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

Miguel Guerrero [a], Sergio Muñoz [a], Josep Ros [a], Teresa Calvet [b], Mercè Font-Bardía [b, c], Josefina Pons[a, *]

a Departament de Química, Universitat Autònoma de Barcelona, 08193, Bellaterra, Barcelona, Spain
b Cristal·lografia, Mineralogia i Dipòsits Minerals, Universitat de Barcelona, Martí i Franquès s/n, 08028, Barcelona, Spain
c Unitat de Difracció de Raig-X, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Universitat de Barcelona, Sol e i Sabarís, 1-3, 08028, Barcelona, Spain

* Corresponding author.
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ABSTRACT

Two new N-pyrazole, P-phosphine hybrids ligands: 1-[2-(diphenylphosphanyl)methyl]-3,5-dimethyl pyrazole (LP1) and 1-[2-(diphenylphosphanyl)propyl]-3,5-dimethylpyrazole (LP3) are presented. The reaction of these two ligands and two other ligands reported in the literature: 1-[2-(diphenylphosphanyl) ethyl]-3,5-dimethylpyrazole (LP2) and 1-[2-(diphenylphosphanyl)ethyl]-3,5-diphenylpyrazole (LP4) with [PdCl2(CH3CN)2] yield [PdCl2(LP)] (LP ¼ LP1 (1), LP2 (2), LP3 (3) and LP4 (4)) complexes. All complexes are fully characterised by analytical and spectroscopic methods and the resolution of the crystal structure of complexes 2 and 3 by single crystal X-ray diffraction is also presented. In these complexes the ligands are coordinated to Pd(II) via k2(N,P) forming metallocycles of six (2) and seven (3) members and finish their coordination with two cis-chlorine atoms. Finally, complex 2 is studied in the palladium-catalysed CeC coupling reaction, being active even for aryl chlorides substrates.

1. INTRODUCTION

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

During the last years, in our group we have studied hybrid ligands that combine pyrazole and amino-, alcohol-, ether-, thioether-, phosphinite- or phosphine-groups. These hybrid ligands have been studied for their potential hemilabile properties, their applications in catalysis and for the construction of discrete molecular architectures with diversified topologies [7]. It is well known that the coordination/chelation properties of these ligands, and, in consequence, their reactivity and catalytic behaviour, in a complex depend on both (i) kind of heteroatoms (i.e. S, O, N, etc.) and (ii) their relative position in the skeleton of the ligands. Thus, in order to expand the scope of our N-pyrazole, P-phospine system, we have modulated the length of the link between these and 1-[2-(diphenylphosphanyl)ethyl]-3,5-diphenylpyrazole (LP4) [6f], we have studied their reactivity with [PdCl2(CH3CN)2]. The synthesis and characterization of these new ligands and their complexes have been investigated. In particular, NMR experiments and X-ray crystal studies. Finally, complex 2 has been studied as a catalyst in the Heck reaction between phenyl halides and tert-butyl acrylate. heteroatoms.

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

2. RESULTS AND DISCUSSION

2.1. Synthesis of the ligands

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

The new ligands 1-[2-(diphenylphosphanyl)methyl]-3,5-dimeth ylpyrazole (LP1) and 1-[2-(diphenylphosphanyl)propyl]-3,5-dimet hylpyrazole (LP3) were prepared by reaction of 1-(chloromethyl)-3,5-dimethylpyrazole (LCl1) [8] or 1-(chloropropyl)-3,5-dimeth ylpyrazole (LCl3) [9], respectively, in presence of PPh2Li, which is generated in situ by deprotonation of PPh2H by n-butyl lithium (n-BuLi) in THF as solvent, at 0 C (Scheme 1a).

These new ligands, isolated in a 99% (LP1) and 95% yields (LP3) as yellowish oils, were characterised by C, H, and N elemental analyses, IR, 1H, 13C{1H} and 31P{1H} NMR spectroscopy, and by MS(ESIþ) mass spectrometry. All of them are in agreement with proposed ligands. In the 31P{1H} NMR spectra, the diphenylphosphanyl moiety gives a singlet at d¼ 18.4 ppm (LP1) and d¼ 19.1 ppm (LP3), indicating the presence of the phosphine group [6e,10,12].

2.2. Synthesis and characterization of the complexes

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

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

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

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

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

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

P signals. The 1H, 13C{1H} and 31P{1H} NMR spectra were consistent with the proposed formulation and showed the coordination of the ligands (LP1, LP2, LP3 and LP4) to the Pd atom. NMR spectroscopic data are reported in Section 4. The 1H NMR spectra of complexes 1e4, present one signal between 6.73 and 5.75 ppm, assigned to the protons of the CH(pz). In the 1H NMR spectrum of 1, the methylene hydrogens appear as one signal, the two protons of the CH2 group in Npz-CH2-P chain are equivalent. Thus, the signal can be assigned as a doublet (4.70 ppm, 2JPH ¼ 8.1 Hz). For 2 and 4, the four protons of the CH2 groups in Npz-CH2-CH2-P chain, appear as two multiplets. The multiplets that correspond to Npz-CH2 appear at 4.81 (2) and 5.03 (4) ppm, and multiplets of the protons CH2-P appear at 2.61 (2) and 2.60 (4) ppm. Finally, for compound 3 the 1H NMR spectrum display four signals as multiplets that corresponds to groups of the signals for Npz-CH2(a)-CH2(b)-CH2(c)-P chain. HMQC spectrumwas used to assign the signals of the protons (a), (b) and (c) of the chain. Two of these multiplets appear at 5.69 and 4.25 ppm corresponding to each one of the protons of the fragment Npz-CH2(a). This behaviour indicates that the two protons are diastereotopic. The other group of signals at 1.89 and 1.21 ppm, are attributable to CH2(b) and CH2-P(c), respectively. The presence of the multiplets for compounds 1e4 is probably due to the diastereotopic properties of CH2 groups. This effect is attributable to the rigid conformation of the ligands once they are complexed. The 13C{1H} NMR spectra of 1e3 complexes, show one signal between 109.9 and 107.6 ppm, assigned to the CH(pz). The signals in the 31P {1H} NMR spectra for all complexes appear at lower fields than for the free respectively ligands and permit to know that phosphorus atom is connected to metallic centre. The spectra show a singlet at (þ35.3 ppm (1), þ23.9 ppm (2), þ11.6 ppm (3), and þ21.0 ppm (4)). Chemical shifts agree with of values of other complexes of Pd(II), Pphosphine complexes described in the literature [6g,6h].

2.3. Crystal and molecular structure of complexes 2 and 3

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

ORTEP pictures and selected bond distances and angles are shown in Fig. 1 (2), Fig. 2 (3) and Table 1. The structures of complexes 2 and 3 consists of discrete Pd(II) molecules. The metal is connected to the pyrazole-phosphine ligands via k2(N,P) building a metallocycle ring of six (2) and seven (3) members, and finishes its coordination with two chlorine atoms in a cis-disposition. A slightly distorted square-planar geometry is observed around Pd(II) atom in both structures. The distortion of the geometry is observed by the values of distances between Pd(II) and the main plane N1-P-Cl1-Cl2 [0.005 Å (2), 0.001 Å (3)], the values of the N1-Pd-P bite angles [82.77(8)º (2), 89.07(6)º (3)]. All of them are in agreement with the ones found in the literature [14].

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)], Pd-Cl1 [2.3885(12) Å (2), 2.3365(7) Å (3)] and Pd-Cl2 [2.2752(15) Å (2), 2.2747(7) Å (3)], are in agreement with the values described in the literature: Pd-N [1.953e2.088 Å], Pd-P [2.201e2.285 Å], Pd-Cl1 [2.282e2.472 Å] and Pd-Cl2 [2.222e2.294 Å] [14].

Due to the different trans effect of the donor atoms in 2 and 3, the Pd-Cl1 bonds trans to phosphorus, are longer than the Pd-Cl2 bonds trans to nitrogen [14]. The N1-Pd-P bite angles for 2 and 3 are smaller than 90 C, but are consistent with the reported angles for similar complexes [14]. It is worth noting that in both structures the six (2) and seven-membered rings (3) formed by the bidentate ligands coordinated to palladium adopt a twisted boat conformation.

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

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

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

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

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

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

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

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

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

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 the results were lower, t ¼ 33 h, % conv. ¼ 2, and TON ¼ 269 (Table 2, entry 5).

3. CONCLUSION

We have presented the synthesis and characterisation of two new ligands (LP1 and LP3), and with these ligands and two other ligands, previously described in the literature (LP2 and LP4), we have assayed the reaction with [PdCl2(CH3CN)2], obtaining [PdCl2(LP)] (LP ¼ LP1 (1), LP2 (2), LP3 (3) and LP4 (4)) compounds. All these new complexes have been characterised by elemental analyses, conductivity measurements, infrared and 1H, 13C{1H} and 31P{1H} NMR spectroscopies, and MS-ESI(þ) and MALDI-TOF spectrometry.

The crystal structure of complexes [PdCl2(LP)] (LP ¼ LP2 (2) and LP3 (3)) were determined by X-ray diffraction methods showing a square planar geometry where the palladium centre is coordinated to one bidentate LP ligand and two chlorine atoms in a cis disposition.

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

4. EXPERIMENTAL SECTION

4.1. General details

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

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

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

4.2. Synthesis of the ligands

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

A solution of nBuLi (16 ml, 25.3 mmol, 1.6 M in hexane) was added dropwise to a stirred solution of PPh2H (1.38 ml, 8.0 mmol) in dry THF (10 ml) at 77 C (acetone/CO2). After 30 min, the solution of PPh2Li was added dropwise to a stirred solution of 1- (chloromethyl)-3,5-dimethylpyrazole (LCl1$HCl) (1.16 g, 8 mmol) for LP1 or 1-(chloropropyl)-3,5-dimethylpyrazole (LCl3$HCl) (1.39 g, 8 mmol) for LP3, in THF (20 ml) at 77 C. The mixture was maintained at 77 C for 1 h. The temperature was then raised to room temperature and after 12 h of stirring the solvent was evaporated under vacuum. 40 ml of dichloromethane were added to the residue and the salts were extracted with 3 10 ml of distilled water. Evaporation of the solvent from the organic phase gives 1- [2-(diphenylphosphanyl)methyl]-3,5-

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

LP1: (Yield: 99%, 2.33 g). Anal. Calc. for C18H19N2P: C, 73.45, H, 6.51; N, 9.52. Found: C, 73.81; H, 6.44; N, 9.39%. MS (ESIþ): m/z (%): 295 (97%) [LP1 þ H]þ, 311 (100%) [LP1(O) þH]þ (LP1(O) ¼ oxidized ligand). IR: (NaCl, cm 1): 3051 n(CeH)ar, 2922 n(CeH)al, 1552 n(C] C/C]N)ar, 1433 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, 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 (s, 3H, pz-CH3) ppm. 13C{1H} NMR (CDCl3 at 298 K, 63 MHz) d: 148.3, 139.9 (pz-CCH3), 136.9 (d, 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 (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 (s, P-C6H5) ppm.

LP3: (Yield: 95%, 2.45 g). Anal. Calc. for C20H23N2P: C, 74.51, H, 7.19; N, 8.69. Found: C, 74.95; H, 7.23; N, 8.33%. MS (ESIþ): m/z (%): 323 (46%) [LP3 þ H]þ, 339 (100%) [LP3(O) þH]þ (LP3(O) ¼ oxidized ligand). IR: (NaCl, cm 1): 3047 n(CeH)ar, 2919 n(CeH)al, 1551 n(C] C/C]N)ar, 1433 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, 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-CH2-P), 2.12 (s, 3H, pz-CH3), 2.08 (s, 3H, pz-CH3) ppm. 13C{1H} NMR (CDCl3 at 298 K, 63 MHz) 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-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, 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-CH3), 7.1 (pz-CH3) ppm. 31P{1H} NMR (CDCl3 at 298 K, 81 MHz) d: 19.1 (s, P-C6H5) ppm.

4.3. Synthesis of the complexes

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

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

1 (Yield: 11%, 0.014 g). Anal. Calc. for C18H19N2PCl2Pd: C, 45.84; H, 4.06; N, 5.94. Found: C, 45.60; H, 3.83; N, 6.21%. MS (MALDITOF): m/z (%): 437 (100%) [PdCl(LP1)]þ. Conductivity (1.02 10 3M in acetonitrile): 2 U 1cm2mol 1. IR: (KBr, cm 1) 3053 n(CeH)ar, 2958, 2915 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, 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, 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 (s, 3H, pz-CH3) ppm. 13C{1H} NMR (CDCl3 at 298 K, 63 MHz) d: 148.1, 139.9 (pz-CCH3), 136.8 (d, 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 (pz-CH3), 12.4 (d, pz-CH3) ppm. 31P{1H} NMR (CDCl3 at 298 K, 81 MHz) d: 35.3 (s, P-C6H5) ppm.

2 (Yield: 86%, 0.113 g). Anal. Calc. for C19H21N2PCl2Pd: C, 46.74; H, 4.20; N, 5.66. Found: C, 47.07; H, 4.64; N, 5.61%. (MALDI-TOF): m/ z (%): 451 (100%) [PdCl(LP2)]þ. Conductivity (1.12 10 3 M in acetonitrile): 7 U 1cm2mol 1. IR: (KBr, cm 1) 3046 n(CeH)ar, 2923 n(CeH)al, 1552 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-N), 347, 328 n(Pd-Cl), 314 n(Pd-P). 1H NMR (CD2Cl2 at 298 K, 250 MHz) d: 7.55 (m,10H, C6H5), 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-

CH3), 2.19 (s, 3H, pz-CH3) ppm. 13C{1H} NMR (CD2Cl2 at 298 K, 63 MHz) d: 152.9, 134.4e127.2 (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-CH3), 11.0 (pz-CH3) ppm. 31P{1H} NMR (CD2Cl2 at 298 K, 81 MHz) d: 23.9 (s, P-C6H5) ppm.

3 (Yield: 40%, 0.054 g). Anal. Calc. for C20H23N2PCl2Pd: C, 47.93; H, 4.41; N, 5.30. Found: C, 47.72; H, 4.13; N, 5.59%. MS (MALDI-TOF): m/z (%): 465 (100%) [PdCl(LP3)]þ, 523 (30%) [PdCl(LP3) þ Na]þ. Conductivity (1.05 U 10 3 M in acetonitrile): 6 U 1cm2mol 1. IR: (KBr, 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 d(CeH)oop; (polyethylene, cm 1) 457 n(Pd-N), 355, 337 n(Pd-Cl), 309 n(Pd-P). 1H NMR (CDCl3 at 298 K, 250 MHz) d: 7.63 (m, 10H, C6H5), 5.99 (s, 1H, pz-CH), 5.69/4.25 (m, 1H/1H, pz-CH2-CH2-CH2-P), 1.89/1.21 (m,2H/ 2H, pz-CH2-CH2-CH2-CH2-P), 2.44 (s, 3H, pz-CH3), 2.23 (s, 3H, pz-CH3) ppm. 13C{1H} NMR (CDCl3 at 298 K, 63 MHz) d: 135.3e128.4 (C6H5), 109.9 (pz-CH), 47.6 (pz-CH2-CH2-CH2-P), 24.9, 23.4 (pz-CH2-CH2- CH2-P), CH2-CH2-CH2-P), 15.7 (pz-CH3), 12.0 (pz-CH3) ppm. 31P{1H} NMR (CDCl3 at 298 K, 81 MHz) d: 11.6 (s, P-C6H5) ppm.

4 (Yield: 56%, 0.092 g). Anal. Calc. for C29H25N2PCl2Pd: C, 57.12; H, 4.13; N, 4.59. Found: C, 56.95; H, 4.05; N, 4.63%. (MALDI-TOF): m/ z (%): 575 (100%) [PdCl(LP4)]þ. Conductivity (1.08 10 3 M in acetonitrile): 8 U 1cm2mol 1. IR: (KBr, cm 1) 3056 n(CeH)ar, 2907 n(CeH)al, 1552 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-N), 360, 345 n(Pd-Cl), 332 n(Pd-P). 1H NMR (CD3CN at 298 K, 250 MHz) d: 7.71 (m, 20H, C6H5), 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-CH3), 1.79 (s, 3H, pz-CH3) ppm. 31P{1H} NMR (CD3CN at 298 K, 81 MHz) d: 21.0 (s, P-C6H5) ppm.

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

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

For 2 and 3, the structure was solved by direct methods, using SHELS-97 computer program [18] and refined by full matrix leastsquares method with SHELXL-97 computer program [19], using 24329 reflections for 2 and 5717 reflections for 3. The function minimized was SwkFor2 - rFcr2r2, where w ¼ [s2(I) þ 4.8616P] 1, and P ¼ (rFo2r2 þ 2 rFcr2)/3 for 2, and w ¼ [s2(I) þ (0.0567P)2 þ 0.4027P] 1 for 3. For 2, all H atoms are computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which is linked. For 3, 2H atoms were located from a difference synthesis and refined with isotropic temperature factor and 21H atoms were computed and refined, using a riding model, with an isotropic temperature factor equal to 1.2 times the equivalent temperature factor of the atom which is linked.

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

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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.

462

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

465

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

468

SCHEME 1

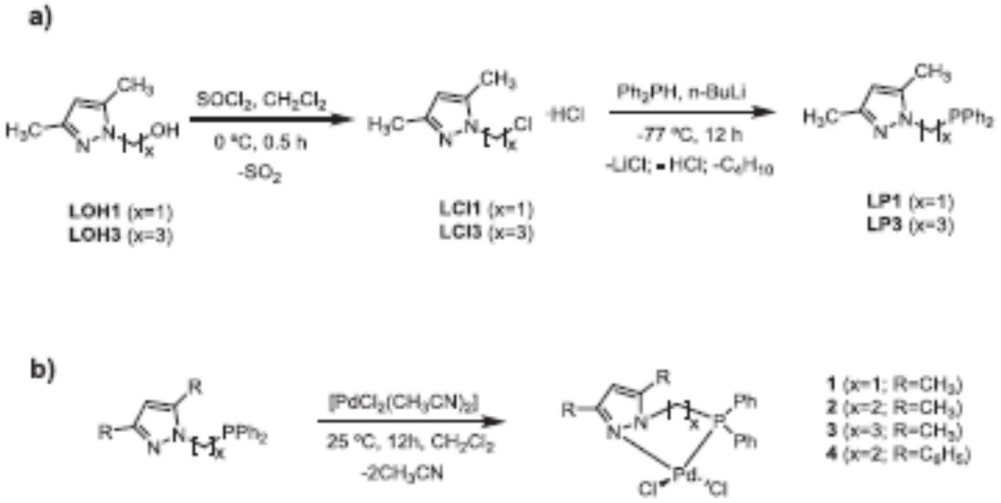

a)
SOCl2, CH2Cl2
0 °C, 0.5 h
-SO2
Ph2PH, n-BuLi
-77 °C, 12 h
-LiCl; -HCl; -C4H10
LOH1 (x=1)
LOH3 (x=3)
LCl1 (x=1)
LCl3 (x=3)
LP1 (x=1)
LP3 (x=3)
b)
[PdCl2(CH3CN)2]
25 °C, 12h, CH2Cl2
-2CH3CN
1 (x=1; R=CH3)
2 (x=2; R=CH3)
3 (x=3; R=CH3)
4 (x=2; R=C6H5)

FIGURE 1

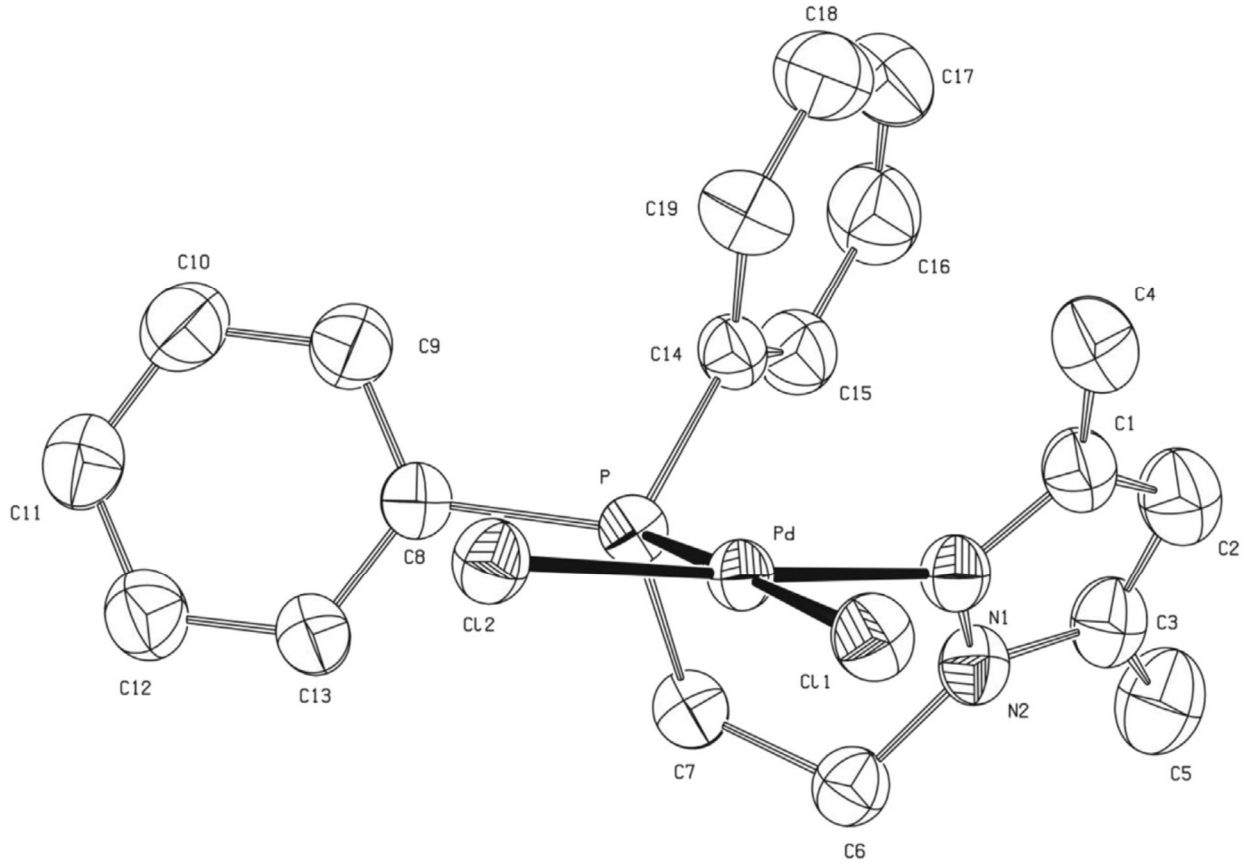

C18
C17
C19
C16
C10
C4
C9
C14
C15
C1
P
C11
Pd
C8
C2
Cl2
N1
C3
Cl1
C12
C13
N2
C7
C5
C6

FIGURE 2

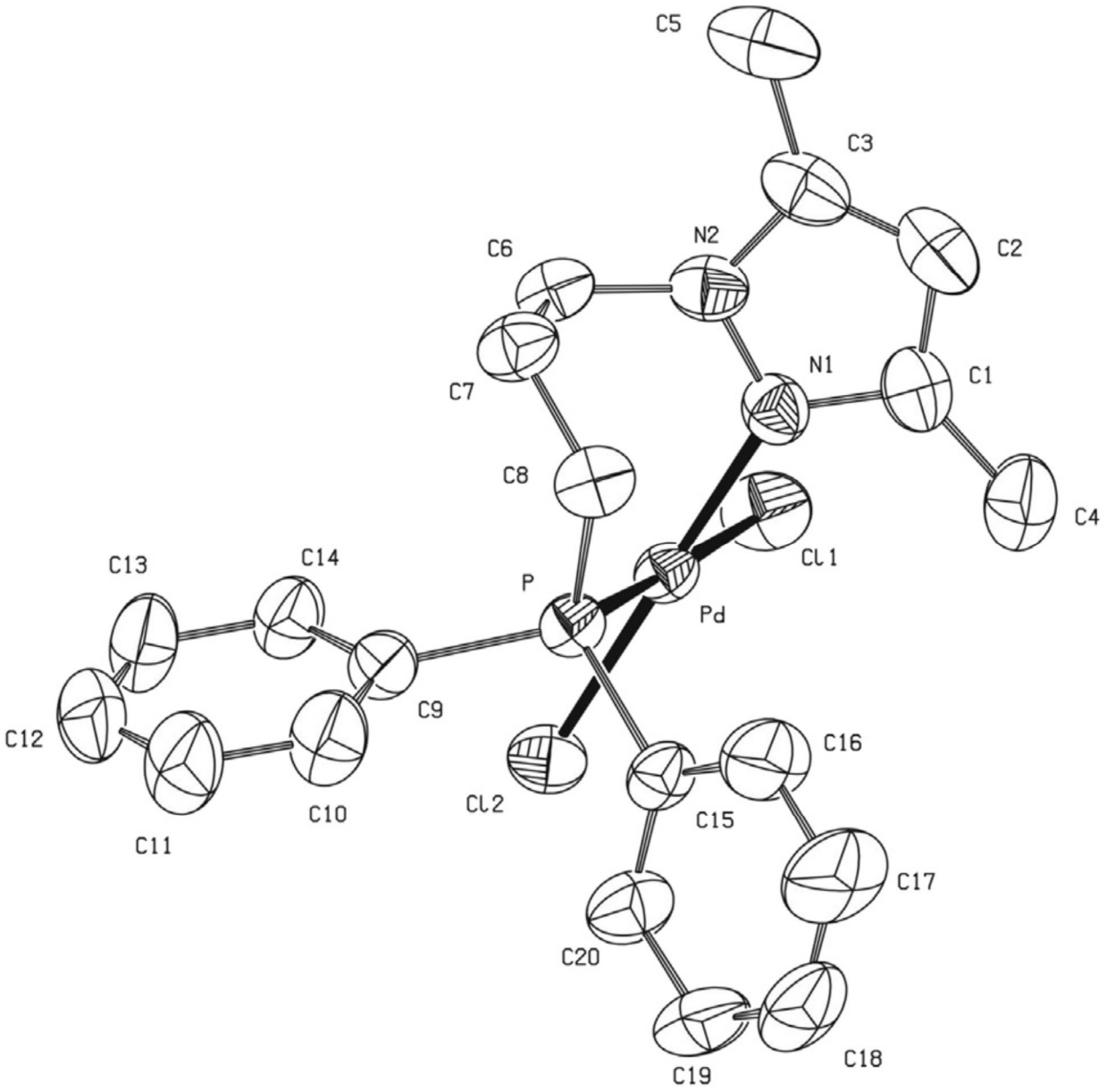

C5
C3
N2
C6
C2
C7
N1
C1
C8
C4
I
Cl1
C13
C14
P
Pd
C9
C12
C16
Cl2
C10
C15
C11
C17
C20
C18
C19

FIGURE 3

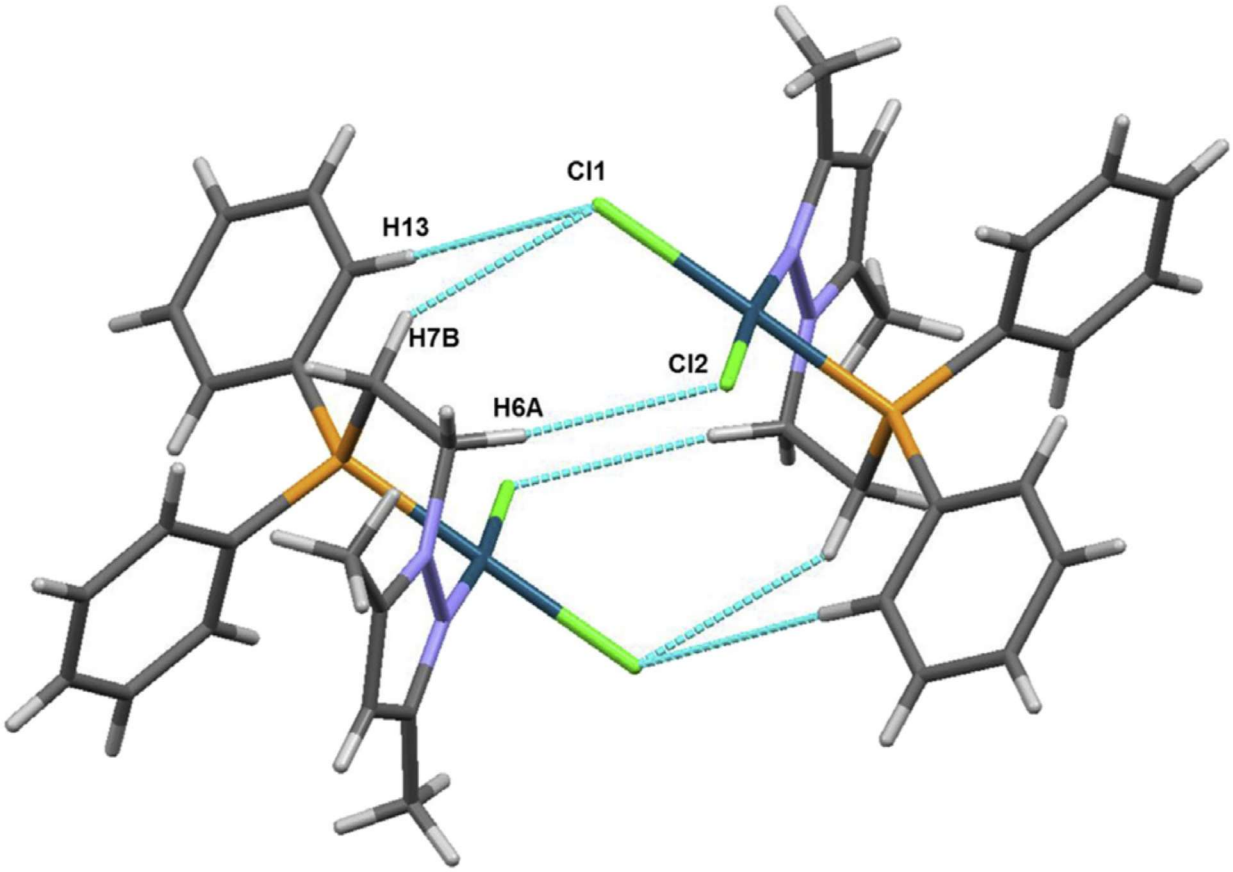
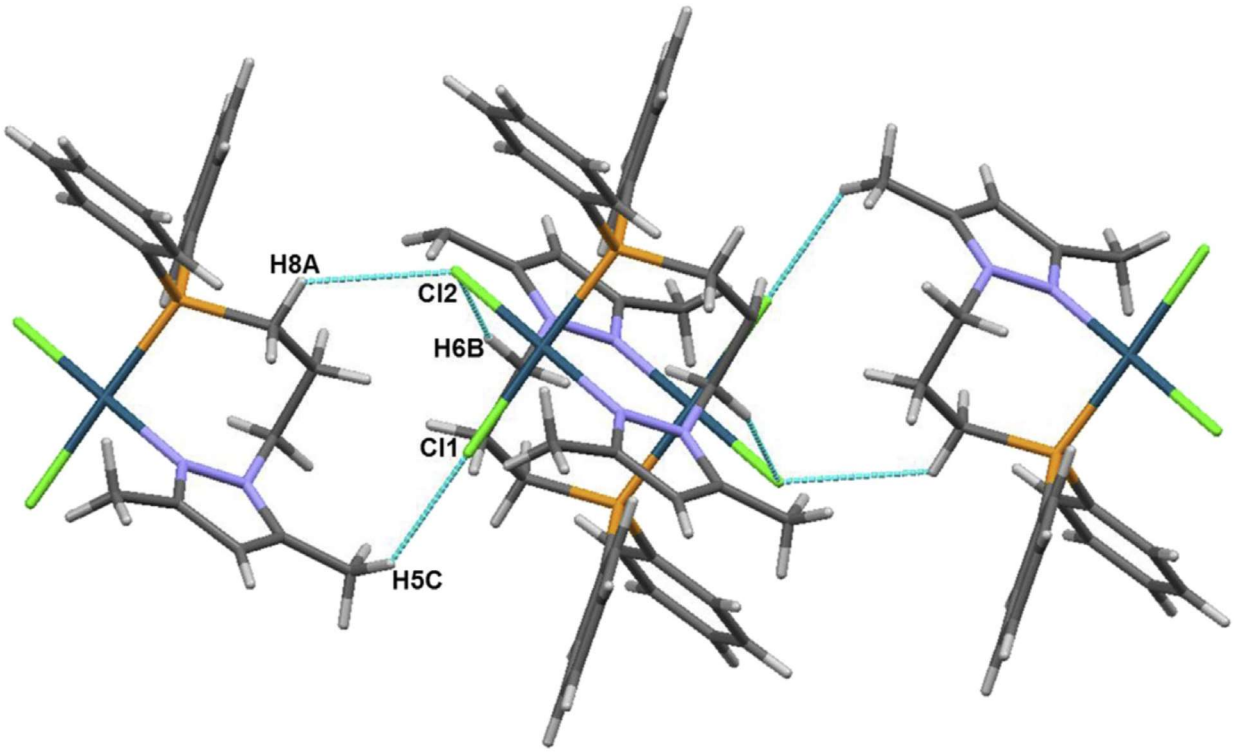


FIGURE 4



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

503

	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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512

513

Table 3. Crystallographic data for 2 and 3.

	2	3
Formula	$C_{19}H_{21}Cl_2N_2PPd$	$C_{20}H_{23}Cl_3N_2PPd$
Formula weigh	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
F(000)	976	1008
Crystal size (mm^3)	0.2 × 0.1 × 0.1	0.2 × 0.1 × 0.1
hkl ranges	$-19 \le h \le 21, -14 \le k \le 13, -23 \le l \le 23$	$-15 \le h \le 15, 0 \le k \le 12, 0 \le l \le 30$
2 θ Range (°)	2.56–30.00	2.63–32.88
Reflections collected/unique/[R_{int}]	24329/5646 [R(int) = 0.0352]	5717/5717 [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/restrains/parameters	5646/3/227	5717/0/245
Goodness-of-fit on F^2	1.324	1.140
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0458$, $wR_2 = 0.0839$	$R_1 = 0.0379$, $wR_2 = 0.0920$
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