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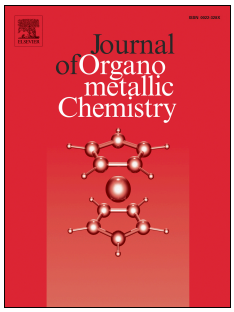

Bis-Cyclometalated Complexes of Pd(II) and Pd(IV) From Iminophosphoranes: Synthesis, Structure and Reactivity

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PII: S0022-328X(14)00261-7

DOI: 10.1016/j.jorganchem.2014.05.024

Reference: JOM 18596

To appear in: *Journal of Organometallic Chemistry*

Received Date: 18 April 2014

Revised Date: 14 May 2014

Accepted Date: 22 May 2014

Please cite this article as: D. Aguilar, G. González, P. Villuendas, E.P. Urriolabeitia, Bis-Cyclometalated Complexes of Pd(II) and Pd(IV) From Iminophosphoranes: Synthesis, Structure and Reactivity, *Journal of Organometallic Chemistry* (2014), doi: 10.1016/j.jorganchem.2014.05.024.

Bis-Cyclometalated Complexes of Pd(II) and Pd(IV) From Iminophosphoranes: Synthesis, Structure and Reactivity

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Dedication: This contribution is dedicated to Prof. Maria Pilar García Clemente, who passed away on May 27, 2013.

MANUSCRIPT JORGANCHEM-D-14-00215

REVISED VERSION

Abstract

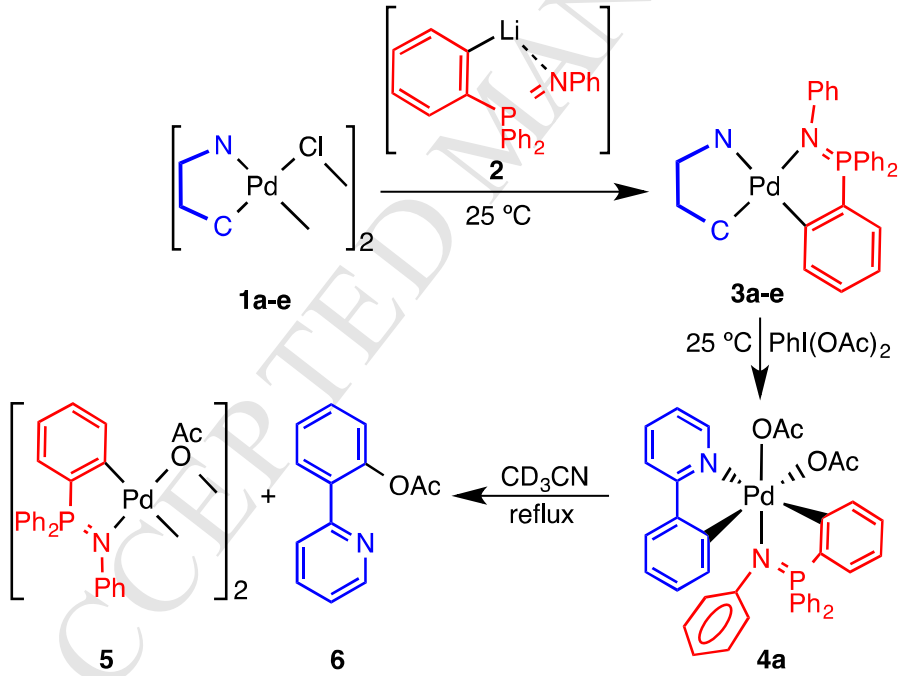
The mononuclear bis-orthopalladated complexes [Pd(C^N){C_6H_4(PPh_2=NPh)-2}] [C^N = (2-(pyridin-2-yl)phenyl) **3a**, (2-((dimethylamino)methyl)phenyl) **3b**, (*S)*-(2-(1-(dimethylamino)ethyl)phenyl) **3c**, (quinolin-8-ylmethyl) **3d**, (4-methoxy-2-((triphenyl-λ^5-phosphanylidene)carbamoyl)phenyl) **3e**] have been synthesized as single isomers by reaction of the corresponding chloride dimers [Pd(μ-Cl)(C^N)]$_2$ (**1a-1e**) with the lithium derivative [Li{C_6H_4(PPh_2=NPh)-2}] (**2**) in Et_2O. Spectroscopic data show that the two palladated C atoms are in *cis* disposition, which is confirmed by the X-ray structure of **3a**. Oxidation of **3a** with PhI(OAc)$_2$ affords the corresponding Pd(IV) derivative (OC-6-32)[Pd(OAc)$_2${C_6H_4(PPh_2=NPh)-2}{C_6H_4-(2'-NC_5H_4)-2}] **4a** also as a single isomer. **4a** undergoes reductive elimination through C-O coupling to give the dimer [Pd(μ-OAc){C_6H_4(PPh_2=NPh)-2}]$_2$ **5** and the *ortho*-acetoxylated phenylpyridine **6**. The reactivity of **3b-3e** towards oxidants is also discussed.

Keywords: orthopalladated, C-O coupling, palladium, high oxidation states, iminophosphoranes, regioselectivity

Synopsis

Transmetallation of iminophosphoranes from [Li{C_6H_4(PPh_2=NPh)-2}]$_2$ to chloride-bridge dimers [Pd(μ-Cl)(C^N)]$_2$ affords mixed bis-cyclopalladated complexes, which were obtained regioselectively as cis(C,C)-isomers. Complex [Pd{C_6H_4(PPh_2=NPh)-2}(C_6H_4-(2'-NC_5H_4)-2)] is regioselectively oxidized to the stable Pd(IV) derivative [Pd(OAc)$_2${C_6H_4(PPh_2=NPh)-2}(C_6H_4-(2'-NC_5H_4)-2)] by treatment with PhI(OAc)$_2$. This compound undergoes reductive elimination, releasing the acetoxylated phenylpyridine and keeping the orthopalladated iminophosphorane.

Graphical Abstract (Pictogram)



Highlights

1.- Transmetallation affords mixed bis(*o*-palladated) complexes **3a-3e** of iminophosphoranes

2.- cis(C,C)-configuration of these complexes was confirmed by X-ray diffraction study

3.- Bis(*o*-palladated) complex **3a** was oxidized regioselectively to Pd^{IV} **4a** with $PhI(OAc)_2$

4.- Pd^{IV} complex **4a** give acetoxylated C-O coupling product by reductive elimination

5.- Acetoxylation is selectively produced at the phenylpyridine fragment

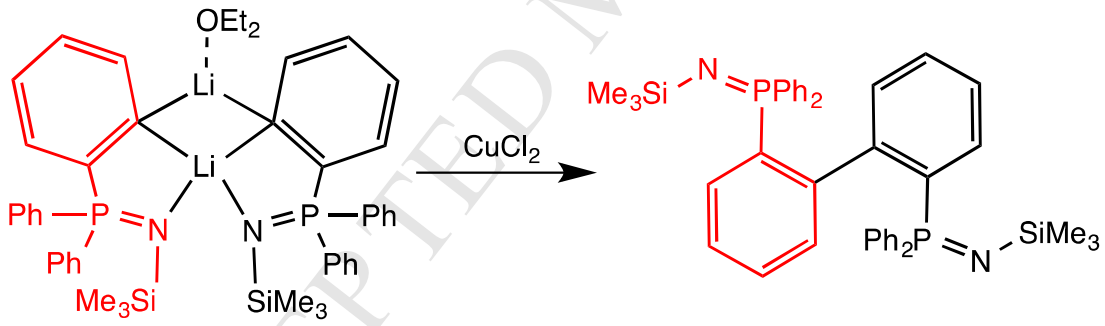
1. Introduction

Cyclopalladated complexes are well known organometallic compounds [1], which are experiencing a "golden age" as useful intermediates in the directed functionalization of organic molecules [2,3]. In this respect, it is really remarkable that a huge number of complexes containing one cyclopalladated unit per palladium atom are known, while the presence of bis-cyclopalladated derivatives (defined as those containing two palladated ligands *on the same* palladium atom) is underrepresented. Specific applications of this type of compounds have been their use as transmetallating reagents [4], in enantioselective synthesis [5-7], or as compounds with liquid crystal properties [8], among others. In spite of this apparent indifference, bis-cyclopalladated derivatives are currently attracting a notable and renewed interest as model intermediate compounds in organic synthesis involving high oxidation states [9]. This is particularly relevant in the preparation of bis-aryl derivatives by C-C coupling [10], and in the functionalization of aryl compounds by C-X (X = halogen) [11], and C-O [12] couplings. In these studies, stable Pd(II) compounds containing two identical metallated aryl fragments (mostly robust phenylpyridine) were subjected to oxidation to the corresponding Pd(IV) complexes, and the subsequent C-C, C-X or C-O bond forming reactions by reductive elimination were in-depth studied [9-12].

A class of substrates of special interest to be subjected to this methodology are iminophosphoranes (IM). These are compounds with general formula $R_3P{=}NR'$, where R and R' can be alkyl, aryl, acyl, ester, vinyl or cyano groups (among others). The first synthesis of IM was reported by Staudinger and Meyer in 1919 [13], and since then they have shown a very interesting behaviour as tunable ligands in coordination chemistry [14]. We have recently studied several aspects of mono-cyclometallated complexes of

IM [15-26], such as their use as catalysts [15,16,24], the regioselectivity of the Pd-induced C-H bond activation in different sites of the IM [17,19-23], their use as auxiliary species to promote singular bonding modes of allyl ligands [18], or their role as intermediates in the synthesis of functionalized organic molecules [25,26].

Aiming to expand the scope of the functionalization of IM, we have attempted the synthesis of biaryl-containing IM from the intramolecular oxidative C-C coupling of bis-cyclopalladated IM. Organic biaryl derivatives display interesting pharmaceutical and biological properties [27,28]. Unfortunately, there are not many examples of biaryl IM. Stalke *et al.* showed that the lithium derivative $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2$ reacted with $CuCl_2$ to yield the product of reductive elimination (Scheme 1) [29], but as far as we know, there are not other examples of similar couplings.



Scheme 1. Synthesis of a bis-aryl-containing IM.[29]

To achieve this task, we have first performed the synthesis of bis-cyclopalladated derivatives containing, at least, one metallated IM. Subsequently, we have studied the reactivity of these complexes towards oxidants, in order to induce the expected C_{aryl}-C_{aryl} coupling. In this contribution we report the obtained results in this chemistry.

2. Experimental Section

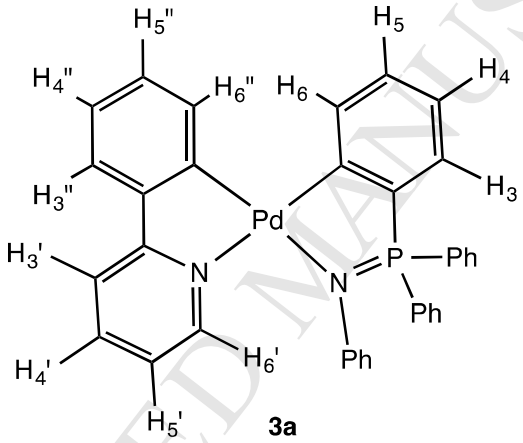
2.1. General Methods. Solvents were dried and distilled using standard procedures before use. All reactions were carried out under Ar atmosphere using standard Schlenk techniques. Elemental analyses were carried out on a Perkin-Elmer 2400-B microanalyser. IR spectra were recorded on a Spectrum 100 Perkin Elmer FTIR spectrophotometer with Universal Attenuated Total Reflectance accesory, which allow the measurement of the spectra in the 4000-250 cm^{-1} region. MALDI-TOF mass spectra were recorded on a Microflex spectrometer (Bruker Daltonic GmBH, Bremen, Germany). HRMS and ESI (ESI+) mass spectra were recorded using a MicroToF Q, API-Q-ToF ESI with a mass range from 20 to 3000 *m/z* and mass resolution 15000 (fwhm). ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded using a Bruker AV300 spectrometer (δ in ppm, J in Hz) at ^{1}H operating frequency of 300.13 MHz in $CDCl_3$ as deuterated solvent. Other solvents and/or temperatures were specified. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the residual solvent signal, and $^{31}P\{^{1}H\}$ was externally referenced to H_3PO_4 (85%). Melting points were taken on a Gallenkamp capillary melting point apparatus (model MPD 350.BM 2.5, Kent, UK). $Ph_3P{=}NPh$ and $PhI(OAc)_2$ were purchased from commercial sources and used without further purification. The lithium derivative $[Li_2(o\text{-}C_6H_4PPh_2NPh)_2]OEt_2$ (**2**) was prepared following known procedures [30], as well as the starting orthopalladated complexes **1a** [31], **1b** [32a], **1c** [32b,c], **1d** [33] and **1e** [17,23].

2.2. General procedure for the synthesis of bis-cyclopalladated compounds 3a-3e

A solution of $[Li_2(o\text{-}C_6H_4PPh_2NPh)_2]OEt_2$ (**2**) (0.71 mmol) was in situ generated from treatment of $Ph_3P{=}NPh$ (0.500 g, 1.42 mmol) with PhLi 1.8 M (1.1 mL, 1.98 mmol) in 20 mL Et_2O under Ar, according to reported methods [30]. To this solution the

corresponding dinuclear Pd compound **1a-1e** (0.71 mmol) was added, and the mixture was stirred at 25 ºC for 3 h. The resulting yellow suspension was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (2×25 mL). The obtained suspension was filtered over celite, the solid was discarded and the resulting solution was evaporated to dryness. The oily residue was treated with Et_2O (15 mL) and continuous stirring, affording complexes **3a-3e** as bright yellow solids, which were filtered, washed with additional Et_2O (3×10 mL) and air-dried.

2.3. Synthesis of [Pd(C_6H_4(PPh_2=NPh)-2)(C_6H_4-(2'-NC_5H_4)-2)] 3a

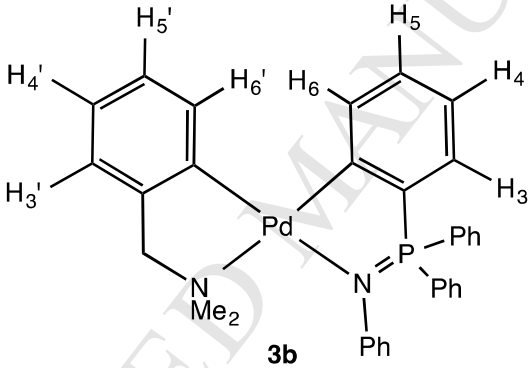


3a

Yield: 0.405 g (46.5 %). ^{1}H NMR ($CDCl_3$, 300.13 MHz), δ_H = 6.69-6.74 (m, 2H, H_p, NPh + $H_{5'}$, py), 6.88-7.04 (m, 6H, H_m + H_o, NPh + H_4 + H_3, PC_6H_4), 7.07 (td, 1H, $H_{5''}$, C_6H_4, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 0.8), 7.17 (td, 1H, $H_{4''}$, C_6H_4, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.1), 7.36-7.44 (m, 5H, H_5, PC_6H_4 + H_m, PPh_2), 7.50-7.60 (m, 4H, $H_{4'}$, py + $H_{6''}$, C_6H_4 + H_p, PPh_2), 7.64-7.72 (m, 5H, $H_{3'}$, py + H_o, PPh_2), 7.77 (d, 1H, $H_{3''}$, C_6H_4, $^3J_{HH}$ = 7.5), 7.86 (d, 1H, $H_{6'}$, py, $^3J_{HH}$ = 6.2), 8.12 (d, 1H, H_6, PC_6H_4, $^3J_{HH}$ = 7.6). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz), δ_C = 117.88 (s, $C_{3'}$, py), 120.10 (s, $C_{5'}$, py), 120.84 (s, C_p, NPh), 122.28 (d, C_4, C_6H_4, $^3J_{PC}$ = 14.7), 123.27, 123.14 (s, $C_{4'}$, py + $C_{5''}$, C_6H_4), 126.50 (d, C_o, NPh, $^3J_{PC}$ = 10.7), 128.08 (s, C_m, NPh), 128.22 (d, C_3, C_6H_4, $^2J_{PC}$ = 20.9, + overlapped $C_{6''}$, C_6H_4), 128.61 (d, C_m, PPh_2, $^3J_{PC}$ = 11.7), 129.31 (s, $C_{4''}$, C_6H_4), 129.89 (d, C_i, PPh_2, $^1J_{PC}$ =

87.6), 129.98 (d, C_5, C_6H_4, $^4J_{PC}$ = 3.3), 132.07 (d, C_p, PPh_2, $^4J_{PC}$ = 2.7), 133.39 (d, C_o, PPh_2, $^2J_{PC}$ = 9.7), 137.45 (s, $C_{3'}$, py), 138.60 (s, $C_{3''}$, C_6H_4), 139.64 (d, C_6, C_6H_4, $^3J_{PC}$ = 15.9), 144.58 (d, C_2, C_6H_4, $^1J_{PC}$ = 144.7), 149.62 (s, $C_{6'}$, py), 146.83 (s, $C_{2''}$, C_6H_4), 149.46 (d, C_i, Ph, $^2J_{PC}$ = 3.2), 161.44 (d, $C_{1''}$, C_6H_4, $^4J_{PC}$ = 1.7), 164.58 (s, $C_{2'}$, py), 170.40 (d, C_1, C_6H_4, $^2J_{PC}$ = 20.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz), δ_P = 28.70. Anal. Calc for [$C_{35}H_{27}N_2PPd$]: C, 68.58; H, 4.44; N, 4.57. Found: C, 68.95; H, 4.20; N, 4.24. IR (ν, cm^{-1}) = 1262 $\nu_{(P=N)}$. MS (MALDI +) *m/z*: 612 (30 %) $[M]^+$. M. p. 249–250 °C (dec).

2.4. Synthesis of [Pd(C_6H_4(PPh_2=NPh)-2)($C_6H_4CH_2NMe_2$-2)] 3b

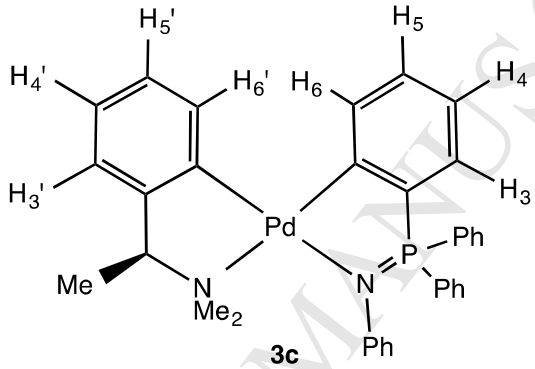


3b

Yield: 0.526 g (62.5 %). ^1H NMR ($CDCl_3$, 300.13 MHz), δ_H = 2.01 (s, 6H, NMe_2), 3.66 (s, 2H, CH_2), 6.67-6.71 (m, 1H, (C_6H_4)'), 6.77 (ddd, 1H, H_3, PC_6H_4, $^3J_{HP}$ = 10.6, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.4), 6.85-6.96 (m, 8H, H_m + H_p + H_o, NPh + H_4, PC_6H_4 + 2H, (C_6H_4)'), 7.20 (tt, 1H, H_5, PC_6H_4, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.6), 7.32 (m, 4H, H_m, PPh_2), 7.41-7.46 (m, 3H, 1H, (C_6H_4)' + H_p, PPh_2), 7.57 (m, 4H, H_o, PPh_2), 7.86 (dd, 1H, H_6, PC_6H_4, $^3J_{HH}$ = 7.2, $^4J_{HH}$ = 1.7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz), δ_C = 49.34 (s, NMe_2), 72.16 (s, CH_2), 120.97 (d, $C_{6'}$, (C_6H_4)', $^4J_{PC}$ = 3.0), 121.74 (s, NPh), 122.15 (d, C_4, PC_6H_4, $^3J_{PC}$ = 14.4), 122.50 (s, NPh), 125.40 (s, (C_6H_4)'), 127.97 (d, C_o, NPh, $^3J_{PC}$ = 9.0), 128.17 (s, (C_6H_4)'), 128.40 (d, C_m, PPh_2, $^3J_{PC}$ = 11.6, + overlapped C_3, PC_6H_4), 130.01 (d, C_5, PC_6H_4, $^4J_{PC}$ = 3.3), 130.27 (C_i, PPh_2, $^1J_{PC}$ = 87.9), 131.32 (d, C_p, PPh_2, $^4J_{PC}$ = 2.7),

133.45 (d, C_o, PPh_2, $^2J_{PC}$ = 9.4), 138.50 (s, (C_6H_4)'), 140.47 (d, C_6, PC_6H_4, $^3J_{PC}$ = 15.7), 142.63 (d, C_2, PC_6H_4, $^1J_{PC}$ = 132.6), 148.05 (s, $C_{2'}$, (C_6H_4)'), 149.87 (d, C_i, Ph, $^2J_{PC}$ = 5.0), 158.08 (s, $C_{1'}$, (C_6H_4)'), 167.40 (d, C_1, PC_6H_4, $^2J_{PC}$ = 19.8). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz), δ_P = 29.40. Anal. Calc for [$C_{33}H_{31}N_2PPd$]: C, 66.84; H, 5.27; N, 4.72. Found: C, 66.49; H, 5.42; N, 4.85. IR (ν, cm^{-1}) = 1257 ($\nu_{P=N}$). MS (MALDI +) *m/z*: 592 (40 %) $[M]^+$. M. p. 201–203 °C (dec).

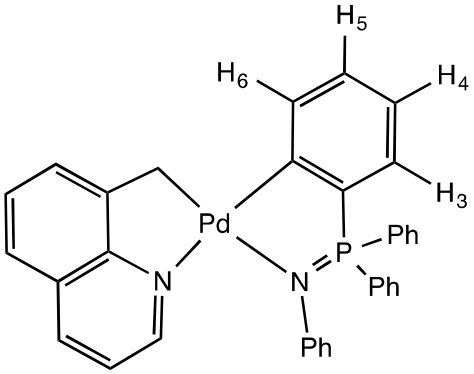
2.5. Synthesis of [Pd(C_6H_4(PPh_2=NPh)-2)((*S*)-C_6H_4CHMeNMe_2-2)] 3c



3c

Yield: 0.420 g (48.9 %). ^1H NMR ($CDCl_3$, 300.13 MHz), δ_H = 1.62 (d, 3H, CHMe, $^3J_{HH}$ = 6.5), 1.98 (s, 3H, NMe_2), 2.28 (s, 3H, NMe_2), 3.66 (q, 1H, CH, $^3J_{HH}$ = 6.5), 6.75 (td, 1H, (C_6H_4)', $^3J_{HH}$ = 7.0, $^4J_{HH}$ = 1.6), 6.77-6.83 (m, 1H, H_3, PC_6H_4), 6.88-7.03 (m, 8H, H_m + H_p + H_o, NPh + H_4, PC_6H_4 + 2H, (C_6H_4)'), 7.29 (tt, 1H, H_5, PC_6H_4, $^3J_{HH}$ = 7.4, $^4J_{HH}$ = 1.6), 7.33-7.43 (m, 7H, H_m, PPh_2 + H_p, PPh_2 + 1H, (C_6H_4)'), 7.77 (m, 4H, H_o, PPh_2), 7.97 (dd, 1H, H_6, PC_6H_4, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz), δ_P = 26.67. Anal. Calc for [$C_{34}H_{33}N_2PPd$]: C, 67.27; H, 5.48; N, 4.61. Found: C, 66.90; H, 5.29; N, 4.48. IR (ν, cm^{-1}) = 1274 ($\nu_{P=N}$). MS (MALDI+) *m/z:* 606 (25 %) $[M]^+$. M. p. 208–210 °C (dec).

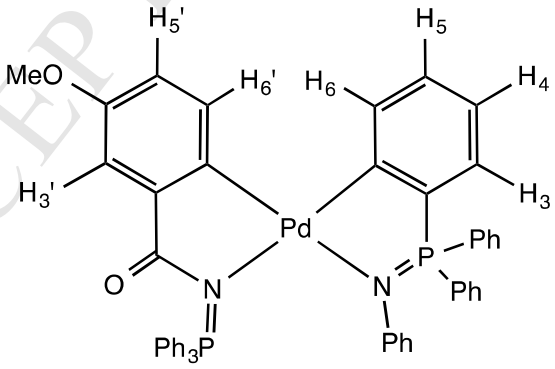
2.6. Synthesis of [Pd(C_6H_4(PPh_2=NPh)-2)(C_9H_6N-8-CH_2)] 3d



3d

Yield: 0.425 g (50.0 %). ^{1}H NMR ($CDCl_3$, 300.13 MHz), δ_H = 3.89 (br, CH_2), 6.37-6.53 (m, 5H, NPh), 6.66 (t, 1H, H_4, PC_6H_4, $^3J_{HH}$ = 7.2), 7.01 (d, 1H, H_3, PC_6H_4, $^3J_{HH}$ = 7.5), 7.24 (t, 1H, H_5, PC_6H_4, $^3J_{HH}$ = 7.5), 7.42-7.79 (m, 15H, 5H, C_9H_6N + H_m + H_p + H_o, PPh_2), 8.27 (d, 1H, H_6, PC_6H_4, $^3J_{HH}$ = 7.4), 8.98 (br, $H_{1'}$, C_9H_6N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz), δ_P = 27.47. Anal. Calc for [$C_{34}H_{27}N_2PPd$]: C, 67.95; H, 4.53; N, 4.66. Found: C, 67.83; H, 4.27; N, 4.44. IR (ν, cm^{-1}) = 1266 ($\nu_{P=N}$). MS (MALDI+) *m/z*: 600 (35 %) $[M]^+$. M. p. 142–144 °C (dec).

2.7. Synthesis of [Pd(C_6H_4(PPh_2=NPh)-2)(C_6H_3-OMe-4-(C(O)N=PPh_3)-2)] 3e

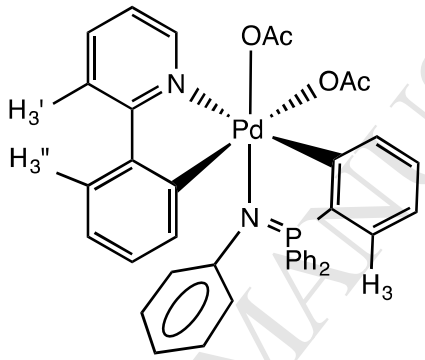


3e

Yield: 0.492 g, 40.0 %. ^{1}H NMR ($CDCl_3$, 300.13 MHz), δ_H = 3.86 (s, 3H, OMe), 6.24 (t, 2H, H_m, NPh, $^3J_{HH}$ = 7.7), 6.38 (t, 1H, H_p, NPh, $^3J_{HH}$ = 7.2), 6.71 (d, 2H, H_o, NPh, $^3J_{HH}$ = 8.0), 6.84-6.97 (m, 3H, 1H, $(C_6H_3)'$ + 2H, C_6H_4), 7.25-7.31 (m, 5H, 1H, C_6H_4 +

H_m, PPh_2), 7.40-7.47 (m, 8H, H_p, PPh_2 + H_m, PPh_3), 7.53-7.74 (m, 15H + 2H, $(C_6H_3)'$, $3H_p$, PPh_3 + $6H_o$, PPh_3 + 4H, H_o, PPh_2), 8.04 (dd, 1H, H_6, C_6H_4, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 2.0). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.49 MHz), δ_P = 19.66 (PPh_2), 24.18 (C(O)N=PPh_3). Anal. Calc for [$C_{50}H_{40}N_2O_2P_2Pd$]: C, 69.09; H, 4.64; N, 3.22. Found: C, 69.51; H, 4.27; N, 3.05. IR (ν, cm^{-1}) = 1590 ($\nu_{C=O}$), 1284 ($\nu_{P=N}$). MS (MALDI +): *m/z*: 868 (20 %) $[M]^+$. M. p. 198–200 °C (dec).

2.8. Synthesis of (OC-6-32)[Pd(OAc)$_2$(C_6H_4(PPh_2=NPh)-2){C_6H_4-(2'-NC_5H_4)-2}] 4a



4a

$PhI(OAc)_2$ (109 mg, 0.326 mmol) was added to a solution of **3a** (200 mg, 0.326 mmol) in 10 mL of CH_2Cl_2 at room temperature, and the resulting solution was stirred for 1 h. During this time the color of the solution changed from yellow to orange. After the reaction time, the solvent was removed under reduced pressure to small volume (1 mL) and Et_2O (4 mL) was added. Further stirring produced the formation of an orange-yellowish solid **4a**, which was filtered, washed with more Et_2O (4 mL) and dried in vacuo. Complex **4a** was recrystallized from CH_2Cl_2/Et_2O affording **4a**·$0.5CH_2Cl_2$, which was used for analytical and spectroscopic purposes. Complex **4a** has to be stored under Ar at -18 °C.

Yield: 200 mg (83 %). ^1H NMR (CD_2Cl_2, 300.13 MHz, 253 K), δ_H = 1.81 (3H, s, OAc), 1.84 (3H, s, OAc), 5.65 (br, 2H, H_o, NPh), 6.41 (br, 2H, H_m, NPh), 6.54 (1H, d, $^3J_{HH}$ =

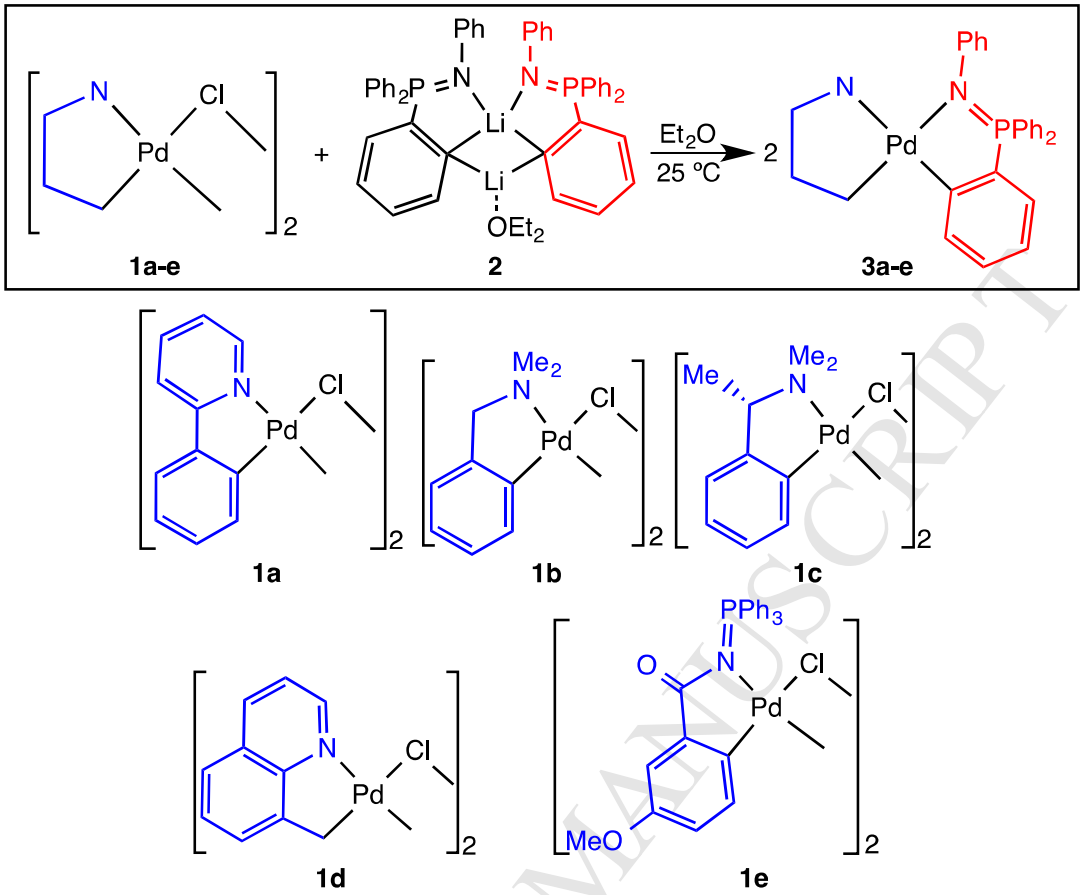
7.4, $H_{5''}$, C_6H_4), 6.70 (1H, t, $^3J_{HH}$ = 7.4, H_p, NPh), 6.9-7.1 (3H, m, $H_{4'}$ py + $H_{5''}$ C_6H_4 + H_6 PC_6H_4), 7.1-7.4 (7H, m, $H_{4''}$ C_6H_4 + H_5 C_6H_4P + $H_{2'}$ py, H_m PPh_2), 7.4-7.8 (9H, m, $H_{3'}$ py + H_3 C_6H_4P + $H_{3''}$ C_6H_4 + H_o + H_p PPh_2), 8.12 (d, 1H, H_6, C_6H_4P , $^3J_{HH}$ = 8.0), 8.94 (d, 1H, $H_{6'}$, py, $^3J_{HH}$ = 4.2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.47 MHz, 253 K), δ_C = 24.9 (CH_3), 115.9 ($C_{3''}$, C_6H_4), 117.7 (C_o, PPh_2), 122.3 ($C_{4'}$, py), 125.1 (C_p, NPh), 125.3 (C_p PPh_2), 125.6 ($C_{4''}$ C_6H_4), 126.2 (C_2 C_6H_4P), 127.3 (C_m NPh), 128.4 (C_m PPh_2), 128.7 ($C_{2'}$ py), 129.2 ($C_{5''}$ C_6H_4), 130.1 (C_6 C_6H_4P), 130.3 (C_o NPh), 132.2 (C_3 C_6H_4P), 133.1 (C_5 C_6H_4P), 133.5 ($C_{6''}$ C_6H_4), 133.7 (C_4 C_6H_4P), 138.1 ($C_{3'}$ py), 142.3($C_{2''}$ C_6H_4), 149.2 ($C_{5'}$ py), 155.9 ($C_{1''}$ C_6H_4), 156.3 (C_i NPh), 157.8 ($C_{6'}$ py), 158.1 (C_i PPh_2), 166.9 (C_1 C_6H_4P), 175.0 (COO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.49 MHz, 253 K), δ_P = 59.06. Anal. Calc for $[C_{39}H_{33}N_2O_4PPd]0.5CH_2Cl_2$: C, 61.33; H, 4.43; N, 3.62. Found: C, 61.68; H, 4.19; N, 3.53. IR (ν, cm^{-1}) = 1616 $\nu_a(CO_2)$, 1357 $\nu_s(CO_2)$, 1295 $\nu_{(P=N)}$. HRMS (ESI-TOF) *m/z*: $[M\text{-}OAc]^+$ calc for $C_{37}H_{30}N_2O_2PPd$ 671.1080, found 671.1126; $[M\text{-}2OAc+OCH_3]^+$ calc for $C_{36}H_{30}N_2OPPd$ 643.1131, found 643.1137.

2.9. X-ray crystallography. X-ray data collection of **3a** was performed on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo-Kα radiation (λ□= 0.71073 Å). A single crystal of **3a** was mounted at the end of a quartz fiber in a random orientation, covered with perfluorinated oil and placed under a cold stream of N_2 gas. A hemisphere of data was collected based on ω-scan or ϕ-scan runs. The diffraction frames were integrated using the program CrysAlisRED [34] and the integrated intensities were corrected for absorption with SADABS [35]. The structure was solved and developed by Patterson and Fourier methods [36]. All non-H atoms were refined with anisotropic displacement parameters. The H atoms were placed at idealized positions and treated as riding atoms. Each H atom was assigned an isotropic

displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structure was refined to F_o^2 and all reflections were used in the least-squares calculations [37].

3. Results and Discussion

With notable exceptions [38], the synthesis of bis-cyclopalladated complexes usually involves a transmetallation step of the metallated ligand from highly charged lithium, sodium or magnesium derivatives to an electrophilic palladium center [39]. Due to the easy availability of lithium phosphinimine complex $[Li_2(o\text{-}C_6H_4PPh_2NPh)_2]OEt_2$ (**2**) [30,40], the synthesis of the bis-cyclometallated derivatives **3a-3e** has been perfomed by reaction of (**2**) with the neutral Pd^{II} dimers $[Pd(\mu\text{-}Cl)(C\text{^}N)]_2$ **1a-1e** [C^N = 2-(pyridin-2-yl)phenyl **1a**, 2-((dimethylamino)methyl)phenyl **1b**, (*S)*-2-(1-(dimethylamino)-ethyl)phenyl **1c**, quinolin-8-ylmethyl **1d**, 4-methoxy-2-((triphenyl-λ^5-phosphanylidene)-carbamoyl)phenyl) **1e**] as shown in Scheme 2. In turn, (**2**) was prepared by reaction of Ph_3P=NPh with excess of PhLi (1:1.4 molar ratio) in Et_2O, following reported procedures [30]. Different classical C,N-cyclopalladated ligands have been selected as ancillary groups in the starting materials **1a-1e** to provide a wide array of different electronic and steric environments, from the electron-rich pyridine-containing ligand **1a** to the electron-poor keto-stabilized IM **1e**. In all studied cases the workup of the reaction is very simple, and allows the synthesis of complexes **3a-3e** as air-stable bright yellow solids in moderate yields.



Scheme 2. Synthesis of bis-cyclopalladated complexes **3a-3e**.

The characterization of **3a-3e** has been accomplished through their analytic and spectroscopic data. The elemental analyses and mass spectra (MALDI+) of **3a-3e** are in good agreement with the stoichiometries proposed in Scheme 2. The IR spectra of **3a-3e** show a strong absorption due to the P=N stretch at 1262 (**3a**), 1257 (**3b**), 1274 (**3c**) and 1266 (**3d**) cm^{-1}, respectively. The position of this band is shifted to low energy with respect to that found in the free iminophosphorane Ph_3P=NPh (1310 cm^{-1}), this fact strongly suggesting the N-bonding to the Pd center. In the case of **3e** two absorption bands (1309 and 1284 cm^{-1}) assigned to the two P=N moieties present in the structure are again different from those found the free iminophosphoranes (1330 and 1310 cm^{-1} respectively). Moreover, the IR spectrum of **3e** also shows a strong band at 1590 cm^{-1},

assigned to the carbonyl stretch ν_{CO}, which appears at a wavenumber similar to that found in other keto-stabilized N-bonded IM [17,23].

The $^{31}P\{^{1}H\}$ NMR spectra of **3a**-**3d** show a single peak at δ = 28.70 (**3a**), 29.40 (**3b**), 26.67 (**3c**) and 27.47 (**3d**) ppm, respectively, which is downfield shifted with respect to the free iminophosphorane (δ = 3.00 ppm), in keeping with the N-bonding to the Pd atom. On the other hand, the $^{31}P\{^{1}H\}$ NMR of **3e** showed two signals at δ = 19.66 and 24.18 ppm. The first one is assigned to the keto-stabilized iminophosphorane ligand while the second one is due to the semi-stabilized iminophosphorane. In all studied cases, the presence of a single set of signals shows that **3a**-**3e** have been obtained as single isomers, this meaning that the reaction takes place with full regioselectivity. The position of the ^{31}P peaks for the $C_6H_4PPh_2$=NPh ligand, in the range 24-30 ppm, is another clear indication of the formation of the neutral bis-cyclometallated complexes. In fact, chemical shifts for other published complexes containing only one cyclometallated $C_6H_4PPh_2$=NPh ligand appear in the range 35-55 ppm [15,40], clearly shifted to low field, while chemical shift for the bis-cyclopalladated complex [Pd($C_6H_4PPh_2$=NPh)$_2$] is reported at 27.8 ppm [40]. This fact can be explained taking into account the higher electron-rich nature of the bis-cyclopalladated complex (with two strong σ-C_{aryl} donors) with respect to those having a single cyclopalladated ligand.

The ^{1}H NMR spectra of **3a**-**3e** show the expected signals for the presence of all functional groups. In addition, the presence of the cyclopalladated Pd(C_6H_4) unit is also clearly inferred from the presence of a deshielded doublet around 8.0-8.2 ppm, assigned to the H_6 proton (ortho to the cyclopalladation position), similar to that reported for the complex [Pd($C_6H_4PPh_2$=NPh)$_2$] [40]. The $^{13}C\{^{1}H\}$ NMR spectra of **3a** and **3b** provide further evidences for the presence of the σ-aryl Pd-C bond, due to the observation of a

very deshielded peak at 170.40 ppm (**3a**) or 167.40 ppm (**3b**), respectively, which appear very near to that reported for [Pd($C_6H_4PPh_2$=NPh)$_2$] (171.2 ppm) [40]. Additional structural information can be obtained from the determination of the X-ray crystal structure of complex **3a**. A draw of the bis-orthopalladated complex is shown in Figure 1, as well as selected bond distances and angles.

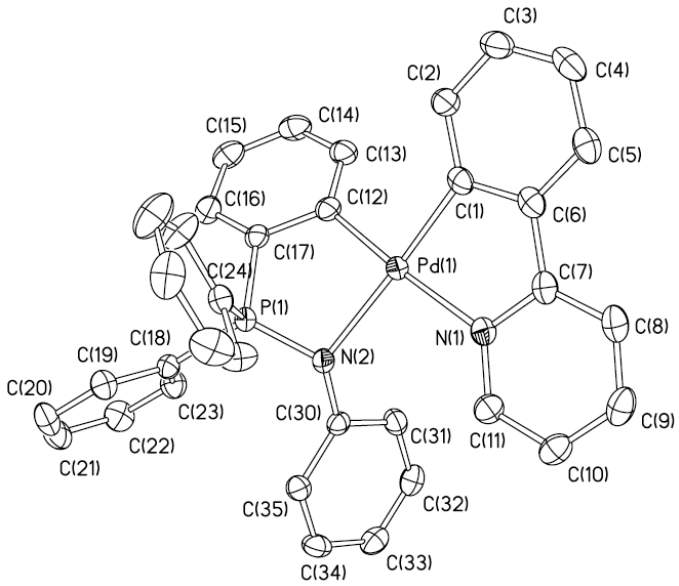


Figure 1. View of complex **3a**. Displacement ellipsoids are scaled to 50% probability level. Selected bond distances (Å) and angles (º): Pd(1)-C(1) = 1.992 (2); Pd(1)-C(12) = 2.003(2); Pd(1)-N(1) = 2.0947(17); Pd(1)-N(2) = 2.1706(17); P(1)-C(17) = 1.785(2); P(1)-N(2) = 1.5963(17); C(1)-C(6) = 1.417(3); C(6)-C(7) = 1.472(3); C(7)-N(1) = 1.356(3); C(12)-C(17) = 1.414(3); C(1)-Pd(1)-C(12) = 96.75(8); C(1)-Pd(1)-N(1) = 81.27 (8); N(1)-Pd(1)-N(2) = 96.68(6); C(12)-Pd(1)-N(2) = 86.21(7); C(1)-Pd(1)-N(2) = 170.48(7); C(12)-Pd(1)-N(1) = 173.82(7); C(6)-C(1)-Pd(1) = 113.61(14); C(1)-C(6)-C(7) = 116.67(18); C(7)-N(1)-Pd(1) = 113.92(13); N(1)-C(7)-C(6) = 114.08(17); N(2)-P(1)-C(17) = 105.95(9).

The Pd atom was located in a slightly distorted square-planar environment, surrounded by the palladated carbon C(1) and the pyridinic nitrogen N(1), derived from the

phenylpyridine ligand, and the metalated carbon C(2) and the phosphinimine nitrogen N(2), from the IM. The slight deviation from the ideal square-planar situation can be deduced from the value of the angle between the best least-square planes defined by N(1)-Pd(1)-C(1) and N(2)-Pd(1)-C(12), which amounts 11.4(2)º. The two Pd-C_{aryl} σ-bonds are in cis(C,C)-arrangement, as it has been found in previous examples [41]. This particular arrangment is easily explained taking into account the antisymbiotic behaviour of the soft Pd(II) center [42,43] and the large trans-influence of the C_{aryl} atoms. In this way, a soft donor (as is the C_{aryl} atom) is more stabilized in trans to a hard donor (in this case the N atom) than in trans to another soft donor [42]. This reasoning has been used in several cases through the bibliography to explain geometrical preferences [43].

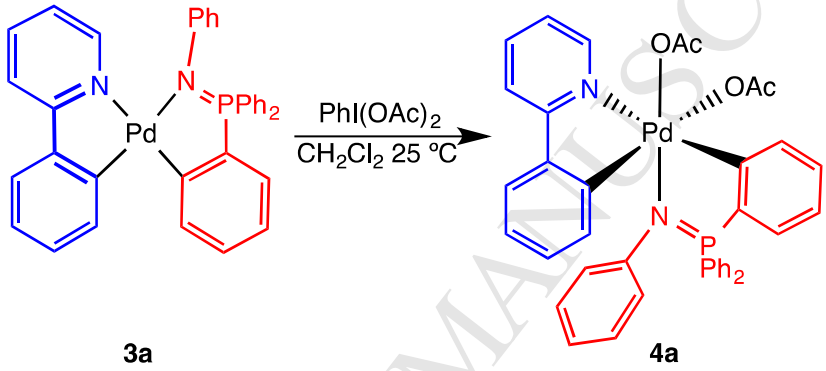
The Pd(1)-C(1) bond distance of the phenylpyridine ligand (1.992(2) Å) is identical, within experimental error, to those found in the dimer $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}NC_5H_4)]_2$ (1.972(5) and 1.978(4) Å, respectively) [44] while the Pd(1)-N(1) bond distance (2.0947(17) Å) is clearly longer than those found in the same dimer [2.005(4) and 2.013(5) Å]. The longer distance of the Pd-N bond in **3a** with respect to $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}NC_5H_4)]_2$ reflects the different influence of the respective trans ligands (C in **3a** versus Cl in the dimer). On the other hand, both the Pd(1)-C(12) (2.003 (2) Å) as well as the Pd(1)-N(2) bond distances (2.1706(17) Å) in the palladated IM are identical, within experimental error, to the respective distances found in the bis-cyclopalladated complex $[Pd(C_6H_4PPh_2{=}NPh)_2]$ [40], probably because the trans environments are similar in both cases (a cyclopalladated ligand). Other internal parameters are as expected, showing values similar to those found in related complexes [40,44] and do not deserve further comment.

Once the synthesis and full characterization of the bis-cyclopalladated complexes **3a-3e** has been accomplished, we have studied their reactivity in different situations in order to promote the C-C coupling of the two palladated ligands. We have first tested the reductive elimination from Pd(II), that is, directly from **3a-3e**, following procedures reported in the literature [45-47]. Thermal treatment of **3a-3e** at reflux temperature in ClC_6H_5 or reaction with CO promoted an unclear decomposition pathway and, although formation of Pd^0 was evident, a very complex mixture of unidentified compounds was obtained. In the case of treatment of **3a-3e** with PPh_3 in MeOH, a clean formation of $Pd(PPh_3)_4$ was observed, but in this case the protonated ligands (Ph_3P=NPh and HC^N) were isolated at the end of the reaction, and the C-C coupling product was not observed. Therefore, even if Pd^0 is detected at the end of the reaction, the expected C-C coupling was not achieved under the studied conditions.

Therefore, we decided to change our strategy, attempting the reactivity of **3a-3e** with oxidants such as $PhI(OAc)_2$. We aimed to promote the oxidation of the square-planar Pd(II) complexes to the respective octahedral Pd(IV) derivatives, which are more prone to undergo the C-C coupling [3h].

The reaction of **3a** with $PhI(OAc)_2$ (1:1 molar ratio) in CD_2Cl_2 was monitored by ^1H and ^{31}P NMR spectroscopy at room temperature. Particularly relevant is the information provided during the reaction by the ^{31}P NMR spectrum, where the disappearance of the peak at 28 ppm (due to **3a**) and the simultaneous grow of another signal at 58 ppm was evident. No other signals were detected in the spectrum, although their existence as low intensity transients cannot be completely excluded. After 1 h of reaction at room temperature, all starting material **3a** was cleanly transformed into a single new species **4a**. The reaction was then scaled up to a 0.3 mmol scale. An equimolar mixture of **3a**

and $PhI(OAc)_2$ was stirred at room temperature for 1 h, then the solvent was partially evaporated and **4a** was precipitated as a yellow solid by Et_2O addition, and recrystallized from CH_2Cl_2/Et_2O. Complex **4a** is stable under Ar at -18 ºC; under these conditions it does not show changes at least in a period of 1 month. The analytical data of **4a** strongly suggest the incorporation of two acetate units to the molecular formula of **3a**. Additional spectroscopic data of **4a** suggest a structure as that depicted in Scheme 3.



Scheme 3. Synthesis and suggested structure of stable Pd(IV) derivative **4a**

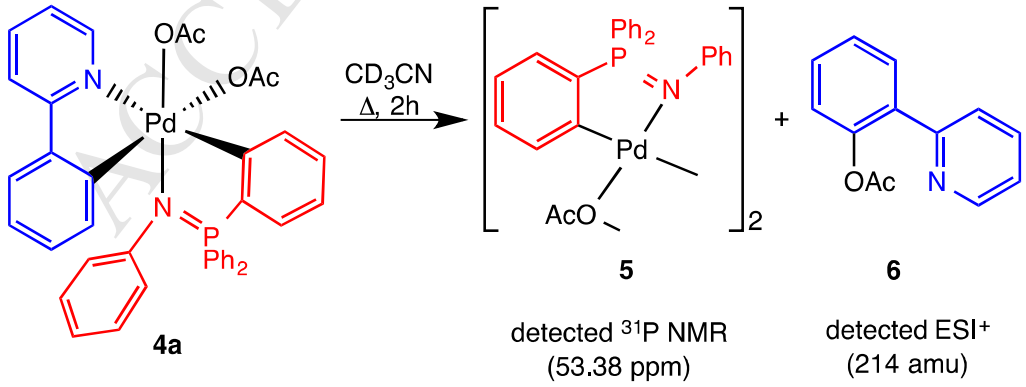
The presence of acetate ligands is clear from the observation of two strong bands in the IR spectrum of **4a** at 1616 and 1357 cm^{-1}, due to the $\nu_a(CO_2^-)$ and $\nu_s(CO_2^-)$ modes, respectively. The separation of these two bands is $\Delta\nu = \nu_a-\nu_s$ = 259 cm^{-1}, this value pointing out to an O-monodentate bonding mode when compared with values reported in the literature (range 228-470 cm^{-1}) for the unidentate coordination [48]. The IR spectrum of **4a** also shows a very strong band at 1295 cm^{-1}, assigned to the $\nu_{(P=N)}$ stretch, which has been shifted to higher energy after oxidation (1262 cm^{-1} in **3a**) indicating a more robust P=N bond in **4a** compared to **3a**.

The ^{31}P NMR spectrum of **4a** shows a single peak at 59.06 ppm, which is downfield shifted with respect to the starting material **3a** (28.70 ppm), in good agreement with the

higher electropositive character of the metal center in **4a** [Pd(IV)] with respect to **3a** [Pd(II)]. It is really worthy of note that, although several isomers are possible for **4a**, only a single set of NMR signals is observed, even at low temperature. At 253 K the molecule behaves as static in the NMR timescale and, therefore, **4a** is obtained as a single isomer. The ^{1}H NMR spectrum of **4a** provides additional structural information. The signal due to $H_{6'}$ proton of the pyridine ring of **4a** appears shifted downfield (8.98 ppm) when compared with **3a** (7.86 ppm). This large shift suggests that the anisotropic shielding undegone by the $H_{6'}$ proton in **3a** due to their close proximity to the phenyl ring of the NPh unit (see Figure 1) is not longer active. The observation of new anisotropic shieldings helps to elucidate the relative disposition of the different groups in the new octahedral structure. Thus, the *ortho* and *meta* protons of the NC_6H_5 ring appear in **4a** strongly shielded (5.65 ppm H_{ortho}, 6.41 ppm H_{meta}) with respect to their respective positions in **3a** (6.88 - 7.04 ppm). Moreover, the $H_{6''}$ proton of the C_6H_4 unit of the phenylpyridine ligand is also suffering a strong shielding in **4a** (6.57 ppm) with respect to its position in the precursor **3a** (overlapped with other signals between 7.50-7.60 ppm). This set of shieldings and deshieldings can be explained assuming a molecular structure for **4a** as that depicted in Scheme 3. If the molecular (equatorial) plane contains the phenylpyridine ligand, one of the acetate ligands and the palladated C atom of the PC_6H_4 moiety, then the axial positions are occupied by the other acetate and by the iminic N atom. In this arrangement the PC_6H_4 ring, which should be normal to the molecular plane, shields the $H_{6''}$ proton of the *cis* C_6H_4 ring which, in turn, shields the *ortho* and *meta* protons of the iminic NPh unit. The relative disposition of the six $C_2N_2O_2$ donor atoms around the Pd atom in **4a** is similar to that displayed in other Pd(IV) compounds characterized by X-ray diffraction methods [12].

Once **4a** has been fully characterized, and prompted by its notable stability, a similar reactivity was attempted with the other derivatives **3b-3e** and $PhI(OAc)_2$. As a first step a similar monitoring of the reactions by ^{1}H and ^{31}P NMR spectroscopy in CD_2Cl_2 was performed. The reaction of **3b** with $PhI(OAc)_2$ is qualitatively much faster than that observed for **3a**, and in few minutes complex **3b** was completely consumed. However, the ^{31}P NMR spectrum only showed a broad resonance near 0 ppm, likely due to the starting material $Ph_3P{=}NPh$ (δ = 3.0 ppm) [49], and two very small peaks around 50 ppm. The latter were probably due to Pd(IV) species analogous of **4a**, but their amount decreases along time and finally vanished, even at low temperature. No definite compound could be isolated from these reaction mixtures. For these reasons and the similarities between **3b** and **3c**, complex **3c** was not studied. The reaction of **3d** with $PhI(OAc)_2$ also took place much faster than observed for **3a**, even at low temperature, and only $[Ph_3PNH_2]^+$ was detected in the ^{31}P NMR spectrum (peak at 36.0 ppm). It is clear that the stability of the presumably formed Pd(IV) intermediates in both cases (**3b**, **3d**) is much lower than for **4a**. It is likely the higher robustness of the phenylpyridine ligand, compared with that of the other classical C,N-orthometalating chelates, the main responsible of the observed behaviour. In this respect, a close inspection of the recent literature dealing with organic synthesis mediated by Pd(IV) complexes shows that most of them use phenylpyridine or analogous rigid-, electron-rich ligands [9-12,50]. Thus, the correct choice of the ancillary ligand is critical in order to prepare, isolate and characterize the Pd(IV) intermediates. However, even being important, it is not the only factor to be taken into account, because the I(III) reagent, the solvent or even the final charge of the complex play a relevant role [51].

As the final step, we have studied the reductive elimination from **4a**. A yellow solution of **4a** in CD_3CN was heated at reflux temperature for 2 h, and a visible change of the color of the solution from bright yellow to orange was observed. The ^{31}P NMR spectrum of this solution shows the presence of a single resonance at 53.38 ppm, showing that only one species containing the IM ligand has been formed. Recent work of Sanford *et al.* reported the reductive elimination of $Pd^{IV}(phpy)_2(OAc)_2$ (phpy = C_6H_4-2-NC_5H_4) affording 2-(2-acetoxyphenyl)pyridine and the dimer $[Pd(\mu\text{-}OAc)(phpy)]_2$ as the only reaction products [12]. The presence of 2-(2-acetoxyphenyl)pyridine **6** in our case is inferred from the observation of a clear peak at 214 amu in the ESI^+ spectrum of the CD_3CN solution. On the other hand, the position of the ^{31}P chemical shift (53.38 ppm) shows that the P-containing species is still palladated, and matches with that reported for the acetate-bridge dimer $[Pd(\mu\text{-}OAc)(C_6H_4PPh_2NC_6H_4Me)]_2$ (53.69 ppm) [52]. Other acetate-bridge dinuclear compounds with minor changes with respect to **5** also appear in the same region [52]. Therefore, on the grounds of the NMR and ESI^+ data, and taking into account the recent results of Sanford, we propose that the reductive elimination of **4a** in CD_3CN takes place affording **5** and **6**, as shown in Scheme 4.



Scheme 4. Reductive elimination of **4a** in CD_3CN to give compounds **5** and **6**.

It is remarkable that, once again, the reaction takes place with full selectivity under the studied conditions. Following the work of Sanford [12], and due to the fact that **4a** contains two different cyclopalladated ligands, one could expect that, after reductive elimination, two different acetate-bridge derivatives, **5** and $[Pd(\mu\text{-}OAc)(phpy)]_2$, could be formed; and that two different C-O couplings and one C-C coupling are also possible in order to obtain organic functionalized products. However, the analysis of the reaction mixtures shows the selective formation of **5** and **6**. Therefore, the study of this system shows that only the C-O coupling in the case of the phenylpyridine ligand is favoured, and that in no case couplings involving the iminophosphorane (neither C-O, nor C-C) were detected. Then, the method seems to be adequate for the functionalization of phenylpyridine, but not for other systems.

4. Conclusions

Bis-aryl Pd(II) complexes containing the metallated iminophosphorane $[C_6H_4PPh_2NPh]$ and another C^N cyclopalladated ligand have been regioselectively synthesized by transmetallation reactions from $[LiC_6H_4PPh_2NPh]_2$. The products were obtained as the cis(C,C)-isomer. The oxidation of the complex $[Pd(phpy)(C_6H_4PPh_2NPh)]$ with $PhI(OAc)_2$ gave the Pd(IV) derivative $[Pd(OAc)_2(phpy)(C_6H_4PPh_2NPh)]$ also as a single stereoisomer, which could be isolated as a stable complex. The oxidation of other examples didn't allow the isolation of stable Pd(IV) complexes. The reductive elimination processes observed on $[Pd(OAc)_2(phpy)(C_6H_4PPh_2NPh)]$ gave in a selective way the acetoxylated phenylpyridine by C-O coupling, while the iminophosphorane remains palladated.

Acknowledgments

Financial support from the Spanish Ministerio de Economía y Competitividad (MINECO) under project CTQ2011-22589 and the Regional Government of Aragón under project E-97 is gratefully acknowledged. P. V. thanks CSIC for a Juan de la Cierva contract.

Appendix A. Supplementary data

CCDC-983329 (**3a**) contains 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.

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