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# Synthesis and characterization of novel five-membered palladacycles

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Dedicated to Professor Jose Jesus Vicente Soler on the occasion of his 66th birthday.

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ABSTRACT

3-(2-Chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxy-phenyl)-pentane-2,4-dione derivatives **3a–b** were conveniently synthesized in excellent yields (82% each) by tandem Knoevenagel condensation reactions of 2-chloro-3-carbaldehyde-quinoline **1a–b** with 3,4,5-trimethoxy acetophenone, followed by a base catalyzed Michael addition, such as DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) with or without solvent. The reactions of **3a–b** with $Pd(dba)_2$ in the presence of $PPh_3$ (1:2) in degassed acetone provided the dinuclear palladium complexes $\{Pd(C,N\text{-}2\text{-}C_9H_4N\text{–}CH\text{–}[\text{–}CH_2CO(3,4,5\text{-}(OMe\text{-})_3\text{–}C_6H_2\text{-}]_2\text{–}3\text{-}R\text{-}6)Cl(PPh_3)\}_2$ [(R = H (**4a**), R = OMe (**4b**)] in moderate yields (38% and 43%), which in turn reacted with an excess of isonitrile XyNC (Xy = 2,6-$Me_2C_6H_3$) to give the corresponding palladacycles **5a–b** in moderate yields (45% and 43%). The palladacycles **5a–b** were also obtained in similar yields (32% and 33%) via a one-pot oxidative addition reaction of **3a-b** with isonitrile XyNC:$Pd(dba)_2$ (4:1). The products were characterized by satisfactory elemental analysis and spectral studies (IR, $^1H$, and $^{31}P$ NMR). The crystal structure of **5a** was determined by X-ray crystallography diffraction studies.



## 1. Introduction

In an earlier paper, we reported on aryl palladium complexes that are of interest as intermediates in important catalytic organic syntheses [1–3]. Some of the catalytic reactions involve *ortho*-functionalized aryl palladium(II) complexes, giving carbo- or heterocycles in which the *ortho* group is not included. A few examples of insertion of isocyanides into *ortho*-functionalized aryl palladium(II) complexes leading to heterocyclic compounds have been reported [3–14]. Thus we have prepared the dinuclear palladium(II) complexes $\{Pd[C_9H_5\text{–}CH\text{–}[\text{–}CH_2CO\text{–}C_6H_2\text{–}(OCH_3)_3]_2\text{–}(3,4,5)]Cl(PPh_3)\}_2$ **4a** and $\{Pd[6\text{-}CH_3O\text{–}C_9H_4\text{–}CH\text{–}[\text{–}CH_2CO\text{–}C_6H_2\text{–}(OCH_3)_3]_2\text{–}(3,4,5)]Cl(PPh_3)\}_2$ **4b** by reacting the prepared compounds 3-(2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)pentane-1,5-dione **3a** and 3-(6-methoxy-2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)pentane-1,5-dione **3b** with $Pd(dba)_2$, in the presence of $PPh_3$ (1:2). In this contribution we present the synthesis and characterization of novel mono- and dimeric palladacycles as well as their utility as precursors for the synthesis of valuable organic products as the most outstanding points. The sequence of the reactions led eventually to compounds that could potentially possess pharmacological properties [3]. The preparation of all the complexes were in one solvent (degassed acetone). The crystal structure of complex **5a** shows some interesting features.

## 2. Results and discussion

To investigate the role of the catalyst and the effect of grinding, first the reaction of 2-chloro-3-carbaldehyde-6-R-quinolines [R = H (**1a**), R = OMe (**1b**)], acetophenone and a catalytic amount of DBU were ground together in a pestle and mortar at room temperature. The reaction started immediately, usually with gentle heat production, with the reaction mixture turning into a brownish viscous liquid, then to a thick brownish mass and finally to a free flowing powder. Surprisingly, the reaction mixture turned into the desired product within a short period of time. When DBU was used as a catalyst in ethanol, stirring for 3 h at room temperature, the reaction proceeded smoothly to afford (2Z)-3-(2-chloroquinolin-3-yl)-1-(phenyl) prop-2-en-1-one in 65% yield [2]. The same result was obtained without solvent after stirring for 3 h. Other solvents such as chloroform, dichloromethane and methanol gave (2Z)-3-(2-chloroquinolin-3-yl)-1-(phenyl) prop-2-en-1-one with the same yield [2].

On the other hand, indication of softening for some seconds followed by immediate hardening were visually observed only in the syntheses with 2-chloro-3-carbaldehyde-6-methoxy-quinolines (**1b**) with 3,4,5-trimethoxy acetophenone. Subsequently, the scope of the Knoevenagel condensation of aldehydes with various active methylene compounds catalyzed by DBU in grinding was investigated. We found that the Knoevenagel condensation of aldehydes with 3,4,5-trimethoxy acetophenones occurred easily in the presence of grinding to form the corresponding products. Both electron-rich and electron-deficient aldehydes worked well to give the corresponding arylidene derivatives (2E)-3-(2-chloro-R-quinolin-3-yl)-1-(3,4,5-trimethoxyphenyl) prop-2-en-1-one [R = H (**2a**),

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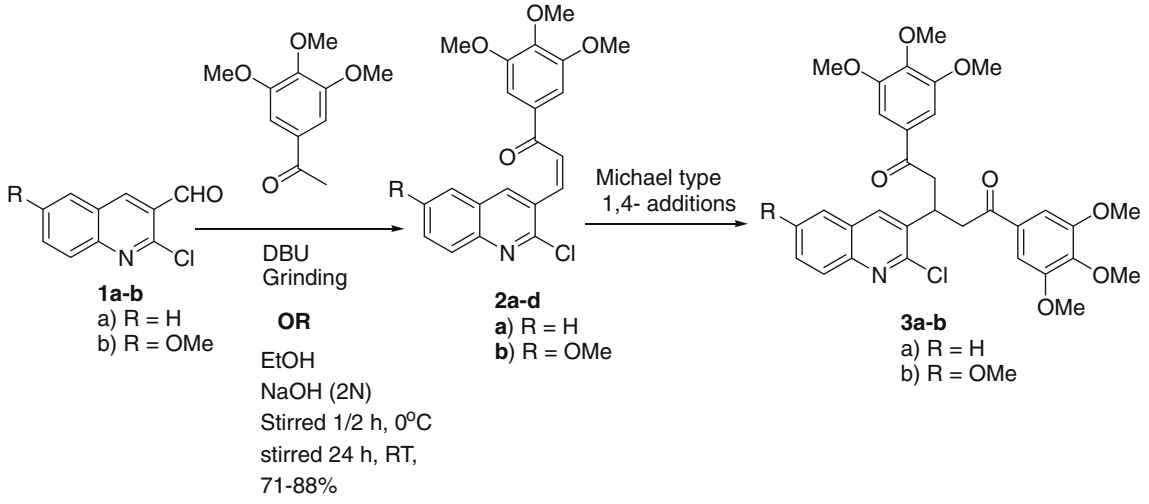
R = OMe, (**2b**)] in excellent yields (72–74%) [2]. Miscibility of DBU with water makes the workup process quite easy as the catalyst can be easily removed from product simply by washing the product with water.

The Knoevenagel condensation [15] reactions have been extensively studied as an example of important carbon–carbon bond formation. In this condensation reaction various catalysts are used, such as ($Te(IV)Cl_4$) [16], ($ZnCl_2$) [17] and ($KF\text{-}Al_2O_3$) [18]. DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) has been widely used as a catalyst in many reactions followed by Michael addition [19–21]. Thus the sequential condensation reactions are achieved in one pot by the reaction of aldehydes **1a–b** with the active methylene compound 3,4,5-trimethoxy acetophenone in the presence of DBU as a base catalyst, to afford arylidene derivatives, followed by Michael addition to give $\delta$ diketones **3a–b** in good yields of 47–75% (Scheme 1).

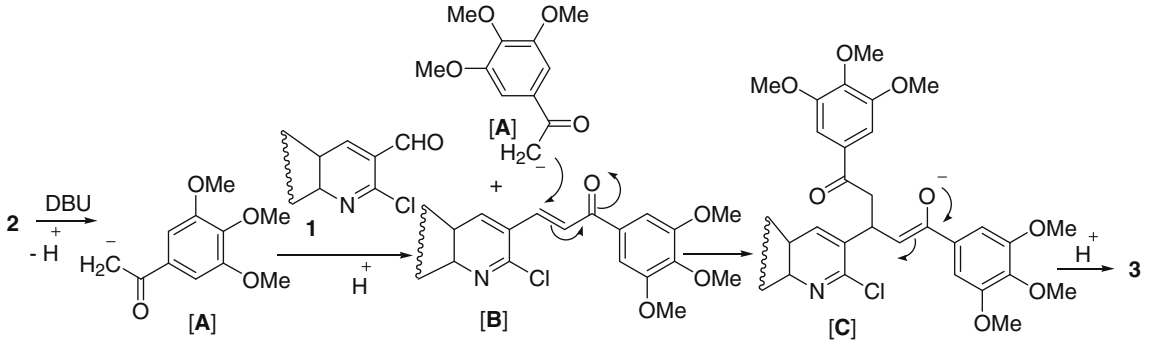
The possible mechanism that could account for the formation of $\delta$ diketones **3a–b** in these reactions of excess 3,4,5-trimethoxy acetophenone with aromatic aldehydes **1** is as follows. First **1** is dehydrated on heating in the basic reaction medium to furnish the highly electrophilic intermediate and thus yielding the corresponding air stable $\alpha,\beta$-unsaturated quinoline [**B**]. The quinoline intermediate [**B**] then undergoes competitive Michael addition by the preformed carbanion [**A**]. The Michael type addition of the enone proceeds in a 1,4-fashion and results in an intermolecular addition to give [**C**], which on hydrolysis during the reaction at reflux temperature under the action of a trace amount of water in the reaction mixture, or during workup on a silica gel column (see Section 3), affords the final product alkane–dione **3a–b**. This mechanism, as outlined in Scheme 2, is consistent with the mechanism described as straight forward by Xu and co-workers [22].

Oxidative addition reactions of 3-(6-R-2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)pentane-1,5-dione [R = H (**3a**), R = OMe (**3b**)] toward a stoichiometric amount of [$Pd(dba)_2$] (=[$Pd_2(dba)_3$].dba; dba = dibenzylideneacetone) [3,23,24] in the presence of a neutral ligand such as $PPh_3$ (1:2:1) under nitrogen in degassed acetone gave the dimeric palladium complexes $Pd[C_9H_5\text{–}CH\text{–}[\text{–}CH_2CO\text{–}C_6H_2\text{–}(OCH_3)_3]_2\text{–}(3,4,5)]Cl(PPh_3)\}_2$ **4a** and $\{Pd[6\text{-}CH_3O\text{–}C_9H_4\text{–}CH\text{–}[\text{–}CH_2CO\text{–}C_6H_2\text{–}(OCH_3)_3]_2\text{–}(3,4,5)]Cl(PPh_3)\}_2$ **4b** in moderate yields (38% and 43%), through the coordination of the quinolinyl nitrogen. Subsequently, the insertion reaction of 2,6-dimethylphenyl isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$) into dinuclear complexes in $CH_2Cl_2$ at room temperature eventually forms the mononuclear five-membered palladacycle complexes **5a–b** in moderate yields (32% and 45%). These five-membered palladacycles **5a–b** are also obtained in similar yields (33% and 43%) by the direct oxidative addition of 3-(6-R-2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)pentane-1,5-dione [R = H (**3a**), R = OMe (**3b**)] with $Pd(dba)_2$ in the presence of a stoichiometric amount of isonitrile XyNC in $CH_2Cl_2$ at room temperature, as depicted in Scheme 3.

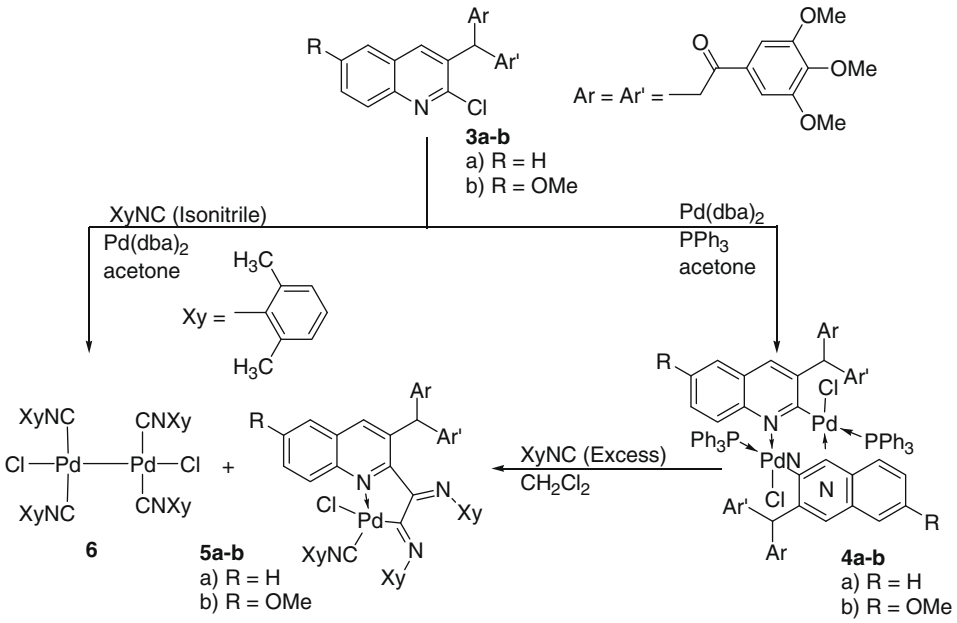
The intermediate species formed in the oxidative addition reaction of **3a–b** with $Pd(dba)_2/PPh_3$ to give **4a–b** follow a very similar pathway as previously described for related quinoline containing palladacycles [3,25], and the structure of the dinuclear complex obtained from the reaction of $Pd(PPh_3)_4$ and 2-bromopyridine,




**Scheme 1.**




**Scheme 2.**




**Scheme 3.**

determined by X-ray analysis, was shown to be *trans*(*P*,*N*)-bis-[bromo(μ-pyridyl-$C^2$,*N*)(triphenylphosphine)palladium(II)], having an approximate symmetry of $C_2$ [26,27].

As far as we are aware, this is the first time these 3-substituted dinuclear palladium complexes **4a–b** and five-membered palladacycles **5a–b** have been synthesized. These complexes were confirmed by the appearance of one singlet signal in their $^{31}P$ NMR spectra. The reaction products were identified by comparison of the $^{31}P$ NMR spectra of the reaction mixture with those of related reported complexes, which showed two AB resonance patterns in the case of R = H (**4a**) and R = OMe (**4b**) at $\delta$ 29.72 and 29.73 ppm. The $^1H$ NMR spectra did not show the presence of impurities for either of complexes **4a** or **4b**, although the quinoline backbone shows slight variations when complexes **4a** or **4b** are compared. However, we feel that not enough was known about the palladium–carbon bonding of these complexes, through 4 bonds.

This promoted us to place an emphasis on these data. While this observation can be rationalized for **4a–b**, we were surprised that the cyclopalladated product showed almost no change in view of the angular distortion involved in forming the five-membered palladacycles. The IR (Nujol, $cm^{-1}$) bands were assignable to $\nu$(C=O), $\nu$(C=N) $\nu$(C=C) modes in **4a–b**, and indicated the non-coordination of the carbonyl group in these complexes. In complex **4a**, IR bands appear at 1672, 1618, 1581 $cm^{-1}$ and for **4b** these bands appear in at slightly higher values at 1673, 1620, 1582 $cm^{-1}$, respectively. Complexes **4a–b** show the strongest band in the IR spectrum at ca. 1672 and 1673 $cm^{-1}$, assignable to $\nu$(C=O) of two ketonic groups. These frequencies are similar to that observed in the starting materials **2a–b** or **3a–b**, indicating that there is no coordination of the ketonic group to the metal atom.

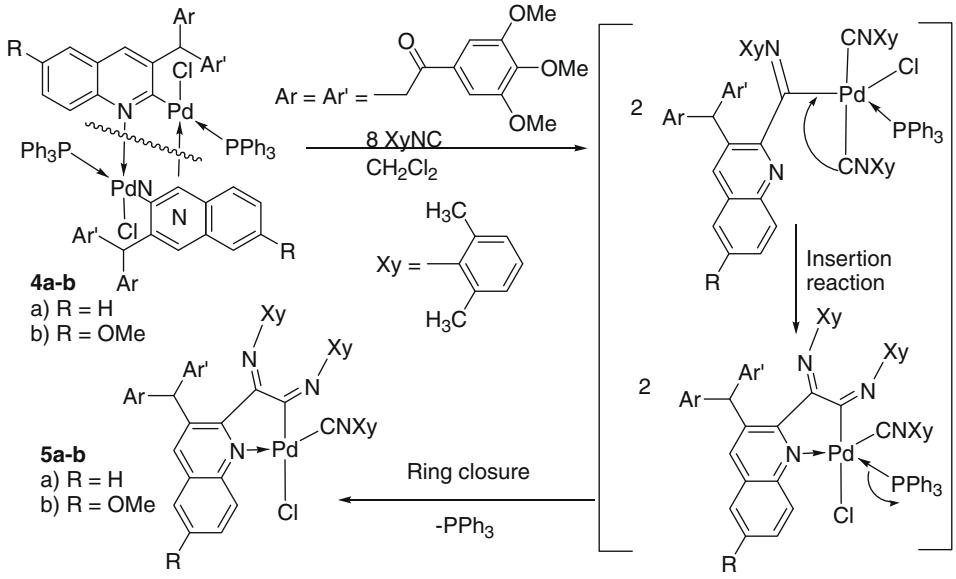
### *2.1. Reactions with XyNC (Xy = 2,6-$Me_2C_6H_3$)*

#### *2.1.1. Reaction of the chloro-quinoline derivatives **3a–b** with XyNC*

Isocyanides behave in many respects like CO and can exhibit terminal or bridging coordination modes. The oxidative addition of 3-(6-R-2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)-pentane-1,5-dione R = H (**3a**), R = OMe (**3b**) (1.5 molar ratio) to a mixture of $Pd(dba)_2$ and 2,6-dimethylphenyl isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$) in a 1:4 molar ratio in degassed acetone at RT, yielded the di-inserted iminoacyl palladium complexes **5a–b** in low yields (32%, 33%), and not the tri-inserted one due to the steric hindrance of the branched side chain. Instead of the required 4:1.5:1 molar ratios of reagents XyNC:**3a–b**:$Pd(dba)_2$ for the formation of **5a** and **5b**, 1:1.5:1 and 1:1:1 stoichiometric amounts of these mixtures were used for both **5a** and **5b**, but unfortunately it was not possible to isolate the inserted products. A mechanistic proposal depicts the formation of possible intermediates and products consistent with literature data [3,28].

#### *2.1.2. Reaction of [$Pd_2$(quinoline-Cl)$_2$($PPh_3$)$_2$] **4a–b** with XyNC*

In order to study the possible aggregation to high nuclearity clusters, the reactions between the dinuclear **4a–b** and XyNC were studied. The reactivity of the dinuclear palladium complexes **4a–b** towards the bulky isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$) depends on the nature of the ligands and on the reaction conditions. Thus when the insertion reaction takes place in different molar ratios of XyNC to complex, the inserted complexes obtained are the result of a di-insertion processes. The mono-insertion of XyNC at 1:1 or 1:2 molar ratios were not isolated. The reaction of the dinuclear palladium complexes **4a–b** with 8 equiv. of XyNC at room temperature with a longer reaction time (24 h) provided the inserted products of the palladacycles **5a–b**. Instead of the required 8:1 equivalents of XyNC:**3a–b**, stoichiometric amounts of 1:1, 2:1, 3:1, 4:1, 5:1 6:1 and 7:1 were used, but it was not possible to isolate complexes **5a–b** in the case of the 1:1, 2:1, 3:1, 4:1 and 5:1 molar ratios. The inserted products are formed by the insertion of XyNC into the Pd–C bond and the displacement of $PPh_3$ by the XyNC ligand. These kinds of complexes are very poorly represented in the literature, the only examples being those recently prepared by Vicente et al. [28], and suggest that the presence of $PPh_3$ during the insertion of XyNC into the dinuclear palladium complexes **4a–b** could be responsible for the change in reactivity of the intermediate complexes. It is possible that free $PPh_3$ coordinates in the intermediate complexes, forcing the insertion of the two isocyanide ligands. A mechanistic scheme depicting the formation of the various products, including possible intermediates consistent with literature data [3,28], is given in Scheme 4.




**Scheme 4.**

Complex **5a** was characterized by $^1$H NMR spectroscopy and single-crystal X-ray diffraction studies. The $^1$H NMR spectra of complexes **5a** and **5b** show three singlets, each corresponding to a methyl group, two signals integrated to the four methyl groups of the inserted Xy–N=C– indicate a *cis* geometry and no free rotation of the Xy groups. Another one singlet signals integrates to two methyl groups of equivalently coordinated isocyanide ligands. This suggests a steric hindrance to rotation of two of the xylyl groups, while the other three rotate freely. Thus the $^1$H NMR spectrum of this reaction mixture in $CDCl_3$ was recorded and was found to contain three resonances at $\delta$ 2.18, 2.08 and 1.53 ppm. These peaks are assigned to the methyl protons adjacent to the phenyl ring on each of the three different xylyl groups. The IR spectra (Nujol, $cm^{-1}$) contain bands assignable to $\nu$(C≡N), $\nu$(C=O) and $\nu$(C=N) for **5a** and **5b**, with no significances difference. In the case of **5a** the bands appear at $\nu$(C≡N) 2184, $\nu$(C=O) 1702 and $\nu$(C=N) 1640 $cm^{-1}$, but in the case of **5b** several bands appear in the $\nu$(C≡N) 2184, $\nu$(C=O) 1710 and $\nu$(C=N) 1610 $cm^{-1}$ region, which are probably attributable to a solid state effect. This suggests little or no change in the carbonyl stretching frequency due to complexation.

In addition, the transformation of **4a–b** into **5a–b** could be achieved by reaction with an excess of XyNC. The Pd(I) dimer of $[Pd_2Cl_2(XyNC)_4]$ **6** was obtained at room temperature after a long reaction time. In the first case, the mixture decomposed to an ill-defined mixture, while in the second, the palladium (I) complex $[Pd_2Cl_2(XyNC)_4]$ **6** is formed.

*2.1.3. Preparation of $[Pd_2Cl_2(XyNC)_4]$ (**6**)*

In addition, the transformation of $[Pd_2(Q\text{-}Cl)_2(PPh_3)_2]$ **4a–b** into **5a–b** can be achieved by reaction with XyNC in a 1:4 molar ratio in $CH_2Cl_2$, following the reported procedure [30]. **5a–b** Could also be prepared by oxidative addition of the corresponding 3-(6-R-2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)pentane-1,5-dione [R = H (**3a**), R = OMe (**3b**)] to "$Pd(dba)_2$" in the presence of XyNC in acetone. In the first case, the mixture decomposed to an ill-defined mixture, while in the second, the palladium (I) complex $[Pd_2Cl_2(CNXy)_4]$ (**6**) formed in a yield of 58%. This complex has recently been prepared by reacting $[Pd_2(\acute{\imath}\text{-}Br)_2(tBu_3P)_2]$ with XyNC [29]. Our one-pot synthesis of complex **6** from "$Pd(dba)_2$" and **3a–b** is simpler and gives a similar yield. When a solution of $[Pd_2(Q\text{-}Cl)_2(PPh_3)_2]$ in $CH_2Cl_2$ was treated with eight equivalents of XyNC, an immediate change of color from green to orange was observed. The reaction was stirred for 2 hr and the $^{31}$P–{$^1$H} NMR spectrum was measured. The $^{31}$P–{$^1$H} NMR spectrum showed only one signal (chemical shift for the free phosphines) suggesting that all the phosphines had been replaced by the XyNC groups. Hexane was added to the reaction mixture and a dark yellow crystalline solid precipitated. On the basis of the IR spectrum and elemental analyses, the product obtained was formulated as $[Pd_2Cl_2(XyNC)_4]$. This type of compound has been previously reported by Yamamoto and Arima [31], and Balch and co-workers [32]. The structure of the Pd(I) dimer **6** is similar to that of the few crystal structures reported of related complexes, $[Pd_2(CNBu^t)_4Cl_2]$ contains two directly bonded Pd atoms, each having two coordinated isocyanides in trans positions and a chloro ligand in the axial position [33,34]. A different behavior was observed in the case of the **4a–b**, as their reaction with XyNC (1:8 molar ratios) in $CH_2Cl_2$ gave intractable mixtures. Workup of the mother liquors rendered a mixture for which $^1$H NMR spectra showed the presence of the Pd(I) dimer **6**. During attempts at chromatographic separation, the fraction at $R_f$ = 0.4 was collected and extracted with acetone to give a solution which was evaporated to dryness.

*2.1.4. X-ray crystal structure of {PdCl(2)–(C=N–Xy)$_2$–(CN–Xy)–$C_9H_5N$-(3)-CH)[$CH_2COC_6H_2$–3,4,5-$(OCH_3)_3$]$_2$} (**5a**)*

To further confirm the structure of the product, the molecular structure of red crystals of **5a**. $CH_2Cl_2$ (Fig. 1) was determined by X-ray analysis. The Pd–C bond distances of the iminoacyl ligands decrease, in agreement with the electron delocalization influence of the extended of electron donating group (3OMe), in complex **5a** in agreement with the *trans* influence of the ligands, thus these values are (in Å) Pd(1)–C(12) = 1.936(3), Pd–C(11) = 1.980(3). The Pd(1)–Cl(1) distance is 2.4317(8) Å. Similarly, the Pd–N bond distance in complex **5a** was compared, Pd(1)–N(1) 2.101(2) Å, showing a greater *trans* influence of the chloro ligand with respect to the carbon-donor iminoacyl ligand. Looking at these scales, our proposal that *transphobia* could be directly related to the *trans* influence is reinforced [35] under this assumption; two ligands with a great *trans* influence will suffer a great *transphobia* [36]. The [Pd]–C=N–Xy bond distance of the iminoacyl ligands in complex **5a** is N(2)–C(10) 1.267(4) Å, and N(3)–C(11) 1.257(4) Å for the C=N distances corresponding to the inserted molecule of XyN=C

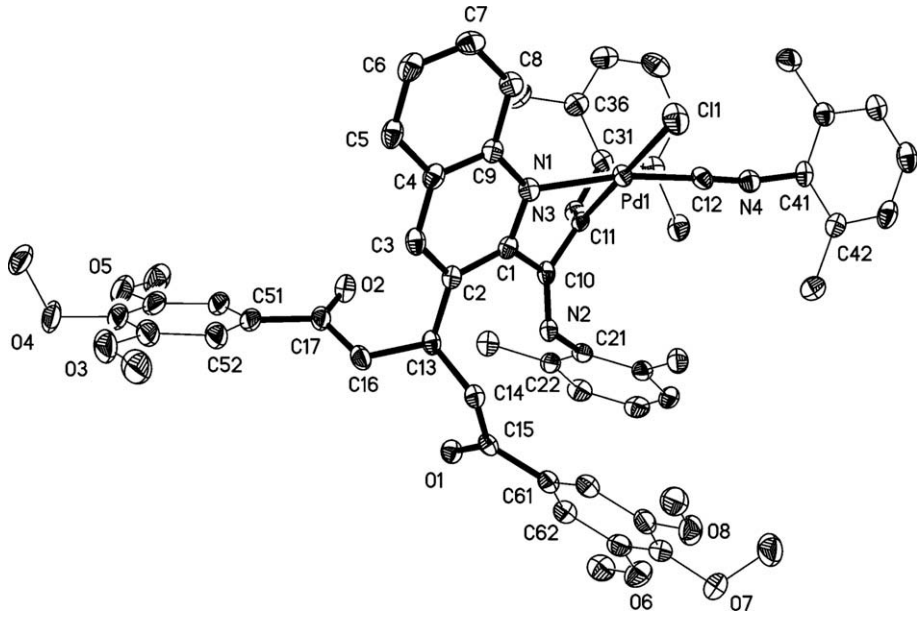



**Fig. 1.** Thermal ellipsoid plot (50% probability level and solvent omitted) of **5a**. Hydrogen atoms attached to N(20) have been displayed for clarity. Selected bond lengths (Å) and angles (deg): Pd–C(12) = 1.936(3), Pd–C(11) = 1.980(3), Pd–N(1) = 2.101(2), Pd–Cl(1) = 2.4317(8), N(1)–C(1) = 1.338(4), N(1)–C(9) = 1.384(3), N(3)–C(11) = 1.257(4), N(3)–C(31) = 1.430(4), N(2)–C(10) = 1.267(4), N(2)–C(21) = 1.432(3), N(4)–C(12) = 1.158(4), N(4)–C(41) = 1.402(4), C(11)–C(10) = 1.508(4), C(10)–C(1) = 1.499(4), C(12)–Pd–C(11) = 92.45(11), C(12)–Pd–N(1) = 168.24(10), C(12)–Pd–Cl(1) = 89.77(8), C(11)–Pd–N(1) = 76.86(10), C(11)–Pd–Cl(1) = 176.63(8), N(1)–Pd–Cl(1) = 100.70(6), C(1)–N(1)–C(9) = 119.8(2), C(1)–N(1)–Pd = 110.71(18), C(9)–N(1)–Pd = 128.70(19), C(11)–N(3)–C(31) = 119.7(2), C(10)–N(2)–C(21) = 123.0(2), C(12)–N(4)–C(41) = 170.1(3), N(1)–C(1)–C(2) = 123.6(2), N(1)–C(1)–C(10) = 111.3(2), C(2)–C(1)–C(10) = 124.8(2), N(3)–C(11)–C(10) = 123.1(2), N(3)–C(11)–Pd = 133.5(2), C(10)–C(11)–Pd = 102.93(17), N(2)–C(10)–C(1) = 122.0(3), C(1)–C(10)–C(11) = 109.8(2), N(2)–C(10)–C(11) = 128.1(2), C(10)–C(1)–C(2) = 124.8(2), N(4)–C(12)–Pd = 177.1(3).

and N(4)–C(12) 1.158(42) Å for the C═N distances corresponding to the inserted molecule of XyNC. All these lengths are as expected for a C═N bond [the mean value for C(aryl)–C═N–R distances is 1.432–1.382 Å] [34–37]. The (aryl)-C═N(–Xy)[Pd] distances corresponding to the second inserted molecule of XyNC in complex **5a** is significantly lower than the other distances, N(2)–C(10) 1.267(4) Å and N(1)–C(1) 1.338(4) Å, as a result of coordination of the nitrogen atom to Pd(II). This fact, and the angles around Pd, C(12)–Pd–C(11) 92.45(11), C(12)–Pd–N(1) 168.24(10), C(11)–Pd–N(1) 76.86(10), C(12)–Pd–Cl(1) 89.77(8), C(11)–Pd–Cl(1)176.63(8) and N(1)–Pd–Cl(1) 100.70(6)°, and the short C(1)–C(10) bond of 1.499(4) Å compared with C(10)–C(11) of 1.508(4) Å, suggest a delocalization of π electron density as compared to the N(2)–C(10)–C(1) angle of 122.0(3)°, and N(2)–C(10)–C(11) angle of 128.1(2)°. This points to a delocalization of π electron density around C(10), the atoms being almost square planar. Crystals suitable for X-ray diffraction of compound **5a**, light red in color and air stable, were obtained by slow evaporation from a $CH_2Cl_2$/ether solution; Diffraction-quality crystals were grown by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of **5a**. The structure is shown in Fig. 2 and reveals chains of molecules connected by hydrogen bonds. Data were collected on an automatic diffractometer using the parameters listed in Table 1.

## 3. Experimental

Reactions were carried out without precautions to exclude light, atmospheric oxygen or moisture, unless otherwise stated. Melting points were determined on a Reicher apparatus and are uncorrected. Elemental analyses were carried out with a Carlo Erba 1106 micro-analyzer. IR spectra were recorded on a Perkin–Elmer 16F P CFT-IR spectrometer with Nujol mulls between polyethylene sheets or KBr pellets. NMR spectra were recorded in a Bruker AC 200, Avance 300 or a Varian Unity 300 spectrometer at room temperature unless otherwise stated. Chemical shifts were referenced to TMS ($^1H$ and $^{13}C$) and $H_3PO_4$ ($^{31}P$). The NMR probe temperature was calibrated using ethylene glycol $^1H$ NMR standard methods. Chromatographic separations were carried out by TLC on silica gel (70–230 mesh).

### 3.1. General method for the synthesis of (2E)-3-(2-chloro-6-R-quinolin-3-yl)-1-(3,4,5-trimethoxyphenyl) prop-2-en-1-one (R = H, (2a), R = OMe, (**2b**))

To a mixture of acetophenone (0.005 mol) and the appropriate aromatic aldehydes (0.005 mol) in oxygen-free ethanol (25 $cm^3$) was added a solution of sodium hydroxide (2 N, 25 $cm^3$) in oxygen-free distilled water with constant shaking of the reaction flask. The reaction mixture was stirred for a specified period with a magnetic stirrer and poured onto crushed ice. The solid mass which separated out was filtered, washed with water and crystallized from a suitable solvent to give the desired product. Purification by chromatography was performed with silica gel.

#### 3.1.1. Compound (**2a**)

This was purified by column chromatography, Silica gel (hexane: $Et_2O$ 2:8) at $R_f$ = 0.56 to isolate a yellow solid of **2a**, yield, 1.6 g, 74%. M.p.: 148–150 °C. IR (Nujol, $cm^{-1}$): ν(C═O) 1664, ν(C═N) 1646, 1580. $^1H$ NMR (300 MHz, $CDCl_3$) (δ ppm): 8.16 (s, 1H, quin-H4), 8.11 (d, 1H, $^3J_{HH}$ = 15.6 Hz, CH═CHCO), 8.06 (d, 1H, $^3J_{HH}$ = 9.2 Hz, quin-H8), 7.49 (d, 1H, $^3J_{HH}$ = 15.8 Hz, CH═CHCO), 7.42 (dd, 2H, $^4J_{HH}$ = 9.2 Hz and $^4J_{HH}$ = 2.6 Hz quin-H5, H7), 7.30 (s, 2H, Ar–H2), 7.14 (dd, 1H, $^4J_{HH}$ = 9.2 and 2.6 Hz quin-H6), 3.92 (s, 6H, 2 OMe), 3.90 (s, 3H, OMe). *Anal.* Calc. for $C_{21}H_{18}ClNO_4$ (383.8): C, 65.71; H, 4.73; N, 3.65. Found: C, 65.67; H, 4.47; N, 3.41%.

#### 3.1.2. Compound (**2b**)

This was purified by column chromatography, silica gel (hexane: $Et_2O$ 2:8) at $R_f$ = 0.59, to isolate a yellow solid of **2b**, yield,

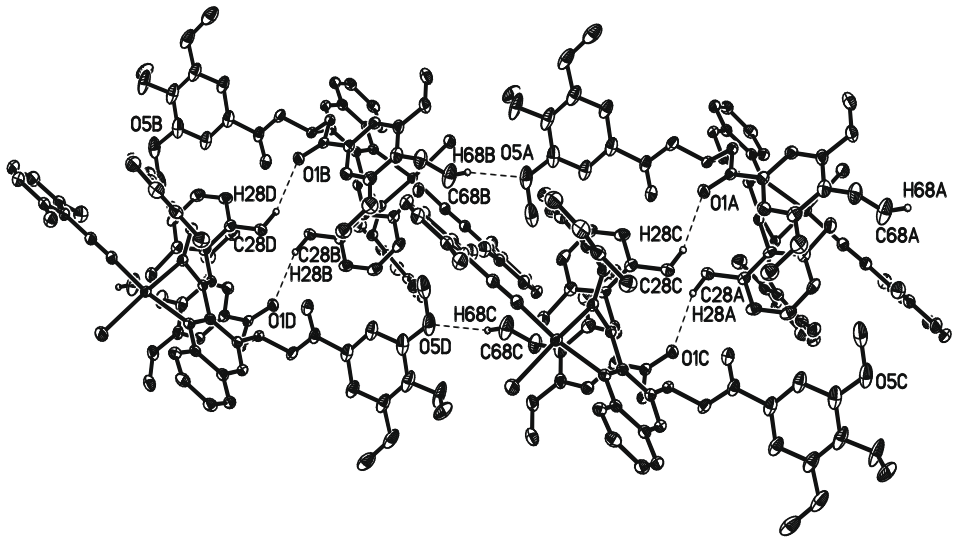



**Fig. 2.** Packing diagram of X-ray crystallographic structure of **5a**, showing chains of molecules connected by hydrogen bonds (dashed lines). Only H atoms involved in hydrogen bonds of $H_{68B}$ with $O_5$ and $H_{28A}$ with $O_1$ together with their neighbors are included in Table 2. View direction perpendicular to the *xy*-plane.

0.8 g, 72%. M.p.: 196–198 °C. IR (Nujol, $cm^{-1}$): $\nu$(C=O) 1664, $\nu$(C=N) 1646, 1580.$^1$H NMR (300 MHz, $CDCl_3$) ($\delta$ ppm): 8.37 (s, 1H, quin-H4), 8.15 (d, 1H, $^3J_{HH}$ = 15.6 Hz, CH=CHCO), 7.93 (d, 1H $^4J_{HH}$ = 9.2 Hz, quin-H8), 7.49 (d, 1H, $^3J_{HH}$ = 15.8 Hz, CH=CHCO), 7.42 (dd, 1H, $^4J_{HH}$ = 9.2 Hz and 2.8 Hz quin-H7), 7.30 (s, 2H, Ar–H), 7.14 (d, 1H, $^4J_{HH}$ = 2.8 Hz quin-H5), 3.96 (s, 6H, 2 OMe), 3.95 (s, 3H, OMe), 3.90 (s, 3H, OMe). *Anal.* Calc. for $C_{22}H_{20}ClNO_5$ (413.9): C, 63.85; H, 4.87; N, 3.38. Found: C, 63.65; H, 4.86; N, 3.35%.

**Table 1**
Crystal data and structure refinement of complex **5a**.

| | |
|---|---|
| Identification code | **5a** |
| Empirical formula | $C_{59}H_{59}ClN_4O_8Pd$ |
| Formula weight | 1093.95 |
| $T$ (K) | 100(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | triclinic |
| Crystal habit | red tablet |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | |
| $a$ (Å) | 11.1555(7) |
| $b$ (Å) | 14.8389(10) |
| $c$ (Å) | 16.7839(11) |
| $\alpha$ (°) | 105.8520(10) |
| $\beta$ (°) | 100.1800(10) |
| $\gamma$ (°) | 96.8170(10) |
| $V$ (Å$^3$) | 2589.4(3) |
| $Z$ | 2 |
| Density (calculated) (Mg/m$^3$) | 1.403 |
| Absorption coefficient ($mm^{-1}$) | 0.471 |
| $F$(0 0 0) | 1136 |
| Crystal size (mm$^3$) | 0.28 × 0.13 × 0.10 |
| $\theta$ Range for data collection (°) | 1.63 to 27.10 |
| Index ranges | $-14 \leqslant h \leqslant 14$, $-18 \leqslant k \leqslant 19$, $-21 \leqslant l \leqslant 21$ |
| Reflections collected | 29 264 |
| Independent reflections | 11 163 [$R_{int}$ = 0.0331] |
| Completeness to theta = 26.00° | 99.4% |
| Absorption correction | semi-empirical from equivalents |
| Max. and min. transmission | 0.9545 and 0.8795 |
| Refinement method | full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 11 163/52/670 |
| Goodness-of-fit on $F^2$ | 1.076 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0493, $wR_2$ = 0.1154 |
| $R$ indices (all data) | $R_1$ = 0.0593, $wR_2$ = 0.1197 |
| Largest difference in peak and hole (e Å$^3$) | 1.941 and −0.781 |

### 3.2. General procedure for the synthesis of 3-(6-R-2-chloroquinolin-3-yl)-1,5-bis(3,4,5-trimethoxyphenyl)pentane-1,5-dione (R = H (**3a**), R = OMe (**3b**))

#### 3.2.1. General procedure method A

An equimolar quantity of the aldehydes **1a–b** (1 mmol), and the active methylene compounds **2** (2 mmol) were mixed thoroughly and then 0.1 mmol of DBU was added. The reaction mixture was ground in a mortar and pestle for 60 s to 5 min. for the appropriate time, the reaction being monitored by TLC for completion of the reaction. The reaction mixture was treated with cold water and the product was filtered, dried, and the crude compounds were recrystallized from a mixture of ethanol and water to get the desired compound in the pure form (**3a–b**) in excellent yields (82% and 84%).

#### 3.2.2. General procedure method B

A solution of 2-chloro-3-quinoline carboxaldehyde **1a–b** (0.005 mol) in ethanol (25 ml) was added dropwise to a solution of 3,4,5-trimethoxyacetophenone (1.00 g, 0.005 mol) in NaOH (2 N, 25 ml) solution at 0 °C then the mixture was stirred for 24 h at RT. The precipitate was filtered and the solid washed 3 times with ethanol/water (1:1 ratio, 25 ml) to give a solid which was air-dried.

#### 3.2.3. Compound **3a**

The solid product was purified by column chromatography using silica gel (hexane:$Et_2O$ 2:8 or hexane:$CH_2Cl_2$ 1:5) to give **3a** as a yellow solid. Yield, 2.4 g, 81%. M.p.: 158–160 °C. IR (Nujol,

**Table 2**
Hydrogen bonds (Å and °).

| D–H···A | d(D–H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| C(68)–H(68B)···O(5)#1 | 0.98 | 2.40 | 3.275(5) | 147.7 |
| C(28)–H(28A)···O(1)#2 | 0.98 | 2.40 | 3.352(3) | 162.6 |

Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z-1$; #2 $-x+2, -y+2, -z+1$.

$cm^{-1}$): $\nu$(C=O) 1748, $\nu$(C=O) 1672, $\nu$(C=N) 1580, 1504. $^1$H NMR (200 MHz, $CDCl_3$) ($\delta$ ppm): 8.16 (s,1H, Quino-$H_8$), 8.00–7.96 (d, 1H $^4J_{HH}$ = 8.4 Hz, Quino-$H_4$), 7.87–7.77 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_5$), 7.73–7.65 (t, 1H, $^3J_{HH}$ = 7.2 Hz, Quino-$H_6$), 7.57-7.46 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Quino-$H_7$), 7.25 (m, 4H), 3.91–3.90 (s, 18H, 6OMe), 3.80–3.71 [(d, 4H, $^3J_{HH}$ = 6.8 Hz, 2(–$CH_2$–)], 3.61–3.46 (quintet, 1H, $^3J_{HH}$ = 6.8 Hz, –$CH_2$–CH–$CH_2$–). *Anal.* Calc. for $C_{32}H_{32}NO_8Cl$ (594.06): C, 64.70; H, 5.43; N, 2.36. Found: C, 64.72; H, 5.47; N, 2.41%.

### 3.2.4. Compound **3b**

The solid product was purified by column chromatography using silica gel (hexane:$Et_2O$ 2:8 or hexane:$CH_2Cl_2$ 1:5) to give **3b** as a yellow solid. Yield 2.6 g, 83%. M.p.: 204–206 °C. IR (Nujol, $cm^{-1}$): $\nu$(C=O)1748, $\nu$(C=O)1674, $\nu$(C=N)1582, 1505. $^1$H NMR (200 MHz, $CDCl_3$) ($\delta$ ppm): 8.37 (s,1H, Quino-$H_8$), 8.06–7.99 (d, 1H $^4J_{HH}$ = 9.4 Hz, Quino-$H_4$), 7.88−7.77 (dd, 1H, $^3J_{HH}$ = 9.2 and 2.6 Hz, Quino-$H_5$), 7.77–7.57 (d, 1H, $^4J_{HH}$ = 2.6 Hz, Quino-$H_7$), 7.25 (m, 4H), 3.962 (s, 3H, OMe), 3.91–3.90 (s, 18H, 6OMe), 3.80–3.71 [(d, 4H, $^3J_{HH}$ = 6.8 Hz, 2(–$CH_2$–)], 3.61–3.46 (quintet, 1H, $^3J_{HH}$ = 6.8 Hz, –$CH_2$–*CH*–$CH_2$–). *Anal.* Calc. for $C_{33}H_{34}NO_9Cl$ (624.077): C, 63.51; H, 5.49; N, 2.24. Found: C, 63.65; H, 5.47; N, 2.39%.

### 3.3. General procedure for the synthesis of {Pd[6-R-$C_9H_4$–CH–[–$CH_2$ CO–$C_6H_2$–$(OCH_3)_3$]$_2$–(3,4,5)]Cl($PPh_3$)}$_2$ [R = H, (**4a**) and [R = OMe, (**4b**)]

[Pd(dba)$_2$] (216 mg, 0.375 mmol), $PPh_3$ (197 mg, 0.75 mmol) and chloroquinoline derivatives of **3a–b** (0.375 mmol) were mixed under $N_2$ in dry acetone (25 ml) and allowed to react with stirring at room temperature for 6 hrs. After evaporation of the solvent and extraction of the residue with $CH_2Cl_2$ (15 + 2 × 5 ml), the combined organic solution was filtered over silica gel/$MgSO_4$ (3:1). The resulting solution was concentrated (2 ml), and a mixture of the complex and dba was precipitated with n-hexane. Purification by chromatography through silica gel with $CH_2Cl_2$ gave **4a** or **4b** as a yellow powder.

### 3.3.1. Complex (**4a**)

Diffraction- quality crystals were grown by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of **4a**. Yield: 274 mg, 38%. M.p.; 210 °C dec., yellow solid. IR (Nujol, $cm^{-1}$); $\nu$(C=O) 1672.2, $\nu$(C=N) 1618, $\nu$(C=C 1580.9. $^1$H NMR (200 MHz, $CDCl_3$) ($\delta$ ppm): 8.16 (s,2H, Quino-$H_8$), 8.00-7.96 (d, 2H, $^4J_{HH}$ = 8.4 Hz, Quino-$H_4$), 7.81–7.77 (d, 2H, $^3J_{HH}$ = 8.2 Hz, Quino-$H_5$), 7.72–7.62 (m, 17H, Quino-$H_6$ + $PPh_3$), 7.60–7.35 (m, 17H, Quino-$H_7$ + $PPh_3$), 7.25 [m, 8H, $(MeO)_3$–$C_6H_2$], 3.91 (s, 24H, 8OMe), 3.90 (s, 12H, 4OMe), 3.69–3.66 (d, 8H, $^4J_{HH}$ = 6.8 Hz, CH–$CH_2$–), 3.61–3.54 (t, 2H, $^4J_{HH}$ = 6.8 Hz –CH–). $^{31}$P {$^1$H} NMR (121 MHz, $CDCl_3$) ($\delta$ ppm): 29.72. *Anal.* Calc. for $C_{100}H_{94}N_2O_{16}Cl_2Pd_2P_2$ (1925.544): C, 62.38; H, 4.92; N, 1.45. Found; C, 62.27; H, 4.83; N, 1.45%.

### 3.3.2. Complex (**4b**)

Diffraction-quality crystals were grown by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of **4b**. Yield: 320 mg, 43%. M.p.: 222 °C dec., yellow solid. IR (Nujol, $cm^{-1}$); $\nu$(C=O) 1673, $\nu$(C=N) 1620, $\nu$(C=C) 1582. $^1$H NMR (200 MHz, $CDCl_3$) ($\delta$ ppm): 8.16 (s,2H, Quino-$H_8$), 8.08–7.966 (d, 2H $^4J_{HH}$ = 8.4 Hz, Quino-$H_4$), 7.81–7.77 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_5$), 7.72–7.62 (m, 15H, $PPh_3$), 7.60–7.35 (m, 17H, Quino-$H_7$+$PPh_3$), 7.25 [m, 8H, $(MeO)_3$–$C_6H_2$], 3.91 (s, 24H, 8OMe), 3.90 (s, 12H, 4OMe), 3.89 (s, 6H, 2OMe), 3.69–3.66 (d, 8H, $^4J_{HH}$ = 6.8 Hz, CH–$CH_2$–), 3.61–3.54 (t, 2H, $^4J_{HH}$ = 6.8 Hz –*CH*–). $^{31}$P {$^1$H} NMR (121 MHz, $CDCl_3$) ($\delta$ ppm): 29.73. *Anal.* Calc. for $C_{101}H_{96}N_2O_{17}Cl_2Pd_2P_2$ (1955.54): C, 62.03; H, 4.95; N, 1.43. Found; C, 62.02; H, 4.89; N, 1.42%.

### 3.4. General procedure for the synthesis of (1Z,2Z)-N-(2,6-dimethylphenyl)-2-(2,6-dimethylphenylimino)-7-R-2-{3-[-1,5-bis(3,4,5-trimethoxyphenyl)-1,5-dioxopenta-3-nyl]quinolin-2-yl}ethanimidoyl palladium cyanidous chloride ([R = H, (**5a**), R = OMe, (**5b**)]

### 3.4.1. General procedure method A

Chloro-quinoline derivatives **3a–b** (0.78 mmol) were added under nitrogen to a suspension of "Pd(dba)$_2$" (300 mg, 0.52 mmol) and XyNC (274 mg, 2.09 mmol) in acetone (15 ml). The suspension was stirred for 5 h at room temperature. After this time the workup is carried out in air. The solvents were evaporated, the residue was extracted with $CH_2Cl_2$, and the extract filtrate was filtered over anhydrous $MgSO_4$/silica gel (1:3).The resulting red solution was evaporated and the residue was triturated with $Et_2O$ (15 $cm^3$). The precipitate was filtered, washed with $Et_2O$ (2 × 5 $cm^3$), and air-dried, giving deep red compounds **5a–b**, in yields 275 mg, 32% and 295 mg, 33%, respectively.

### 3.4.2. General procedure method B

XyNC (125 mg, 0.96 mmol) was added to a suspension of **4a–b** (0.12 mmol) in $CH_2Cl_2$ (15 ml). The suspension was stirred for 16 hrs at room temperature. The color changed from pale yellow to pale red and then dark red on monitoring the reaction mixture. After this time the workup was carried out in air. The solvents was filtered over anhydrous $MgSO_4$/silica gel (1:3). The resulting red solution was evaporated and the residue was triturated with $Et_2O$ (15 $cm^3$). The precipitate was filtered, washed with $Et_2O$ (2 × 5 $cm^3$), and air-dried, giving deep red compounds **5a–b**, in yields 60 mg, 45% and 59 mg, 43%, respectively.

### 3.4.3. {PdCl(2)–(C=N–Xy)$_2$–(CN–Xy)–$C_9H_5N$–(3)–CH)[$CH_2COC_6H_2$–3,4,5-$(OCH_3)_3$]$_2$} (**5a**)

The solid red compound was purified by chromatography using silica gel (acetone/hexane; 9:1). TLC: $R_f$ = 0.88; Yield: 275 mg, 32%. Diffraction-quality crystals were grown by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution of **5a**. M.p.: 139–140 °C. IR (Nujol, $cm^{-1}$): $\nu$(C≡N) 2184, $\nu$(C=O)1672, $\nu$(C=N) 1640, 1582, 1504. $^1$H NMR (200 MHz, $CDCl_3$) ($\delta$ ppm): 9.27−9.24 (d,1H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_8$), 8.72 (s, 1H, Quino-$H_4$), 8.16 (s, 1H, Ar–H), 7.99–7.94 (t, 2H, $^3J_{HH}$ = 8.4 Hz), 7.87–7.85 (t, 1H, $^3J_{HH}$ = 6.9 Hz), 7.80–7.77 (d, 1H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_7$), 7.73–7.66 (m, 2H), 7.56–7.51 (t, 1H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_6$), 7.25–7.24 (s, 4H), 7.17–7.11 (t, 1H, $^3J_{HH}$ = 7.8 Hz), 6.99–6.97 (d, 2H, $^3J_{HH}$ = 7.5 Hz), 6.93–6.90 (d, 2H, $^3J_{HH}$ = 7.5 Hz), 6.85–6.80 (d, 1H, $^3J_{HH}$ = 6.6 Hz), 6.72–6.65 (t, 2H, $^3J_{HH}$ = 6.9 Hz), 6.62–6.60 (d, 1H, $^3J_{HH}$ = 6.6 Hz), 3.91(s, 6H, 2OMe), 3.90 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.87 (s, 6H, 2OMe), 2.18 (s, 6H, 2 Me), 2.08 (s, 6H, 2 Me), 1.52 (s, 6H, 2 Me). *Anal.* Calc. for $C_{59}H_{59}N_4O_8ClPd$ (1093.995): C, 64.77; H, 5.44; N, 5.12. Found: C, 64.75; H, 5.45; N, 5.10%.

### 3.4.4. {PdCl(2)–(C=N–Xy)$_2$–(CN–Xy)–6-OMe–$C_9H_4N$–(3)-CH)[$CH_2COC_6H_2$–3,4,5-$(OCH_3)_3$]$_2$} (**5b**)

The solid red compound was purified by chromatography using silica gel (acetone); the fraction at $R_f$ = 0.66 was collected and extracted to give a solution which was evaporated to dryness. Yield: 295 mg, 33%. M.p.: 142–144 °C. IR (Nujol, $cm^{-1}$): $\nu$(C≡N) 2184, $\nu$(C=O) 1710, 1664, $\nu$(C=N) 1610, 1580, 1498. $^1$H NMR (200 MHz, $CDCl_3$) ($\delta$ ppm): 8.65 (d,1H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_8$), 8.39 (s, 1H, Quino-$H_5$), 8.19 (s, 1H) 8.11–8.07 (d,1H, $^3J_{HH}$ = 8.4 Hz, Quino-$H_7$), 7.95–7.90 (d, 2H, $^3J_{HH}$ = 9.2 Hz), 7.54 (s, 2H), 7.46–7.43 (m, 2H), 7.40–7.37 (m, 1H), 7.31 (s, 4H), 7.17–7.12 (m, 3H), 7.08–7.04 (m, 2H), 7.00–698 (m, 2H), 6.90 (s 2H), 6.83 (s, 2H), 3.96 (s, 6H, 2OMe), 3.90 (s, 12H, 4OMe), 3.82 (s, 3H, OMe), 2.58 (s, 3H, Me), 2.51 (s, 3H, Me), 2.32 (s, 3H, Me), 2.18 (s, 6H, 2 Me),

2.02 (s, 3H, Me), 1.52 (s, 6H, 2 Me). *Anal.* Calc. for $C_{60}H_{61}N_4O_9ClPd$ (1124.021): C, 64.11; H, 5.47; N, 4.98. Found: C, 64.10; H, 5.47; N, 4.92%.

*3.4.5. Synthesis of $[Pd_2Cl_2(CNXy)_4]$ (**6**)*

This compound was prepared by following the procedure method A described for **5a–b**, from "Pd(dba)2" (300 mg, 0.52 mmol), XyNC (274 mg, 2.09 mmol) and the chloro-quinoline derivatives **3a–b** (0.78 mmol). In this case, the isolated yellow solid is identified as **6**, which had previously been described [37]. The fraction at $R_f = 0.4$ was collected and extracted with acetone to give a solution which was evaporated to dryness.

Yield: 366 mg, 58%. $^1$H NMR (300 MHz, $CDCl_3$) ($\delta$ ppm) 7.25–7.09 (m, 12H), 2.52 (s, Me, 24H). $^{13}$C NMR (50 MHz, CDCl3) ($\delta$ ppm): 142.9 (C≡N), 135.6 (CMe), 129.8 (CH), 128.0 (CH), 126.4 (CNC), 19.1 (Me). *Anal.* Calc. for $C_{36}H_{36}N_4Cl_2Pd_2$ (808.44): C, 53.48; H, 4.49; N, 6.93. Found: C, 53.40; H, 4.37; N, 6.72%.

*3.4.6. X-ray crystallographic study of (**5a**)*

Details of data collection and refinement are given in Table 1. The single-crystal X-ray diffraction study of **5a** was carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms placed in calculated positions. The structure solution and refined were performed by using the SHELXL-97 package [38].

## 4. Conclusions

To illustrate the capacity of {Pd[6-R-$C_9H_4$–CH–[–$CH_2$CO–$C_6H_2$–$(OCH_3)_3$]$_2$–(3,4,5)]Cl($PPh_3$)}$_2$ [R = H (**4a**), R = OMe, (**4b**)] to prepare chloro-palladium(II) complexes, we have isolated complexes of the type PdCl(2)(C≡N–Xy)$_3$(R-(6)-$C_9H_4$N–3-CH)[$CH_2COC_6H_2$-3,4,5-$(OCH_3)_3$]$_2$ [R = H (**5a**), R = OMe, (**5b**)]. We have studied the thermal transformation of these compounds into C-palladated $\alpha$ and $\beta$-ketoenimine complexes resulting from the insertion of excess or 3 moles of the isocyanide followed by an $\alpha$- to $\beta$-ketoimine process. The resulting complexes are the first palladium compounds containing five-membered rings with insertion two molecules of isocyanide. We report here for the first time the isolation of both types, adducts and insertion products of isocyanides into Pd–C bonds.

## Supplementary data

CCDC 715598 contains the supplementary crystallographic data for **5a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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