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Conversion of novel palladacycles into oxopyrrolo[3,4-b]quinolines

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ABSTRACT

The quinolinylcyclopalladated complexes **3a–b** were synthesised in good yields (81% and 77%) by the insertion reaction of the prepared dinuclear palladium complexes [Pd(*C,N*-2-C_9H_4N-CHO-3-R-6)Cl(PPh_3)]$_2$ [(R = H (**2a**), R = OMe (**2b**)] with isonitrile XyNC (Xy = 2,6-$Me_2C_6H_3$). The cyclopalladated complexes **3a–b** were also obtained in low yields (39% and 33.5%) via a one pot oxidative addition reaction of quinoline chloride **1a–b** with isonitrile XyNC:Pd(dba)$_2$ (4:1). The reactions of **3a–b** with Tl(TfO) (TfO = triflate, CF_3SO_3) in the presence of H_2O or EtOH causes depalladation reactions of the complexes to provide the corresponding organic compounds **4a–b**, **5a–b** and **6a–b** in yields (41%, 27% and 18–19%). The products were characterized by satisfactory elemental analyses and spectral studies (IR, ^{1}H, ^{13}C and ^{31}P NMR). The crystal structures of **2a**, **3a** and **3b** were determined by X-ray diffraction studies.

1. Introduction

The chemistry of arylpalladium complexes is a topic of great interest because such compounds participate in many organic reactions [1–12]. Cyclopalladated complexes (CPCs) are one of the most popular classes of organopalladium derivatives, which are widely applied in organic synthesis, organometallic catalysis and new molecular materials. Among them, the most investigated cyclopalladated complexes are five- or six-membered rings fused with an aromatic ring, and the metallated carbon is usually an aromatic sp^2 carbon [13–17]. However, six-membered palladacycles with iminoyl (C=N–) sp^2 carbon are rather rare [18]. This is probably due to poor stability which brings difficulties of preparation, isolation and characterization of these complexes. The limitation can be overcome by changing the nature of the metallated carbon atom, the type of donor groups and their substituents. Some of these reactions involved *ortho*-functionalized aryl complexes that after insertion of isocyanides gave heterocyclic products in which the ortho group is included [19–21]. Establishing synthetic procedures for these complexes invariably involve the presence of other strongly coordinated ligands, such as PPh_3 [22–24], and these are attracting our interest. There is relatively little known concerning the cyclometallation of aldehyde functionalities [25–34]. The interest of this subject has prompted us to prepare arylpalladium complexes containing *ortho*-–CHO functionalized groups. 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. The structure of dimeric [*N*-aryl-Pd-Cl(PPh_3)]$_2$, **2a–b**, with non common '$Pd_2C_2N_2$' central cores formed by oxidative addition of the chloroquinolines **1a–b** to a Pd(0) is supported by X-ray structures. The utility of the cyclopalladated complexes **3a–b** in organic synthesis via their depalladation reactions to provide amidic acid or esters (**4a–b**, **5a–b** and **6a–b**) are the most outstanding points of this manuscript. The sequence of the reactions led eventually to compounds that could potentially possess pharmacological properties [35–53].

2. Results and discussion

Oxidative addition reactions of 2-chloro-6-R-3-quinolinecraboxaldehydes R = H (**1a**), R = OMe (**1b**) toward a stoichiometric amount of [Pd(dba)$_2$] = ([Pd$_2$(dba)$_3$] · dba; dba = dibenzylideneacetone) [54] 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-CHO(3)]Cl(PPh_3)}$_2$ **2a**, {Pd[-6-OCH_3-C_9H_4-CHO(3)]Cl(PPh_3)}$_2$ **2b** in moderate yields (43% and 31%), 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 the dinuclear complexes in CH_2Cl_2 at room temperature eventually formed the monuclear complexes **3a–b** in high yields (81% and 77%). These palladacycles **3a–b** could also be obtained in low yields (39% and 33.5%) by direct oxidative addition of 2-chloro-6-R-3-quinolinecraboxaldehydes **1a–b** toward Pd(dba)$_2$ in the presence of a stoichiometric amount of isocyanide XyNC in degassed acetone at room temperature, as depicted in Scheme 1.

It was envisaged that the oxidative addition reaction of **1a–b** with Pd(dba)$_2$/PPh_3 could give the expected complex in a *transoid* form (**A**). However, isolation of the *trans* complexes failed, and only a yellow powder solid was isolated in the pure form that

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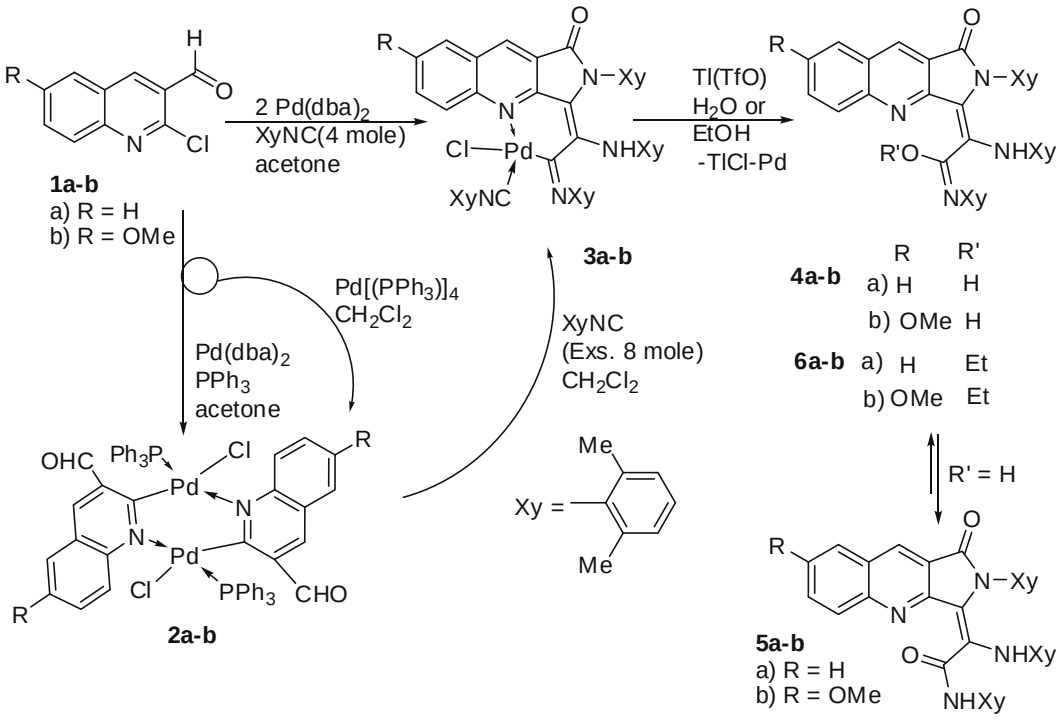
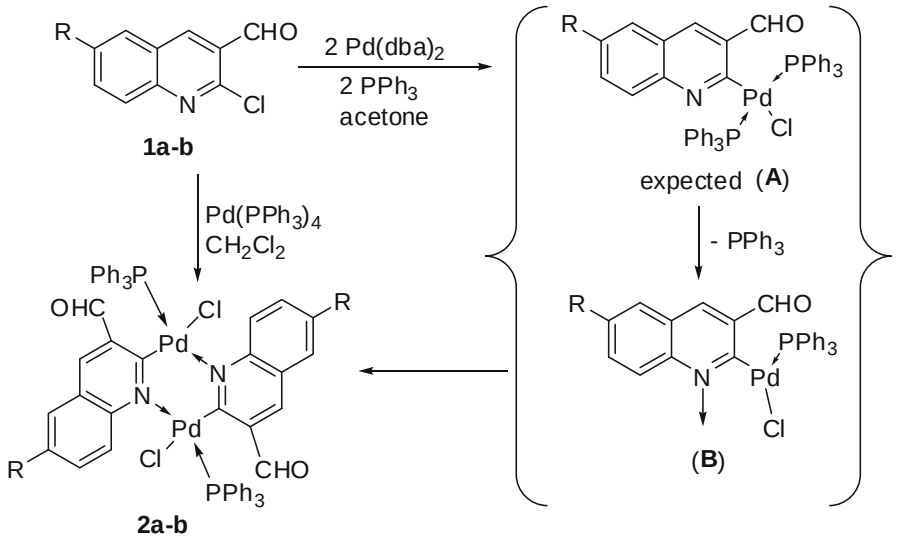


Scheme 1.

corresponded to the dimeric palladium complexes **2a–b**, as outlined in Scheme 2. This is probably due to the result of the interchange between the nitrogen donor of the quinoline ring and the PPh_3 ligand of palladium, which is a very well-known process [55]. One might believe that complexes (**A**) and (**B**) are intermediates for the formation of complexes **2a–b** and also suggest that the presence of PPh_3 as a ligand could be responsible for the interchange of the ligands and existence of complex **2a** or **2b** in solution as a mixture of complexes derived from two *trans* forms. The formation of the dimeric complexes **2a–b** are consistent with the related dimeric palladium complex $[Pd(\mu\text{-pyridine})Cl(PPh_3)]_2$, formed by the oxidative addition of 2-chloropyridine to the complex $Pd(PPh_3)_4$ [56].

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. The ^{31}P NMR spectra recorded in case of R = H (**2a**) and R = OMe (**2b**) showed resonances at δ 20.67 and 21.37 ppm.

The ^{1}H NMR spectra did not show the presence of any impurities for either of the complexes **2a** or **2b**, although the quinoline backbone shows slight variations when complexes **2a** or **2b** are compared. However, we feel that not enough was known about palladium–carbon bonds of these complexes, through four bonds. This promoted us to place emphasis on these data. While this



Scheme 2.

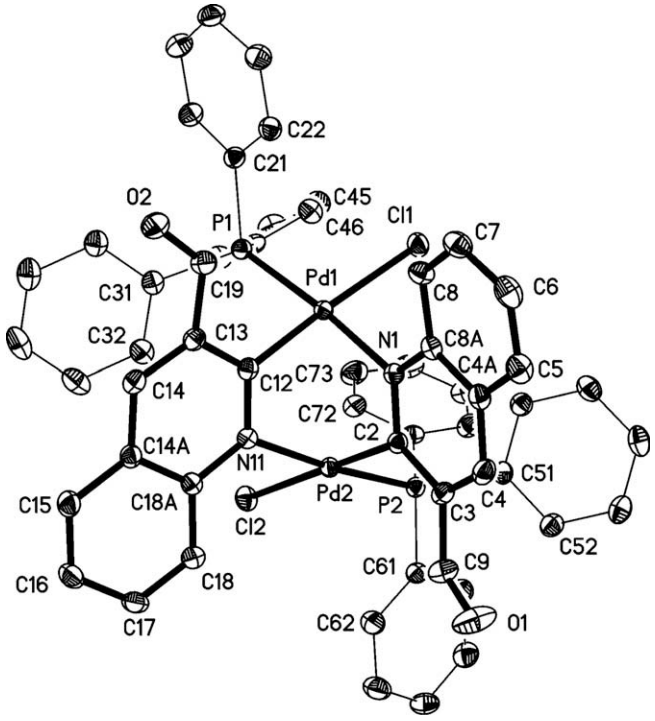


Fig. 1. Thermal ellipsoid plot (50% probability level and solvent omitted CH_2Cl_2) of **2a**. Selected bond lengths (Å) and angles (°): Pd(1)–C(12) = 1.9919(17), Pd(1)–N(1) = 2.0944(14), Pd(1)–P(1) = 2.2906(5), Pd(1)–Cl(1) = 2.3816(6), Pd(1)–Pd(2) = 3.0818.(5), Pd(2)–C(2) = 2.0081(6), Pd(2)–N(11) = 2.1115(14), Pd(2)–P(2) = 2.2661(7), Pd(2)–Cl(2) = 2.3812(5), N(1)–C(2) = 1.330(2), N(11)–C(12) = 1.324(2), C(12)–Pd(1)–N(1) = 82.22(6), C(12)–Pd(1)–P(1) = 92.32(5), N(1)–Pd(1)–P(1) = 174.53(4), C(12)–Pd(1)–Cl(1) = 173.90(5), N(1)–Pd(1)–Cl(1) = 92.30(4), P(1)–Pd(1)–Cl(1) = 93.14(2), C(12)–Pd(1)–Pd(2) = 66.01(5), N(1)–Pd(1)–Pd(2) = 63.12(4), P(1)–Pd(1)–Pd(2) = 114.865(14), Cl(1)–Pd(1)–Pd(2) = 113.865(19), C(2)–Pd(2)–N(11) = 84.88(6), C(2)–Pd(2)–P(2) = 93.24(5), N(11)–Pd(2)–P(2) = 175.12(4), C(2)–Pd(2)–Cl(2) = 174.14(5), N(11)–Pd(2)–Cl(2) = 90.20(4), P(2)–Pd(2)–Cl(2) = 91.91(2), C(2)–Pd(2)–Pd(1) = 66.30(5), N(11)–Pd(2)–Pd(1) = 63.27(4), P(2)–Pd(2)–Pd(1) = 111.854(17), Cl(2)–Pd(2)–Pd(1) = 114.188(16).

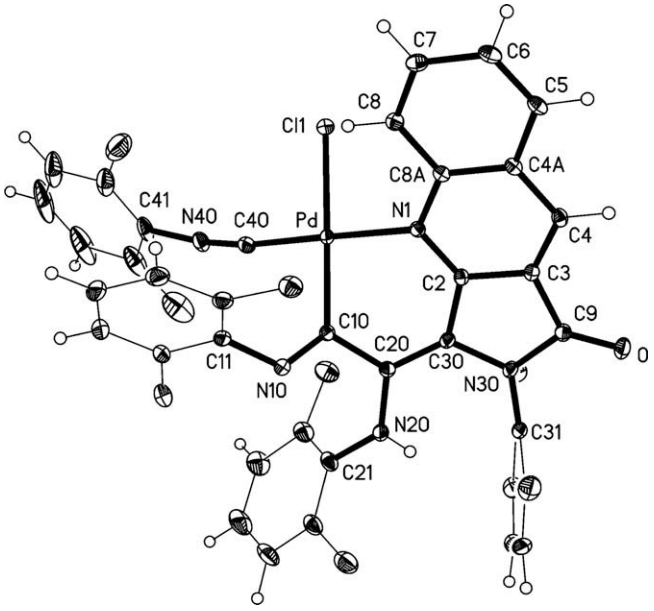


Fig. 2. Thermal ellipsoid plot (50% probability level and solvent omitted) of **3a**. The hydrogen atom attached to N(20) has been displayed for clarity. Selected bond lengths (Å) and angles (°): Pd–C(40) = 1.9425(18), Pd–C(10) = 1.9999(17), Pd–N(1) = 2.0864(14), Pd–Cl(1) = 2.4398(4), N(1)–C(2) = 1.325(2), N(1)–C(8A) = 1.388(2), N(10)–C(10) = 1.270(2), N(10)–C(11) = 1.420(2), N(20)–C(20) = 1.372(2), N(20)–C(21) = 1.418(2), N(30)–C(9) = 1.389(2), N(30)–C(30) = 1.429(2), N(30)–C(31) = 1.434(2), N(40)–C(40) = 1.151(2), N(40)–C(41) = 1.409(2), C(2)–C(30) = 1.452(2), C(3)–C(9) = 1.479(2), C(9)–O = 1.221(2), C(10)–C(20) = 1.505(2), C(20)–C(30) = 1.366(2), C(40)–Pd–C(10) = 91.93(7), C(40)–Pd–N(1) = 178.97(6), C(40)–Pd–Cl(1) = 84.21(5), C(10)–Pd–N(1) = 87.11(6), C(10)–Pd–Cl(1) = 173.33(5), N(1)–Pd–Cl(1) = 96.78(4), C(2)–N(1)–C(8A) = 116.44(14), C(2)–N(1)–Pd = 116.23(11), C(8A)–N(1)–Pd = 126.75(11), C(10)–N(10)–C(11) = 123.11(15), C(20)–N(20)–C(21) = 129.41(17), C(9)–N(30)–C(30) = 112.76(14), C(9)–N(30)–C(31) = 122.82(15), C(30)–N(30)–C(31) = 124.29(14), C(40)–N(40)–C(41) = 171.2(2), N(1)–C(2)–C(3) = 123.94(15), N(1)–C(2)–C(30) = 127.31(15), C(3)–C(2)–C(30) = 108.75(15), C(2)–C(3)–C(9) = 108.26(14), O–C(9)–N(30) = 125.39(17), O–C(9)–C(3) = 129.47(16), N(30)–C(9)–C(3) = 105.12(14), N(10)–C(10)–C(20) = 116.45(15), N(10)–C(10)–Pd = 127.94(13), C(20)–C(10)–Pd = 115.61(11), C(30)–C(20)–N(20) = 122.27(16), C(30)–C(20)–C(10) = 118.02(15), N(20)–C(20)–C(10) = 118.83(15), C(20)–C(30)–N(30) = 127.76(15), C(20)–C(30)–C(2) = 126.11(16), N(30)–C(30)–C(2) = 104.88(13), N(40)–C(40)–Pd = 171.71(16).

observation can be rationalized for **2a–b**, we were surprised that the cyclopalladated product showed almost no change in view of the angular distortion involved in forming the six-membered palladacycles. The IR (Nujol, cm^{-1}) bands assignable to the ν(C=O), ν(C=N) and ν(C=C) modes in **2a–b** indicating the non-coordination of the carbonyl group in these complexes. In complex **2a**, the IR spectrum shows bands at 1688, 1612 and 1582 cm^{-1} and for **2b** these bands appear at slightly lower values at 1678, 1584 and 1546 cm^{-1} respectively. The complexes **2a–b** show in their IR spectra a strong band at ca. 1688 and 1678 cm^{-1} assignable to ν(C=O) of the formyl group. These frequencies are similar to that observed in the starting materials **1a–b**, indicating that there is no coordination of the formyl group to the metal atom.

2.1. Insertion of 2,6-dimethylphenyl isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$)

Oxidative addition of 2-chloro-6-R-3-quinolinecarboxaldehydes **1a–b** [R = H (**1a**), R = OMe (**1b**)] (1.5) to a mixture of $Pd(dba)_2$ and XyNC (Xy = 2,6-$Me_2C_6H_3$) in 1:4 ratios in acetone at room temperature yields the tri-inserted iminoacyl palladium complexes **3a–b** in low yields (39%, 33.5%). Instead of the required 4:1.5:1 molar ratios of reagents XyNC:**1a–b**:$Pd(dba)_2$ for the formation of **3a–b**, the stoichiometric amounts of this mixtures used were 3:1.5:1, 2:1.5:1, 2:1:1, 1:1.5:1, 1:1:1 (**3a**) and 3:1.5:1, 2:1.5:1, 2:1:1, 1:1.5:1, 1:1:1 (**3b**), unfortunately, it was not possible to isolate the inserted products in this regard.

A mechanistic proposal depicts the formation of the possible intermediates [Pd{C(=NXy)$_3$Ar}Cl(CNXy)] [**I**] which are quickly cyclized to give iminoacyl quinolinylpalladium **3a** and **3b**, and not the expected complex [**II**]. We believe that a nucleophilic attack of the nitrogen of the primarily inserted isocyanide at the formyl carbon could give the isoindole ring [**III–V**]. The intermediate [**IV**] could evolve to [**V**], bearing a carbon–carbon double bond, which could undergo an intermolecular proton migration from the OH group of the intermediate [**V**] to the nitrogen of the second inserted isocyanide. There is no precedent for this type of structure conformation with migration of the proton to the nitrogen atom of the second inserted isocyanide, it was supported by X-ray structures, displaying the nitrogen proton at N(20)–H (**3a**, Fig. 2) and N(5)–H (**3b**, Fig. 3). The favored attack of the quinolinyl nitrogen at the (Pd) metal center in intermediate [**VI**] could turn into iminoacyl quinolinylpalladium **3a** or **3b**. The reported [57–62] synthesis of a highly functionalized ketenimine from di-insertion of XyNC into an (*o*-formylaryl) palladium complex is consistent with the result described here. The formation of such a ketenimine is also the result of the attack of the nitrogen of the primarily inserted isocyanide at the formyl carbon. A mechanistic proposal consistent with literature data [63], is given in Scheme 3.

The reactivity of the dinuclear palladium complexes **2a–b** were examined toward the bulky isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$),

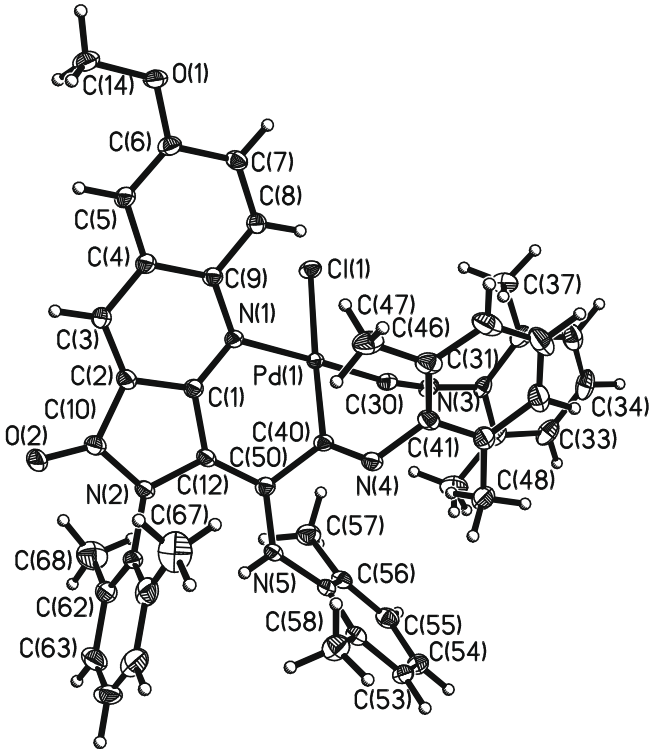


Fig. 3. Thermal ellipsoid plot (50% probability level and solvent omitted) of **3b**. The hydrogen atom attached to N(5) has been displayed for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(30) = 1.944(2), Pd(1)–C(40) = 2.002(2), Pd(1)–N(1) = 2.0905(18), Pd(1)–Cl(1) = 2.4283(5), N(1)–C(1) = 1.332(3), N(1)–C(9) = 1.382(3), N(2)–C(10) = 1.383(3), N(2)–C(12) = 1.432(3), N(2)–C(61) = 1.438(3), N(3)–C(30) = 1.153(3), N(3)–C(31) = 1.404(3), N(4)–C(40) = 1.266(3), N(4)–C(41) = 1.429(3), N(5)–C(50) = 1.363(3), C(30)–Pd(1)–C(40) = 91.67(8), C(30)–Pd(1)–N(1) = 178.75(8), C(40)–Pd(1)–N(1) = 87.14(8), C(30)–Pd(1)–Cl(1) = 84.53(6), C(40)–Pd(1)–Cl(1) = 175.94(6), N(1)–Pd(1)–Cl(1) = 96.64(5), C(1)–N(1)–C(9) = 116.68(18), C(1)–N(1)–Pd(1) = 116.25(14), C(9)–N(1)–Pd(1) = 126.45(14), C(10)–N(2)–C(12) = 112.44(18), C(10)–N(2)–C(61) = 119.09(18), C(12)–N(2)–C(61) = 127.39(18), C(30)–N(3)–C(31) = 170.0(2), C(40)–N(4)–C(41) = 120.57(18), C(50)–N(5)–C(51) = 129.11(19), C(6)–O(1)–C(14) = 116.23(18), N(1)–C(1)–C(2) = 122.76(19), N(1)–C(1)–C(12) = 128.49(19).

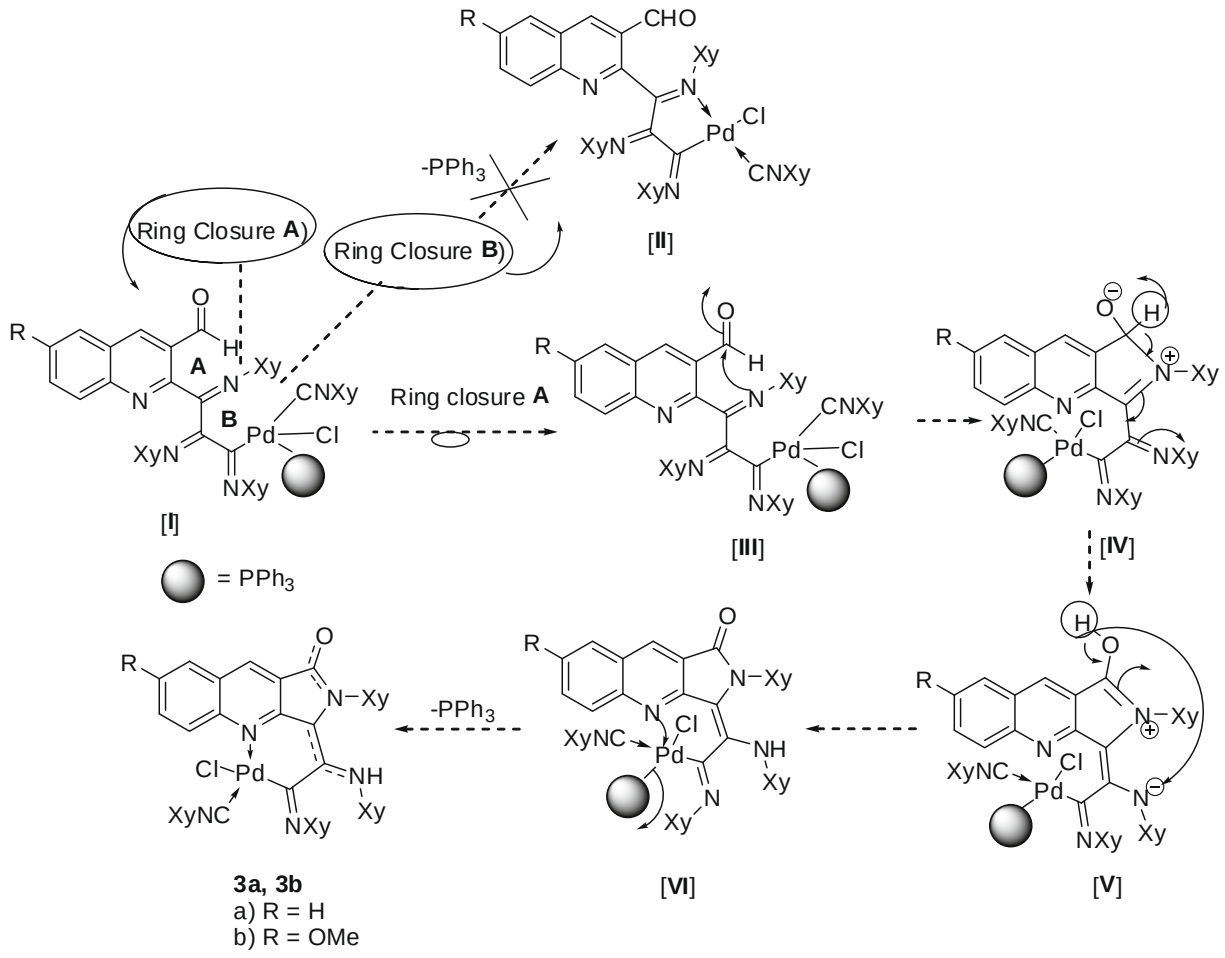
and it depends on nature of the ligands and on the reaction conditions. Thus when the insertion reaction takes place at different molar ratios of XyNC to complex, the inserted products obtained are the result of tri-insertion processes. The mono-insertion and di-insertion of XyNC at 1:1 or 1:2 molar ratios are not being isolated. The reaction of the dinuclear palladium complexes **2a–b** with 8 equiv. of XyNC at room temperature with a longer reaction time (16 h) provided the inserted products of iminoacyl quinolinylpalladium complexes **3a–b**. Instead of the required (8:1) equivalents of XyNC:**2a–b**, the stoichiometric amounts of 3:1, 4:1, 5:1, 6:1 and 7:1 were used, and it was not possible to isolate complexes **3a–b** in case of 3:1, 4:1 and 5:1 molar ratios.

The inserted products were formed from the insertion of 2,6-dimethylphenyl isocyanide (XyNC) into the C–Pd bond and the displacement of PPh_3 by the XyNC ligand. These kinds of complexes are very poorly represented in the iterature, the only example being those recently prepared by Vicente et al. [63] and suggested that the presence of PPh_3 during the insertion of XyNC into the dinuclear palladium complexes **2a–b** could be responsible for the change of 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 [63] is given in Scheme 4.

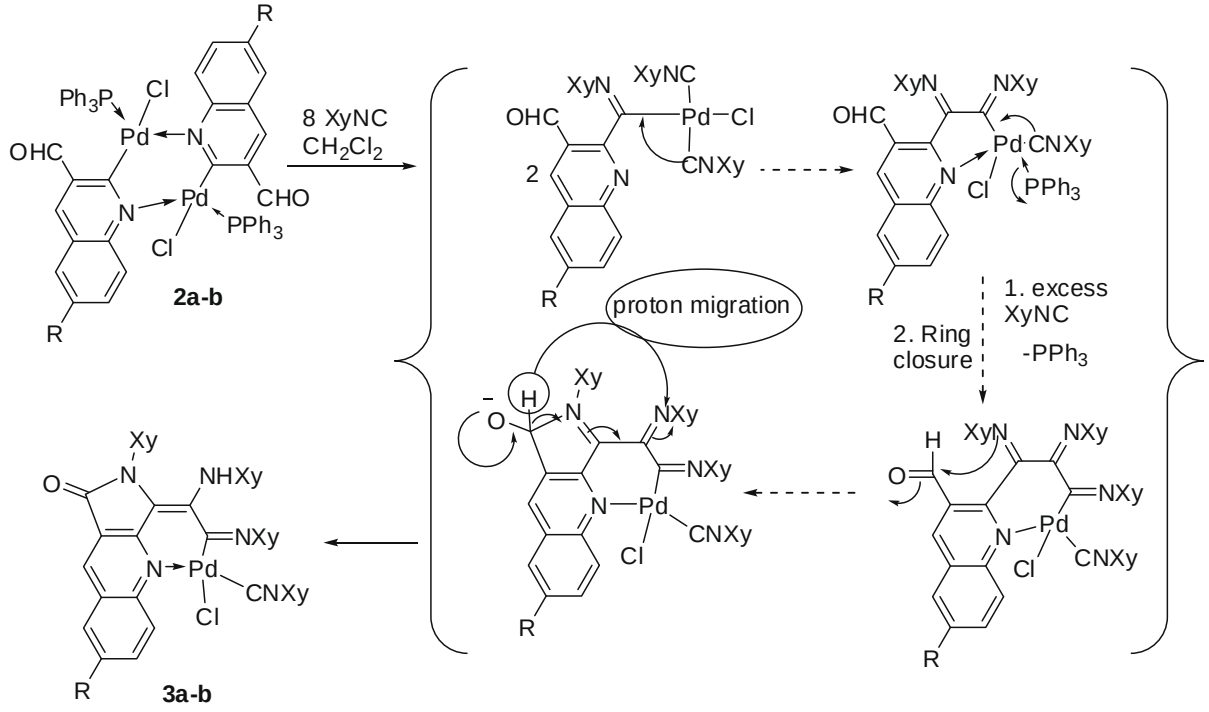
The products were analyzed by IR, ^1H NMR spectroscopy and single-crystal X-ray diffraction studies. IR (Nujol, cm^{-1}) bands were assignable to ν_{NH}, $\nu_{C\equiv N}$, $\nu_{C=O}$ and $\nu_{C=N,}$ for the iminoacyl quinolinylpalladium complexes **3a** and **3b** with no significances differences, indicating the cyclization of the carbonyl group within those complexes. In the case of **3a** the bands appear at ν(NH, broad band) 3338, ν(C≡N) 2361, ν(C=O) 1716 and ν(C=N) 1558 cm^{-1}, and in the case of **3b** the bands appear at ν(NH, broad band) 3360, ν(C≡N) 2182, ν(C=O) 1704 and ν(C=N) 1602 cm^{-1}. This suggests little change in the carbonyl stretching frequency of **3a** or **3b** due to complexation, and the electron releasing methoxyl group could confer special properties to the formyl group, for example, facilitating its coordination to the primarily inserted isocyanide (C=NXy) intermediate and nucleophilic attack of the nitrogen on the formyl carbon could give cyclometallated species of the important isoindolinone. The complexes **3a** and **3b** show a strong band in their IR spectra at 1716 and 1704 cm^{-1} assignable to ν(C=O). This frequency is not similar to that observed in the starting materials **1a–b** or **2a–b** and indicates the coordination of the carbonyl group to the isoindolinone ring. The ^1H NMR spectrum of complex **3a** in $CDCl_3$ was recorded and found to contain seven singlet resonances at different chemical shifts, each corresponding to methyl groups, appearing at δ 2.55 (s, Me, 3H), 2.49 (s, Me, 3H), 2.30 (s, Me, 3H), 2.19 (s, Me, 6H), 2.11 (s, Me, 3H), 1.58 (s, Me, 3H) and 0.62 (s, Me, 3H) ppm. There is one singlet signals integrated for 2 equiv. methyl groups of the coordinated isocyanide (CNXy) which appears at δ 2.19. The ^1H NMR spectrum of complex **3b** in $CDCl_3$ was recorded and found to contain six singlet resonances at different chemical shifts, each corresponding to methyl groups, appearing at δ 2.54 (s, Me, 3H), 2.49 (s, Me, 3H), 2.29 (s, Me, 3H), 2.18 (s, Me, 6H), 2.12 (s, Me, 6H) and 0.62 (s, Me, 3H) ppm. There are two singlet signals for the four methyl groups appearing at δ 2.18 (s, 6H, 2Me(Xy)) and 2.12 (s, 6H, 2Me(Xy)), one of which is for the inserted XyNC, indicating a *cis* geometry and no free rotation of the Xy groups. The other of the two singlet signals integrated to 2 equiv. methyl groups is from the coordinated isocyanide. This suggests steric hindrance that prevents the rotation of three xylyl groups, while the fourth one rotates freely.

2.2. Depalladation via reactions with Tl(TfO)

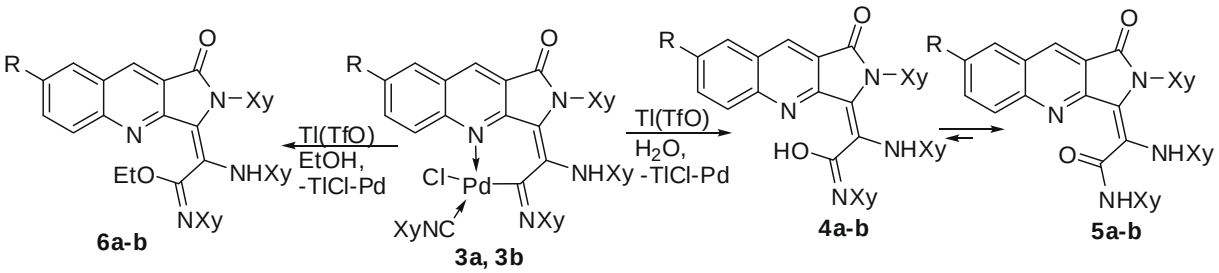
The reaction of complexes **3a–b** with Tl(TfO) was carried out in CH_2Cl_2 to give after 20 h at room temperature a precipitate of TlCl plus metallic palladium and a solution from which the highly functionalized **4a**–**b** and **5a–b** could be isolated (70% total yield, Scheme 5). These tautomers could not be separated by chromatography, but they displayed an exploitable difference in solubility. Thus, when a solution of both products in Et_2O was evaporated to dryness and Et_2O added again, the major tautomer did not redissolve and could be isolated by filtration, while the other tautomer could be similarly separated from the mother liquor. In the solid state **5a–b** and **4a–b** are stable and they do not interconvert. However, if **4a–b** are dissolved in CH_2Cl_2 and refluxed for 16 h, they transform completely into **5a–b**. The latter are stable at room temperature in $CDCl_3$ for several days, while under the same conditions **4a–b** transform partially into **5a–b**. The addition of an acid does not accelerate the interconversion of these products. Several reviews dealing with imidoyl compounds have discussed the question of whether imidic acids can exist in general [64]. They are unstable compounds that may be in equilibrium with the stable amide (**5a–d**) molecules. This is confirmed by theoretical investigations, which demonstrate that the amide form is about 11 kcal/mol more stable than the tautomeric imidic acid (**4a–d**) [65]. When the reaction of **3a–b** with Tl(TfO) was carried out in CH_2Cl_2 plus a drop of EtOH, **6a–b** were obtained and the yields varied from 18% to 40%, depending on the amount of added of EtOH.



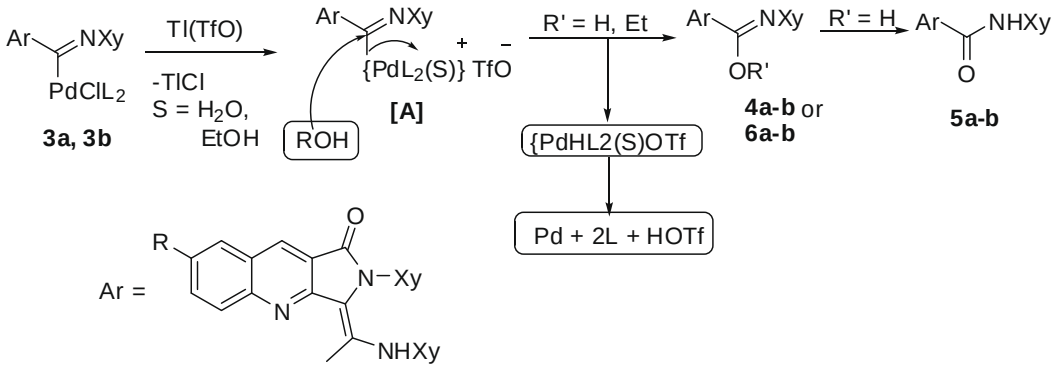
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

Therefore, the depalladation of these inserted complexes represents a stoichiometric synthesis of functionalized arene, *N*-heterocyclic compounds from chloroarenes. As mentioned above, we fruitlessly attempted the synthesis of some of these organic compounds under catalytic conditions. However, catalytic applications of these stoichiometric reactions could still be an objective for future studies. We believe that all depalladation reactions reported here share three common steps, as outlined in Scheme 6

(i) The substitution of the chloro ligand in the iminoacyl quinolinylpalladium complexes **3a–b** by TfO to give the intermediates [**A**], which are formulated as cationic species, assuming that the very labile TfO is substituted by H_2O or EtOH.
(ii) The nucleophilic attack of the iminoacyl carbon (C=NXy)-Pd of intermediate [**A**] by EtOH alcoholysis or H_2O hydrolysis, the latter coming from atmospheric or solvent moisture.
(iii) The decomposition of the resulting adduct (probably through an intermediate) gives the hydrido palladium complex, metallic palladium, neutral ligand L, HOTf and Ar C(=NXy)OR′.

Although the very simple reaction pathways proposed in Scheme 6 allow systematization of the formation of such products, some questions remain unanswered because too many factors can influence the results. Finally, we do not attempt to explain the formation of the enol or ketone form and which of these is more stable, as we cannot account for the influence of the impurities present in the starting material. A mechanistic scheme depicting the formation of various products, including possible intermediates, is outlined in Scheme 6.

2.3. X-ray crystal structures

To further confirm the structures of the products, the molecular structures of yellow crystals of **2a** (Fig. 1), red crystals of **3a** · CH_2Cl_2 (Fig. 2) and reddish crystals of **3b** · CH_2Cl_2 · C_2H_6O (Fig. 3) were determined by X-ray analysis. The Pd–C bond distances of the iminoacyl ligands decrease, in agreement with the decreasing electron delocalization influence of the extended of electron donating group (OMe) located in position (6), as shown in complexes **3a–b** compared with **2a**, or may be decreased due to the *trans* influence of the ligands, thus these values are (in Å): Pd(1)–C(12) 2.0081(16), Pd(2)–C(2) 1.9919(17) (**2a**); Pd–C(40) = 1.9425(18), Pd–C(10) = 1.9999(17) (**3a**); Pd–C(30) = 1.944(2), Pd–C(40) = 2.002(2) (**3b**).

The Pd–Cl distances in (Å) are: Pd(1)–Cl(1) 2.3816(6), Pd(2)–Cl(2) 2.3812(5) **2a**; Pd–Cl 2.4398(4) **3a**, Pd–Cl 2.4283(5) **3b**. Similarly, the Pd–N bond distance in complexes **2a**, **3a** and **3b** were compared: Pd(1)–N(1) 2.0944(14), Pd(2)–N(2) 2.1115(14) **2a**; Pd–N(1) 2.0864(14) **3a** and 2.0905(18) **3b**. Those show the greater *trans* influence of the carbon-donor iminoacyl ligand with respect to the chloro ligand. Looking at these scales, our proposal that the *transphobia* could be directly related to the *trans* influence is reinforced [66] under this assumption; the two ligands with a great *trans* influence will suffer a great *transphobia* [67].

The structure of **2a** (Fig. 1) clearly shows the formation of a palladium atom in a square-planar environment due to the coordination environment consisting of *trans* phosphine, chloro ligands and nitrogen, carbon quinolinyl ligands. The mean deviation of atoms Pd(1), P(1), N(1), Cl(1), C(1) and Pd(2), P(2), N(2), Cl(2), C(2) from the best plane is [Pd(2)–C(2)–Pd(1)–C(12) = 0.0162 Å], [Pd(2)–P(2)–Pd(1)–P(1) = 0.7912 Å], [Pd(2)–Cl(2)–Pd(1)–Cl(1) = 0.004 Å] and [Pd(2)–N(11)–Pd(1)–N(1) = 0.0171 Å]. As expected, for the Pd–C bond distances, Pd(2)–C(2) (2.0081(16) Å) is significantly longer than Pd(1)–C(12) (1.9919(17) Å), the difference being 0.0162 Å. The Pd–N bond distance Pd(2)–N(11) (2.1115(14) Å) is significantly longer than that for Pd(1)–N(1) (2.0944(14) Å), and the difference here is 0.0171 Å, as a result of coordination of the nitrogen atom to Pd(II). However, the Pd–Cl bond distance Pd(2)–Cl(2) (2.3812(5) Å) is just a little bit longer than Pd(1)–Cl(1) (2.3816(6) Å), the difference being 0.004 Å. The Pd–P distance

Pd(2)–P(2) (3.0818(5) Å) is significantly longer than Pd(1)–P(1) (2.2906 Å) and the difference is 0.7912 Å. The reason for the deviation of the Pd(2) compared to Pd(1) in the bond distances for all the ligands around it is due to the greater steric hindrance of PPh_3 and also the trigonal pyramids for the phosphine atom. The angles around Pd(1) and Pd(2) have been compared: C(2)–Pd(2)–N(11) (84.88(6)°) is significantly larger than C(12)–Pd(1)–N(1) (82.22 (6)°) and the difference is 2.66°; C(2)–Pd(2)–P(2) (93.24(5)°) is slightly larger than C(12)–Pd(1)–P(1) (92.32(5)°) and the difference is 0.92°; N(11)–Pd(2)–P(2) (175.12(4)°) is slightly larger than N(1)–Pd(1)–P(1) (174.53(4)°) and the difference is 0.59°; C(2)–Pd(2)–Cl(2) (174.14(5)°) is slightly larger than C(12)–Pd(1)–Cl(1) (173.90(5)°) and the difference is 0.24°; N(11)–Pd(2)–Cl(2) (90.20(4)°) is smaller than N(1)–Pd(1)–Cl(1) (92.30(4)°) by 2.10°; P(2)–Pd(2)–Cl(2) (91.91(2)°) is smaller than P(1)–Pd(1)–Cl(1) (93.14(2)°) by 1.23°; C(2)–Pd(2)–Pd(1) (66.30(5)°) is slightly larger than C(12)–Pd(1)–Pd(2) (66.01(5)°) and the difference is 0.29°; N(11)–Pd(2)–Pd(1) (63.27(4)°) is very slightly larger than N(1)–Pd(1)–Pd(2) (63.12(4)°) and the difference is 0.15°; P(2)–Pd(2)–Pd(1) (111.854(17)°) is smaller than P(1)–Pd(1)–Pd(2) (114.865(14)°) by 3.015°; Cl(2)–Pd(2)–Pd(1) (114.188(16)°) is slightly larger than Cl(1)–Pd(1)–Pd(2) (113.865(19)°) and the difference is 0.323°. These results suggest a delocalization of π electron density around N(1) and P(1) as compared to N(2) and P(2) and distortion of the bond angles around the Pd(1) and Pd(2) due to the greater steric hindrance of PPh_3.

Fig. 2 clearly shows the structure of the red crystalline quinolinepalladium complex **3a**, with the Pd–C distances Pd–C(40) 1.9425(18) Å and Pd–C(10) 1.9999(17) Å. The Pd–Cl(1) distance is 2.4398(4) Å and the Pd–N(1) bond distance is 2.0864(14) Å; these show the greater *trans* influence of the C-donor iminoacyl ligand is with respect to the chloro ligand. The *transphobia* [*T*] is directly related to the *trans* influence of the two ligands and the complex suffers a great *transphobia* effect. The [Pd]C═NXy bond distance of the iminoacyl ligand in complex **3a** is N(10)–C(10) 1.270(2) Å; N(20)–C(20) 1.372(2) Å and N(30)–C(30) 1.429(2) Å are the C═N distances corresponding to the inserted molecule of XyN═C and N(40)–C(40) 1.151(2) Å is the C═N distance corresponding to the inserted molecule of CNXy. All these lengths are as expected for a C═N bond [mean values for the C(aryl)–C═NR distances lie in the range 1.432–1.382 Å] [68–70]. The aryl C═N(Xy)[Pd] distance corresponding to the third inserted molecule of XyNC in **3a** is significantly longer than the other related distances, N(10)–C(10) 1.270(2) Å and N(1)–C(2) 1.325(2) Å, as a result of coordination of the nitrogen atom to Pd(II). This fact, the angles around Pd (C(40)–Pd–C(10) 91.93(7)°, C(40)–Pd–N(1) 178.97(6)°, C(10)–Pd–N(1) 87.11(6)°, C(40)–Pd–Cl(1) 84.21(5)°, C(10)–Pd–Cl(1) 173.33(5)°, N(1)–Pd–Cl(1) 96.78(4)°) and the short C(20)–C(30) bond 1.366(2) Å compared with C(10)–C(20) 1.505(2) Å, suggest a delocalization of π electron density around C(20)–C(30)–N(30) (angle (127.76(15)°) as compared to N(30)–C(30)–C(2) (angle 104.88(13)°), N(20)–C(20)–C(30) (angle 122.27(16)°) and N(20)–C(20)–C(10) (angle 118.83(15)°). The coordination environment of the Pd(II) centre is almost square planar.

Red crystals of **3b**, also suitable for X-ray analysis, were obtained in a similar manner to its analogue **3a**, and the structure of **3b** (Fig. 3) is identical to **3a** except for the different substituents of the OMe group. The Pd–C distances of the iminoacyl quinolinylpalladium complex **3b** are Pd(1)–C(30) 1.944(2) Å and Pd(1)–C(40) 2.002(2) Å. The Pd–Cl distance (Pd(1)–Cl(1) 2.4283(5) Å) and the Pd–N bond distance, Pd(1)–N(1), is 2.0905(18) Å; these again show the greater *trans* influence of the C-donor iminoacyl ligand is with respect to the chloro ligand. Looking at these scales, our proposal that the *transphobia [T]* could be directly related to the *trans* influence is reinforced under this assumption; the two ligands with a great *trans* influence will suffer a great *transphobia [T]* [67]. The [Pd]C═NXy bond distance of the iminoacyl ligand in complex **3b** is N(4)–C(40) 1.266(3) Å; N(5)–C(50) 1.363(3) Å and N(2)–C(12) 1.432(3) Å are the C═N distances corresponding to the inserted molecule of XyN═C and N(3)–C(30) 1.153(3) Å is the C═N distance corresponding to the inserted molecule of CNXy. All these lengths are as expected for a C═N bond [mean values for the C(aryl)–C═NR distances lie in the range 1.432–1.382 Å] [68–70]. The aryl C═N(Xy)[Pd] distance corresponding to the third inserted molecule of XyNC in **3b** is significantly longer than the other related distance, N(4)–C(40) 1.266(3) Å, as a result of coordination of the nitrogen atom to Pd(II). This fact, the angles around Pd (C(30)–Pd(1)–C(40) 91.67(8)°, C(30)–Pd(1)–N(1) 178.75(8)°, C(40)–Pd(1)–N(1) 87.14(8)°, C(30)–Pd(1)–Cl(1) 84.53(6)°, C(40)–Pd(1)–Cl(1) 175.94(6)°, N(1)–Pd(1)–Cl(1) 96.64(5)°) and the short C(12)–C(50) bond 1.365(3) Å compared to C(40)–C(50) 1.507(3) Å, suggest a delocalization of π electron density around the C(50)–C(12)–N(2) (angle 127.34(19)°) as compared to N(2)–C(12)–C(1) (angle 105.08(18)°), N(5)–C(50)–C(12) (angle 123.2(12)°) and N(5)–C(50)–C(40) (angle 119.57(19)°). The coordination environment of the Pd(II) centre is almost square planar.

3. Experimental

Reactions were carried out without precautions to exclude light, atmospheric, oxygen and 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 microanalyzer. 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). Some of the preparations required the use of highly hazardous Tl(I) salts and they should be handle with caution.

3.1. General method for the synthesis of aryl palladium complexes (*2a–b*)

A mixture of [Pd(dba)$_2$] (432 mg, 0.75 mmol), PPh_3 (393.45 mg, 1.5 mmol) and 2-chloro-6-R-3-quinolinecarboxaldehyde **1a–b** (0.75 mmol) was mixed under N_2 in dry acetone (25 ml). The reaction mixture was stirred for 3–5 h at room temperature, then was concentrated (ca. 2 ml) and CH_2Cl_2 (25 ml) was added. The solution was passed through a pad of silica gel/$MgSO_4$ (3:1) in a fritted funnel, and then evaporated under reduced pressure, and Et_2O (15 ml) was added. The resulting solution was concentrated (ca. 2 ml); a mixture of the complex and dba was precipitated with *n*-hexane. The suspension was stirred for 10 min at RT, filtered off, washed with Et_2O (5 ml), and air-dried to give the yellow solid of **2a–b**.

3.1.1. {Pd[C_9H_5-CHO-(3)]Cl(PPh_3)}$_2$ (*2a*)

Purification via flash column chromatography silica gel (1:1 CH_2Cl_2/acetone) afforded a yellow solid **2a**, Yield: 398 mg, 43%. M.p.: 177–179 °C dec. A diffraction-quality crystal was grown by slow diffusion of Et_2O into a CH_2Cl_2 solution. IR (Nujol, cm^{-1}); *ν*(HC═O) 1688.4, *ν*(C═N and C═C) 1612.0, 1582.0, 1572.0 and 1538.0. ^1H NMR (400 MHz, $CDCl_3$); *δ* 10.39 (s, 2H, CHO), 7.34–7.90 (m, 17H, Ar–H), 7.25–6.91 [(m, 23H, Ar–H and (PPh_3)$_2$], 5.28 [(s, 1H, 1/2 (CH_2Cl_2)] ppm. ^{31}P {^1H} NMR (121 MHz, $CDCl_3$); 20.67 ppm. *Anal.* Calc. for $C_{56}H_{42}N_2O_2Cl_2Pd_2P_2$ (1120.62): C, 60.02; H, 3.78; N, 2.50. Found; C, 60.01; H, 3.75; N, 2.35%.

*3.1.2. [Pd[-6-OCH_3-C_9H_4-CHO-(3)]Cl(PPh_3)}$_2$ (**2b**)*

Purification via flash column chromatography silica gel (1:1 CH_2Cl_2/acetone) afforded a yellow-solid **2b**, Yield: 277 mg, 31.2%. M.p.: 180–182 °C dec. A diffraction-quality crystal was grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **2b**. IR (Nujol, cm^{-1}); ν(HC=O) 1678.0, ν(C=N and C=C) 1584.0, 1546.0. ^1H NMR (400 MHz, $CDCl_3$); δ 10.43 (s, 2H, CHO), 7.79–7.46 (m, 15H, Ar–H), 7.41–7.05 [(m, 22H, Ar–H and $(PPh_3)_2$], 6.60 (d, 1H, J = 2.6Hz), 3.84 (s, 6H, OMe) ppm. ^{31}P {^1H} NMR (121 MHz, $CDCl_3$); 21.37 ppm. *Anal.* Calc. for $C_{58}H_{46}N_2O_4Cl_2Pd_2P_2$ (1180): C, 59.00; H, 3.93; N, 2.37. Found; C, 59.08; H, 4.04; N, 2.32%.

*3.2. 4-(2,6-Dimethyl-phenyl)-3-(2,6-dimethyl-phenylamino)-2-(2,6-dimethyl-phenylimino)-1-[(2,6-dimethyl-phenylisonitrile)]-2,4-dihydro-1H-4,10b-diaza-acephenanthrylene-5-one-1-palladium(II)chloride complex (**3a**)*

3.2.1. Method (A)

To a suspension of 'Pd(dba)$_2$' (300 mg, 0.52 mmol) and XyNC (274 mg, 2.09 mmol) in acetone (15 ml), 2-chloro-3-quinoline carboxaldehyde **1a** (149.4 mg, 0.78 mmol) was added under nitrogen. The suspension was stirred for 5 h at room temperature, then the solvent was evaporated. The resulting residue was extracted with CH_2Cl_2 (25 ml) and the extract filtrate was filtered over anhydrous $MgSO_4$/silica gel (1:3) in a fritted funnel. The resulting red solution was evaporated and the residue was triturated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving the red compound **3a**, yield, 254 mg, 39%. Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **3a**. M.p.: Dec. pt: 255 °C. IR (Nujol, cm^{-1}):): ν(NH, broad band) 3353, ν(C=O) 1716, 1699, ν(C≡N) 2361, 2338, ν(C=N) 1558, 1541. ^1H NMR (200 MHz, $CDCl_3$) δ 8.87 (s, 1H, NH), 8.83–8.78 (d, 1H, *J* = 8.6 Hz), 7.99–7.87 (q, 2H, *J* = 8.6 Hz), 7.63–7.55 (t, 1H, *J* = 7.6 Hz), 7.35–7.22 (m, 3H), 7.19–6.97 (m, 5H), 6.91–6.73 (m, 4H), 6.40–6.37 (d, 1H, *J* = 7.2 Hz), 2.55 (s, Me, 3H), 2.49 (s, Me, 3H), 2.30 (s, Me, 3H), 2.19 (s, Me, 6H), 2.11 (s, Me, 3H), 1.58 (s, Me, 3H) 0.62 (s, Me, 3H) ppm. *Anal.* Calc. for $C_{46}H_{42}N_5OClPd$ (822): C, 67.15; H, 5.15; N, 8.50. Found: C, 67.04; H, 5.09; N, 8.14%.

3.2.2. Method (B)

To a suspension of {Pd[C_9H_5-CHO (3)]Cl(PPh_3)}$_2$ **2a** (268 mg, 0.24 mmol) in CH_2Cl_2 (15 ml), XyNC (248 mg, 1.92 mmol) was added. The suspension was stirred for 24 h at room temperature. The color changed from pale yellow into pale red and then dark red whilst the reaction mixture was monitored. The solvents were filtered over a pad of anhydrous $MgSO_4$/silica gel (1:3) in a fritted funnel. The resulting red solution was evaporated and the residue was triturated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving the red compound **3a**. Yield: 160 mg, 81%. Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **3a**.

*3.3. 4-(2,6-Dimethyl-phenyl)-3-(2,6-dimethyl-phenylamino)-2-(2,6-dimethyl-phenylimino)-1-[(2,6-dimethyl-phenylisonitrile)]-8-methoxy-2,4-dihydro-1H-4,10b-diaza-acephenanthrylene-5-one-1-palladium(II) chloride complex (**3b**)*

3.3.1. Method (A)

2-Chloro-6-methoxy-3-quinoline carboxaldehyde **1b** (172.86 mg, 0.78 mmol) was added to a suspension of 'Pd(dba)$_2$' (300 mg, 0.52 mmol) and XyNC (274 mg, 2.09 mmol) in acetone (15 ml) under nitrogen. The suspension was stirred for 5 h at room temperature. The solvents were evaporated, the residue was extracted with CH_2Cl_2, and the extract filtrate was filtered over a pad of anhydrous $MgSO_4$/silica gel (1:3) in a fritted funnel. The resulting red solution was evaporated and the residue was triturated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving the red solid compound **3b**.Yield: 223 mg, 33.5%. Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **3b**. M.p.: 238–240 °C. IR (Nujol, cm^{-1}): ν(NH, broad band) 3360, ν(C≡N) 2182.7, ν(C=O) 1704.5, ν(C=N) 1602.4, 1570.1. ^1H NMR (200 MHz, $CDCl_3$) δ 8.75 (s, 1H, NH), 8.71 (d, 1H, $^3J_{HH}$ = 8.6 Hz), 7.67–7.57 (dd, 1H, $^4J_{HH}$ = 2.6, $^3J_{HH}$ = 9.6 Hz, quinoline-H_8), 7.27–7.18 (m, 5H), 7.14–7.11 (s, 1H), 7.07–6.96 (m, 3H), 6.89–6.80 (m, 4H), 6.40–6.36 (d, 1H, $^3J_{HH}$ = 7.6 Hz, quinoline-H), 3.96 (s, 3H, OMe), 2.54 (s, Me, 3H), 2.49 (s, Me, 3H), 2.29 (s, Me, 3H), 2.18 (s, Me, 6H), 2.12 (s, Me, 6H), 0.62 (s, Me, 3H) ppm. *Anal.* Calc. for $C_{47}H_{44}N_5O_2ClPd$ (852) + H_2O = (870.79): C, 64.83: H, 5.32: N, 8.04. Found: C, 64.91: H, 5.12: N, 8.04%.

3.3.2. Method (B)

To a suspension of {Pd[6-OCH_3-C_9H_5-CHO (3)]Cl(PPh_3)}$_2$ (**2b**) (283 mg, 0.24 mmol) in CH_2Cl_2 (15 ml), XyNC (248 mg, 1.92 mmol) was added. The suspension was stirred for 24 h at room temperature and the color changed from pale yellow into pale red and then dark red whilst the reaction mixture was monitored. The solvents were filtered over a pad of anhydrous $MgSO_4$/silica gel (1:3) in a fritted funnel. The resulting red solution was evaporated and the residue was triturated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving the red compound **3b**. Yield, 158 mg, 77%. Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **3b**.

4. Depalladation procedure

*4.1. General procedure for the acetamidic acids (**4a**–**b**) and acetamide (**5a**–**b**)*

Tl(TfO) (314 mg, 0.89 mmol) was added to a suspension of **3a–b** (0.89 mmol) in Me_2CO (20 ml). The resulting red suspension was stirred for 20 h. During this time decomposition to metallic palladium was observed and a dark brownish suspension formed. This was filtered over Celite, and the filtrate was concentrated and applied to a preparative TLC plate (eluant: *n*-hexane/Et_2O, 1:2). A yellow band at R_f = 0.25 was collected and extracted with Me_2CO (30 ml). The resulting solution was dried with anhydrous $MgSO_4$ for 1 h and filtered, and the filtrate was evaporated to dryness, giving a 2:3 mixture of both tautomers **5a–b** and **4a–b**. A sample of this mixture (200 mg) was dissolved in Et_2O (30 ml), the solution was evaporated to dryness, and the residue was treated with Et_2O (30 ml), causing the precipitation of a solid, which was filtered and air-dried to give yellow **4a–b** (41%). The same process was repeated with the mother liquor, giving **5a–b** (27%).

*4.2. N-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylamino)-2-[2-(2,6-dimethylphenyl)-1-oxo-1,2-dihydro-pyrrolo[3,4-b]quinolin-3-ylidene]-acetimidic acid (**4a**)*

M.p.: 206–208 °C. IR (cm^{-1}): ν(OH), ν(NH) 3420, 3232 b, ν(C=O), ν(C=N) 1682, 1668. ^1H NMR (200 MHz, $CDCl_3$) δ 8.77 (d, 1H, quinol-H_4), 8.37 (dd, 1H, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.6 Hz, quinol-H_8), 7.97 (d, 1H, $^3J_{HH}$ = 8.6 Hz, quinol-H_5), 7.73 (dd, 1H, $^3J_{HH}$ = 8.6 and 6.9 Hz, quinol-H_7), 7.43 (dd, 1H, $^3J_{HH}$ = 8.6 and 6.8 Hz, quinol-H_6), 7.30–7.21 (m, 3H), 7.14–6.96 (m, 6H), 6.89 (s, 1H, NH), 5.58 (s, 1H, NH), 2.39 (s, 2Me, 6H), 2.29 (s, 2Me, 6H), 1.63 (s, Me, 6H), 1.54 (s, 1H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 (C=O), 164.9 (quaternary C), 156.8 (quaternary C), 151.4 (quaternary C), 148.8 (quaternary C), 147.2 (quaternary C), 139.7 (quaternary C), 137.9 (CH), 131.1 (CH), 130.1 (CH), 129.9 (quaternary C), 129.7

(quaternary C), 128.6 (CH), 127.5 (CH), 127.4 (quaternary C), 127.2 (CH), 127.0 (CH), 126.8 (CH), 126.4 (quaternary C), 124.7 (quaternary C), 124.7 (CH), 124.1 (CH), 123.1 (CH), 122.0 (quaternary C), 105.5 (quaternary C), 18.8 (2 × Me), 18.3 (2 × Me), 18.1 (2 × Me). *Anal.* Calc. for $C_{37}H_{34}N_4O_2$ (566.7): C, 78.42; H, 6.05; N, 9.89. Found: C, 78.36; H, 6.06; N, 9.87%.

4.3. N-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylamino)-2-[2-(2,6-dimethylphenyl)-7-methoxy-1-oxo-1,2-dihydro-pyrrolo[3,4-b]quinolin-3-ylidene]-acetimidic acid (**4b**)

M.p.: 211–213 °C. IR (cm^{-1}): ν(OH), νNH) 3420, 3232 b, ν(C=O), ν(C=N) 1668. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.79 (d, 1H, quinol-H_4), 8.42 (dd, 1H, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.7 Hz, quinol-H_8), 7.97 (d, 1H, $^3J_{HH}$ = 8.7 Hz, quinol-H_5), 7.73 (dd, 1H, $^3J_{HH}$ = 8.7 and 6.8 Hz, quinol-H_7), 7.43 (dd, 1H, $^3J_{HH}$ = 8.7 and 6.8 Hz, quinol-H_6), 7.3–7.2 (m, 3H), 7.14–6.95 (m, 6H), 5.58 (s, 1H, NH), 3.96 (s, 3H, OMe), 2.39 (s, 2Me, 6H), 2.29 (s, 2Me, 6H), 1.63 (s, Me, 6H), 1.54 (s, 1H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 (C=O), 164.9 (quaternary C), 156.8 (quaternary C), 151.4 (quaternary C), 148.8 (quaternary C), 147.2 (quaternary C), 139.7 (quaternary C), 137.9 (CH), 131.1 (CH), 130.1 (CH), 129.9 (quaternary C), 129.7 (quaternary C), 128.6 (CH), 127.5 (CH), 127.4 (quaternary C), 127.2 (CH), 127.0 (CH), 126.8 (CH), 126.4 (quaternary C), 124.7 (quaternary C), 124.7 (CH), 124.1 (CH), 123.1 (CH), 122.0 (quaternary C), 105.5 (quaternary C), 57.34 (OMe), 18.8 (2 × Me), 18.3 (2 × Me), 18.1 (2 × Me). *Anal.* Calc. for $C_{38}H_{36}N_4O_3$ (596.7): C, 78.49; H,6.06; N, 9.39. Found: C, 78.46; H, 6.04; N, 9.36%.

4.4. N-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylamino)-2-[2-(2,6-dimethylphenyl)-1-oxo-1,2-dihydro-pyrrolo[3,4-b]quinolin-3-ylidene]-acetamide (**5a**)

M.p.: 146–148 °C. IR (cm^{-1}): ν(NH) 3388, 3366, 3262 broad, ν(C=O) 1698, ν(C=N), 1668. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.77 (d, 1H, quinol-H_4), 8.37 (dd, 1H, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.6 Hz, quinol-H_8), 7.97 (d, 1H, $^3J_{HH}$ = 8.6 Hz, quinol-H_5), 7.73 (dd, 1H, $^3J_{HH}$ = 8.6 and 6.9 Hz, quinol-H_7), 7.43 (dd, 1H, $^3J_{HH}$ = 8.6 and 6.8 Hz, quinol-H_6), 7.30–7.21 (m, 3H), 7.14–6.96 (m, 6H), 6.89 (s, 1H, NH), 5.07 (s, 1H, NH), 2.44 (s, 2Me, 6H), 2.29 (s, 2Me, 6H), 2.02 (s, Me, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8 (C=O), 162.6 (C=O), 157.8 (quaternary C), 147.8 (quaternary C), 146.8 (quaternary C), 139.8 (quaternary C), 139.6 (quaternary C), 137.8 (CH), 135.9 (quaternary C), 135.7 (quaternary C), 135.6 (quaternary C), 134.9 (quaternary C), 132.7 (quaternary C), 132.1 (CH), 131.9 (CH), 129.14 (CH), 129.11 (CH), 128.6 (CH), 127.54 (CH), 127.48 (quaternary C), 127.3 (CH), 126.8 (CH), 126.4 (CH), 124.0 (CH), 122.0 (CH), 112.9 (quaternary C), 18.8 (2 × Me), 18.3 (2 × Me), 18.1 (2 × Me). *Anal.* Calc. for $C_{37}H_{34}N_4O_2$ (566.7): C, 78.42; H, 6.05; N, 9.89. Found: C, 78.31; H, 6.12; N, 9.84%.

4.5. N-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylamino)-2-[2-(2,6-dimethylphenyl)-7-methoxy-1-oxo-1,2-dihydro-pyrrolo[3,4-b]quinolin-3-ylidene]-acetamide (**5b**)

Mp: 146–148 °C. IR (cm^{-1}): ν(NH) 3388, 3366, 3262 broad, ν(C=O) 1698, ν(C=N), 1668. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.77 (d, 1H, quinol-H_4), 8.37 (dd, 1H, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.6 Hz, quinol-H_8), 7.97 (d, 1H, $^3J_{HH}$ = 8.6 Hz, quinol-H_5), 7.73 (dd, 1H, $^3J_{HH}$ = 8.6 and 6.9 Hz, quinol-H_7), 7.43 (dd, 1H, $^3J_{HH}$ = 8.6 and 6.8 Hz, quinol-H_6),7.30–7.21 (m, 3H), 7.14–6.96 (m, 6H), 6.89 (s, 1H, NH), 5.07 (s, 1H, NH), 3.96 (s, 3H, OMe), 2.44 (s, 2Me, 6H), 2.29 (s, 2Me, 6H), 2.02 (s, Me, 6H), ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8 (C=O), 162.6 (C=O), 158.8 (quaternary C), 154.8 (quaternary C), 148.8 (quaternary C), 143.8 (quaternary C), 139.8 (quaternary C), 139.6 (quaternary C), 136.9 (CH), 135.9 (quaternary C), 135.7 (quaternary C), 135.6 (quaternary C), 134.9 (quaternary C), 132.7 (quaternary C), 131.7 (CH), 129.11 (CH), 128.6 (CH), 127.54 (CH), 127.48 (quaternary C), 127.3 (CH), 126.8 (CH), 126.4 (CH), 124.0 (CH), 122.0 (CH), 112.9 (quaternary C), 57.34 (OMe), 18.8 (2 × Me), 18.3 (2 × Me), 18.1 (2 × Me). *Anal.* Calc. for $C_{38}H_{36}N_4O_3$ (596.7): C, 76.49; H, 6.06; N, 9.39. Found: C, 76.41; H, 6.02; N, 9.34%.

4.6. General Procedure of the ethyl esterification of acetamidic acids (**6a**–**b**)

Tl(TfO) (374 mg, 1.06 mmol) and EtOH (one drop) were added to a solution of **3a–b** (1.06 mmol) in CH_2Cl_2 (20 ml). The resulting black suspension was stirred for 20 h and filtered over Celite, and the yellow filtrate was concentrated and applied to a preparative TLC plate (eluant: *n*-hexane/Et_2O, 1:2), where two main yellow bands separated. From the band at R_f = 0.25 a 2:1 mixture of **5a–b** and **4a–b** was obtained in moderate yield. The band at R_f = 0.62 was collected and extracted with Me_2CO (30 ml). The extract was treated with anhydrous $MgSO_4$ for 1 h, filtered and evaporated to dryness, affording the yellow ester **6a–b** in low yields (18–19%).

4.7. N-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylamino)-2-[2-(2,6-dimethylphenyl)-1-oxo-1,2-dihydro-pyrrolo[3,4-b]quinolin-3-ylidene]acetimidic acid ethyl ester (**6a**)

A suspension solution of **3a** (871.32 mg, 1.06 mmol) in CH_2Cl_2 (20 ml) was used under the reaction conditions to produce **6a** in the yield 122 mg, 19%. M.p.: 210–212 °C. IR (cm^{-1}): ν(NH) 3384, ν(C=O), ν(C=N) 1698, 1694, 1660. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.86 (d, 1H, quinol-H_4), 8.34 (dd, 1H, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.4 Hz, quinol-H_8), 7.87 (d, 1H, $^3J_{HH}$ = 8.4 Hz, quinol-H_5), 7.73 (dd, 1H, $^3J_{HH}$ = 8.4 and 6.8 Hz, quinol-H_7), 7.45 (dd, 1H, $^3J_{HH}$ = 8.4 and 6.8 Hz, quinol-H_6), 7.10–7.05 (m, 3H), 6.80–6.69 (m, 6H), 4.79 (s, NH, 1H), 4.39 (q, CH_2Me, 2H, $^2J_{HH}$ = 7 Hz), 2.22 (s, 2 × Me, 6H), 1.48 (bs, 4 × Me, 12H), 1.39 (t, CH_2Me, 3H, $^2J_{HH}$ = 7 Hz) ppm. *Anal.* Calc. for $C_{39}H_{38}N_4O_2$ (594.7): C, 78.76; H,6.44; N, 9.42. Found: C, 78.74; H, 6.22; N, 9.35%.

4.8. N-(2,6-Dimethylphenyl)-2-(2,6-dimethylphenylamino)-2-[2-(2,6-dimethylphenyl)-7-methoxy-1-oxo-1,2-dihydro-pyrrolo[3,4-b]quinolin-3-ylidene]acetimidic acid ethyl ester (**6b**)

A suspension solution of **3b** (903.12 mg, 1.06 mmol) in CH_2Cl_2 (20 ml) was used under the reaction conditions to produce **6b** in the yield 120 mg, 18%. M.p.: 206–208 °C. IR (cm^{-1}): ν(NH) 3384, ν(C=O), ν(C=N) 1698, 1694, 1660. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, 1H, quinol-H_4), 8.34 (dd, 1H, $^4J_{HH}$ = 1.6, $^3J_{HH}$ = 8.4 Hz, quinol-H_8), 7.87 (d, 1H, $^3J_{HH}$ = 8.4 Hz, quinol-H_5), 7.73 (dd, 1H, $^3J_{HH}$ = 8.4 and 6.8 Hz, quinol-H_7), 7.45 (dd, 1H, $^3J_{HH}$ = 8.4 and 6.8 Hz, quinol-H_6), 7.10–7.05 (m, 3H), 6.80–6.69 (m, 6H), 4.79 (s, NH, 1H), 4.39 (q, CH_2, 2H, $^2J_{HH}$ = 7 Hz), 2.22 (s, 2 × Me, 6H), 1.48 (bs, 4 × Me, 12H), 1.39 (t, CH_2Me, 3H, $^2J_{HH}$ = 7 Hz) ppm. *Anal.* Calc. for $C_{40}H_{40}N_4O_3$ (624.8): C, 76.90; H, 6.45; N, 8.97. Found: C, 76.83; H, 6.42; N, 9.02%.

4.9. X-ray crystallographic studies

Details of data collection and refinement are given in Table 1. The crystal structures from the single-crystal X-ray diffraction studies for **2a**, **3a** and **3b** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 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

Table 1
Details of data collection and structure refinement for the complexes {Pd[C_9H_5-CHO(3)]Cl(PPh_3)}$_2$ **2a**, {PdCl[(C=N-Xy)$_2$-(C-NHXy) (CNXy)C_9H_5N-(3)-CO]} **3a** and {PdCl[(C=N-Xy)$_2$-(C-NHXy) (CNXy) 6-MeO-C_9H_5N-(3)-CO]}**3b**.

	2a · CH_2Cl_2	**3a** · CH_2Cl_2	**3b** · C_2H_6O · CH_2Cl_2
Empirical formula	$C_{56}H_{42}Cl_2N_2O_2P_2Pd_2$	$C_{46}H_{42}ClN_5OPd$	$C_{47}H_{43}ClN_5O_2Pd$
E. F. as X-ray measure	$C_{57}H_{44}C_{l4}N_2O_2P_2Pd_2$	$C_{47}H_{44}Cl_3N_5OPd$	$C_{50}H_{51}Cl_3N_5O_3Pd$
Formula weight	1205.48	907.62	982.71
Temperature (K)	133(2)	133(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal habit	yellow rectangular prim	red tablet	red prism
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P21/c$	$P2(1)/c$
Unit cell dimensions			
a (Å)	11.8384(11)	11.7167(8)	8.3018(3)
b (Å)	13.451(2)	20.1516(14)	19.8319(8)
c (Å)	17.804(3)	18.7484(12)	27.3429(11)
α (°)	106.116(11)	90	90
β (°)	96.793(15)	108.055(4)	95.2830(10)
γ (°)	111.512(12)	90	90
V (Å^3)	2456.0(6)	4208.7(5)	4482.6(3)
Z	2	4	4
D_{calc} (Mg/m^3)	1.630	1.432	1.456
Absorption coefficient (mm^{-1})	1.062	0.674	0.642
F(000)	1212	1864	2028
Crystal size (mm^3)	0.36 × 0.15 × 0.11	0.25 × 0.19 × 0.10	0.25 × 0.15 × 0.14
θ Range for data collection (°)	1.23–30.04	1.53–30.04	1.81–27.10
Index ranges	$-16 \leqslant h \leqslant 16$, $-18 \leqslant k \leqslant 18$, $-25 \leqslant l \leqslant 25$	$-16 \leqslant h \leqslant 16$, $-28 \leqslant k \leqslant 28$, $-26 \leqslant l \leqslant 26$	$-10 \leqslant h \leqslant 10$, $-25 \leqslant k \leqslant 25$, $-35 \leqslant l \leqslant 34$
Reflections collected	46379	66861	50825
Independent reflections (R_{int})	14268 (0.0293)	12314 (0.0476)	9847 (0.0231)
Completeness to θ = 30.00° (%)	99.4	100.0	99.7
Absorption correction	numerical	numerical	semi-empirical from equivalents
Maximum and minimum transmission	0.9069 and 0.7461	0.9387 and 0.8509	0.9155 and 0.8559
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	14268/0/622	12314/0/526	9847/32/571
Goodness-of-fit on F^2	1.029	0.982	1.065
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0251, $wR2$ = 0.0630	$R1$ = 0.0306, $wR2$ = 0.0724	$R1$ = 0.0352, $wR2$ = 0.0909
R indices (all data)	$R1$ = 0.0335, wR2 = 0.0664	$R1$ = 0.0478, $wR2$ = 0.0778	$R1$ = 0.0395, $wR2$ = 0.0938
Largest difference in peak and hole (e Å^{-3})	0.997 and −0.960	1.037 and −0.887	1.671 and −0.527

absorption. The structures were 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. Structure solution and refinement were performed by using the SHELXL-97 package. [71] Crystal data and processing parameters for **2a**, **3a** and **3b** are summarized in Table 1.

5. Conclusion

We successfully developed a new type of iminoacyl quinolinyl palladium complexes and palladacycles that allows the preparation of new carbocycles via a depalladation reaction. Overall, this methodology provides an alternative approach to novel quinolinylpalladium complexes and amide **5a–b** or imidic acid **4a–b** from three simple and readily available building blocks via a one-pot, multi-component process. These novel arylpalladium complexes are air- and moisture stable, and further scope of this class of arylpalladium complexes and applications are currently under investigation in our laboratory.

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Appendix A. Supplementary data

CCDC 680962, 680963, 680964 contain the supplementary crystallographic data for **2a**, **3a**, **3b**. 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. ^{1}H and ^{31}P NMR spectra for compounds **2a**, **3a** and **3b**. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.10.054.

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