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Conversion of iminoacyl quinolinylpalladium (II) complexes into novel oxo-pyrrolo[3,4-*b*] quinolines via depalladation reactions

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Oxidative addition reactions of quinolines 1a, b with $Pd(dba)_2$ in the presence of PPh_3 (1 : 2) in acetone gave dinuclear palladium complexes $[Pd(C,N\text{-}2\text{-}C_9H_4N\text{-}CHO\text{-}3\text{-}R\text{-}6)Cl(PPh_3)]_2$ [(R = H (2a), R = OMe (2b), which were reacted with isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$) to give novel iminoacyl quinolinylpalladium complexes 3a, b in good yields (81 and 77%). Cyclopalladated complexes3a, b were also obtained in low yields (39 and 33.5%) via one-pot reaction of 1a, b with isonitrile XyNC : $Pd(dba)_2$ (4 : 1). The reaction of 3a,b with Tl(TfO) (TfO = triflate, CF_3SO_3) in the presence of H_2O or EtOH causes depalladation reactions of complexes to provide the corresponding organic compounds 4a, b, 5a, b and 6a, b in yields of 41, 27 and 18 −19%, respectively. The products were characterized by satisfactory elemental analyses and spectral studies (IR, ^1H, ^{13}C and ^{31}P NMR). The crystal structures 2a, 3a and3b were determined by X-ray diffraction studies.

Keywords: quinoline; arylpalladium complexes; oxopyrrolo[3,4-b]quinolines; acetimidic acid ethyl ester; isocyanides

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 metalated carbon is usually an aromatic sp^2 carbon.[13–17] However, six-membered palladacycles with iminoyl (C═N-) sp^2 carbon are rather rare. This is probably due to poor stability, which causes difficulties in preparation, isolation and characterization of these complexes. The limitation can be overcome by changing the nature of the metalated carbon atom, the type of donor groups and their substituents. Some of these reactions involve *ortho*-functionalized aryl complexes that, after insertion of isocyanides, give heterocyclics in which the *ortho* group is included.[18–20] Establishing synthetic procedures for these complexes invariably involves the presence of other strongly coordinated ligands, such as PPh_3,[21–23] and these are attracting interest. Relatively little is known concerning the cyclometalation of aldehyde functionalities.[24–33] The interest in this subject has prompted us to prepare arylpalladium complexes **2a-b** of quinoline containing *ortho*-CHO functionalized. 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 $[N\text{-aryl-Pd-Cl}(PPh_3)]_2$, **2a**, **b**, with uncommon '$Pd_2C_2N_2$' central cores formed by oxidative addition of a chloroquinolines **1a**, **b** to a Pd(0) is supported by X-ray structures. The utility of cyclopalladated complexes**3a**, **b** in organic synthesis via their depalladation reactions to provide amidic acid or esters (**4a**, **b**, **5a**, **b**, **6a**, **b**) is the subject of interest of this manuscript. The sequence of the reactions leads eventually to compounds that could potentially possess pharmacological properties.[34–52]

Results and Discussion

Oxidative addition reactions of 2-chloro-6-R-3-quinoline-craboxaldehydes [R = H (**1a**), R = OMe (**1b**)] with stoichiometric amounts of $[Pd(dba)_2]$ = ($[Pd_2(dba)_3]$.dba; dba = dibenzylideneacetone)[53] in the neutral ligand such as PPh_3 (1 : 2 : 1) under nitrogen in degassed acetone giving the dimeric palladium complexes$\{Pd[C_9H_5\text{-}CHO(3)]Cl(PPh_3)\}_2$ **2a** and $\{Pd[\text{-}6\text{-}OCH_3\text{-}C_9H_4\text{-}CHO(3)]Cl(PPh_3)\}_2$ **2b** in moderate yields (43 and 31%), through the coordination of 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 formed monuclear complexes **3a**, **b** in high yields (81 and 77%). The palladacycles **3a**, **b** were also obtained in low yields (39 and 33.5%) by direct oxidative addition of 2-chloro-6-R-3-quinolinecraboxaldehydes**1a**, **b** to $Pd(dba)_2$ in the presence of stoichiometric amounts of isocyanide XyNC in degassed acetone at room temperature, as depicted in Scheme 1.

It is envisioned that the oxidative addition reaction of **1a**, **b** with $Pd(dba)_2$−PPh_3 could give the expected complex in a *transoid* form (**A**). The *trans* complexes could not be isolated, and the only yellow powder solid was isolated in the pure form of the dimeric palladium complexes **2a**, **b**, as outlined in Scheme 2. This is probably due to the result of the interchange between the

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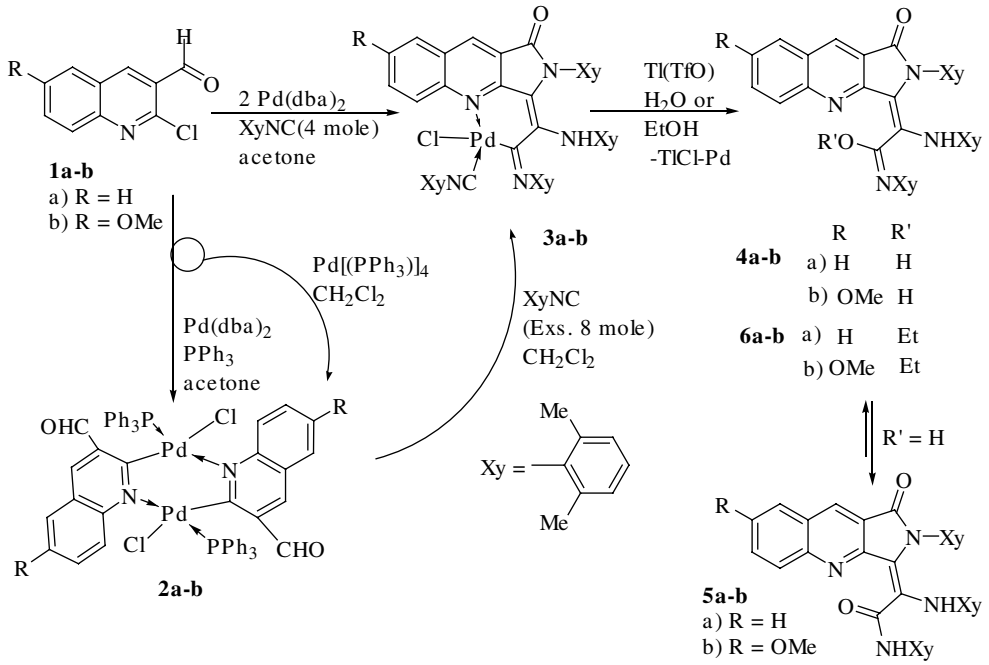
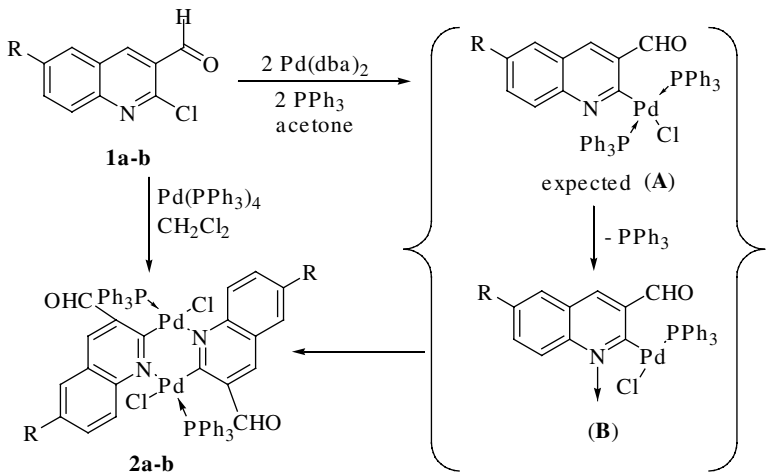


Scheme 1. Conversion the 2-chloroquinolines-3-carbaldehyde into the corresponding isoindolinones.



Scheme 2. Displayed the selective conformation of the dinuclear complexes **2a-b**.

nitrogen donor of the quinoline ring and the PPh_3 ligand of palladium, which is a very well-known process.[54] It is possible that **A** and**B** are intermediates for the formation of complexes **2a**, **b** and the presence of PPh_3 as ligand could be responsible for the interchange of the ligands and the existence of complex **2a** or **2b** in solution as a mixture of complexes derived from two *trans* form. The formation of the dimeric complexes **2a**, **b** are consistent with related dimeric palladium complex $[Pd(\mu\text{-pyridine})Cl(PPh_3)]_2$ formed by oxidative addition of a 2-chloropyridine to a $Pd(PPh_3)_4$ complex.[55]

These complexes were confirmed by the appearance of one singlet signal in their ^{31}P NMR spectrum, corresponding to an**AB** system. The reaction products were identified by comparison of the ^{31}P-NMR spectra of the reaction mixture with those of the related reported complexes, which showed two **AB** resonance patterns after explanation of the ^{31}P-NMR spectra recorded where R = H (**2a**) and R = OMe (**2b**) at δ20.67 and 21.37 ppm, as shown in Fig. 1.

The ^1H NMR spectrum did not show the presence of impurities for all of the complexes **2a** or**2b**, although the quinoline backbone showed slight variations when complexes **2a** or **2b** were compared. However, not enough is known about the palladium-carbon bonds of these complexes, through four bonds. This promoted us to place emphasis on these data, while this 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 ν(C═O), ν(C═N), ν(C═C) mode in **2a**, **b** indicated the non-coordination of the carbonyl group in these complexes. In complex **2a**, IR appeared at 1688, 1612 and 1582 cm^{-1} and **2b** appeared slightly shorter at 1678, 1584 and 1546 cm^{-1}. The complexes **2a**,**b** showed in their IR spectra a strong band at ca. 1688 and 1678 cm^{-1} assignable to

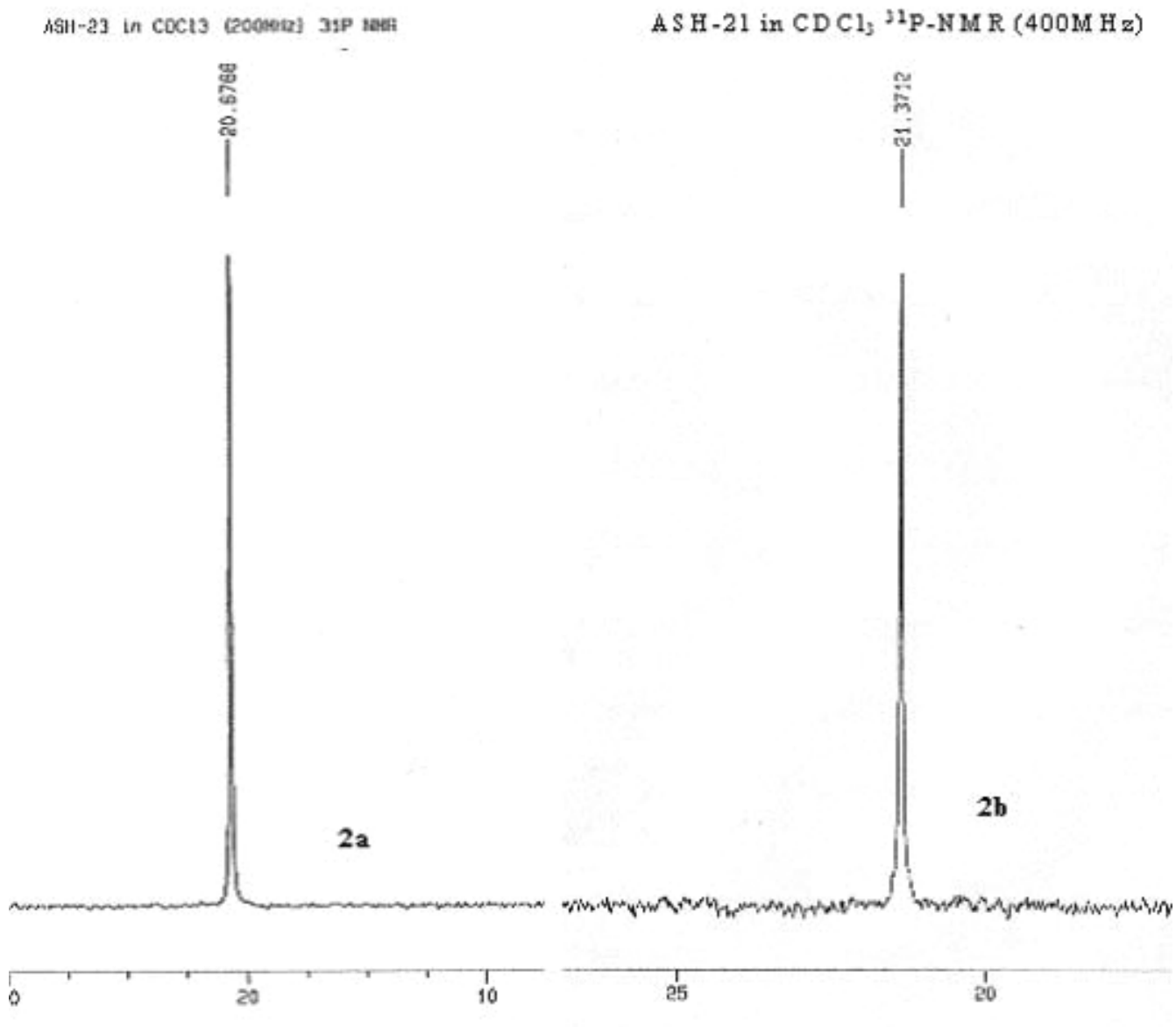


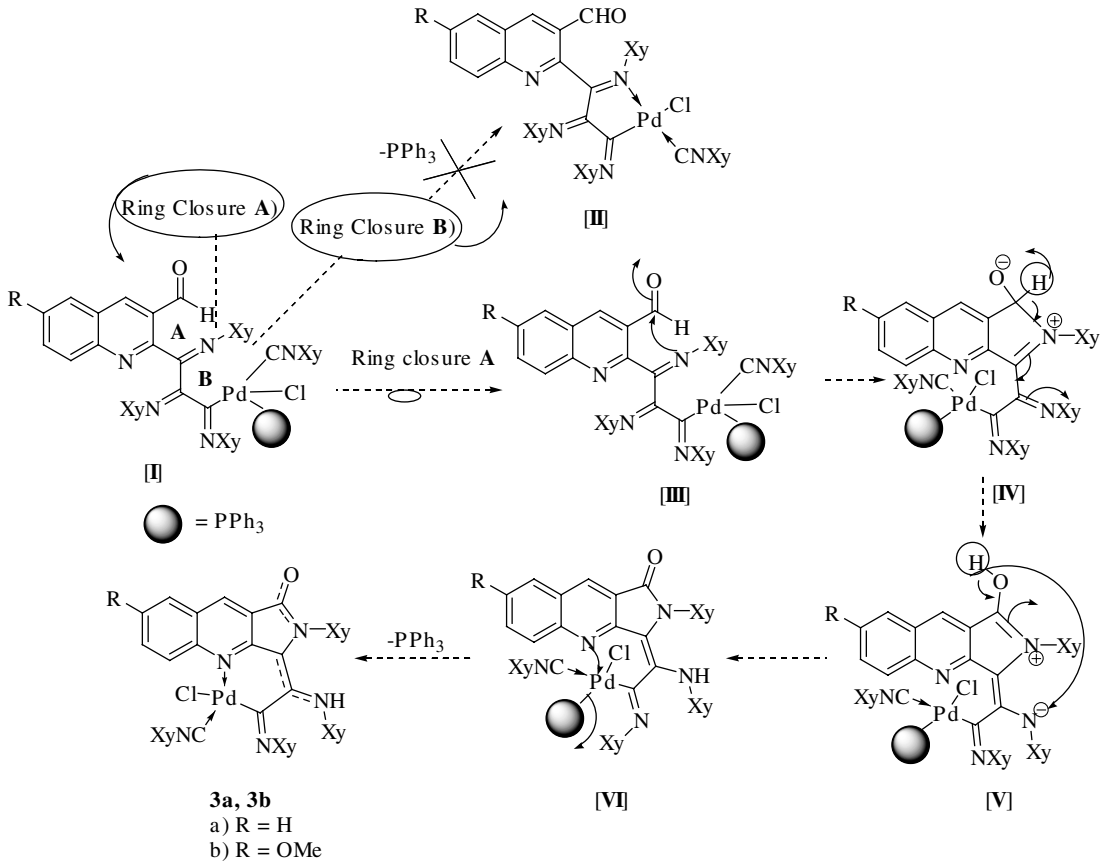
Figure 1. ^{31}P-NMR spectrum for the complexes **2a** and **2b**.

ν(C═O) of the formyl group. These frequencies are similar to that observed in the start materials **1a**,**b** and indicate that there was no coordination of the formyl group to the metal atom.

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 M) to a mixture of 'Pd(dba)$_2$' (1 M) and XyNC (Xy = 2,6-$Me_2C_6H_3$) (4 M) in acetone at room temperature yields a triinserted iminoacyl palladium complexes **3a** and **3b** in low yields (39 and 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** and **3b**, the stoichiometric amounts of this mixtures were used at [(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 depicted the formation of possible intermediates [Pd{C(═NXy)$_3$Ar}Cl(CNXy)] (**I**) 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, followed by 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 into the nitrogen atom of the second inserted isocyanide, which was supported by X-ray structures and displayed the nitrogen proton at N(20)-H (**3a**, Fig. 3) and N(5)-H (**3b**, Fig. 4). The favored attack of quinolinyl nitrogen at the (Pd) metal center in intermediate (**VI**), could in turn lead to iminoacyl quinolinylpalladium **3a** or **3b**. The previously reported[56–61] synthesis of a highly functionalized ketenimine from di-insertion of XyNC into an (*o*-formylaryl) palladium complex is consistent



Scheme 3. A mechanistic sequence for the formation of mononuclear palladium complexes.

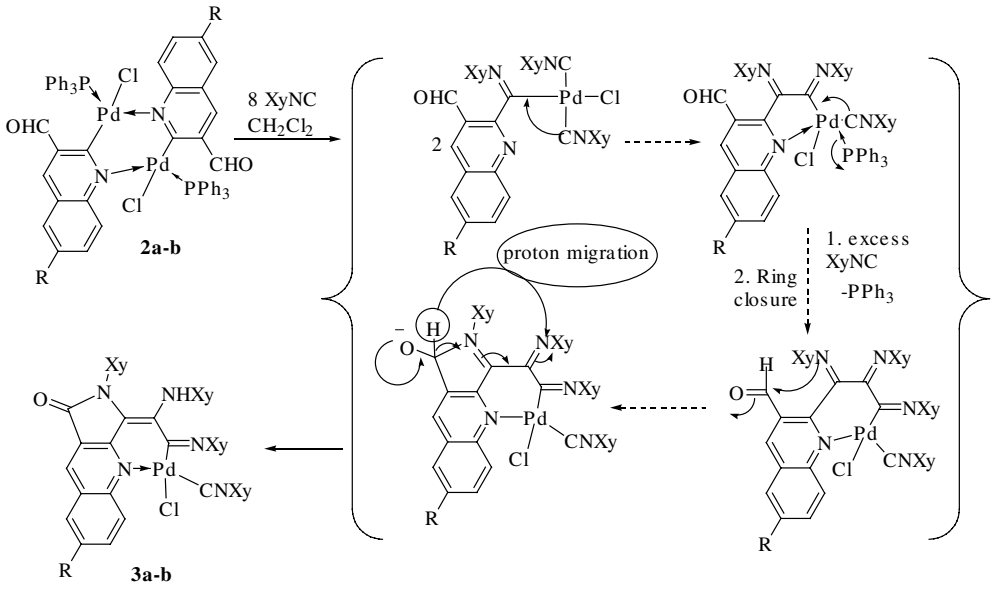
with the result described here. The formation of such a ketenimine is also the result of the attack of the nitrogen on the primarily inserted isocyanide at the formyl carbon. A mechanistic proposal is consistent with the literature data,[62] given in Scheme 3.

The reactivity of the dinuclear palladium complexes **2a**, **b** toward bulky isocyanide XyNC (Xy = 2,6-$Me_2C_6H_3$) was examined and depends on the nature of the ligands and the reaction conditions. Thus, when the insertion reaction takes place in different molar ratios of XyNC, the inserted products obtained are the result of triinsertion processes. The monoinsertion and diinsertion of XyNC at a 1 : 1 or 1 : 2 molar ratio(s) are not isolated. The reaction of dinuclear palladium complex **2a**, **b** with eight equivalents 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 stiochiometric 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.

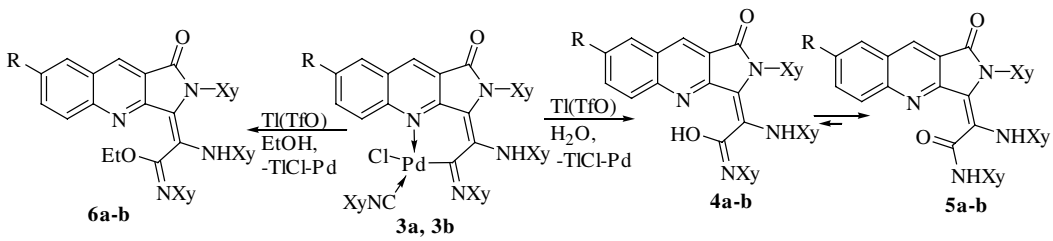
The inserted products were formed from the insertion of 2,6-dimethylphenyl isocyanide (XyNC) into the C–Pd bond and the displacement of PPh_3 by XyNC ligand. These kinds of complexes are very poorly represented in the literature, the only example being those recently prepared by Vicente *et al*.,[62] and suggest that the presence of PPh_3 during the insertion of XyNC into dinuclear palladium complexes **2a**,**b**, could be responsible for the change of reactivity of intermediate complexes. It is possible that free PPh_3 coordinates in that intermediate complex forces the insertion of the two isocyanide ligands. A mechanistic scheme depicting the formations of various products, including possible intermediates, is consistent with the literature data,[62] given in Scheme 4.

The products were analyzed by IR, ^{1}H NMR spectroscopy and single-crystal X-Ray diffraction studies. IR (Nujol, cm^{-1}) bands assignable to ν(NH), ν(C≡N), ν(C═O) and ν(C═N), for iminoacyl quinolinylpalladium complexes**3a** and **3b** with no significances differences appeared and indicated the cyclization of the carbonyl group comparable to those complexes. In case of **3a**, bands appear at ν(NH, broad band), 3338, ν(C≡N) 2361, ν(C═O) 1716 and ν(C═N) 1558 cm^{-1} regions and, in the case of **3b**, 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 a small 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. The nucleophilic attack of the nitrogen on the formyl carbon could give cyclometalated species of the importance isoindolinone. The complexes **3a** and **3b** show their IR spectra in a strong band at 1716 and 1704 cm^{-1} assignable to the ν(C═O) of the group. This frequency is not similar to that observed in start materials **1a**, **b** or**2a**, **b** and indicates the coordination of the carbonyl group to the isoindolinone ring.

The ^{1}H NMR of complex **3a** in $CDCl_3$ was recorded and found to contain seven resonances of singlet signals at different chemical shifts, each corresponding to methyl group appears at δ2.55 (s, 3H, Me), 2.49 (s, 3H, Me), 2.30 (s, 3H, Me), 2.19 (s, 6H, 2Me), 2.11 (bs, 3H, Me), 1.58 (s, 3H, Me) and 0.62 (s, 3H, Me) ppm. There was one singlet signal integrated for two methyl groups of the



Scheme 4. A mechanistic sequence for the formation of mononuclear palladium complexes from dinuclear palladium complexes.



Scheme 5. Depalladation reaction by Tl(TfO), (TfO = triflate, CF_3SO_3).

equivalent coordinated isocyanide (CNXy) appearing at δ2.19. ^{1}H NMR of this complex **3b** in $CDCl_3$ was recorded and found to contain seven resonance singlet signals at different chemical shifts, each corresponding to a methyl group appearing at δ2.54, 2.49, 2.29, 2.18, 2.02 and 0.62 ppm. There were two singlet signals for the four methyl groups appearing at δ2.18 [s, 6H, 2Me(Xy)] and 2.11 [s, 6H, 2Me(Xy)], one of which was for the inserted XyNC, indicating the *cis* geometry and no free rotation of the Xy groups. One of the two singlet signals integrated into two methyl groups of the equivalents coordinated isocyanide. This suggests that a steric hindrance prevents the rotation of the three of xylyl groups, while the fourth one rotates freely.

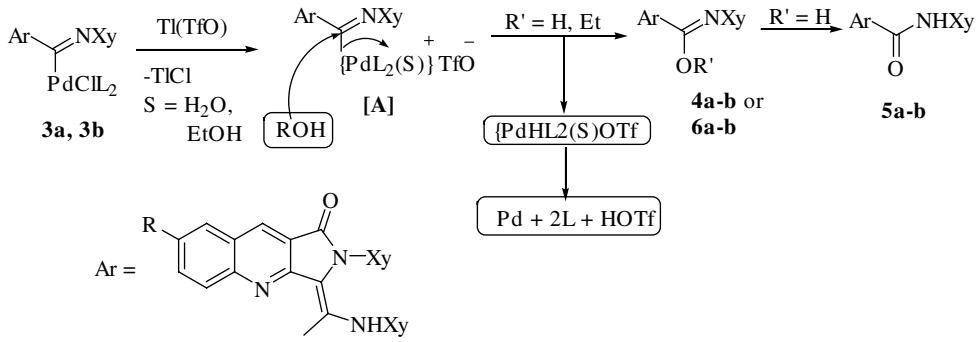
Depalladation via reactions with Tl(TfO)

The reaction of complex **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 could be similarly separated from the mother liquors. In the solid state **5a**, **b** and **4a**, **b** are stable and they do not interconvert.

However, if **4a**, **b** is dissolved in CH_2Cl_2 and refluxed for 16 h, it transforms completely into **5a**, **b**. The latter is stable at room temperature in $CDCl_3$ for several days, while under the same conditions **4a**, **b** transforms 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.[52] They are unstable compounds that may be in equilibrium with the stable amide (**5a–d**) molecule. This has been confirmed by theoretical investigations, which demonstrate that the amide form is about 11 kcal mol^{-1} more stable than the tautomeric imidic acid (**4a–d**).[63] When the reaction of**3a**, **b** with Tl(TfO) was carried out in CH_2Cl_2 plus a drop of EtOH, **6a**, **b** was obtained and the yields varied from 18 to 40%, depending on the added amount of EtOH.

Therefore, the depalladation of these inserted complexes represents a stoichiometric synthesis of functionalized arenes, *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:

(1) 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 assuming that the very labile TfO is substituted by H_2O or EtOH;



Scheme 6. A mechanistic proposal for the depalladation reactions.

(2) the nucleophilic attack of the iminoacyl carbon (C═NXy)-Pd of intermediate **A** by alcoholysis (EtOH) or hydrolysis (H_2O), the latter coming from the atmosphere or solvent moisture;
(3) the decomposition of the resulting adduct (probably through an intermediate) to give 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 a 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 enol or ketone forms and which of them 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.

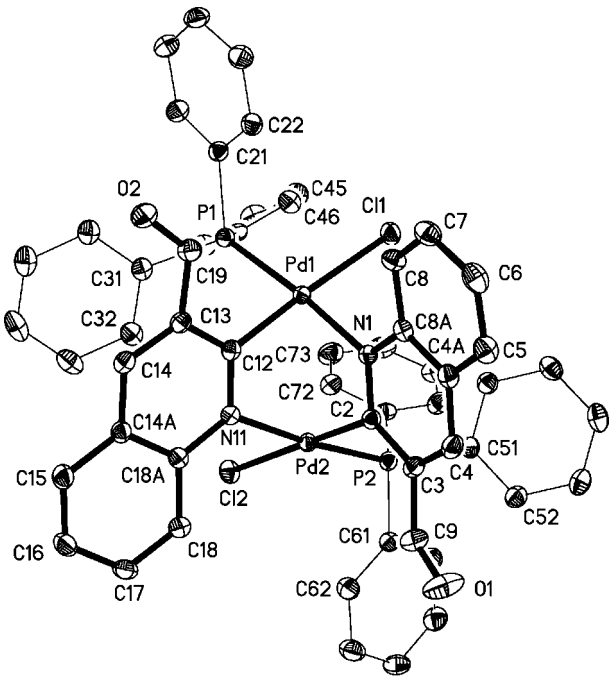


Figure 2. Thermal ellipsoid plot (50% probability level and solvent omitted CH_2Cl_2) of **2a**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(12) = 1.9919(17), Pd(1)–N(1) = 2.0944(14), Pd(1)–P(1) = 2.2906(5), Pd(1)–Cl(1) = 2.3816(6), Pd(1)–Pd(2) = 3.0818.(5), Pd(2)–C(2) = 2.0081(6), Pd(2)–N(11) = 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).

X-ray crystal structures

To further confirm the structures of the products, the molecular structures of yellow crystals of **2a** (Fig. 2), red crystals of **3a**·CH_2Cl_2 (Fig. 3) and reddish crystals of **3b**·$CH_2Cl_2C_2H_6O$ (Fig. 4) were determined by X-ray analysis. The Pd–C bond distances of the iminoacyl ligands decreased, in agreement with the decreasing electron delocalization influence of the electron donating group (OMe) located in the side chain position, as shown in complexes **3a**, **b** compared with **2a**, or possibly decreased in agreement with 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 distances 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**). This shows 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[64] under this assumption: two ligands with great *trans* influence will suffer a great *transphobia*.[65]

The structure of **2a** (Fig. 2) clearly shows the formation of a palladium atom in a square-planar 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, Pd–C bond distances [Pd(2)–C(2) 2.0081(16) Å] are significantly longer than Pd(1)–C(12)1.9919(17) Å and the difference is 0.0162 Å. The Pd–N bond distance, Pd(2)–N(11) 2.1115(14) Å, is significantly longer than that in Pd(1)–N(1) 2.0944(14) Å and the difference 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 a little longer than Pd(1)–Cl(1) 2.3816(6) Å and the difference is 0.004 Å. The Pd–P distance in 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) from Pd(1) in bond distances for all the ligands around it is due to the greater steric hindrance of PPh_3 and also the trigonal pyramides for the phosphine atom. The angles around Pd (1) and Pd(2) were compared and C(2)–Pd(2)–N(11)84.88(6) is significantly longer than C(12)–Pd(1)–N(1)82.22(6), the difference being 2.66°; C(2)–Pd(2)–P(2)93.24(5) is slightly longer than C(12)–Pd(1)–P(1)92.32(5), the difference being 0.92°; N(11)–Pd(2)–P(2)175.12(4) is slightly longer than N(1)–Pd(1)–P(1)174.53(4), the difference being 0.59°; C(2)–Pd(2)–Cl(2) 174.14(5) is slightly longer than C(12)–Pd(1)–Cl(1)173.90(5), the difference being 0.24°; N(11)–Pd(2)–Cl(2)90.20(4) is significantly shorter than N(1)–Pd(1)–Cl(1)92.30(4), the difference being 2.10°; P(2)–Pd(2)–Cl(2)91.91(2) is significantly shorter than P(1)–Pd(1)–Cl(1)93.14(2), the difference being 1.23°; C(2)–Pd(2)–Pd(1)66.30(5) is slightly longer than C(12)–Pd(1)–Pd(2) 66.01(5), the difference being 0.29°; N(11)–Pd(2)–Pd(1)63.27(4) is very slightly longer than N(1)–Pd(1)–Pd(2)63.12(4), the difference being 0.15°; P(2)–Pd(2)–Pd(1)111.854(17) is significantly shorter than P(1)–Pd(1)–Pd(2)114.865(14), the difference is 3.015°; Cl(2)–Pd(2)–Pd(1)114.188(16) is slightly longer than Cl(1)–Pd(1)–Pd(2)113.865(19), the difference being 0.323°. These values suggest a delocalization of π electron density around the N(1) and P(1) as compared with N(2) and P(2) and the distortion of the bond angles around the Pd(1) and Pd(2) due to the greater steric hindrance of PPh_3. These are attributed to a delocalization of π electron density along the Pd(1), Pd(2) and the atoms are almost square planar.

Figure 3 clearly shows the formation of red crystal of quinolinepalladium complex **3a** with Pd–C(40) 1.9425(18) Å and Pd–C(10) 1.9999(17) Å. The Pd–Cl distance is Pd–Cl(1) 2.4398(4). Similarly, the Pd–N bond distance of Pd–N(1) is 2.0864(14) Å; these show the greater *trans* influence of the C-donor iminoacyl ligand with respect to the chloro ligand. The *transphobia* [*T*] is directly related to the *trans* influence of the two ligands and is large. The [Pd]C═NXy bond distances of the iminoacyl ligands in complex **3a** are 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. C═N distances correspond to the inserted molecule of XyN═C and N(40)–C(40) 1.151(2) Å of C═N distances corresponding to the inserted molecule of CNXy. All these lengths are as expected for a C═N bond [the mean value for the C(aryl-C═NR distance is 1.432 -1.382 Å).[66–68] The (aryl C═N(Xy)[Pd] distances corresponding to the third inserted molecule of XyNC in **3a** is significantly longer than the other 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 are 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). The short C(20)–C(30) bond 1.366(2) Å compared with C(10)–C(20) 1.505(2) Å suggests a delocalization of π electron density around the C(20)–C(30)–N(30) angle [127.76(15)]° as compared with 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)°. This points to a delocalization of π electron density along the C(30), as the atoms are almost square planar.

Red crystals of **3b** suitable for X-ray analysis were also obtained in a similar manner to its analog **3a** and the structure of **3b** (Fig. 4) is identical to **3a** except for the different substituents of the OMe group. An ORTEP plot of **3b** of iminoacyl quinolinylpalladium complex (Fig. 4) shows ~1.944(2)–2.002(2) of Pd(1)–C(30) 1.944(2) and Pd(1)–C(40) 2.002(2) Å. The Pd–Cl distances also allow us to correlate longer distance with greater *trans* influence. These values are Pd(1)–Cl(1) 2.4283(5) Å. Similarly, the Pd–N bond distance is Pd(1)–N(1) 2.0905(18) Å; these values show the greater *trans* influence of the C-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 under this assumption; the two ligands with great *trans* influence will suffer a large *transphobia*.[65] The [Pd]C═NXy bond distance of the iminoacyl ligands 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. C═N distances correspond to the inserted molecule of XyN═C and N(3)–C(30) 1.153(3) Å of C═N distances correspond to the inserted molecule of CNXy. All these lengths are as expected for a C═N bond [the mean value for the C(aryl-C═NR) distances is 1.432 −1.382 Å].[66–68] The (aryl C═N(Xy)[Pd]) distances corresponding to the third inserted molecule of XyNC in **3b** is significantly longer than the other, N(4)–C(40) 1.266(3) Å, as a result of the coordination of the nitrogen atom to Pd(II). This fact, and that the angles around Pd are C(30)–Pd(1)–C(40) 91.67(8); C(30)–Pd(1)–N(1)

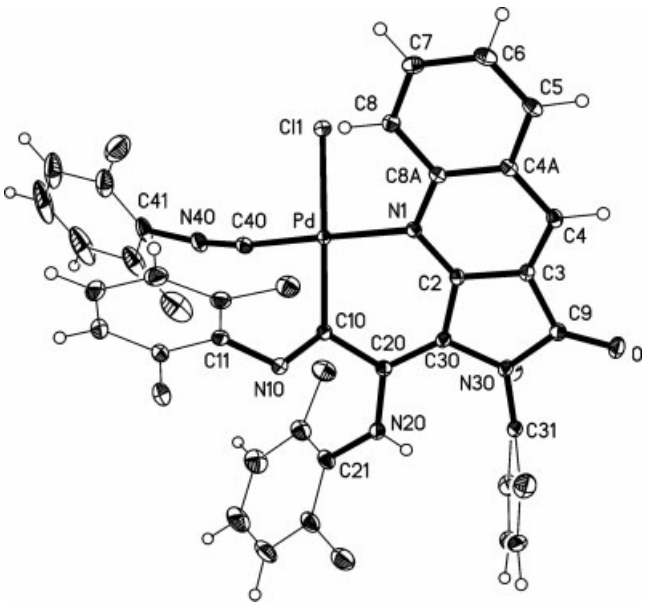


Figure 3. Thermal ellipsoid plot (50% probability level and solvent omitted) of **3a**. Hydrogen atoms attached to N(20) have been displayed for clarity. Selected bond lengths (Å) and angles (deg): Pd–C(40) = 1.9425(18), Pd–C(10) = 1.9999(17), Pd–N(1) = 2.0864(14), Pd–Cl(1) = 2.4398(4), N(1)–C(2) = 1.325(2), 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).

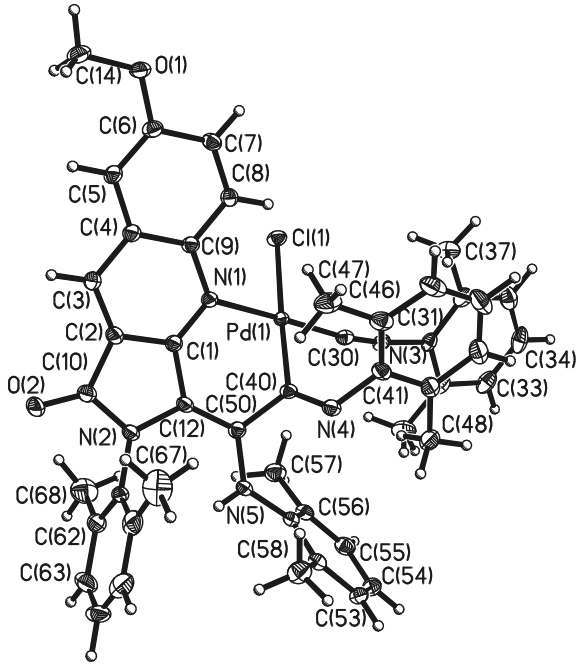


Figure 4. Thermal ellipsoid plot (50% probability level and solvent omitted) of **3b**. Hydrogen atoms attached to N(5) have been displayed and omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(30) = 1.944(2), Pd(1)–C(40) = 2.002(2), Pd(1)–N(1) = 2.0905(18), Pd(1)–Cl(1) = 2.4283(5), 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).

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 with 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 with 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)°. This points to a delocalization of π electron density along the C(12), as the atoms are almost square planar.

Experimental Section

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 [^{1}H, ^{13}C(^{1}H) and H_3PO_4 (^{31}P)]. The NMR probe temperature was calibrated using ethylene glycol ^{1}HNMR 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 were handled with caution.

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 room temperature (RT), filtered off, washed with Et_2O (5 ml), and air-dried to give a yellow solid of **2a**, **b**.

*{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. 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 cm^{-1}, ν(C═N and C═C) 1612.0, 1582.0, 1572.0 and 1538.0. ^{1}H NMR (400 MHz, $CDCl_3$); δ10.39 (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 {^{1}H} NMR (121 MHz, $CDCl_3$); 20.67 ppm. Anal. calcd 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.

*{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. 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 cm^{-1}, ν(C═N and C═C) 1584.0, 1546.0; ^{1}H NMR (400 MHz, $CDCl_3$); δ10.43 (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 = 2.6 Hz), 3.84 (s, 6H, OMe) ppm. ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$); 21.37 ppm. Anal. calcd 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.

*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**)*

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) and 2-chloro-3-quinoline carboxaldehyde **1a** (149.4 mg, 0.78 mmol) were added under nitrogen. The suspension was stirred for 5 h at room temperature then the solvent was evaporated. The resulting residue was extra cted 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 titrated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving 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(cm^{-1}) (Nujol, cm^{-1}): ν(NH, broad band), 3353, ν(C═O) 1716, 1699, ν(C≡N) 2361, 2338, ν(C═N) 1558, 1541. ^{1}H NMR (200 MHz, $CDCl_3$) δ8.87 (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. calcd 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.

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) and XyNC (248 mg, 1.92 mmol) was added. The suspension was stirred for 24 h at room temperature. The color was changed from pale yellow into pale red and then dark red during monitoring of the reaction mixture. 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 titrated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving a 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**.

*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**)*

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 titrated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving 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 (cm^{-1}) (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. ^{1}H NMR (200 MHz, $CDCl_3$) δ8.75 (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. calcd 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.

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) and XyNC (248 mg, 1.92 mmol) were added. The suspension was stirred for 24 h at RT and the color changed from pale yellow into pale red and then dark red during, during monitoring of the reaction mixture. 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 titrated with Et_2O (15 ml). The precipitate was filtered, washed with Et_2O (2 × 5 ml), and air-dried, giving 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**.

Depalladation procedure

*General procedure of 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%).

*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. ^{1}H NMR (200 MHz, $CDCl_3$) δ8.77 (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, $CDCl_3$): δ166.5 (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. calcd 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.

*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), ν(NH) 3420, 3232 b,ν(C═O), ν(C═N), 1668. ^{1}H NMR (200 MHz, $CDCl_3$) δ8.79 (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, $CDCl_3$): δ166.5 (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. calcd 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.

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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	C56 H42 Cl2 N2 O2 P2 Pd2	C46 H42 Cl N5 O Pd	C47 H43 Cl N5 O2 Pd
E. F. as X-ray measurement	C57 H44 Cl4 N2 O2 P2 Pd2	C47 H44 Cl3 N5 O Pd	C50 H51 Cl3 N5 O3 Pd
Formula weight	1205.48	907.62	982.71
Temperature	133(2) K	133(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal habit	Yellow rectangular prim	Red tablet	Red prism
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P −1	P 21/c	P2(1)/c
Unit cell dimensions			
	$a = 11.8384(11)$ Å	$a = 11.7167(8)$ Å	$a = 8.3018(3)$ Å
	$b = 13.451(2)$ Å	$b = 20.1516(14)$ Å	$b = 19.8319(8)$ Å
	$c = 17.804(3)$ Å	$c = 18.7484(12)$ Å	$c = 27.3429(11)$ Å
	$\alpha = 106.116(11)^\circ$	$\alpha = 90^\circ$	$\alpha = 90^\circ$
	$\beta = 96.793(15)^\circ$	$\beta = 108.055(4)^\circ$	$\beta = 95.2830(10)^\circ$
	$\gamma = 111.512(12)^\circ$	$\gamma = 90^\circ$	$\gamma = 90^\circ$
Volume	2456.0(6) Å^3	4208.7(5) Å^3	4482.6(3) Å^3
Z	2	4	4
Density (calculated)	1.630 mg m^{-3}	1.432 mg m^{-3}	1.456 mg m^{-3}
Absorption coefficient	1.062 mm^{-1}	0.674 mm^{-1}	0.642 mm^{-1}
F(000)	1212	1864	2028
Crystal size	0.36 × 0.15 × 0.11 mm^3	0.25 × 0.19 × 0.10 mm^3	0.25 × 0.15 × 0.14 mm^3
Theta range for data collection	1.23 −30.04°	1.53 −30.04°	1.81 −27.10°
Index ranges	−16 ≤h ≤16, −18 ≤k ≤18, −25 ≤l ≤25	−16 ≤h ≤16, −28 ≤k ≤28, −26 ≤l ≤26	−10 ≤h ≤10, −25 ≤k ≤25, −35 ≤l ≤34
Reflections collected	46 379	66 861	50 825
Independent reflections	14 268 [R(int) = 0.0293]	12 314 [R(int) = 0.0476]	9847 [R(int) = 0.0231]
Completeness to theta = 30.00°	99.4%	100.0%	99.7%
Absorption correction	Numerical	Numerical	Semi-empirical from equivalents
Max. and min. 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	14 268/0/622	12 314/0/526	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 peak and hole	0.997 and −0.960 e Å^{-3}	1.037 and −0.887 e Å^{-3}	1.671 and −0.527 e Å^{-3}

*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, $CDCl_3$) δ8.77 (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, $CDCl_3$): δ165.8 (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), 8.1 (2 × Me). Anal. calcd 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.

*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**)*

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, $CDCl_3$) δ8.77 (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, $CDCl_3$): δ165.8 (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. calcd 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

*General procedure of the ethyl ester 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%).

*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) used under the reaction condition to produce **6a** in 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, $CDCl_3$) δ8.86 (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, $\underline{CH_2}Me$, 2H, $^2J_{HH}$ = 7 Hz), 2.22 (s, 2 × Me, 6H), 1.48 (bs, 4 × Me, 12H), 1.39 (t, $CH_2\underline{Me}$, 3H, $^2J_{HH}$ = 7 Hz) ppm. Anal. calcd 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.

*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) used under the reaction condition to produce **6b** in 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, $CDCl_3$): δ8.86 (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. calcd 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.

X-ray crystallographic studies

Details of data collection and refinement are given in Table 1. The crystal structures of 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 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 refined were performed using the SHELXL-97 package.[69] Crystal data and processing parameters for**2a**, **3a** and **3b** are summarized in Table 1.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 680962 (**2a**), 680963 (**3a**) and 680964 (**3b**).

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. The further scope of this class of arylpalladium complexes and applications is currently under investigation in our laboratory.

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