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Synthesis and characterization of pyrido[1,2-*a*]quinoline palladacycles

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Abstract Palladacycles of pyrido[1,2-*a*]quinoline complexes were synthesized *via* a one pot reaction of quinolines with *Xy*NC (*Xy* = 2,6-$Me_2C_6H_3$) in the presence of Pd(*dba*)$_2$ (4:1). These palladacycles were also obtained *via* reaction of quinolines with Pd(*dba*)$_2$ in the presence of P*Ph*$_3$ (1:2) in acetone to give the intermediate complexes of dinuclear palladaphosphaquinoline complexes. Dinuclear complexes were converted into palladacycles *via* reaction with *Xy*NC in CH_2Cl_2. The crystal structure of the dinuclear palladium complex was determined by X-ray diffraction studies.

Keywords Insertions; Metallacycles; Quinolines; Palladacycles; Isonitrile.

Introduction

Palladacycles are one of the most important and investigated classes of organometallic compounds [1]. The importance of cyclopalladated compounds (CPCs) is documented by the numerous articles published each year on the subject [2–17]. After the discovery of cyclopalladation by *Cope* and *Siekman* in 1965 [18], it has been believed that this reaction could afford only five-membered metallacycles. Meanwhile, palladacycles of different sizes have been reported, including six-membered cycles [19]. One of the most abundant classes of CPCs contains a CN-type metallacycle. Several such CN-complexes are derived from imines and other C=N bond-containing compounds, including quinolines. On the basis of the position of the C=N bond relative to the palladacycle, CPCs form either *endo*- or *exo*-metallacycles (Fig. 1).

The vast majority of known imine-derived CPCs contain *endo*-palladacycles with the C=N bond being *endo*-cyclic. This preference of C=N bond-containing ligands for the formation of *endo*-palladacycles is so strong that it has been referred to as the ''*endo* effect'' [20, 21]. *Exo*-cyclopalladation of imines can be achieved only when *endo*-metalation is impossible [21–25] or strongly disfavored [25–28] for electronic or steric reasons. Thus far, there has been no example of quinoline-derived *endo*-CPCs. Palladacycles are widely applied also in organic synthesis, organometallic catalysis, and new molecular materials [29–39]. Among them, the best investigated palladacycles are five- or six-membered rings fused with an aromatic ring, and the metalated carbon is usually an aromatic sp^2 carbon [40–44]. For this reason, there is a lot of interest in developing new strategies for the straightforward synthesis of substituted palladacycles. However, the above methods often suffer from one or more synthesis limitations for large-scale preparation of cyclopalladated complexes and six-membered palladacycles with a metalated imine (C=N–) sp^2 carbon are rather rare. During our ongoing investigations [45] into the cyclopalladation reactions of quinolines and

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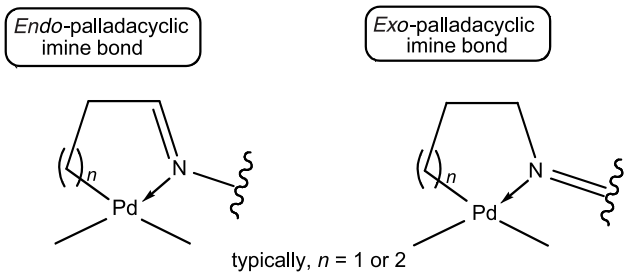


Fig. 1 General structures of *endo*- and *exo*-palladcycles

applications of their corresponding CPCs, chalcones **3a**–**3d** were synthesized. In this paper, we report the successful cyclopalladation of compounds **4a**–**4d** resulting in the formation of unique CPCs **5a**–**5d** containing an *endo*-palladacycle exhibiting a direct Pd(II) sp^2 carbon contact. Some of these reactions involve *ortho*-functionalized aryl complexes that after insertion of isocyanides give heterocycles incorporating the *ortho* group. A few examples of insertion of isocyanides into other *ortho*-functionalized arylpalladium (II) complexes leading to heterocyclic compounds have been reported [46–48]. Thus, we have prepared a chalcone by reacting 2-chloro-3-quinolinecarboxaldehydes [$R = H$ (**1a**), $R = OMe$ (**1b**)] with acetophenone **2a** or 3,4,5-trimethoxyacetophenone **2b**. The interest of this subject has prompted us to prepare arylpalladium complexes containing *ortho*-functionalized aryl groups such as –CH=CHCO–C_6H_5– or CH=CHCO–[C_6H_2–(OMe)$_3$] as well as cyclopalladated complexes. The trimethoxylaryl moiety is present in organic molecules of pharmaceutical interest, for example the antileukemic lactones steganacin and steganangin [49–52], the antibacterial agent trimethoprim [53], or the cytotoxic colchicines [54]. The crystal structure of the palladium complex **4d** containing α,β-unsaturated ketones has been determined and the structure shows interesting features.

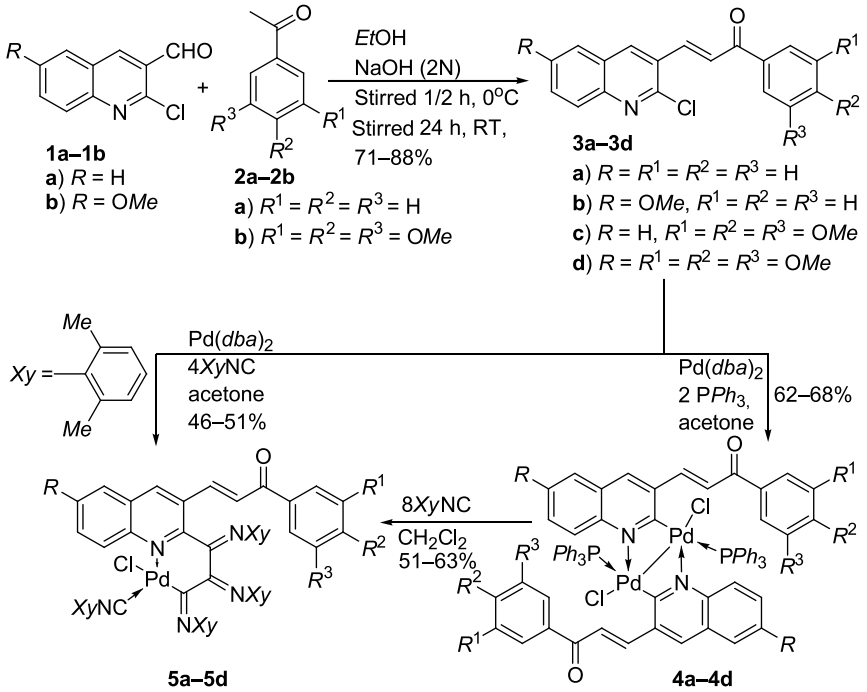
Recently, considerable interest has been shown in palladium (II) dimers as possible intermediates in catalytic systems for organic transformations. Several compounds of this type containing a Pd–Pd bond have been previously synthesized and their reactivities studied [55–57]. Interestingly, the simple CN bridged dimers **4a**–**4d** have not been described until recently. The reaction between [$Pd_2(dba)_3$] (dba = dibenzylideneacetone), PPh_3, and the halocarbons Ar–Cl leads to the formation of the Pd^1–Pd^2 dimers [$Pd_2(Ar\text{–}Cl)_2(PPh_3)_2$]. These dimers represent interesting precursors for the formation of high nuclearity clusters. On the other hand, their unsaturated electronic state, suggests that they may readily react with organic fragments to form organometallic compounds. In this paper we report a detailed study of their reactions with 2,6-dimethylphenyl isonitrile (CNXy) ($Xy = 2,6\text{-}Me_2C_6H_3$).

Results and discussion

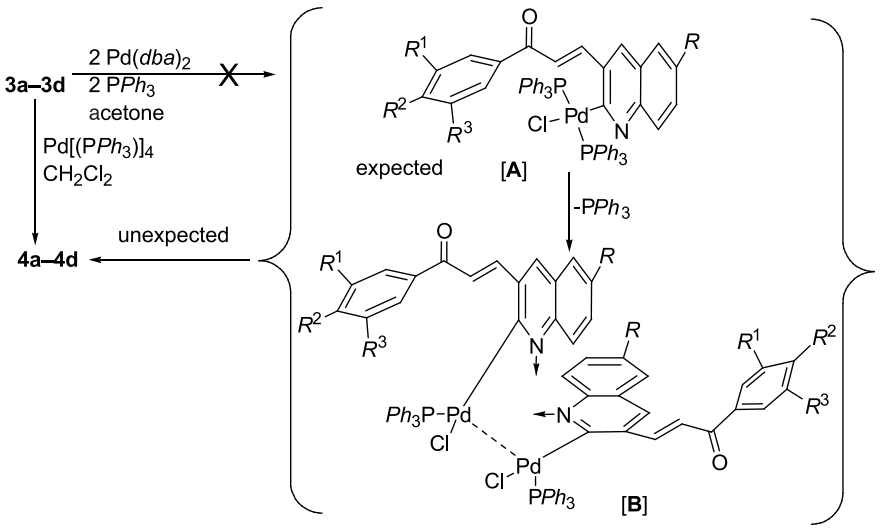
Knoevenagel condensation [58–67] of 2-chloro-3-carbaldehyde-6-*R*-quinolines [$R = H$ (**1a**), $R = OMe$ (**1b**)] with acetophenone (**2a**) or 3,4,5-trimethoxyacetophenone (**2b**) in ethanol furnishes the enones **3a**–**3d** in good yields (71–88%). Under an intert atmosphere of nitrogen quinoline derivatives **3a**–**3d** react with [Pd(dba)$_2$]($=$[$Pd_2(dba)_3$]$\cdot dba$) [68] in the presence of stoichiometric amounts of a neutral ligand such as PPh_3 furnishing the dinuclear palladium complexes **4a**–**4d** in good yields (62–68%) *via* oxidative addition reaction. The reaction mixture was analyzed by ^{31}P-{1H} NMR spectroscopy which showed the formation of different products. By careful recrystallization these products were separated and characterized as dinuclear palladium complexes **4a**–**4d** (Scheme 1).

The reaction of chalcones **3a**–**3d** with Pd(dba)$_2$ and PPh_3 in molar ratio (1:2:1) under N_2 in degassed acetone was expected to give the *trans*-complexes **A** (Scheme 2). However, no *trans* mononuclear palladium complexes (**A** or **B**) could be isolated, but instead the only yellow solid isolated in pure form contains the unexpected dinuclear palladium complexes **4a**–**4d** (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 [69–70]. It is believed that complexes **A** and **B** are intermediates in the formation of complexes **4a**–**4d**. This suggests that the presence of PPh_3 as a ligand could be responsible for the interchange of the ligands, as outlined in Scheme 2.

The complexes **4a**–**4d** were confirmed by the appearance of one singlet signal at $\delta = 23.60$, 23.63, 23.53, and 23.64 ppm in their ^{31}P NMR spectrum corresponding to an AB system. We believe that this is due to the existence of complexes **4a**–**4d** in solution as a mixture of complexes derived from two *trans* forms. The structure of compounds

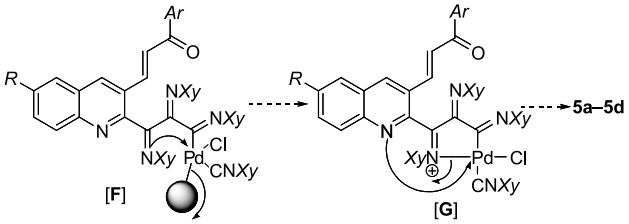


Scheme 1



Scheme 2

4a–**4d** was unambiguously assigned by comparison with published NMR data and further proven by X-ray crystallography (Fig. 2). The ^{1}H NMR spectra did not show the presence of impurities for all of the complexes **4a**–**4d**, even the quinoline fragments show only slight variations when complexes **4a**–**4d** are compared. However, we feel that not enough is known about the reactivity of Pd–C bonds of quinoline palladium, through four bonds to permit us to place emphasis on these data. While this observation can be rationalized for **4a**–**4d**, we were surprised that the cyclopalladated **4a**–**4d** showed almost no change, in view of the angular distortion involved in forming the six-membered ring. This yellow product was characterized on the basis of ^{31}P-{^{1}H} NMR, IR, and elemental analyses. A single-crystal X-ray analysis of **4d** is depicted in Fig. 2.



Scheme 3

We also investigated the reaction of chalcones **3a**–**3d** with isonitrile *Xy*NC. Oxidative addition reaction of halo quinolines **3a**–**3d** with a mixture of Pd(*dba*)$_2$ and *Xy*NC in acetone takes place at room temperature and yielded the novel iminoacyl palladium complexes of pyrido[1,2-*a*]quinoline **5a**–**5d** (Scheme 1) in moderate yields (46–51%). We believe that the triinserted (C=N*Xy*) complex **F** (Scheme 3) could be an intermediate and a nucleophilic attack of the nitrogen of the primarily inserted isocyanide at the metal center could give the five membered ring of **G** as an intermediate too. This unstable complex could then be attacked by the nitrogen of the quinoline ring to give the pyrido[1,2-*a*]quinolines **5a**–**5d** as the stable unexpected product (Schemes 1 and 2). A mechanistic proposal depicting the formation of desirable product, including possible intermediates, is given in Scheme 3.

The reactivity of the dinuclear palladium complexes **4a**–**4d** was examined towards bulky isocyanide *Xy*NC depending on the nature of substitution, ligands, and reaction conditions. The products obtained are the result of mono-, di-, or tri-insertion processes. The mono-inserted and di-inserted complexes with *Xy*NC in 1:1 or 1:2 molar ratios could not be isolated and show an intractable mixture.

*Triple insertion of 2,6-dimethylphenylisocyanide (XyNC) into **4a**–**4d** complexes*

The insertion reaction of excess *Xy*NC into dinuclear palladium complexes **4a**–**4d** in a 8:1 molar ratio for 16 h afforded tri-inserted palladacycles **5a**–**5d** in good yields (51–55%). These complexes resulted from the insertion of *Xy*NC into the sp^2 carbon-palladium bond and the displacement of P*Ph*$_3$ by two *Xy*NC ligands. There is only one example of such a complex type in literature, which has recently been reported by *Vicente et al.* [71]. It is possible that free P*Ph*$_3$ coordinates in that intermediate complexes, forcing the insertion of the two isocyanide ligands.

*Spectroscopic properties of arylpalladium complexes **4a**–**4d***

The IR bands assignable to the ν(C=O), ν(C=N), ν(C=C) mode in **4a**–**4d** indicate the non-coordination of the carbonyl group of the ligand side chain with these arylpalladium complexes. These bands appear in complex **4a** at $\bar{\nu} = 1677, 1665, 1575\,cm^{-1}$, in complex **4b** slightly shorter at $\bar{\nu} = 1664, 1622.0, 1610, 1580\,cm^{-1}$, in complex **4c** at $\bar{\nu} = 1665, 1620, 1580\,cm^{-1}$, and in **4d** slightly shorter again at $\bar{\nu} = 1664, 1622, 1610, 1580\,cm^{-1}$ due to the extended conjugation of the side chain.

The IR bands assignable to the ν(C=O), ν(C=N), and ν(C≡N) of pyrido[1,2-*a*]quinoline palladacycles **5a**–**5d** appear with no significant differences to the above complexes indicating that there is no cyclization of the carbonyl group in those complexes. This suggests a little change in the carbonyl stretching frequency of **5a**–**5d** due to complexation (see Experimental section). The structure of compounds **5a**–**5d** was unambiguously assigned by comparison to published NMR data. The ^{1}H NMR spectra of complex **5a** show three singlet signals at different chemical shifts each corresponding to two methyl groups appearing at $\delta = 2.30$ (s, 6H, 2*Me*), 2.10 (s, 6H, 2*Me*), 1.55 (s, 6H, 2*Me*) ppm. There is one singlet signal integrating for two methyl groups of coordinated isocyanide (CN*Xy*) appearing at $\delta = 2.20$ (s, 6H, 2*Me*) ppm. The ^{1}H NMR spectra of complex **5b** show four singlet signals at different chemical shifts each corresponding to two methyl groups appearing at $\delta = 2.31$ (s, 6H, 2*Me*), 2.19 (s, 6H, 2*Me*), 2.09 (s, 6H, 2*Me*), 1.53 (s, 6H, 2*Me*) ppm. Two singlet signals for the four methyl groups appear at $\delta = 2.19$ and 2.09 ppm, one of which for the inserted *Xy*NC, indicating the *cis* geometry and no free rotation of the *Xy* groups. One of the two singlet signals integrates for two methyl groups of the coordinated isocyanide. This suggests a steric hindrance of the rotation of three of the xylyl groups, while the fourth one rotates freely. The rigidity of the palladacycles was checked by variable temperature (−60 to +60°C) ^{1}H NMR experiments using the mononuclear complexes in $CDCl_3$. Minor changes in the multiplicities and resonance frequencies of the aromatic protons in the spectra of **5a**–**5d** over the studied temperature range suggest that both *endo* palladacycles in these complexes have a rigid conformation in solution. The singlet signals integrating for two

methyl groups of the coordinated 2,6-dimethylphenyl isocyanides (CN*Xy*) appearing at $\delta = 2.20$ (**5a**), 2.19 (**5b**), 2.19 (**5c**), 2.18 (**5d**) ppm, due to the free rotation of the 2,6-dimethylphenyl isocyanide, are consistent with the results described more recently by *Vicente* [71].

*X-Ray crystal structure of the dinuclear complex **4d***

To further confirm the structure of the product, a yellow crystal of **4d** suitable for X-ray analysis was obtained from its solution in CH_2Cl_2 at room temperature. The general view of this complex and atom-numbering scheme are presented in Fig. 2. The complex adopts a transoid conformation and exists as a palladium bridged dimer in *endo*-palladacycles. The Pd(1)–Pd(2) bond length covers a range from 2.562(5)–3.077(1) Å. The longest Pd–Pd distance between Pd(1) and Pd(2) is attributed to the report of X-ray data for six-membered palladacycles, they usually adopt a boat conformation in the solid state [57]. This bond is bridged by two CN ligands and is longer than the equivalent distance. From the molecular structure, it is possible to see that a phosphine in the structure stops the aggregation process at the dinuclear stage. Unfortunately, it was impossible to determine the *endo* palladacycles conformation in complexes **4a**–**4d** using NMR spectroscopy.

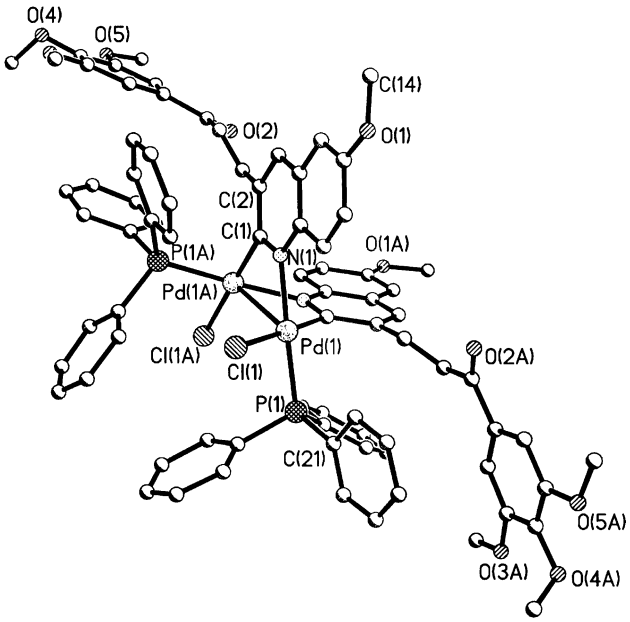


Fig. 2 Thermal ellipsoid plot (50% probability level and solvent omitted CH_2Cl_2) of **4d**. Selected bond lengths (Å) and angles (deg): Pd(1)–C(1A) = 1.9911(17), Pd(1A)–C(1) = 2.0021(16), Pd(1A)–N(1A) = 2.0855(14), Pd(1)–P(1) = 2.2905(5), Pd(1)–Cl(1) = 2.3515(6), Pd(1)–Pd(1A) = 3.077(1), Pd(1)–N(1) = 2.4220(14), Pd(1A)–P(1A) = 2.481(7), Pd(1A)–Cl(1A) = 2.3512(4), N(1)–C(1) = 1.330(2), N(1A)–C(1A) = 1.329(2), C(1A)–Pd(1)–N(1) = 82.25(6), C(1A)–Pd(1)–P(1) = 92.66(5), N(1)–Pd(1)–P(1) = 174.53(4), C(1A)–Pd(1)–Cl(1) = 173.99(5), N(1)–Pd(1)–Cl(1) = 92.30(4), P(1)–Pd(1)–Cl(1) = 93.14(2), C(1A)–Pd(1)–Pd(1A) = 66.01(5), N(1)–Pd(1)–Pd(1A) = 63.12(4), P(1)–Pd(1)–Pd(1A) = 114.865(14), Cl(1)–Pd(1)–Pd(1A) = 113.888(19), C(1)–Pd(1A)–N(1A) = 84.88(6), C(1)–Pd(1A)–P(1A) = 93.35(5), N(1A)–Pd(1A)–P(1A) = 175.15(4), C(1A)–Pd(1)–Cl(1) = 174.33(5), N(1A)–Pd(1A)–Cl(1A) = 90.20(4), P(1A)–Pd(1A)–Cl(1A) = 91.91(2), C(1)–Pd(1A)–Pd(1) = 66.30(5), N(1A)–Pd(1A)–Pd(1) = 63.27(4), P(1)–Pd(1)–Pd(1A) = 111.854(17), Cl(1)–Pd(1)–Pd(1A) = 113.999 (18)

Taking into account that this structure is the first example of a structurally characterized quinoline derived CPC with a (sp^2)C–Pd bond, it will be compared with other known complexes of *exo*-imine N-donor groups [72]. The coordination environment of the palladium atom in complex **4d** may be described as square planar with very slight tetrahedral distortion. The angle between the planes N–Pd–C and P–Pd–N is equal to 2.9°. It is of note that an almost ideal square planar geometry is a common feature in pure heterocyclic six-membered –C=N cyclopalladated complexes, where the tetrahedral distortion angles in complexes fall in the range 1.9–3.1° [73–76]. Consequently, heterocyclic *ortho*-palladated derivatives with pronounced flexibility allow for retention of a square-planar configuration environment, which is optimal for a d^8-metal center such as Pd(II).

The Pd–C bond distances of the iminoacyl ligands decrease, in agreement with the decreasing electron delocalization influence of the electron donating group (O*Me*) located in the side chain position. Also, the Pd–C bond distances of the iminoacyl ligands decrease, in agreement with the *trans* influence of the ligand located in the *trans* position with chloro ligand. Thus, these values are as follows (in Å); Pd(1)–C(1) 2.0021(16), Pd(1A)–C(1A) 1.9911(17). The Pd–C bond length for complex **4d** falls in the narrow ranges reported for related CPCs with (sp^2)C–Pd–Cl axes (1.99–2.05 Å), despite the expected difference in the *trans*-influence of the quinoline ring and chloride ligands. The Pd–Cl distances also allow us to correlate shorter distances with greater delocalization influence of side chain. Thus, the order is as follows Pd(1)–Cl(1) 2.3515(6) Å, Pd(1A)–Cl(1A)

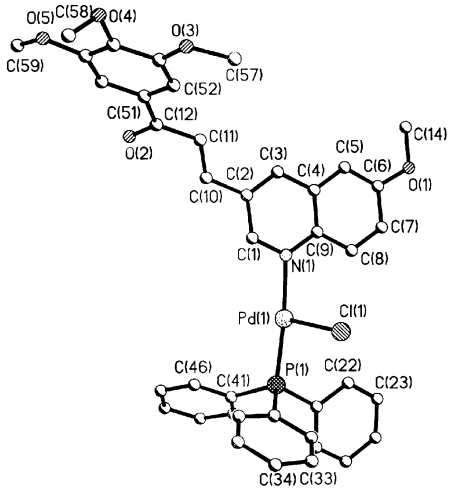


Fig. 3 Structure conformations of half of the dinuclear complex in X-ray structure of complex **4d** (30% probability ellipsoids)

2.3512(4) Å. Similarly, the Pd–N bond length in complex **4d**, Pd(1)–N(1) 2.1220(14) Å, Pd(1A)–N(1A) 2.0855(12) Å, is longer than known examples of *ortho*-palladated derivatives (1.886–2.085 Å), but is between the normal values of 2.060–2.062 and 2.142–2.188 Å found for phosphane adducts of *ortho*-palladated heterocycles with an *endo* C=N bond [77, 80]. Some elongation of the Pd–N bond in the *endo*-adduct **4d** compared to heterocyclic derived *endo*-analogues may be explained as resulting from less efficient palladium bonding with the imino-donor group located in the *endo*-cyclic position, due to the absence of intracyclic conjugation with this double bond. This assumption can be supported by similar values of Pd–N bond length (2.103–2.112 Å) found for P*Ph*$_3$ derivatives of *endo*-cyclopalladated imines [81]. This shows 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 [82, 83] under this assumption; two ligands with great *trans* influence will suffer a great *transphobia*.

The Pd–P bond length in complex **4d**, Pd(1)–P(1) 2.2905(5) Å, Pd(1A)–P(1A) 2.2481(7) Å, is in good agreement with values (2.243–2.248 Å) reported for neutral *exo*-imine derivatives [81]. These values fall within the ranges found previously for the neutral P*Ph*$_3$ adducts of *ortho*-palladated heterocyclic of *endo*-type (2.235–2.256 Å) [84,85] and *ortho*-palladated arylamines (2.243–2.256 Å) [86–89].

Another structural peculiarity of complex **4d** is the nearly coplanar orientation of the trimethoxyphenyl ring and one of the P*Ph*$_3$ phenyl rings (A) (Fig. 2) characterized by the torsion angle C1–Pd(1A)–P(1A)–C^{ipso} of −174.6° and an interplanar angle between these two aromatic rings of 16.5°. Non-covalent attractive interactions between π–π-systems are invoked to account for stabilization and orientation in many systems [90, 91]. In recent theoretical studies of intermolecular π–π-stacking in simple arene dimers, three geometries are most commonly discussed: sandwich (D_{6h}), parallel-displaced (C_{2h}, ''slipped sandwich''), and T-shaped (C_{2v}, ''point-to-face'') [90–98]. In structure **4d**, the orientation of the 3,4,5-(*Me*O)–C$_6$H$_2$–CH=CH–CO– and P–*Ph*^{A} rings resembles the parallel-displaced geometry of two arenes. The closest contact distance between the two aromatic rings is 3.5 Å (C$^{51}\cdots$C^{44A}) (Fig. 4), which is in accord with experimental values of 3.3–3.5 Å found to be the average interplanar spacing in porphyrin aggregates [90]. For comparison, a study of substituent effects on π–π-interactions performed by *Sinnokrot* and *Sherrill* [91] found a vertical displacement of 3.6–3.8 Å for a sandwich benzene-benzotrimethoxy dimer. Due to the restricted geometry of the arene moieties in **4d**, horizontal displacement of the two arenas is 1.39 Å (Figs. 2, 3; defined as the distance between the *Ph*^{A}-

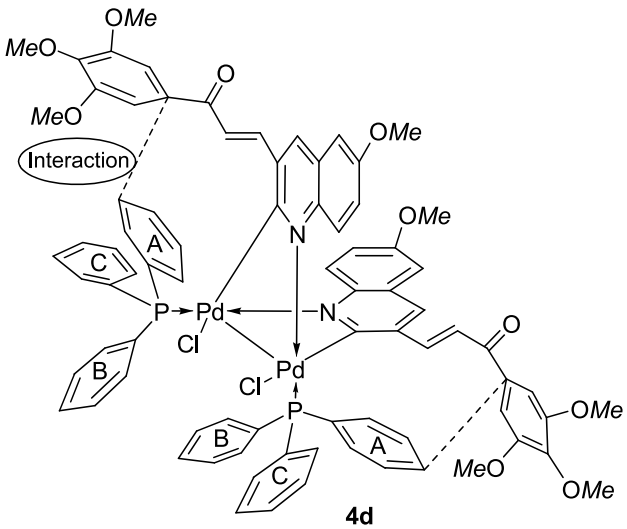


Fig. 4 Structure of complex **4d** with showing the interaction of P–*Ph*^{A} and aromatic ring of trimethoxy aroyl. π–π-Stacking interactions between two adjacent molecules in structure **4d**. The distance between planes of P–*Ph*^{A} and ligand in adjacent aryl is 3.5 Å

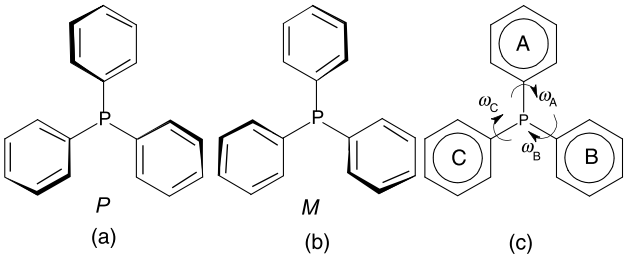


Fig. 5 Possible chiral rotameric states (*P*) (a) and (*M*) (b) for the Pd–P*Ph*$_3$ moiety derived from achiral C_3-symmetric structures *via* the *Ph*-ring rotation around the P–C^{ipso} bonds (c)

centroid to C^{44A}), which is slightly shorter than the calculated horizontal displacements for benzene dimers (1.54–2.10 Å) [91, 94–98]. Since the geometric parameters of complex **4d** are in good agreement with both theoretical and experimental values for systems with known $\pi-\pi$-interactions, one can reasonably interpret the nearly coplanar orientation of the two arene rings in complex **4d** (Fig. 4) as due to intramolecular $\pi-\pi$-interactions.

The stereochemistry of the coordinated P*Ph*$_3$ ligand in complex **4d** is of special interest since its propeller-like rotameric states can provide additional chirality [99–102]. The *Ph*$_3$P–*M* fragment remains achiral only if all P–*Ph* rings are positioned either parallel (''parallel'' conformation) or orthogonal (''orthogonal'' conformation) to the C_3 axis of the P*Ph*$_3$ moiety (Fig. 5) [99–100]. Between the two extremes lie the rotameric states that result from synchronous twisting of the three P–*Ph* rings (starting from the orthogonal conformation) about the P–C^{ipso} axes [99–100]. Rotation can be either clockwise or counterclockwise (Fig. 5), which generates the chiral propeller-like configurations (*P*) and (*M*). Unfortunately, studies of the influence of other chirality elements on P*Ph*$_3$ stereochemistry have been mainly restricted to cyclopentadienyl compounds with planar chirality and an asymmetric metal center [101–103]. Recently, a detailed analysis [104] of available X-ray structure data for P*Ph*$_3$ derivatives of C- and N-palladacycles has shown that the spirality (helicity) of the phosphane ligand is dependent upon both the palladacycle conformation and the nature of the N-donor atom.

The rotameric states of the aromatic rings in the phosphane ligand (relative to the corresponding P–C^{ipso} bonds) in complex **4d** were estimated using averaged values of the pair of torsion angles that include the *ortho-Ph* carbons, *i.e.*, Pd–P–C^{ipso}–C$^{ortho-1}$(ω_{i1}) and Pd–P–C^{ipso}–C$^{ortho-2}$(ω_{i2}), according to the known equation $\omega_i = (\omega_{i1} + \omega_{i2} + 180°)/2$. The torsion angle range of 0–90° is indicative of the (*P*) propeller configuration, while the range 90–180° corresponds to the (*M*) configuration. For complex **4d**, the angles ω_A–ω_B are equal to 90.3°, 141.0°, and 177.4° for P*Ph*$_3$ rings A(C^{ipso} = C^{41} or C^{41A}), B(C^{ipso} = C^{21} or C^{21A}), and **C**(C^{ipso} = C^{31} or C^{31A}) (Fig. 5). These data allow us to describe the P*Ph*$_3$ conformation as an (*M*) propeller, distorted due to interaction of ring **A** with the quinoline derivative ligand.

For comparison, the P*Ph*$_3$ ligands also adopt a helical conformation in related phosphane adducts and correspond to the (*M*) propeller configuration of the phosphane ligand. In all reported X-ray data for P*Ph*$_3$ derivatives of palladacycles [104] only two P–*Ph* rings exist in the twisted state, while the third P–*Ph* ring adopts a nearly parallel disposition, presumably due to secondary interactions that were not investigated.

Conclusions

Despite the unfavorable combination of the reduced propensity of (sp^2)C–Cl bonds to be activated by Pd(II) and the disadvantageous *exo*-position of the C=N bond in the target palladacycles, cyclopalladation of quinoline derivatives was achieved using palladium(II) dibenzylideneacetone as metallation agent. This is the first example of direct cyclopalladation of quinoline derivatives through the (sp^2)C–Cl and having an enone side chain group at position 3. Spectral investigations of the initial dimeric complex and its dinuclear palladaphosphane derivatives and X-ray diffraction study of an unusual pyrido[1,2-*a*]quinoline palladaphosphane complex confirmed a very high degree of cyclopalladated puckering and its existence in both the crystal and solution states. This conformation is fixed by the bicyclic structure formed by cyclopalladated ring and the quinoline ring. Peculiarities of the new cyclopalladated structures, such as its very pronounced twisting and high conformational stability, create the best conditions for efficient transmetallation transfer from the phosphane to other imine (*Xy*NC) ligands in the palladium environment. Further research into (sp^2)C–Cl activation toward formation of optically active CPCs and their applications is ongoing at this time in our laboratory.

Experimental

Reactions were carried out without precautions to exclude light, atmospheric oxygen, and moisture, unless otherwise stated. Melting points were determined on a *Reichert* apparatus. Elemental analyses were carried out with a Carlo Erba 1106 microanalyzer results agreed favorably with IR calculated values. IR spectra were recorded on a Perkin-Elmer ^{16}F PC FT-IR spectrometer with Nujol mulls between polyethylene sheets or KBr pellets. NMR spectra were recorded on 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 and ^{13}C(^{1}H) and H_3PO_4 (^{31}P). The NMR probe temperature was calibrated using ethylene glycol ^{1}H NMR standard methods. Chromatographic separations were carried out by TLC on silica gel (70–230 mesh).

*Synthesis of chalcones **3a–3d**: general method*

To a mixture of 0.59 g acetophenone (5 mmol) and 5 mmol appropriate aromatic aldehydes in 25 cm^3 oxygen-free ethanol was added 25 cm^3 2 *N* NaOH solution in oxygen-free distilled water with constant shaking of the reaction flask. The reaction mixture was stirred for a specified period on a magnetic stirrer and poured onto crushed ice. The solid mass which separated was filtered off, washed with water, and crystallized from a suitable solvent to give the desired product. Purification by chromatography was performed with silica gel.

(2E)-3-(2-Chloroquinolin-3-yl)-1-phenylprop-2-en-1-one (**3a**, $C_{18}H_{12}ClNO$)

It was purified by column chromatography (*n*-hexane/Et_2O 2/8, $R_f = 0.55$) to yield 1.3 g **3a** (88%). Yellow solid; mp 168–170°C; IR (Nujol): $\bar{\nu} = 1678$ (C=O), 1664, 1594, 1578 (C=N) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.16$ (s, 1H, quinoline-H4), 7.98–7.96 (d, 3H, $^4J_{HH} =$ 9.26 Hz), 7.77–7.75 (d, 1H, $^3J_{HH} = 8.2$ Hz) 7.69–7.64 (m, 1H), 7.58–7.49 (m, 3H), 7.46–7.42 (m, 3H) ppm.

(2E)-3-(2-Chloro-6-methoxy-quinolin-3-yl)-1-phenylprop-2-en-1-one (**3b**, $C_{19}H_{14}ClNO_2$)

It was purified by column chromatography (*n*-hexane/Et_2O 2/8, $R_f = 0.52$) to yield 1.15 g **3b** (71%). Yellow solid; mp 173–175°C; IR (Nujol): $\bar{\nu} = 1665$ (C=O), 1645, 1585 (C=N) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.36$ (s, 1H, quinoline-H4), 8.14–8.09 (d, 1H, $^3J_{HH} = 15.3$ Hz, CH=CHCO) 7.93–7.90 (d, 1H, $^4J_{HH} = 9.3$ Hz, quinoline-H8), 7.89–7.86 (d, 1H, $^4J_{HH} = 9.3$ Hz, quinoline-H7), 7.73–7.67 (d, 1H, $^3J_{HH} = 15.3$ Hz, CH=CHCO) 7.42–7.32 (m, 4H), 7.13–7.12 (d, 1H, $J = 2.7$ Hz), 6.74–6.68 (d, 2H, $^3J_{HH} = 7.8$ Hz), 3.95 (s, 3H, O*Me*) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 190.6$ (C=O), 158.4 (quin-C6), 151.2 (quin-C2), 147.8 (quin-C8a), 143.8 (quin-*C*H=CH), 137.6 (*Ph*–C1), 134.6 (quin-C4), 134.6 (*Ph*-C4), 131.0 (quin-C3), 129.7 (*Ph*–C2,6), 128.4 (CH=*C*H–CO*Ph*), 128.1 (quin-C8), 127.2 (*Ph*-C3,5), 124.1 (quin-C4a), 118.4 (quin-C7), 105.1 (quin-C5), 55.5 (O*Me*) ppm.

(2E)-3-(2-Chloroquinolin-3-yl)-1-(3,4,5-trimethoxyphenyl)-prop-2-en-1-one (**3c**, $C_{21}H_{18}ClNO_4$)

It was purified by column chromatography (*n*-hexane/Et_2O 2/8, $R_f = 0.56$) to yield 1.6 g **3c** (74%). Yellow solid; mp 148–150°C; IR (Nujol): $\bar{\nu} = 1664$ (C=O), 1646, 1580 (C=N) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.16$ (s, 1H, quin-H4), 8.11 (d, 1H, $^3J_{HH} = 15.6$ Hz, CH=CHCO) 8.06 (d, 1H, $^3J_{HH} = 9.2$ Hz, quin-H8), 7.49 (d, 1H, $^3J_{HH} = 15.8$ Hz, CH=CHCO) 7.42 (dd, 2H, $^4J_{HH} = 9.2$, 2.6 Hz, quin-H5, H7), 7.30 (s, 2H, Ar–H2), 7.14 (dd, 1H, $^4J_{HH} = 9.2$, 2.6 Hz, quin-H6), 3.92 (s, 6H, 2O*Me*), 3.90 (s, 3H, O*Me*) ppm.

(2E)-3-(2-Chloro-6-methoxyquinolin-3-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (**3d**, $C_{22}H_{20}ClNO_5$)

It was purified by column chromatography (*n*-hexane/Et_2O 2/8, $R_f = 0.59$) to yield 0.8 g **3d** (72%). Yellow solid; mp 196–198°C; IR (Nujol): $\bar{\nu} = 1664$ (C=O), 1646, 1580 (C=N) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.37$ (s, 1H, quin-H4), 8.15 (d, 1H, $^3J_{HH} = 15.6$ Hz, CH=CHCO) 7.93 (d, 1H, $^4J_{HH} = 9.2$ Hz, quin-H8), 7.49 (d, 1H, $^3J_{HH} = 15.8$ Hz, CH=CHCO) 7.42 (dd, 1H, $^4J_{HH} = 9.2$, 2.8 Hz, quin-H7), 7.30 (s, 2H, Ar–H), 7.14 (d, 1H, $^4J_{HH} = 2.8$ Hz, quin-H5), 3.96 (s, 6H, 2O*Me*), 3.95 (s, 3H, O*Me*), 3.90 (s, 3H, O*Me*) ppm.

*Synthesis of chalcone palladium complexes **4a–4d***: general method

A mixture of 216 mg [Pd(*dba*)$_2$] (0.375 mmol), 195 mg P*Ph*$_3$ (0.75 mmol), and 0.375 mmol halochalcones **3a–3d** was stirred under N_2 in 25 cm^3 dry acetone for 3–5 h at room temperature. Then it was concentrated to *ca.* 2 cm^3 and 25 cm^3 CH_2Cl_2 were added. The solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. Then it was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to *ca.* 2 cm^3, a mixture of the complex and *dba* was precipitated with *n*-hexane. The suspension was stirred for 10 min at RT. The precipitate was collected by filtration, washed with 5 cm^3 Et_2O, and air-dried to give a yellow solid of **4a–4d**.

Bis[(1E)-3-oxo-3-phenyl-1-propenyl(quinolin-2-yl)-(triphenylphosphine)palladium(II) chloride] (**4a**, $C_{72}H_{54}N_2O_2Cl_2Pd_2P_2$)

It was purified by chromatography (CH_2Cl_2/Et_2O 1/1, $R_f = 0.44$) to give 340 mg **4a** (68%). Yellow-orange powder; mp 158–160°C (dec); IR (Nujol): $\bar{\nu} = 1677$ (C=O), 1665 (C=N), 1575 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 9.32$ (s, 2H, quin-H4), 8.42 (d, 2H, $^3J_{HH} = 9.3$ Hz, quin-H8), 8.17 (d, 2H, $^3J_{HH} = 15.5$ Hz, CH=CHCO–), 7.75 (15H, P*Ph*$_3$), 7.52 (dd, 2H, $^3J_{HH} = 9.3$ Hz, $^4J_{HH} = 2.6$ Hz, quin-H7), 7.22 (m, 18H, quin-H6, H5, and P*Ph*$_3$), 6.67 (d, 2H, $^3J_{HH} = 15.5$ Hz, CH=CCO–), 6.66–6.43 (m, 10H, *Ph*–H) ppm; ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): $\delta = 23.60$ ppm.

Bis[(1E)-3-oxo-3-phenyl-1-propenyl(6-methoxyquinolin-2-yl)(triphenylphosphine)palladium(II) chloride] (**4b**, $C_{74}H_{58}N_2O_4Cl_2Pd_2P_2$)

It was purified by chromatography (CH_2Cl_2/Et_2O 1/1, $R_f = 0.45$) to give 339 mg **4b** (65%). Yellow-orange powder;

mp 162–164°C (dec); IR (Nujol): $\bar{\nu} = 1664$, 1622 (C=O), 1610, 1580, 1572, 1538 (C=N, C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.38$ (s, 2H, quin-H4), 8.51 (d, 2H, $^3J_{HH} = 15.6$ Hz, CH=CCO–), 8.15 (d, 2H, $^3J_{HH} = 9.3$ Hz, quin-H8), 7.90–7.76 (m, 15H, P*Ph*$_3$), 7.59 (dd, 2H, $^3J_{HH} = 9.3$ Hz, $^4J_{HH} = 2.6$ Hz, quin-H7), 7.45–7.15 (m, 15H, P*Ph*$_3$), 7.13 (d, 2H, $^4J_{HH} = 2.6$ Hz, quin-H5), 6.81 (d, 2H, $^3J_{HH} = 15.6$ Hz, C=CHCO–), 6.70–6.45 (m, 10H, 2*Ph*–H), 3.77 (s, 3H, O*Me*) ppm; ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): $\delta = 23.63$ ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 193.6$ (C=O), 162.8 (quin-C6), 152.3 (quin-C2), 148.5 (quin-C8a), 142.8 (quin-*C*H=CH), 138.2 (*Ph*–C1), 134.5 (*Ph*–C4), 134.3 (quin-C4), 132.1 (P–*Ph*–C1), 131.2 (quin-C3), 130.4 (P–*Ph*–C4), 129.8 (quin-C8), 129.7 (*Ph*–C2,6), 129.4 (P–*Ph*–C2,6), 129.3 (CH=*C*H–CO*Ph*), 129.2 (quin-C4a), 129.0 (*Ph*–C3,5), 128.8 (P–*Ph*–C3,5), 122.5 (quin-C7), 105.5 (quin-C5), 57.2 (O*Me*) ppm.

Bis[(1E)-3-oxo-3-(3,4,5-trimethoxyphenyl)-1-propenyl-(quinolin-2-yl)(triphenylphosphine)palladium(II) chloride] (**4c**, $C_{78}H_{66}N_2O_8Cl_2Pd_2P_2$)

It was purified by chromatography (CH_2Cl_2/Et_2O 1/1, $R_f = 0.46$) to give 398 mg **4c** (67%). Yellow-orange powder; mp 155–156°C (dec); IR (Nujol): $\bar{\nu} = 1663$ (C=O), 1620 (C=N), 1580 (C=C) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.36$ (d, 2H, $^3J_{HH} = 9.3$ Hz, quin-H8), 8.81–8.73 (d, 2H, $^3J_{HH} = 8.7$ Hz, quin-H5), 8.50–8.45 (d, 2H, $^3J_{HH} = 15.6$ Hz, CH=CHCO–), 8.38 (s, 2H, quin-H4), 8.18–8.12 (d, 2H, $^3J_{HH} = 15.6$ Hz, CH=CCO–), 7.94–7.91 (d, 2H, $^3J_{HH} = 9.3$ Hz, quin-H7), 7.85–7.54 (m, 15H, P*Ph*$_3$), 7.57–7.54 (dd, 2H, $^3J_{HH} = 6.4$ Hz, $^4J_{HH} = 2.7$ Hz, quin-H6), 7.45–7.40 (m, 15H, P*Ph*$_3$), 7.03 (s, 4H, Ar–H), 3.95 (s, 6H, 2O*Me*) 3.91 (s, 12H, 4O*Me*) ppm; ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): $\delta = 23.53$ ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 190.6$ (C=O), 152.5 (quin-C2), 150.5 (*Ph*–C3,5), 149.0 (*Ph*–C4), 148.8 (quin-C4), 146.8 (quin-*C*H=CH), 145.5 (quin-C8a), 135.2 (*Ph*–C1), 132.6 (P–*Ph*–C1), 130.8 (quin-C3), 130.3 (P–*Ph*–C4), 130.1 (CH=*C*H–CO*Ph*), 129.9 (quin-C8), 129.6 (P–*Ph*–C2,6), 129.5 (quin-C5), 129.2 (quin-C4a), 128.9 (P–*Ph*–C3,5), 128.8 (quin-C7), 127.5 (quin-C6), 110.2 (*Ph*–C2,6), 57.0 (*Ph*–C3,5-O*Me*), 56.8 (*Ph*–C4-O*Me*) ppm.

Bis[(1E)-3-oxo-3-(3,4,5-trimethoxyphenyl)-1-propenyl-(6-methoxyquinolin-2-yl)(triphenylphosphine)palladium(II) chloride] (**4d**, $C_{81}H_{72}N_2O_{10}C_{l4}Pd_2P_2$)

It was purified by chromatography (CH_2Cl_2/Et_2O 1/1, $R_f = 0.43$) to give 365 mg **4d** (62%). Diffraction-quality crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of **4d**. Yellow-orange solid; mp 144–146°C (dec); IR (Nujol): $\bar{\nu} = 1664$, 1622 (C=O), 1610, 1580 (C=N, C=C) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.39$ (d, 2H, $^4J_{HH} = 9.4$ Hz, quin-H8), 8.51 (d, 2H, $^3J_{HH} = 15.6$ Hz, CH=CCO–), 8.17–7.73 (m, 15H, P*Ph*$_3$ + 2H of quin-H4), 7.62–7.56 (dd, 2H, $^4J_{HH} = 2.6$ Hz, quin-H5), 7.45–7.03 (m, 15H, P*Ph*$_3$ + 2H of quin-H7), 6.84–6.76 (d, 2H, $^3J_{HH} = 15.6$ Hz, C=CHCO–), 6.70 (s, 4H, Ar–H), 4.01 (s, 6H, 2O*Me*) 3.93 (s, 12H, 4O*Me*), 3.77 (s, 3H, O*Me*) ppm; ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): $\delta = 23.64$ ppm; ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 191.8$ (C=O), 165.9 (quin-C6), 155.4 (quin-C4), 150.2 (*Ph*–C3,5), 148.5 (quin-C2), 146.8 (quin-*C*H=CH), 145.5 (quin-C8a), 141.0 (*Ph*–C4), 136.4 (*Ph*–C1), 132.2 (P–*Ph*–C1), 130.6 (CH=*C*H–CO*Ph*), 129.9 (quin-C8), 129.8 (P–*Ph*–C4), 129.7 (P–*Ph*–C2,6), 129.0 (quin-C3), 129.0 (quin-C4a), 127.9 (P–*Ph*–C3,5), 118.3 (quin-C7), 115.3 (quin-C5), 110.8 (*Ph*–C2,6), 57.5 (*Ph*–C4–O*Me*), 57.2 (*Ph*–C3,5-O*Me*), 56.0 (quin-C6-O*Me*) ppm.

2,3,4-Tris(2,6-dimethylphenylimino)-5-(3-oxo-3-phenylpropenyl)-1,2,3,4-tetrahydropyrido[1,2-a]quinoline-1-(2,6-dimethylphenylisocyano)palladium(II) chloride (**5a**, $C_{54}H_{48}N_5OClPd$)

Method A. Chalcone **3a** (110 mg, 0.375 mmol) was added to a suspension of 300 mg Pd(*dba*)$_2$ (0.52 mmol) and 274 mg *Xy*NC (2.09 mmol) in 15 cm^3 acetone under nitrogen. The reaction mixture was stirred for 5 h at room temperature, then evaporated under reduced pressure, and 25 cm^3 CH_2Cl_2 were added. The resulting solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give 160 mg red solid of palladacycle **5a** (46%). Mp 182–184°C (dec); IR (Nujol): $\bar{\nu} = 2180$ (C≡O), 1675 (C=O), 1645, 1585, 1505 (C=N) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): $\delta = 9.27$–9.24, (s, 1H, quin-H4), 8.72 (d, 1H, $^3J_{HH} = 8.6$ Hz, quin-H8), 8.57–8.50 (d, 1H, $^3J_{HH} = 15.7$ Hz, CH=CCO–), 8.16 (d, 1H, $^3J_{HH} = 8.4$ Hz, quin-H5), 7.99–7.94 (dd, 1H, $^3J_{HH} = 8.6$, 7.4 Hz, quin-H7), 7.80–7.65 (m, 12H), 7.56–7.51 (dd, 1H, $^3J_{HH} = 8.4$, 7.4 Hz, quin-H6), 6.98–6.91 (d, 1H, $^3J_{HH} = 15.7$ Hz, C=CHCO–), 6.77–6.60 (s, 5H, *Ph*–H), 2.31 (s, 6H, 2*Me*), 2.20 (s, 6H, 2*Me*), 2.10 (s, 6H, 2*Me*), 1.55 (s, 6H, 2*Me*) ppm.

Method B. To a suspension of 0.158 g arylpalladium **4a** (0.12 mmol) in 15 cm^3 CH_2Cl_2 0.125 g *Xy*NC (0.96 mmol) were added. The suspension was stirred for 16 h at room temperature. The color changed from pale yellow into pale red and then dark red during monitoring of the reaction. The suspension was stirred for 5 h more at room temperature, then evaporated under reduce pressure, and 25 cm^3 CH_2Cl_2 were added. The resulting solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give 62 mg red solid of palladacycle **5b** (55%).

2,3,4-Tris(2,6-dimethylphenylimino)-8-methoxy-5-(3-oxo-3-phenylpropenyl)-1,2,3,4-tetrahydropyrido[1,2-a]quinoline-1-(2,6-dimethylphenylisocyano)palladium(II) chloride (**5b**, $C_{55}H_{50}N_5O_2ClPd$)

Method A. Chalcone **3b** (252.5 mg, 0.78 mmol) was added to a suspension of 300 mg Pd(*dba*)$_2$ (0.52 mmol) and 274 mg

*Xy*NC (2.09 mmol) in 15 cm^3 acetone under nitrogen. The reaction mixture was stirred for 5 h at room temperature, then evaporated under reduced pressure and 25 cm^3 CH_2Cl_2 were added. The solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give 375 mg red solid of palladacycle **5b** (51%). Mp 177–179°C; IR (Nujol): $\bar{\nu} = 2185$ (C≡N), 1675 (C=O), 1642, 1582, 1506 (C=N) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.24$ (d, 1H, $^3J_{HH} =$ 8.6 Hz, quin-H8), 8.72 (s, 1H, quin-H4), 8.51 (d, 2H, $^3J_{HH} =$ 15.7 Hz, CH=CCO–), 8.16 (d, 1H, $^3J_{HH} = 8.4$ Hz, quin-H5), 7.94 (dd, 1H, $^3J_{HH} = 8.6$, 8.4 Hz, quin-H7), 7.80–7.51 (m, 12H), 6.91 (d, 2H, $^3J_{HH} = 15.7$ Hz, C=CHCO–), 6.77–6.63 (m, 5H, *Ph*–H), 3.88 (s, 3H, O*Me*), 2.31 (s, *Me*, 6H), 2.19 (s, 6H, 2 *Me*), 2.09 (s, 6H, 2 *Me*) , 1.53 (s, 6H, 2 *Me*) ppm.

Method B. To a suspension of 166 mg arylpalladium **4b** (0.12 mmol) in 15 cm^3 CH_2Cl_2 124 mg *Xy*NC (0.96 mmol) were added. The suspension was stirred for 16 h at room temperature. The color changed from pale yellow into pale red and then dark red during monitoring of the reaction. The suspension was stirred for 5 h more at room temperature, then evaporated under reduce pressure and 25 cm^3 CH_2Cl_2 were added. The resulting solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give 59 mg red solid of palladacycle **5b** (53%).

2,3,4-Tris(2,6-dimethylphenylimino)-5-[3-oxo-3-(3,4,5-trimethoxyphenyl)propenyl]-1,2,3,4-tetrahydropyrido [1,2-a]quinoline-1-(2,6-dimethylphenylisocyano) palladium(II) chloride (**5c**, $C_{57}H_{54}N_5O_4ClPd$)

Method A. Chalcone **3c** (144 mg, 0.375 mmol) was added to a suspension of 300 mg Pd(*dba*)$_2$ (0.52 mmol) and 274 mg *Xy*NC (2.09 mmol) in 15 cm^3 acetone under nitrogen. The reaction mixture was stirred for 5 h more at room temperature, then evaporated under reduce pressure and 25 cm^3 CH_2Cl_2 were added. The solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give 180 mg red solid of palladacycle **5c** (47%). Mp 173–175°C (dec); IR (Nujol): $\bar{\nu} = 2185$ (C≡N), 1678 (C=O), 1643, 1586, 1502 (C=N) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.29$ (d, 1H, $^3J_{HH} = 8.6$ Hz, quin-H8), 8.72 (s, 1H, quin-H4), 8.53 (d, 2H, $^3J_{HH} = 15.7$ Hz, CH=CCO–), 8.16 (s, 1H, quin-H5), 7.97 (dd, 1H, $^3J_{HH} = 8.7$, 8.4 Hz, quin-H7), 7.80–7.66 (m, 12H), 7.54 (d, 1H, $^3J_{HH} = 8.4$ Hz, quin-H6), 6.95 (d, 2H, $^3J_{HH} = 15.7$ Hz, C=CHCO–), 6.77 (s, 2H, Ar–H), 3.91 (s, 6H, 2O*Me*), 3.87 (s, 3H, O*Me*), 2.30 (s, *Me*, 6H), 2.19 (s, 6H, 2*Me*), 2.08 (s, 6H, 2*Me*), 1.53 (s, 6H, 2*Me*) ppm.

Method B. To a suspension of 180 mg arylpalladium **4c** (0.12 mmol) in 15 cm^3 CH_2Cl_2 125 mg *Xy*NC (0.96 mmol) were added. The suspension was stirred for 16 h at room temperature. The color changed from pale yellow into pale red and then dark red during monitoring of the reaction mixture. The suspension was stirred for 5 h more at room temperature, then evaporated under reduced pressured and 25 cm^3 CH_2Cl_2 were added. The resulting solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give 62 mg red solid of palladacycle **5c** (51%).

2,3,4-Tris(2,6-dimethylphenylimino)-8-methoxy-5-[3-oxo-3-(3,4,5-trimethoxyphenyl)propenyl]-1,2,3,4-tetrahydropyrido-[1,2-a]quinoline-1-(2,6-dimethylphenylisocyano)-palladium(II) chloride (**5d**, $C_{58}H_{56}N_5O_5ClPd$)

Method A. Chalcone **3d** (322.5 mg, 0.78 mmol) was added to a suspension of 300 mg Pd(*dba*)$_2$ (0.52 mmol) and 274 mg *Xy*NC (2.09 mmol) in 15 cm^3 acetone under nitrogen. The reaction mixture was stirred for 5 h at room temperature, then evaporated under reduced pressure and 25 cm^3 CH_2Cl_2 were added. The solution was passed through a pad of silica gel: $MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, 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 5 cm^3 Et_2O, and air-dried to give red solid of palladacycle **5d** which was purified by chromatography (acetone:CH_2Cl_2 1:1, $R_f = 3.6$). Yield: 385 mg (47%); mp 152–154°C; IR (Nujol): $\bar{\nu} = 2184$, 1672 (C≡N), 1640, 1582, 1504 (C=N); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.27$ (d, 1H, $^3J_{HH} = 8.6$ Hz, quin-H8), 8.72 (s, 1H, quin-H4), 8.57 (d, 2H, $^3J_{HH} = 15.7$ Hz, CH=CCO–), 8.16–8.05 (s, 1H, quin-H5), 7.99–7.94 (d, 1H, $^3J_{HH} = 8.6$, quin-H7), 7.80–7.51 (m, 12H), 6.98–6.91 (d, 2H, $^3J_{HH} = 15.7$ Hz, C=CHCO–), 6.77 (s, 2H, *Ph*–H), 3.96 (s, 3H, O*Me*), 3.91 (s, 6H, 2O*Me*), 3.87 (s, 3H, O*Me*), 2.30 (s, *Me*, 6H), 2.18 (s, 6H, 2 *Me*), 2.08 (s, 6H, 2*Me*), 1.52 (s, 6H, 2*Me*).

Method B. To a suspension of 187.8 mg arylpalladium **4d** (0.12 mmol) in 15 cm^3 CH_2Cl_2 124 mg *Xy*NC (0.96 mmol) were added. The suspension was stirred for 16 h at room temperature. The color changed from pale yellow into pale red and then dark red during monitoring of the reaction. The suspension was stirred for 5 h more at room temperature, then evaporated under reduce pressure and 25 cm^3 CH_2Cl_2 were added. The resulting solution was passed through a pad of silica gel:$MgSO_4$ (3:1) in a fritted funnel. The resulting filtrate was evaporated under reduced pressure and 15 cm^3 Et_2O were added. The resulting solution was concentrated to 2 cm^3, a mixture of the complex and *dba* was precipitated with *n*-hex-

ane. The suspension was stirred for 10 min at RT, filtered off, washed with 5 cm^3 Et_2O, and air-dried to give 69 mg red solid of palladacycle **5d** (55%).

*X-Ray structure determination of dinuclear palladium(II) complex **4d***

Details of data collection and refinement are given in Table 1. The crystal structure of **4d** was determined by single crystal X-ray diffraction. Measurements were recorded for **4d** on a Bruker SMART 1000 CCD, a Siemens P4 diffractometer using monochromated Mo Kα radiation in *w*-scan and *f*-scan mode for **4d**. The structure was solved by the heavy atom method and refined anisotropically on F^2 with the program SHELXL-97 (*G.M. Sheldrick*, University of Göttingen, Gemany). Hydrogen atoms were included using a riding model or rigid methyl groups. Disordered groups were refined using appropriate systems of similarity restraints. 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, CambridgeCB2 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 number 680965.

Table 1 Details of data collection and structure refinement for the complex {Pd[6-OCH_3–C_9H_4–CH=CHCO–C_6H_2–(3,4,5)–$(OCH_3)_3$]Cl (PPh_3)}$_2 \cdot CH_2Cl_2$ (**4d**)

	4d $\cdot CH_2Cl_2$
Empirical formula	$C_{81}H_{72}Cl_4N_2O_{10}P_2Pd_2$
Formula weight	1650
Temperature/K	166(2)
Wavelength/Å	0.76274
Crystal habit	Yellow rectangular prim
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	
a/Å	11.8585(11)
b/Å	14.462(2)
c/Å	18.822(3)
α/deg	107.226(11)
β/deg	99.993(15)
γ/deg	112.555(12)
Volume/Å^3	2444.0(6)
Z	2
Density (calculated)/Mg m^{-3}	1.730
Absorption coefficient/mm^{-1}	1.072
F(000)	1414
Crystal size/mm^3	$0.38 \times 0.16 \times 0.22$
θ range for data collection	1.26 to 30.09
Index ranges	$-18 \le h \le 18$, $-19 \le k \le 19$, $-27 \le l \le 27$
Reflections collected	47779
Independent reflections	14288 [R(int) = 0.0399]
Completeness to $\Theta = 30.00°$	99.5%
Absorption correction	Numerical
Max. and min. transmission	0.9070 and 0.7471
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14270/0/633
Goodness-of-fit on F^2	1.030
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0261$, $wR2 = 0.0631$
R indices (all data)	$R1 = 0.0336$, $wR2 = 0.0666$
Largest diff. peak and hole/eÅ^{-3}	0.998 and −0.966

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