Journal of Organometallic Chemistry 834 (2017) 10–21

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Reactions of palladium(0) olefin complexes stabilized by some different hetero- and homo-ditopic spectator ligands with propargyl halides

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ARTICLE INFO

Article history:
Received 7 December 2016
Received in revised form
31 January 2017
Accepted 5 February 2017
Available online 7 February 2017

Keywords:
Allenyl
Propargyl
Palladium(0) complexes
Oxidative addition

ABSTRACT

Several new allenyl and propargyl complexes have been obtained by oxidative addition with propargyl chlorides of palladium (0) olefin complexes stabilized by N–N, P–P, N–P, N–S. and N–C homo– and hetero–ditopic spectator ligands. The oxidative addition of some of the isolated palladium(0) olefin derivatives with 3–chloro–1–propyne and 3–chloro–1– phenyl–propyne has been investigated and the ensuing tautomeric mixtures bearing propargyl and allenyl fragmenst η^1– coordinated isolated. As a consequence of a detailed kinetic study, we have analyzed the influence of the electronic and steric parameters of the involved reactants and hypothesized the mechanism of reaction. The tautomeric rearrangement of one allenyl isomer into its propargyl counterpart was also investigated and in this case the complete determination of all the rate constants involved has been obtained. Beside these studies, two very rare η^3–propargyl palladium derivatives have been isolated and characterized.

1. Introduction

Oxidative addition and the related reductive elimination are processes of remarkable importance in the field of homo– [1] and hetero–cross coupling [2] catalysis. In this respect, we have been recently involved in theoretical and experimental studies of oxidative reactions of Pd(II) or Pd(0) complexes with halogens and interhalogens [3] and alkyl or aryl halides [4]. As a matter of fact, despite the vast literature dealing with the application of palladium derivatives in catalysis [5], some interesting aspects related to the mechanism of the oxidative reaction with organic halides are still controversial [6]. In this context, the present work represents a remarkable extension from the synthetic and the mechanistic points of view of a former paper dealing with the oxidative addition of 3–chloro–1–propyne or 3–chloro–1– phenyl–propyne to Pd(0) derivatives bearing heteroditopic bidentate moieties as spectator ligands [4a]. Since we wished to expand our knowledge on the mechanism of formation of propargyl and/or allenyl derivatives we have endeavored a more detailed kinetic investigation in order to understand the involvement and the importance of the nature of the spectator ligands and olefin in the oxidative process. Hence, in order to remove complications arising from *cis–trans* isomerization in complexes bearing monodentate spectator ligands [7], we have extended our investigation to palladium(0) species stabilized by bidentate frames. The hetero– or homo–ditopic spectator ligands we used are characterized by the presence of nitrogen, phosphorus, sulfur or carbenic carbon as coordinating atoms, whereas the stabilizing olefins were dimethylfumarate (dmfu) and naphthoquinone (nq), both representing a reasonable compromise between the stability imparted to their Pd(0) derivatives and the reactivity of the complexes themselves [4a,8]. Moreover, the spectroscopic characteristics of such complexes allow a detailed kinetic investigations by UV–Vis technique. The complexes synthesized and a schematic representation of the reactions studied are reported in the following Schemes 1 and 2, respectively.

2. Results and discussion

2.1. Synthesis of the novel palladium(0) complexes

Only the starting complexes **1'b** and **1j** are newly synthesized species which were obtained by mixing under inert atmosphere and in anhydrous acetone $Pd_2(DBA)_3 \cdot CHCl_3$, naphthoquinone and 8–(diphenylphosphino)–2–methylquinoline [9] (DPPQ–Me;

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http://dx.doi.org/10.1016/j.jorganchem.2017.02.003
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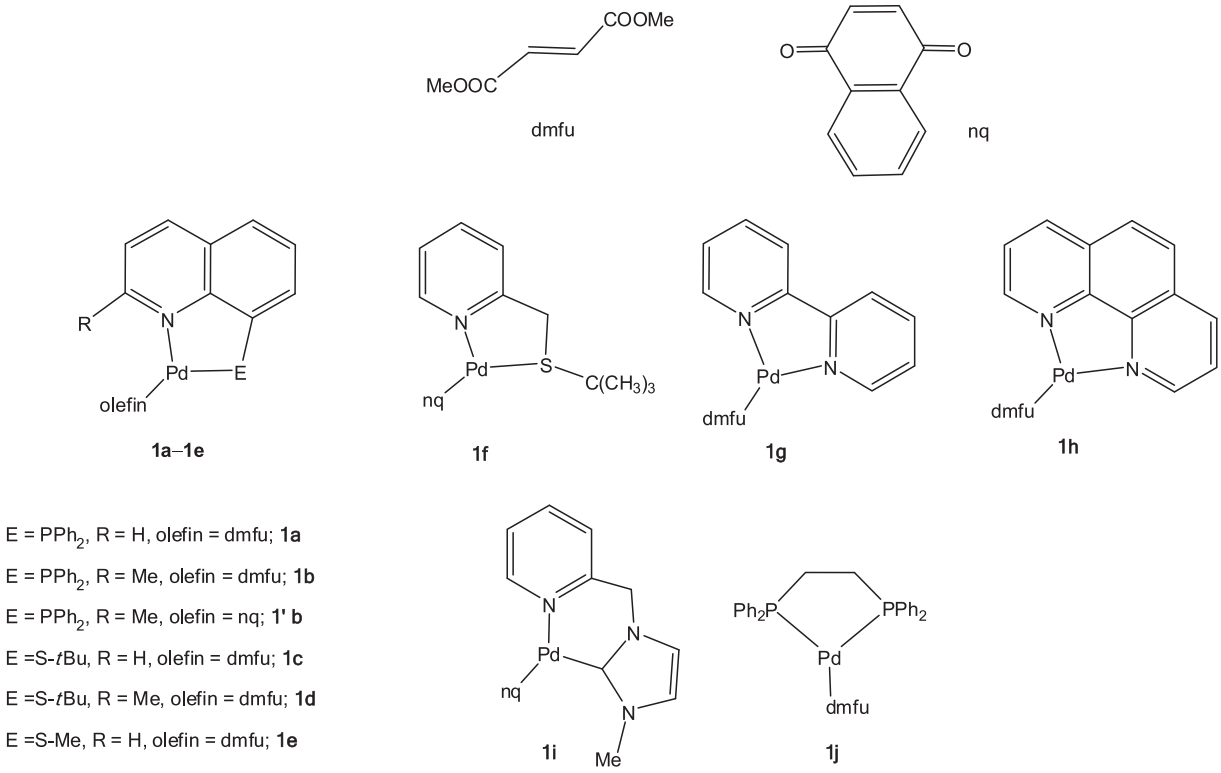
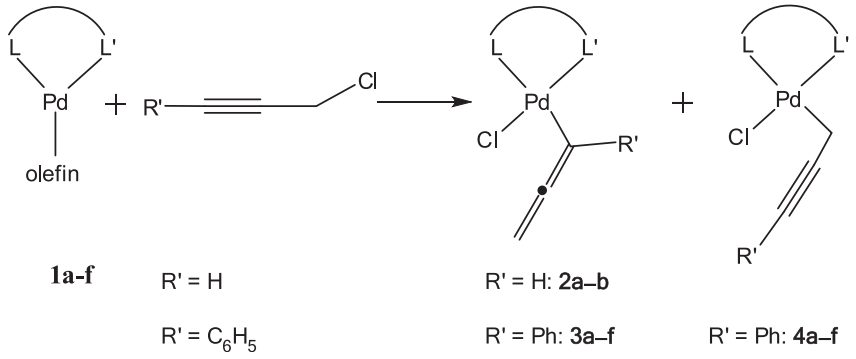


Scheme 1. Studied complexes.



Scheme 2. Schematic representation of the investigated process.

complex **1'b**) in stoichiomeric ratio or $Pd_2(DBA)_3 \cdot CHCl_3$, dmfu in slight excess and 1,2–bis(diphenylphosphino)ethane (dppe; complex **1j**). The separated stable pale-orange complex **1'b** and the pale–yellow **1j** where characterized by ^{1}H and ^{13}C NMR and elemental analysis, which are in accord with the formulated structure. As for the NMR spectra, it is noteworthy that all the signals belonging to the spectator ligands are detected at different fields with respect to those of the free ligands, whereas the protons and carbons of the olefin shift significantly up-field upon coordination [10] ($\Delta\delta_H \approx 5$, $\Delta\delta_C \approx 65$ ppm, **1'b**; $\Delta\delta_H \approx 2.4$, $\Delta\delta_C \approx 80$ ppm, **1j**). In particular, in the case of complex **1'b**, due to the heteroditopicity of the DPPQ–Me ligand, the two olefin protons are not equivalent and coupled with phosphorus of the ligand and therefore resonate as a multiplet. Owing to the persistence of the coupling with phosphorus, the dmfu protons of the symmetric complex **1j** resonate as a single AA'BB′ system. (See **Supplementary Material** Figs. S1 and S2). The ^{31}P NMR signals and IR spectra are in accord with the formulated structures and the ^{31}P NMR spectra display in both cases only a single peak, clearly indicating the presence of a unique species in solution whereas the IR signals between 1610 and 1685 cm^{-1} related to the CO stretching confirm the presence of the carbonyl (**1'b**) and carboxylate groups (**1e**) in the isolated complexes (see **Experimental**).

2.2. Reactivity of complexes *1a*, *1b* and *1'b* with 3–chloro–1–propyne and 3–chloro–1–phenyl–propyne

The reactivity of complex **1a** with 3–chloro–1–propyne has been recently studied and it was unequivocally established that the reaction gave only the allenyl derivative **2a**, whereas an almost equimolecular mixture of the allenyl **3a** and propargyl **4a** isomers was obtained when 3–chloro–1–phenyl–1–propyne was used in the oxidative addition [4a]. In this work, we have proved that the regioselectivity of the reaction was maintained and only the allenyl derivative **2b** was detected in solution at the end of the reaction of complexes **1b** and **1'b** with 3–chloro–1–propyne. This result is

confirmed by the presence of *i)* the signals due to allenyl protons at 5.41 (Pd–CH=C=) and 3.90 (CH=C=CH_2) ppm, in the ^{1}H NMR spectrum, *ii)* the signals related to allenyl carbons at 77.5 (Pd–CH), 6.84 (=C=CH_2) and 200.9 (C=C=C) ppm, in the in the $^{13}C\{^1H\}$ NMR spectrum, *iii)* the peak at 35 ppm in the ^{31}P NMR spectrum indicating the occurred oxidation of palladium (in the Pd(0) derivative the phosphorus resonates at ca. 20 ppm) and finally, *iv)* by the asymmetric stretching of the C=C=C group at 1919 cm^{-1} in the IR spectrum (Figs. S3a and b in **Supplementary Material**).

Complex **1b** (or **1'b**) reacts with 3–chloro–1–phenyl–1–propyne initially yielding a tautomeric mixture of complexes **4b** and **3b** (molar ratio **4b**/**3b** ≈ 0.33). However, the more abundant allenyl species **3b** rearranges to give in about four hours a new isomeric distribution in which the comparatively more stable propargyl tautomer prevails with a molar ratio of **4b**/**3b** ≈ 7.3.

As can be seen in Fig. S4 (**Supplementary Material**), the ^{1}H NMR spectrum is characterized by the presence of the signal of the Pd-CH_2 protons (propargyl tautomer **4b**) at 2.48 ppm and a small peak at 4.31 ppm related to the =C=CH_2 (allenyl tautomer). The tautomeric distribution is also confirmed by the ^{31}P NMR spectrum in which the phosphorus of the propargyl and that of the allenyl tautomer respectively resonate at 35.0 and 32.9 ppm. Owing to the remarkably different concentrations of the isomers only the signals due to the predominant **4b** isomer are detectable in the ^{13}C NMR and IR spectra of the final mixture (See **Experimental**). The DFT calculation related to the energy of the tautomers considered and the kinetic study of the isomeriation are reported in dedicated sections (*vide infra*).

2.3. Reactivity of complexes *1c, 1d, 1e* and *1f* with 3–chloro–1–phenyl–propyne

Complexes **1c**, **1d,** **1f** and **1e** react with 3–chloro–1–phenyl–1–propyne to give a mixture of tautomers which in the case of complexes **1c** **1d** and **1f** yields a final distribution ratio molar ratio of ca. **4**/**3** ≈ 9.0 whereas in the case of **1e** the **4e**/**3e** ratio is ca. 6. As a matter of fact, in the ^{1}H NMR spectra of the isolated complexes both tautomers are detected from the resonance frequencies of the propargyl (Pd-CH_2-C≡) and allenyl (=C=CH_2) protons at ca. 2.7÷2.8 and 4.8÷4.9 ppm, respectively (See Fig. S5 **Supplementary Material** case of **3e**/**4e**). However, due to the predominance of the propargyl isomer in the ^{13}C NMR and IR spectra, only the signals of the isomers **4** (Pd-CH_2 within −4.9 and −9.2, CH_2-C≡ ≈ 84, ≡Ph ≈ 98 ppm; $\nu_{C\equiv C}$ ≈ 2180 cm^{-1}) are clearly detectable. (See Figs. S6a and b in **Supplementary Material**). Interestingly, the CH_2-S protons of both the propargyl and allenyl fragments of complexes **3e** and **4e** at low temperature resonate as two separated AB systems owing to their proximity to sulfur which becomes a stereocentre as a consequence of the freezing of the fast inversion of its absolute structure [11 and Refs. therein]. (Fig. S7 **Supplementary Material**).

2.4. Reactivity of complexes *1g* and *1h* with 3–chloro–1–phenyl–1–propyne

The reaction of the Pd(0) complexes bearing symmetric nitrogen di-substituted spectator ligands bi–pyridine and *o*–phenanthroline with 3–chloro–1– phenyl–1–propyne is fast and yields the expected mixture of allenyl (**3g** or **3h**) and propargyl isomers (**4g** or **4h**) although in a reduced ratio (**4**/**3** ≈ 3).

As can be seen in Fig. S8 (**Supplementary Material**) the signals characterizing both the tautomers are immediately recognized. Thus, the signals between 2.60 and 2.80 and at 4.80 ppm are traceable back to the propargyl (Pd-CH_2-C≡) and allenyl (=C=CH_2) protons, whereas only the ^{13}C NMR spectrum of the complexes **3g** and **4g** is available owing to the insufficient solubility of the *o*–phenanthroline (**3h** and **4h**) derivatives. The ^{13}C NMR spectrum of the soluble tautomer **4g** is characterized by the peaks at 3.70 (Pd–CH_2; $J_{C,P}$ = 9.8 Hz), 81.1 (C≡C–Ph, $J_{C,P}$ = 4.4 Hz) and 98.6 ppm (C≡C–Ph) whereas the carbons of **3g** resonate at 68.7 (–C=CH_2), 97.1 (Pd–C(Ph)=) and 196.4 (C=C=C) ppm. Finally, the sharp IR signals of the $\nu_{C\equiv C}$ and $\nu_{C=C=C}$ vibration modes can be detected at 2170 and 1900 cm^{-1}, respectively.

2.5. Reactivity of complex *1i* with 3–chloro–1–phenyl–1–propyne

Complex **1i** reacts with 3–chloro–1– phenyl–1–propyne and in about one hour the typical signals ascribable to the tautomeric mixture of **3i** and **4i** can be detected by the NMR technique. At variance with the usual findings, in this case the allenyl isomer is slightly predominant over its propargyl counterpart (**3i**/**4i** ≈ 3.0). Such an unexpected isomeric distribution is confirmed by the DFT calculation we have carried out for some selected couples of tautomers, as summarized in Table 1 of the dedicated section (*vide infra*).

The immediately recognizable signals in the ^{1}H NMR spectrum ascribable to the tautomers **4i** and **3i**, are at 2.46 (Pd-CH_2-C ≡) and 4.68 ppm (=C=CH_2), whereas the low field resonance (9.21–9.31 ppm) of both the pyridine ^{6}H identifies the usual geometric distribution of the palladium substituents with the chloride *cis* to the pyridine nitrogen (Fig. S9, **Supplementary Material**) [3b and Refs. therein].

The ^{13}C NMR experiment is fully consistent and the allenyl carbons of the preponderant tautomer resonate at 68.0 (=C=CH_2), 92.1 (Pd–C(Ph)=) and at 200.4 (C=C=C) ppm together with the coordinated carbene carbon at 165.1 ppm. Finally, the IR shows the contemporary presence of the $\nu_{C\equiv C}$ and $\nu_{C=C=C}$ at 2181 and 1900 cm^{-1} vibrations, respectively.

Due to the bent structure of the chelating carbene-pyridine ring and the vertical coordination mode of the allenyl or propargyl fragment, two geometric isomers for each tautomer are possible together with their enantiomers without taking into consideration the position of the chloride which is always *cis* to pyridine, (Schematic representation in Fig. S10 **Supplementary Material**). Apparently, at RT a general fluxional rearrangement takes place so that, only one broad singlet ascribable to the C–CH_2–N protons of both tautomers can be detected. On decreasing the temperature, two AB systems at different intensity (one for each tautomer) were observed indicating the presence of only two groups of diastereotopic C–CH_2–N protons at different concentration (Fig. S11 **Supplementary Material**). The observed occurrence can be explained whether *i)* the rotation of the allenyl (or propargyl) fragment is operative and the fluxionality of the chelating heteroditopic ring frozen, or *ii)* the fluxionality of the chelate ring is operative and the rotation of the allenyl (or propargyl fragment) frozen. A further explanation is the less probable existence of only one isomer (for each tautomer) in which the rotation of the allenyl or propargyl fragments and the fluxionality of the chelate ring were both frozen. Of the two possible geometric arrangements (*exo* and *endo*), the less energetic *exo* species should be the more probable but a dedicated computational investigation does not allow an unequivocal choise ($\Delta E_{exo/endo}$ << 2 kcal mol^{-1}) and therefore we propend for the exclusion of such a possibility. However, since no more specific investigation was carried out, we do not provide a definitive interpretation.

Table 1
Calculated isomeric distribution and related free energy for the equilibrium.
3⇌4

Complexes	Allenyl tautomer (%) 3	Propargyl tautomer (%) 4	ΔG^0 (Kcal/mol)[a]
3a/**4a**	34	66	−0.4
3b/**4b**	15	85	−1.0
3c/**4c**	18	82	−0.9
3e/**4e**	30	70	−0.5
3g/**4g**	34	66	−0.4
3i/**4i**	55	45	+0.1

[a] $\Delta G^0 = G^0$allenyl − G0propargyl.

2.6. Reactivity of complex **1j** with 3−chloro−1−phenyl−1−propyne

Complex **1j** reacts with 3−chloro−1− phenyl−1−propyne yielding the expected tautomeric mixture in which the propargyl isomer is prevailing (**4j**/**3j** ≈ 9.0). The ^{1}H NMR spectrum displays the signal of Pd-CH_2-C ≡ protons (propargyl isomer) at ca. 2.13 and that of =C=CH_2 (allenyl isomer) at ca. 3.97 ppm.

For concentration reasons only the IR peak at 2176 cm^{-1} ($\nu_{C\equiv C}$) is detectable, whereas the ^{31} P NMR spectrum is characterized by two AX systems owing to the asymmetry of the chemical environment of the dppe ligands. (Fig. S12 **Supplementary Material**).

The experimental findings were computationally validated. The small difference in energy between the allenyl and propargyl tautomers was established within the errors affecting this sort of calculation and the experimentally detected concomitant presence in solution of both the species, theoretically confirmed. The calculated tautomeric distribution is reported in the following Table 1. (Details on the DFT calculation in Experimental).

2.7. Palladium complexes bearing the propargyl fragment η^3−coordinated

At variance with the palladium η^3−allyl derivatives which are characterized by a wide variety of spectator ligands [12], palladium complexes bearing the η^3−propargyl fragment are very rare and obtained only in the case of monodentate ligands [13]. Moreover, for a better comprehension of the following discussion, it is worth recalling that at variance with the orthogonal allyl, the η^3−coordinated propargyl fragment lays parallel to the main coordination plane of the complexes, as can be deduced from the published structures of the uncommon η^3−coordinated propargyl derivatives of palladium and platinum.

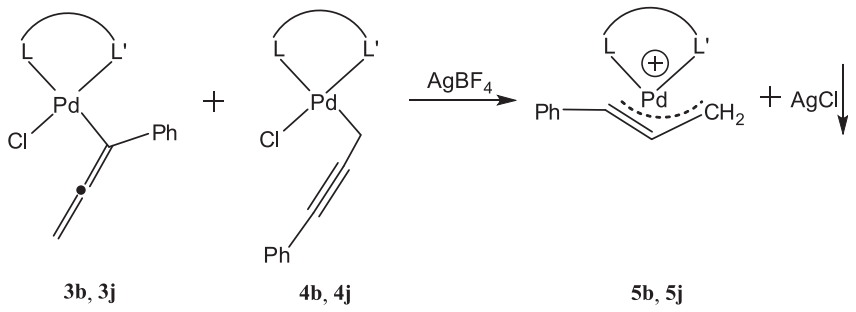
Using the proven protocol based on the dechloridations of the η^1− species we have systematically tried to obtain the title complexes using different combination of dechloridation agents and solvents with all the available propargyl/allenyl mixtures. However, in the majority of cases we have obtained spectra of difficult interpretation characterized by the presence of more than one compound in solution. Fortunately, in the case of the couples **3j**/**4j** and **3b**/**4b** we have obtained and isolated the species **5j** and **5b** (Scheme 3). In this respect, it is worth noting that complexes **5j** and **5b** represent the first cases of η^3−propargyl derivatives bearing a chelating diphosphine (**5j**) and a nitrogen containing ligand (**5b**), respectively.

Unfortunately, despite several attempts we were not able to obtain crystals suitable for a diffractometric determination. Hence, we have been forced to base our structural hypotheses on detailed NMR studies and elemental analysis.

The ^{31}P{^{1}H}NMR spectrum of complex **5j** which was isolated from the filtered solution of the reacting mixture of complexes **3j** and **4j** and $AgBF_4$ can be seen in Fig. 1. The dramatic change of the final spectrum with respect to that of the initial mixture is evident since the two initial AX signals revert into one single AB system (J_{PP} =29 Hz) owing to the similarity of the chemical environment of the two phosphorus both *trans* to carbon.

The ^{1}H NMR spectrum fully confirms the hypothesized structure, and beside the low field splitting (0.2 ppm) of the multiplet ascribable to $-CH_2-CH_2-$ protons, which is probably due to the positive charge of the new complex, the diagnostic spectral features of the CH_3 propargyl group should be considered. The latter resonates as a doublet of doublets characterized by two different coupling constants with phosphorus (J_{PHcis} = 2.2 Hz; $J_{PHtrans}$ = 7.8 HZ) (see Fig. S13 in **Supplementary Material**). Eventually, in the ^{13}C{^{1}H}NMR spectrum the presence of three distinct signals related to the carbons Ph−C=C−CH_2 (δ = 47.5 ppm; doublet of doublets, J_{CP} = 37.6 and 6 Hz), Ph−C=C−CH_2 (δ = 98.2 ppm; doublet, J_{CP} = 7 Hz) and Ph−C=C−CH_2 (δ = 103.7 ppm; doublet of doublets, J_{CP} = 46 and 6 Hz) supports our conclusion based on the similarity with the spectrum of the literature complex [Pt(η^3−propargyl)(PPh_3)$_2$] [14].

Complex **5b** was obtained by dechloridation of the mixture of **3b**/**4b**, at low temperature (273 K) in order to minimize decomposition. Both the ^{1}H and ^{31}P{^{1}H}NMR spectra indicate that the only species obtained was the charged derivative as can be deduced from the low field shifts of the proton and phosphorus signals.



3b, **3j** **4b**, **4j** **5b**, **5j**

Scheme 3. Schematic representation of the synthetic approach to type **5** complexes.

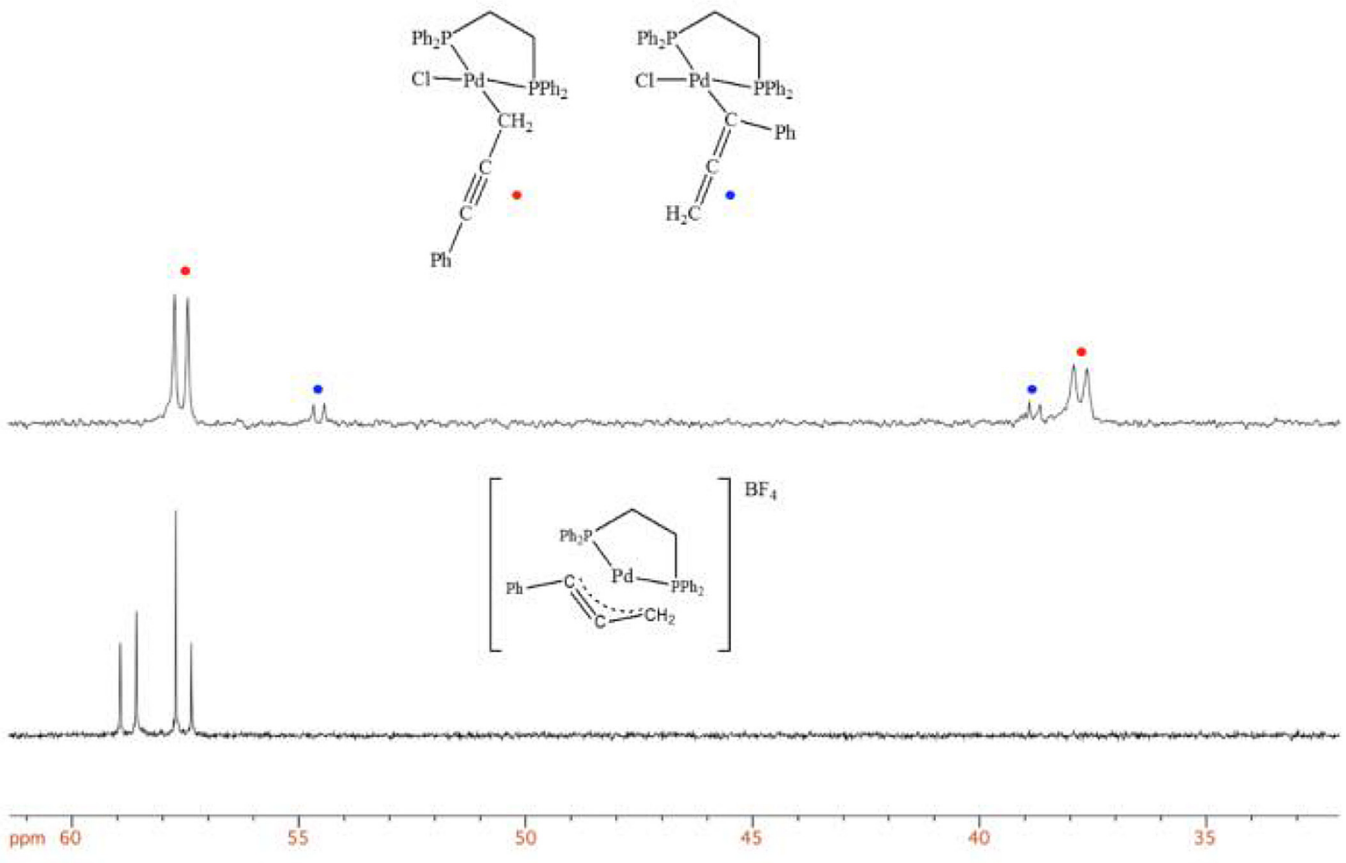


Fig. 1. $^{31}P\{^{1}H\}$NMR spectra of the **3j**/**4j** starting mixture (top) and of complex **5j** (bottom) in CD_2Cl_2 at 253 K.

Moreover, we suggest that the unique isolated isomer is the less hindered complex with the phenyl group *trans* to phosphorus. The NMR spectra and in particular the doublet related to the Ph–C≡C–CH_2 protons at 2.81 ppm with its small coupling constant (J_{PH} = 1.7 Hz) testifies their *cis* position to phosphorus. Moreover, this structural hypothesis is confirmed by the shift to high field of the protons of the methyl group in position 2 of the quinoline ligand ($\Delta\delta \approx 0.7$ ppm) due to the *cis* position of the quinolinic nitrogen and the phenyl substituted terminal propargyl carbon. The signals of the η^3-propargyl fragment are detected in the $^{13}C\{^{1}H\}$ NMR spectrum at 25.9 ppm (terminal $-CH_2$ carbon; doublet, J_{CP} = 5.6 Hz), 82.6 ppm (central propargyl carbon; doublet, J_{CP} = 9.7 Hz) and 103.7 ppm (terminal CPh carbon; doublet, J_{CP} = 35.3 Hz), where the markedly high coupling constant of the latter is traceable back to the *trans* position of the coordinated phopsphine.

(^{1}H, ^{31}P and ^{13}C NMR spectra in Figs. S14 and S15 in **Supplementary Material**; NMR details in **Experimental** sections).

2.8. Kinetic and mechanistic studies

In order to study the kinetics of oxidative reaction of the complexes **1** with 3–chloro–1–propyne and 3–chloro–1– phenyl–propyne, we have resorted to the UV–Vis spectrophotometric technique which in case of adequate reaction rates and absorbance changes is comparatively faster than NMR spectrometry.

In Fig. 2 and in Figs. s16–s17 SM (**Supplementary Material**), we report as examples of spectrophotometric experiments *i)* the spectral change in the 480–280 nm wavelengths range *vs*. time [15] and *ii)* the absorbance change at a fixed wavelength *vs*. time (Fig. s16 SM) and *iii)* the related linear regression analysis (Fig. s17 SM).

Spectral analysis *i)* provides the experimental conditions, whereas from investigation *ii)* the observed rate constant at a given concentration of organic halide (under *pseudo*–first order conditions) can be deduced from the non linear regression analysis based of the monoexponential model:

$$A_t - A_\infty = (A_0 - A_\infty)e^{-k_{obs}t}$$

where A_0, A_∞ and A_t are the initial, the final and the absorbance at time t, respectively.

Eventually, the slope of the linear regression of the observed rate constants *vs*. the concentration of the organic halide gives the second order rate constant k_2 for each complex studied (Scheme 4).

Owing to the monoexponential nature of the absorbance *vs* time change and the insignificant value of the intercept in the linear regression, we may conclude that the reaction is first order in both complex and chloropropynes. According to our previous findings [4a], we think that also in this case the mechanism involved in the oxidative addition entails the formation of a 18–electron five–coordinate intermediate which rapidly collapses into the final products (Scheme 4). In such a case the second order k_2 is the slope of the linear regression of k_{obs} *vs*. organic halide concentration. The alternative dissociative mechanism involving displacement of the olefin and formation of a 14–electron intermediate was ruled out since no dependence on added olefin was detected. Moreover, in the absence of added olefin the monoexponential model should no longer be valid.

The rate determining step (k_2) however, involves one or two

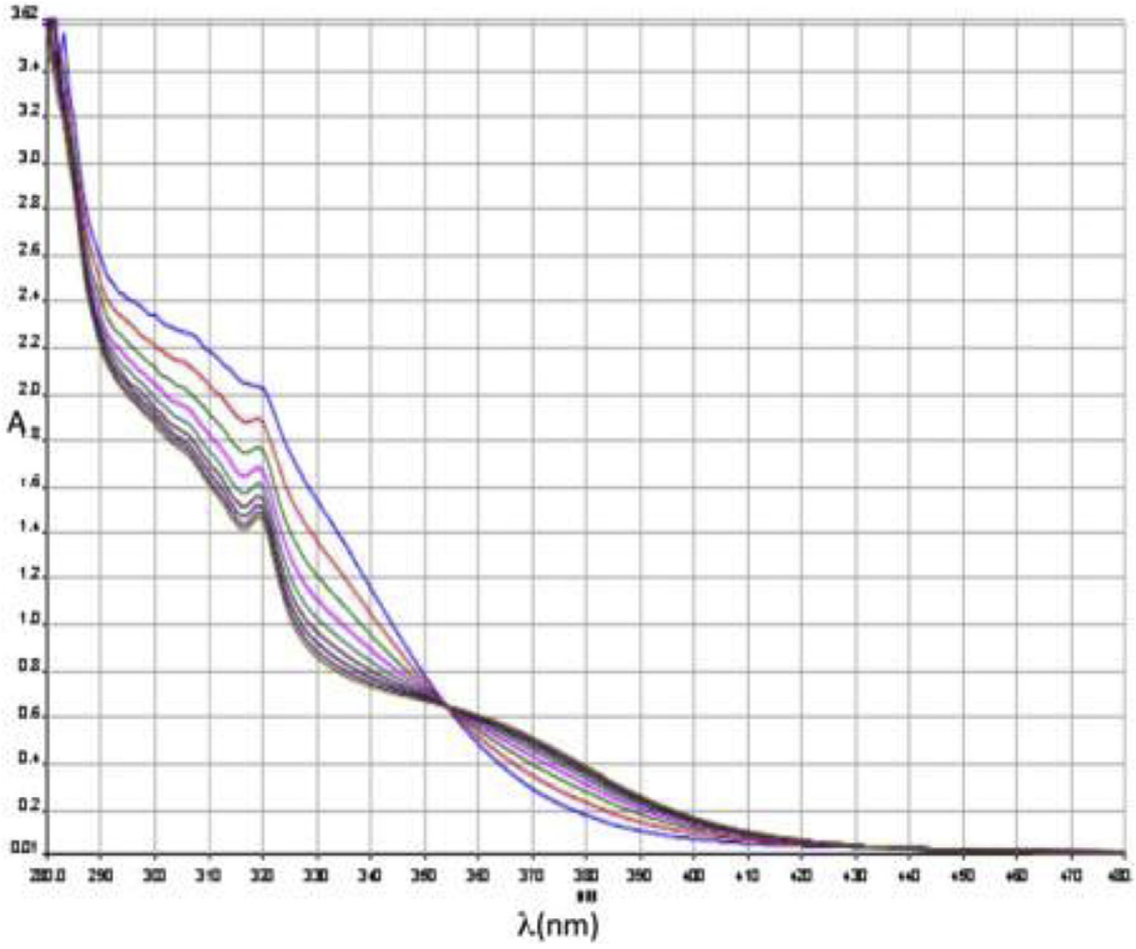
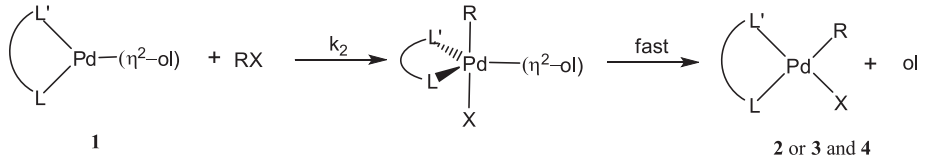


Fig. 2. Absorbance vs. wavelengths change for the reaction between **1a** and 3–chloro–1–phenyl–1–propyne in $CHCl_3$ at 298 K [**1a**] = 1 × 10^{-4}, 3–chloro–1–Phenyl–1–propyne] = 2.44 × 10^{-3} mol dm^{-3}.



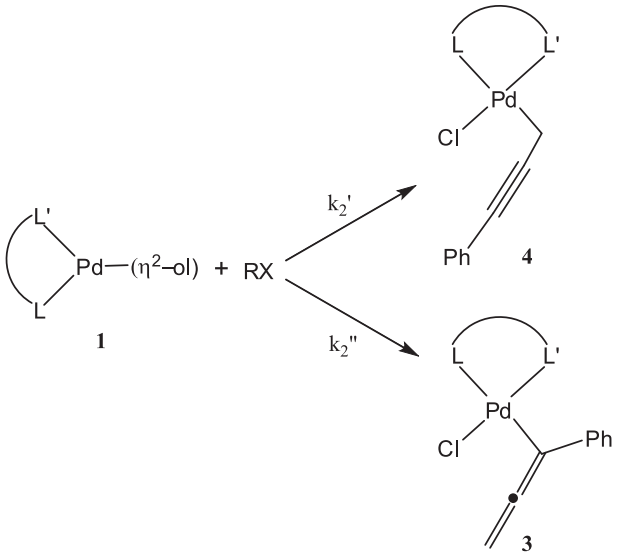
Scheme 4. Schematic representation of the mechanism of the reaction between type **1** complexes and chloropropynes.

parallel bimolecular second order steps which lead to the reaction product **2** or **3** and **4**, respectively. In the latter case hence, the reaction network is better described in Scheme 5, where k_2' and k_2'' represent the rate constants of the elementary processes yielding the propargyl and the allenyl isomers, respectively.

The complete summary of the k_2 values determined for all the studied complexes is reported in the following Table 2.

Owing to the nature of the studied reactions, the measured k_2 should in any case be a function of the single mechanistic steps yielding the final tautomeric mixture. For instance, if the formation of the isomers is concomitant, the value of k_2 will be the sum of two rate constants k_2' and k_2'' related to the two parallel S_N2 and S_N2' processes involving attack of the palladium to the methylene or to the phenyl substituted carbon, respectively. In any case the determined k_2 is related to the propensity of type **1** complexes to undergo oxidative addition. In this respect, on the basis of the data of Table 2 we may conclude that:

1) The nature of the second substituent on the quinoline ligand does not affect dramatically the reactivity of complexes **1a**, **1b**, (E = PPh_2), **1c** (E = StBu) and **1g** (L-L' = bipy) all showing k_2 values of similar magnitude. Only in the case of **1c** was a slight decrease detected probably due to steric factors.
2) The reduced reactivity of complex **1'b** as compared with that of **1b** (ca. 20–fold) is probably due to the electron withdrawing ability of the olefin naphthoquinone which renders the palladium centre less effective as nucleophile.
3) In the case of complex **1j** steric demand becomes very important and thus the k_2 rate constant is the smallest among the measured ones.
4) No remarkable difference can be noticed in the reaction rates related to the reactions of 3–chloro–1–propyne and 3–chloro–1–phenyl–1–propyne with **1a** and **1b.** Apparently, a leveling effect due to a balance between the favorable steric demand of 3–chloro–1–propyne and conjugative electronic



Scheme 5. Schematic representation of the mechanism of the reaction between type **1** complexes and 3-chloro-1-phenyl-1-propyne.

stabilization imposed by the phenyl group of 3–chloro–1–phenyl–1–propyne, may be operative.

We have described above the case of the reaction of **1b** (or **1'b**) with 3–chloro–1–phenyl–1–propyne giving an isomeric mixture of **4b**/**3b** ≈ 0.33 which evolves into a final **4b**/**3b** ≈ 7.3 M ratio (*vide supra*).

As can be deduced from the reaction progress detected by ^{1}HNMR (Fig. 3).

the complete isomerization is over within ca. 4 h, whereas the reaction yielding the initial tautomeric mixture in few minutes. Under such experimentally observed condition, the isomerization process can be independently monitored and the time dependent concentration of the tautomers determined by ^{1}H NMR. Thus, the non linear regression analysis based on the rate equations:

$$-\frac{d[3\boldsymbol{b}]}{dt} = k_1[3\boldsymbol{b}] - k_{-1}[4\boldsymbol{b}]$$

$$\frac{d[4\boldsymbol{b}]}{dt} = k_1[3\boldsymbol{b}] - k_{-1}[4\boldsymbol{b}]$$

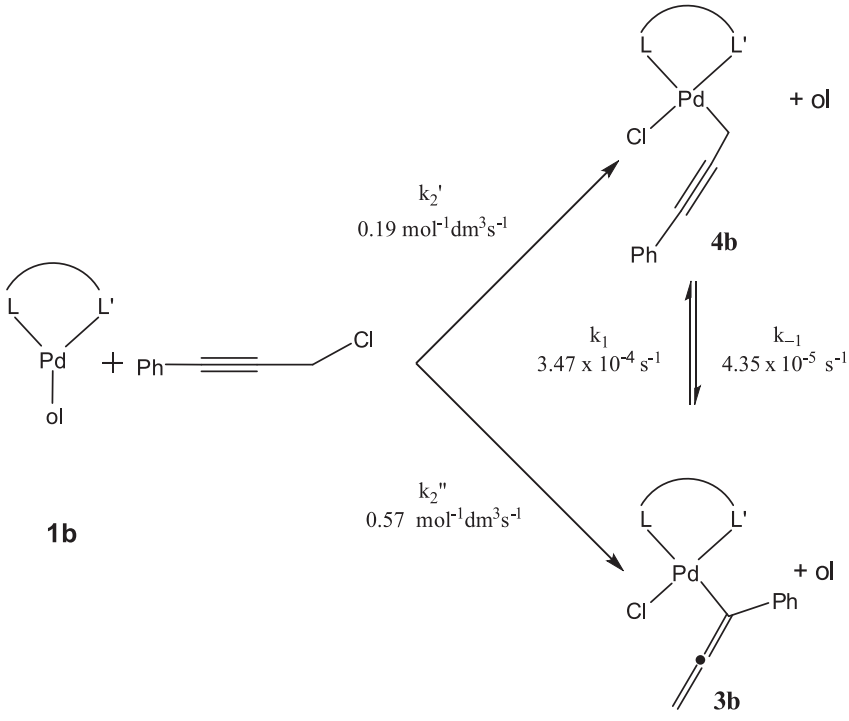
$$[3\boldsymbol{b}] + [4\boldsymbol{b}] = [3\boldsymbol{b}]_0 + [4\boldsymbol{b}]_0$$

gives the values of k_1 = (3.47 ± 0.01) x 10^{-4} and k_{-1} = (4.35 ± 0.01) x 10^{-5} s^{-1}, respectively (see Fig. S18 **Supplementary Material**). The equilibrium constant K_E, calculated as the ratio k_1/k_{-1} = 7.98 ± 0.03 fits nicely with the value K_E ≈ 7.3 determined from the estimated final concentrations of the NMR spectrum (*vide supra*). Therefore, the general mechanism (at least valid for the reaction of **1b** with 3–chloro–1–phenyl–1–propyne) reported in Scheme 6 can be proposed and a final evaluation deduced. Thus, from the initial isomeric distribution **4b**/**3b** ≈ 0.33 = k_2''/k_2' and $k_2 = k_2' + k_2''$ = 0.76 mol^{-1} dm^3 s^{-1} the values k_2' ≈ 0.19 and k_2'' ≈ 0.57 mol^{-1} dm^3 s^{-1} were calculated and the overall mechanistic network disentangled.

Table 2
Set of the calculated k_2 values (dm^3 $mol^{-1}s^{-1}$) for the reaction carried out in $CHCl_3$ at 298 K: **1** + 3–chloro–1 –propyne → **2**; **1** + 3–chloro–1–phenyl–propyne → **3/4**.

Complex	3-chloro-1-propyne	3-chloro-1-phenyl-1-propyne
1a	0.34[a] ± 0.01	0.66 ± 0.01
1b	0.90 ± 0.02	0.76 ± 0.01
1'b	//	0.033 ± 0.001
1c	//	0.255 ± 0.006
1g	//	0.75 ± 0.02
1j	//	0.0390 ± 0.0004

[a] Ref. [4a].



Scheme 6. Reactivity network and related rate constants for the reaction: **1b** + Ph-C≡C-CH_2Cl → **3b** + **4b.**

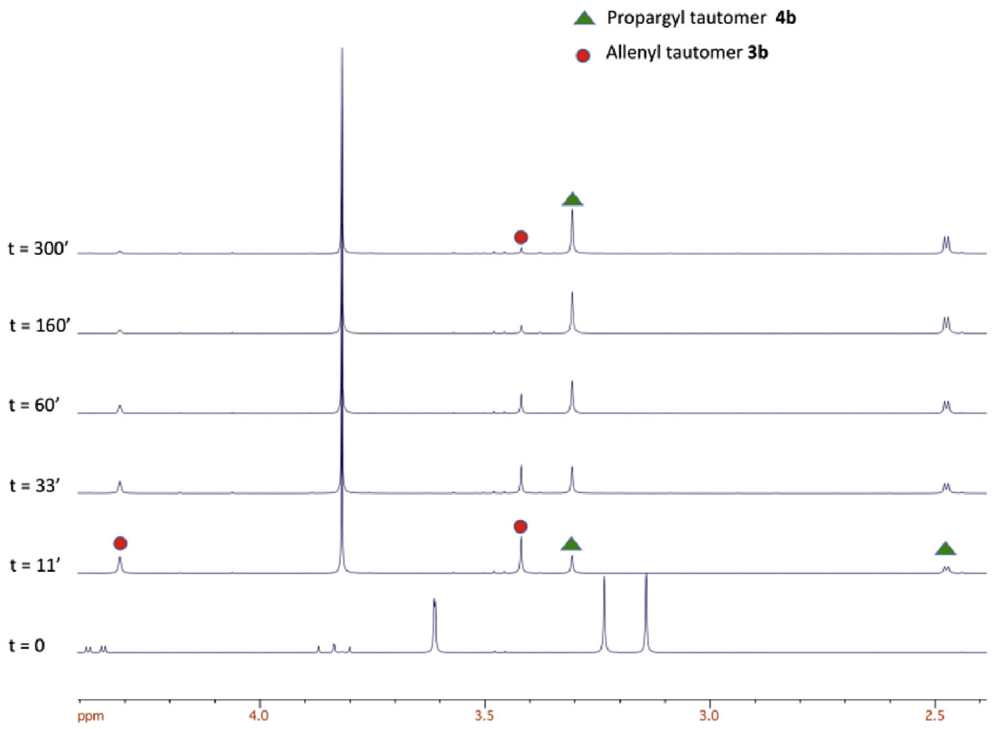


Fig. 3. Time depending ^{1}HNMR spectra evolution of the initial tautomeric mixture (**4b**/**3b** ≈ 0.33) into the final one (**4b**/**3b** ≈ 7.3) in CD_2Cl_2 at 298 K.

3. Conclusion

The information obtained can be summarized in the following points:

i) We have synthesized and characterized allenyl and allenyl/propargyl palladium complexes bearing some different spectator ligands by oxidation of the Pd(0) olefin precursors with chloro–propyne derivatives. The tautomeric composition is thermodynamically modulated and depends on the spectator ligands and the nature of the used chloro–propyne as supported by the dedicated DFT calculation.
ii) As an interesting corollary two novel complexes containing the very rare η^3– coordinated propargyl fragment have been obtained.
iii) The kinetics of the oxidative addition reactions were studied in detail and an overall common mechanistic network proposed. In the case involving complex **2b** and 3–chloro–1–phenylpropyne the mechanistic network was completely resolved.

4. Experimental

4.1. Solvents and reagents

All the following distillation processes were carried out under inert atmosphere (argon). Acetone and CH_2Cl_2 were distilled over 4 Å molecular sieves and CaH_2, respectively. $CHCl_3$ was distilled over silver foil. Tetrahydrofurane was distilled over benzophenone and metallic sodium. Anhydrous acetonitrile was used as purchased and stored under Argon atmosphere. All the other chemicals were commercially available grade products and were used as purchased.

4.2. Data analysis

Non linear and linear analysis of the data related to equilibrium and kinetics measurements were performed by locally adapted routines written in ORIGIN® 7.5 or SCIENTIST ® environments.

4.3. IR, NMR, UV–Vis and elemental analysis measurements

The IR, ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer, respectively. UV–Vis spectra were taken on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Perkin-Elmer PTP6 (Peltier temperature programmer) apparatus. Elemetal analysis was carried out using an Elementar CHN "CUBO Micro Vario" analyzer.

4.4. Preliminary studies and kinetic measurements

All the reactions were preliminarily studied by ^{1}H NMR technique by dissolving the complex under study in 0.6 ml of CD_2Cl_2 ($[Complex]_0 \approx 10^{-2}$ mol dm^{-3}) and adding microaliquots of a concentrated CD_2Cl_2 solution of the organic halide under study ($[RX] \approx 4 \times 10^{-2}$ mol dm^{-3}) by monitoring the signal for the disappearance of the starting complex and the concomitant appearance of the final products.

The UV–Vis preliminary study was carried out by placing 3 ml of freshly prepared solution of the complex under study ($[Complex]_0 = 1 \times 10^{-4}$ mol dm^{-3}) in the thermostatted (298 K) cell compartment of the UV–Vis spectrophotometer. Microaliquots of solutions containing the organic chloride in adequate concentrations ($[RX] = \min 1 \times 10^{-3}$ mol dm^{-3}) were added and the absorbance changes were monitored in the 250–500 nm wavelength interval or at an optimized fixed wavelength.

4.5. Computational details

Theoretical calculations were performed with the Gaussian09 [16] package using the functional hybrid GGA PBE0 [17] (PBE1PBE in Gaussian09 formalism) and the Def2-SVP basis set [18]; solvent effects (dichloromethane, $\varepsilon = 8.93$) were included using CPCM [19]. The geometry optimization was performed without any symmetry constraint, followed by analytical frequency calculation to confirm that a minimum had been reached.

4.5.1. Synthesis of the Pd(0) olefin complexes

The complexes $[Pd_2(DBA)_3\cdot CHCl_3]$ [20], **1a**, **1b** [21], **1c**, **1e** [4a], **1d** [4b], **1f** [22], **1g** [23], **1h** [24] and **1i** [25] were synthesized according to published procedures.

4.5.2. Synthesis of complex ***1'b***

0.1328 g (0.4057 mmol) of 8−diphenylphosphine−2−methylquinoline, 0.0674 g (0.4261 mmol) of naphthoquinone and 0.2003 g(0.1935 mmol) of $[Pd_2(DBA)_3\cdot CHCl_3]$ were dissolved under inert atmosphere (Ar) in 30 ml of anhydrous acetone in a 100 ml necked flask. The mixture was stirred for 60 min at RT, the resulting orange solution treated with activated charcoal, filtered on a celite filter and concentrated under vacuum. The title complex was precipitated as a pale−orange solid by slow addition of diethylether, filtered off on a gooch, and washed with diethylether and n-pentane.

0.2039g (yield 89%) of complex **1'b** was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 3.12 (s, 3H, quinoline-CH_3), 4.98−5.05 (m, 2H, CH=CH) 7.06−7.13 (m, 2H, aryl naphthoquinone), 7.29−7.71 (m, 13H, H^3, PPh_2, aryl naphthoquinone), 7.79 (ddd, 1H, J = 8.1, 7.5, 1.4 Hz, H^6), 7.90 (d, 1H, J = 8.1, H^7), 8.05 (dd, 1H, J = 7.5, 1.6 Hz, H5), 8.19 (dd, 1H, J = 8.4, 1.4 Hz, H^4).

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.3 (CH_3, quinoline-CH_3), 62.7 (CH, CH=CH *trans*-N), 66.3 (d, CH, J_{CP} = 21 Hz, CH=CH *trans*−P), 123.9 (CH, C^3), 125.1 (CH, C^5), 131.1 (CH, C^7), 137.8 (CH, C^6), 138.4 (CH, C^4), 165.7 (d, C, J_{CP} = 22.1 Hz, C^9), 165.7 (C, C^2), 184.0 (d, C, J_{CP} = 6.2 Hz, CO *trans*−P), 185.2 (C, CO *trans*−N).

31P{1H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 23.4.

IR (KBr, pellet, cm^{-1}): 1641 (ν_{CO}).

Anal. Calcd. for $C_{32}H_{24}NO_2PPd$: C 64.93, H 4.09, N 2.37. Found: C 65.06, H 3.98, N 2.21.

4.5.3. Synthesis of complex ***1j***

0.1624 g (0.4076 mmol) of 1,2-bis(diphenylphosphine)ethane, 0.1671 g (1.159 mmol) of dmfu and 0.2002 g (0.1934 mmol) of $[Pd_2(DBA)_3\cdot CHCl_3]$ were dissolved under inert atmosphere (Ar) in 30 ml of anhydrous acetone and vigorously stirred for 60 min. Owing to the progressive dissolution of $[Pd_2(DBA)_3\cdot CHCl_3]$, the violet color of the mixture gradually disappeared and the concomitant precipitation of the scarcely soluble pale yellow complex **1j** was observed. The solution was dried under vacuum, the residue dissolved in CH_2Cl_2, treated with activated charcoal and filtered on a celite filter. The clear pale yellow solution was concentrated under vacuum and the title complex precipitated by slow addition of diethylether. Complex **1j** was filtered off on a gooch, washed with diethylether and dried under vacuum. 0.2027 g (yield 81%) of the title complex **1j** as a pale yellow solid was obtained.

^{1}H NMR (300 MHz, CDCl3, T = 298 K, ppm) δ: 2.11−2.61 (m, 4H, CH2P), 3.40 (s, 3H, OCH3), 4.33−4.42 (m, 2H, CH=CH), 7.32−7.53 (m, 16H, PPh), 7.79−7.85 (m, 4H, PPh).

^{13}C{^{1}H} NMR (CDCl3, T = 298 K, ppm selected peaks) δ: 26.7 (m CH2, CH2P), 50.5 (CH3, OCH3), 52.9 (m, CH, CH=CH), 173.7 (C, CO).

^{31}P{^{1}H} NMR (CD2Cl2, T = 298 K, ppm) δ: 39.0.

IR (KBr, pellet, cm^{-1}): 1683 (ν_{CO}).

Anal. Calcd. for $C_{32}H_{32}O_4P_2Pd$: C 59.22, H 4.97. Found: C 59.11, H 5.03.

4.5.4. Synthesis of the allenyl/propargyl Pd(II) complexes

Complexes **2a**, **3a** and **4a** have been synthesized according to published procedure [4a].

4.5.5. Synthesis of complex ***2b***

0.0800 g (0.1384 mmol) of **1b** and 20.1 μL (0.2778 mmol) of 3−chloro−1−propyne were dissolved in 8 ml of anhydrous CH_2Cl_2 under inert atmosphere (Ar) in a necked 100 ml flask. The solution was stirred for 20 min and concentrated under vacuum. Addition of diethylether induces the precipitation of complex **2b** as a yellow solid which was filtered off on a gooch, washed with diethylether and dried under vacuum. 0.0694 g (yield 98%) of the title complex was obtained.

^{1}H-NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 3.32 (s, 3H, quinoline- CH_3), 3.90 (dd, 2H, J = 6.2, 1.5 Hz, CH_2=), 3.77 (t, 2H, J = 6.2, =CH-Pd), 7.47−7.72 (m, 13H, H^3, H^6, H^7, PPh_2), 8.04 (dt, 1H, J = 7.7, 1.4 Hz, H^5), 8.26 (dd, 1H, J = 8.5, 1.8 Hz, H^4).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 253 K, ppm) δ: 29.11(CH_3, quinoline-CH_3 68.4 (d, J_{CP} = 3.3 Hz, CH_2, CH_2=), 75.5 (CH, =CH-Pd), 125.6 (CH, C^3), 127.7 (d, J_{CP} = 8.5 Hz, CH, C^6), 129.0 (d, J_{CP} = 9.1 Hz, C, C^{10}), 131.5 (CH, C^5), 132.8 (d, J_{CP} = 46.3 Hz, C, C^8), 135.9 (CH, C^7), 138.3 (CH, C^4), 151.0 (d, J_{CP} = 17.7 Hz, C, C^9), 167.0 (CH, C^2), 200.9 (d, d, J_{CP} = 3.9 Hz, C, =C=).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 35.0.

IR (KBr, pellet, cm^{-1}): 1919 (νC=C=C).

Anal. Calcd. for $C_{25}H_{21}ClNPPd$: C 59.07, H 4.16, N 2.76. Found: C 60.04, H 4.12, N 2.61.

4.5.6. Synthesis of the ***3b*/*4b*** *tautomeric mixture*

0.0800 g (0.1384 mmol) of **1b** and 29.0 μL (0.2109 mmol) of 3−chloro−1−phenyl−propyne were dissolved in 8 ml of anhydrous CH_2Cl_2 under inert atmosphere (Ar) in a necked 100 ml flask. The solution was reacted for 4 h, cooled in an ice bath and evaporated to small volume under vacuum. Addition of diethylether induces the precipitation of a yellow solid which was filtered off on a gooch washed with diethylether and dried under vacuum. 0.0651 g (yield 80%) of the mixture of complexes **3b/4b** was obtained.

Propargyl isomer ***4b*** (92%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 2.48 (d, 2H, JHP = 2.5 Hz, CH_2-Pd), 3.31 (s, 3H, quinoline-CH3), 7.43−7.58 (m, 7H, H^3, PPh_2), 7.60 (dd, 1H, J =8.0, 7.7, H6), 7.73−7.66 (m, 5H, H7, PPh2), 8.01 (d, 1H, J = 8.0, H5), 8.22 (dd, 1H, J = 8.5, 1.7 Hz, H4).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 0.7 (d, JCP = 3.5 Hz, CH2, CH2Pd), 28.7 (CH3, quinoline-CH3), 84.5 (d, C, JCP = 3.5 Hz, C≡), 97.6 (C, ≡CPh), 125.4 (CH, C^3), 126.3 (CH, C^6), 131.2 (CH, C^5), 134.4 (CH, C^7), 137.7 (CH, C^4), 150.7 (d, C, JCP = 17.6 Hz, C^9), 166.6 (C, C^2).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 35.0.

Allenyl isomer ***3b*** (15%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm; selected peaks) δ: 3.42 (s, 3H, quinoline-CH_3), 4.32 (s, 2H, CH_2=), 8.02 (d, 1H, J = 8.0, H^5), 8.26 (dd, 1H, J = 8.5, 1.7 Hz, H^4).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 32.9.

IR (KBr, pellet, cm^{-1}): 2182 ($\nu_{C\equiv C}$).

Anal. Calcd. for $C_{31}H_{25}ClNPPd$: C 63.71, H 4.31, N 2.40. Found C 63.63, H 4.28, N 2.47.

4.5.7. Synthesis of the ***3c*/*4c*** *tautomeric mixture*

0.0800 g (0.1710 mmol) of **1c** and 36.0 μL (0.2109 mmol) of 3−chloro−1−phenyl−propyne were dissolved in 8 ml of anhydrous CH_2Cl_2 under inert atmosphere (Ar) in a necked 100 ml flask. The solution was reacted for 20 min, cooled in an ice bath and evaporated to dryness under vacuum. The residue was ground in

diethylether, filtered off on a gooch and washed with diethylether. 0.0605 g (yield 76%) of the title complexes as a yellow powder was obtained.

Propargyl isomer ***4c*** (91%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 263 K, ppm) δ: 1.41 (s, 9H, *t*Bu), 2.51, 2.80 (AB system, 2H, J = 11.6 Hz, CH_2Pd), 7.25–7.27 (m, 2H, Ph), 7.40–7.43 (m, 3H, Ph), 7.62 (dd, 1H, J = 8.2, 4.7 Hz, H^3), 7.74 (dd, 1H, J = 7.9, 7.2 Hz, H^6), 8.00 (d, 1H, J = 7.2, Hz, H5), 8.13 (d, 1H, J = 7.9, Hz, H7), 8.46 (d, 1H, J = 8.2, H4), 9.41 (d, 1H, J = 4.7, Hz, H2).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 263 K, ppm) δ: −9.0 (CH_2, CH_2Pd), 30.0 (CH_3, C*Me*$_3$), 58.3 (C, *C*Me$_3$), 83.6 (C, C≡), 98.5 (C, ≡CPh), 123.2 (CH, C^3), 126.7 (C, Ph), 125.8 (CH, Ph), 127.4 (CH, C^6), 128.4 (CH, Ph), 129.2 (C, C^{10}), 129.7 (C, C^8), 130.7 (CH, Ph), 131.6 (CH, C^7), 137.3 (CH, C^5), 138.9 (CH, C^4), 148.4 (C, C^9), 152.7 (CH, C^2).

Allenyl isomer ***3c*** (9%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 263 K, ppm) δ: 1.33 (s, 9H, *t*Bu), 4.85, 4.78 (AB system, 2H, J = 9.8 Hz, CH_2=), 7.25–7.27 (m, 2H, Ph), 7.40–7.43 (m, 3H, Ph), 7.67 (dd, 1H, J = 8.2, 4.7 Hz, H^3), 7.78 (dd, 1H, J = 7.9, 7.2 Hz, H^6), 8.00 (d, 1H, J = 7.2, Hz, H^5), 8.16 (d, 1H, J = 7.9, Hz, H^7), 8.51 (d 1H, J = 8.2, H^4), 9.61 (d, 1H, J = 4.7, Hz, H^2).

IR (KBr, pellet, cm^{-1}): 2183 ($\nu_{C\equiv C}$).

Anal. Calcd. for $C_{22}H_{22}ClNPdS$: C 55.70, H 4.67 N 2.95. Found: C 55.83, H 4.71 N 3.07.

The following complexes were obtained according to the above described protocols using the appropriate starting complexes. The yield, color, reaction time and where necessary, some supplementary information will be reported under the title.

4.5.8. Synthesis of the ***3d*****/****4d*** *tautomeric mixture*

The mixture was separated after 20 min as a yellow powder in 77% yield.

Propargyl isomer ***4d*** (91%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 253 K, ppm) δ: 1.38 (s, 9H, *t*Bu), 2.70, 2.85 (AB system, 2H, J = 11.1 Hz, CH_2Pd), 3.17 (s, 3H, quinoline-CH_3), 7.21–7.44 (m, 6H, Ph, H^3), 7.60 (dd, 1H, J = 8.1, 7.3 Hz, H^6), 7.96 (dd, 1H, J = 7.3, 1.3 Hz, H^5), 8.02 (dd, 1H, J = 8.1, 1.3 Hz, H^7), 8.25 (d, 1H, J = 8.5, H^4).

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 253 K, ppm) δ: −4.6 (CH_2, CH_2Pd), 28.7 (CH_3,quinoline-CH_3), 29.9 (CH_3, C*Me*$_3$), 56.8 (C, *C*Me$_3$), 84.8 (C, C≡), 97.3 (C, ≡CPh), 125.3 (CH, C^3), 125.9 (C, Ph), 126.2 (CH, C^6), 126.7 (CH, Ph), 127.7 (C, C^{10}), 128.3 (CH, Ph), 128.9 (C, C^8), 131.1 (CH, Ph), 131.4 (CH, C^7), 136.4 (CH, C^5), 138.3 (CH, C^4), 149.0 (C, C^9), 165.8 (C, C^2).

Allenyl isomer ***3d*** (9%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 253 K, ppm) δ: 1.28 (s, 9H, *t*Bu), 4.99, 4.85 (AB system, 2H, J = 9.9 Hz, CH_2=), 7.21–7.44 (m, 6H, Ph, H^3), 7.61 (dd, 1H, J = 7.9, 7.2 Hz, H^6), 7.91 (d, 1H, J = 7.2, Hz, H^5), 8.05 (d, 1H, J = 7.9, Hz, H^7), 8.30 (d 1H, J = 8.2, H^4).

IR (KBr, pellet, cm^{-1}): 2184 ($\nu_{C\equiv C}$).

Anal. Calcd. for $C_{23}H_{24}ClNPdS$: C 56.56, H 4.95, N 2.87. Found: C 56.74, H 5.10, N 2.72.

4.5.9. Synthesis of the ***3e*****/****4e*** *tautomeric mixture*

The mixture was separated after 10 min as a yellow powder in 61% yield.

Propargyl isomer ***4e*** (85%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.71 (s, 2H, CH_2-Pd), 3.04 (s, 3H, SCH_3), 7.27–7.32 (m, 3H, Ph), 7.42–7.47 (m, 2H, Ph), 7.70 (dd, 1H, J = 8.3, 4.9 Hz, H^3), 7.78 (dd, 1H, J = 8.1, 7.4 Hz, H^6), 8.07 (d, 1H, J = 8.1 Hz, H^5), 8.19 (d, 1H, J = 7.4, Hz, H^7), 8.47 (dd, 1H, J = 8.3, 1.6 Hz, H^4), 9.72 (dd, 1H, J = 4.9, 1.6 Hz, H^2).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 228 K, ppm) δ: −9.2 (CH_2, CH_2Pd), 28.0 (CH_3, S*Me*), 83.6 (C, C≡), 98.2 (C, ≡CPh), 123.2 (CH, C^3), 125.6 (C, Ph), 126.8 (CH, Ph), 127.9 (CH, C^6), 128.3 (CH, Ph), 129.1 (C, C10), 130.2 (C, C^8), 130.5 (CH, C^7), 130.8 (CH, Ph), 135.1 (CH, C^5), 138.8 (CH, C^4), 147.3 (C, C^9), 152.8 (CH, C^2).

Allenyl isomer ***3e*** (15%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.83 (s, 3H, SCH3), 4.82 (s, 2H, CH2=), 7.27–7.32 (m, 3H, Ph), 7.42–7.47 (m, 2H, Ph), 7.75 (dd, 1H, J = 8.3, 4.9 Hz, H3), 7.82 (dd, 1H, J = 8.1, 7.4 Hz, H6), 8.11 (d, 1H, J = 8.1 Hz, H5), 8.19 (d, 1H, J = 7.4, Hz, H7), 8.51 (dd, 1H, J = 8.3, 1.6 Hz, H4), 9.79 (dd, 1H, J = 4.9, 1.6 Hz, H2).

IR (KBr, pellet, cm^{-1}): 2179 ($\nu_{C\equiv C}$), 1899 ($\nu_{C=C=C}$).

Anal. Calcd. for $C_{19}H_{16}ClNPdS$: C 52.79, H 3.73, N 3.24. Found: C 52.83, H 3.65, N 3.13.

4.5.10. Synthesis of the ***3f*****/****4f*** *tautomeric mixture*

The mixture was separated after 30 min as a yellow powder in 89% yield.

Propargyl isomer ***4f*** (91%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 263 K, ppm) δ: 1.41 (s, 9H, *t*Bu), 2.45, 2.69 (AB system, 2H, J = 11.5 Hz, CH_2Pd), 4.15, 4.50 (AB system, 2H, 17.4 Hz, CH_2S), 7.26–7.42 (m, 6H, H^5, Ph), 7.51 (d, 1H, J = 7.8 Hz, H^3), 7.85 (dd, 1H, J = 7.7, 1.7 Hz, H^4), 9.19 (d, 1H, J = 5.5 Hz, H^6).

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 263 K, ppm) δ: −8.0 (CH_2, CH_2Pd), 30.3 (CH_3, C*Me*$_3$), 41.2 (CH_2, CH_2S), 52.0 (C, *C*Me$_3$), 84.3 (C, C≡), 98.2 (C, ≡CPh), 122.1 (CH, C^5), 123.8 (CH, Ph), 125.9 (C, Ph), 126.7 (CH, C^3), 128.3 (CH, Ph), 131.1 (CH, Ph), 138.8 (CH, C^4), 150.6 (CH, C^6), 158.1 (CH, C^2).

Allenyl isomer ***3f*** (9%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 263 K, ppm) δ: 1.31 (s, 9H, *t*Bu), 4.16, 4.51 (AB system, 2H, 17.4 Hz, CH_2S), 4.70, 4.79 (AB system, 2H, J = 9.9 Hz, CH_2=), 7.26–7.42 (m, 6H, H^5, Ph), 7.55 (d, 1H, J = 7.8 Hz, H^3), 7.90 (dd, 1H, J = 7.7, 1.7 Hz, H^4), 9.23 (d, 1H, J = 5.5 Hz, H^6).

IR (KBr, pellet, cm-1): 2177 ($\nu_{C\equiv C}$).

Anal. Calcd. for $C_{19}H_{22}ClNPdS$: C 52.06, H 5.06, N 3.20. Found: C 52.19, H 4.98, N 3.13.

4.5.11. Synthesis of the ***3g*****/****4g*** *tautomeric mixture*

The mixture was separated after 12 min as an orange powder in 96% yield. The complexes were obtained from a small volume solution of the complexes in CH_2Cl_2 by slow addition of diethylether.

Propargyl isomer ***4g*** (74%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 2.61 (s 2H, CH_2Pd), 7.59 (ddd, 1H, J = 7.3, 5.3, 1.5 Hz, 5-pyr), 9.04 (d, 1H, J = 5.3 Hz, 6-pyr'), 9.20 (d, 1H, J = 5.3 Hz, 6-pyr).

^{13}C{^{1}H}-NMR (CDCl3, T = 298 K, ppm selected peaks) δ: −3.7 (CH_2, CH_2Pd), 81.1 (C, C≡), 98.2 (C, ≡CPh), 153.3 (CH, 6-Pyr), 156.4 (CH, 6-Pyr').

Allenyl isomer ***3g*** (26%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 4.80 (s, 2H, CH_2=), 7.50 (ddd, 1H, J = 7.3, 5.3, 1.5 Hz, 5-pyr), 8.86 (d, 1H, J = 5.3 Hz, 6-pyr'), 9.26 (d, 1H, J = 5.3 Hz, 6-pyr').

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 298 K, ppm selected peaks) δ: 68.7 (CH_2, CH_2=), 97.3 (C, =(Ph)CPd), 153.3 (CH, 6-Pyr), 156.1 (CH, 6-Pyr'), 196.5 (C, =C=).

IR (KBr, pellet, cm^{-1}): 2173 ($\nu_{C\equiv C}$), 1907 ($\nu_{C=C=C}$).

Anal. Calcd. for $C_{19}H_{15}ClN_2Pd$: C 55.23, H 3.66, N 6.78. Found: C 55.31, H 3.74, N 6.69.

4.5.12. Synthesis of the ***3h*****/****4h*** *tautomeric mixture*

The mixture was separated after 5 min as a pale red brown powder in 89% yield. The complexes were obtained from a small volume solution in CH_2Cl_2 by slow addition of diethylether.

Propargyl isomer ***4h*** (74%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 2.79 (s 2H, CH_2Pd), 7.17–7.37 (m, 5H, Ph), 7.93 (dd, 1H, J = 8.2, 5.3 Hz, $H^{3\prime}$), 8.02 (dd, 1H, J = 8.2, 5.3 Hz, H^3), 8.03 (s, 1H, $H^{5\prime}$), 8.04 (s, 1H, H^5), 8.55 (dd, 1H, J = 8.2, 1.4 Hz, $H^{4\prime}$), 8.64 (dd, 1H, J = 8.2, 1.4 Hz, H^4), 9.39 (dd, 1H, J = 5.3, 1.4 Hz, $H^{2\prime}$), 9.48 (d, 1H, J = 5.3, 1.4 Hz, H^2).

Allenyl isomer ***3h*** (26%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 4.85 (s, 2H, CH_2=), 7.17–7.37 (m, 5H, Ph),

7.83 (dd, 1H, J = 8.2, 5.3 Hz, $H^{3\prime}$), 7.93 (dd, 1H, J = 8.2, 5.3 Hz, H^{3}), 8.03 (s, 1H, $H^{5\prime}$), 8.04 (s, 1H, H^{5}), 8.57 (dd, 1H, J = 8.2, 1.4 Hz, $H^{4\prime}$), 8.60 (dd, 1H, J = 8.2, 1.4 Hz, H^{4}), 9.13 (dd, 1H, J = 5.3, 1.4 Hz, $H^{2\prime}$), 9.53 (d, 1H, J = 5.3, 1.4 Hz, H^{2}).

IR (KBr, pellet, cm^{-1}): 2170 ($\nu_{C\equiv C}$).

Anal. Calcd. for $C_{21}H_{15}ClN_2Pd$: C 57.69, H 3.46, N 6.41. Found: C 57.85, H 3.59, N 6.27.

*4.5.13. Synthesis of the **3i**/**4i** tautomeric mixture*

The mixture was separated after 60 min as a pale red brown powder in 96% yield. The complexes were obtained from a small volume solution in CH_2Cl_2 by slow addition of diethylether.

*Propargyl isomer **4i*** (22%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 2.46 (s, 2H, CH_2Pd), 4.05 (s, 2H, CH_2N), 6.94 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.13 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.41 (dd, J = 7.7, 5.4, 1H, 5-Pyr), 7.51 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.83 (td, J = 7.7, 1.7 Hz, 1H, 4-Pyr), 9.19 (d, J = 5.4 Hz, 1H, 6-Pyr).

^{13}C{^{1}H}-NMR ($CDCl_3$, T =253 K, ppm, selected peaks) δ: −9.2 (CH_2, CH_2Pd), 37.6 (CH_3, Py-CH_3), 55.5 (CH2, Py-CH_2),79.8 (C, C≡), 100.1 (C, ≡CPh), 121.2 (CH, Im-CH), 121.9 (CH, Im-CH), 153.1 (CH, 6-Pyr) 169.1(C, NCN).

*Allenyl isomer **3i*** (78%): **^{1}H-NMR** (300 MHz, CD_2Cl_2, T = 298 K, ppm, selected peaks) δ: 3.75 (s, 2H, CH_2N), 4.47 (s, 2H, CH_2=), 6.80 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.10 (d, J = 1.9 Hz, 1H, CH=CH Im), 7.47 (dd, J = 7.7, 5.4, 1H, 5-Pyr), 7.51 (d, J = 7.7 Hz, 1H, 3-Pyr), 7.88 (td, J = 7.7, 1.7 Hz, 1H, 4-Pyr), 9.31 (d, J = 5.4 Hz, 1H, 6-Pyr).

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 253 K, ppm selected peaks) δ: 38.1 (CH_3, Py-CH_3), 55.5 (CH_2, Py-CH_2), 68.0 (CH_2, CH_2=), 92.1 (C, =(Ph) CPd), 121.0 (CH, Im-CH), 122.2 (CH, Im-CH), 153.4 (CH, 6-Pyr), 165.1(C, NCN), 200.4 (C,=C=).

IR (KBr, pellet, cm^{-1}): 2181 ($\nu_{C\equiv C}$), 1903 ($\nu_{C=C=C}$).

Anal. Calcd. for $C_{19}H_{18}ClN_3Pd$: C 53.04, H 4.22, N 9.77. Found: C 52.97, H 4.28, N 9.69.

*4.5.14. Synthesis of the **3j**/**4j** tautomeric mixture*

The mixture was separated after 60 min as a yellow powder in 81% yield. The complexes were obtained from a small volume solution in CH_2Cl_2 by slow addition of diethylether.

*Propargyl isomer **4j*** (90%): **^{1}H-NMR** (300 MHz, $CDCl_3$, T = 253 K, ppm) δ: 2.13 (dd, 2H, J_{HP} = 11.0, 3.2 Hz, CH_2Pd), 2.11–2.59 (m, 4H, CH_2P), 7.04–7.06 (m, 2H, Ph), 7.19–7.21 (m, 3H, Ph), 7.43–7.89 (m, 20H, PPh).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 253 K, ppm) δ: 37.8 (d, J_{PP} = 35.0 Hz), 57.6 (d, J_{PP} = 35.0 Hz).

*Allenyl isomer **3j*** (10%): **^{1}H-NMR** (300 MHz, $CDCl_3$, T = 253 K, ppm, selected peaks) δ: 3.77 (d, 2H, J_{HP} = 8.1 Hz, CH_2=), 7.95–6.97 (m, 2H, Ph), 7.30–7.37 (m, 3H, Ph).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 253 K, ppm) δ: 38.8 (d, J_{PP} = 29.0 Hz), 54.5 (d, J_{PP} = 29.0 Hz).

IR (KBr, pellet, cm^{-1}): 2176 ($\nu_{C\equiv C}$).

Anal. Calcd. for $C_{35}H_{31}ClP_2Pd$: C 64.14, H 4.77. Found: C 64.22, H 4.83.

*4.5.15. Synthesis of complex **5b***

To 0.0501 (0.086 mmol) g of the complexes **4b** (separated before the slow isomerization) dissolved in 8 ml of anhydrous CH_2Cl_2 ca.3 ml of a solution of 0.0171 g (0.088 mmol) of $AgBF_4$ in anhydrous THF under inert atmosphere were added (Ar). The cloudy mixture was stirred under dark for 20 min, filtered by a millipore apparatus to remove AgCl and cooled in an ice bath. The cold clear yellow-orange solution was concentrated under vacuum and the title complex precipitated by slow addition of diethylether. The complex was filtered off on a gooch, washed with diethyleter and dried under vacuum. 0.0467 g (84% yield) of the complex **5b** as an orange solid was obtained.

^{1}H-NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.64 (s, 3H, quinoline-CH_3), 2.81 (dd, J_{HP} = 1.7, Hz, C=CH_2), 7.47–7.52 (m, 2H, Ph), 7.47–7.56 (m, 2H, Ph), 7.57–7.70 (m, 14H, H^3, Ph, PPh_2), 7.83 (ddd, 1H, J =8.1, 7.2, 1.5 Hz, H^6), 8.00 (ddd, 1H, J = 10.7, 7.2, 1.4 Hz, H^7), 8.26 (dt, 1H, J = 8.1, 1.4 Hz, H^5), 8.51 (dd, 1H, J = 8.5, 2.0 Hz, H^4).

^{13}C{^{1}H}-NMR (CD_2Cl_2, T = 253 K, ppm) δ: 25.9 (d, J_{CP} = 5.6 Hz, CCH_2), 31.1 (CH3, quinoline-CH_3), 82.6 (d, J_{CP} = 9.7 Hz, *C*CPh), 109.3 (d, J_{CP} = 35.3 Hz, *C*Ph), 124.4 (CH, C^3), 127.8.

(CH, C^6), 133.1 (CH, C^5), 137.8 (CH, C^7), 140.4 (CH, C^4), 151.2 (d, C, J_{CP} = 19.2 Hz, C^9), 165.4 (C, C^2).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 41.7.

IR (KBr, pellet, cm^{-1}): 1083 (ν_{BF}).

Anal. Calcd. for $C_{31}H_{25}BF_4NPPd$: C 58.57, H 3.96 N 2.20. Found: C 58.71, H 4.04 N 2.06.

*4.5.16. Synthesis of complex **5j***

The synthesis of the title complex was carried following the same procedure described above starting from an in situ prepared mixture of complexes **3j** and **4j**. Complex **5j** was obtained as a yellow compound in 84% yield.

^{1}H-NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.62–2.80 (m, 4H, CH_2P), 3.70 (dd, J_{HP} = 7.8, 2.2 Hz, C=CH_2), 7.00–7.12 (m, 3H, Ph), 7.25–7.48 (m, 9H, Ph, PPh), 7.56–7.71 (m, 13 H, PPh).

^{13}C{^{1}H}-NMR ($CDCl_3$, T = 298 K, ppm, selected peaks) δ: 28.1 (m, CH_2, PCH_2), 47.5 (dd, J_{CP} = 37.6, 6.0 Hz, CCH_2), 98.2 (t, J_{CP} = 7.2 Hz, *C*CPh), 103.7 (dd, J_{CP} = 46.0, 6.0 Hz, *C*Ph).

^{31}P{^{1}H}-NMR (CD_2Cl_2, T = 298 K, ppm) δ: 56.4, 59.9 (AB system, J_{PP} = 42.4 Hz).

IR (KBr, pellet, cm^{-1}): 1054 (ν_{BF}).

Anal. Calcd. for $C_{35}H_{31}BF_4P_2Pd$: C 59.48, H 4.42. Found: C 59.63, H 4.57.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.02.003.

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