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Oxidative addition of organic halides on palladium(0) complexes stabilized by dimethylfumarate and quinoline-based N–P or N–S spectator ligands

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ABSTRACT

We have studied the oxidative addition of some organic halides on palladium(0) dimethylfumarate complexes bearing heteroditopic (N–P or N–S) quinoline-based spectator ligands from the experimental and theoretical point of view. We have measured the half-life of some oxidative addition reactions carried out in two different solvents (CD_2Cl_2 and CD_3CN). The reactions were studied under mild conditions by NMR and the reactivities of different oxidants towards the complexes under study were compared. The rates of reaction were influenced by the nature of the spectator ligands and the solvent. The thioquinoline derivatives display a higher reactivity than that of the phosphoquinoline complexes and in general the reaction rates are higher in CD_3CN than in CD_2Cl_2, although such a behavior is not always observed. We propose a plausible mechanism for the oxidative reaction in different solvents based on the experimental results and an adequate computational approach. Finally, the solid state structures of two reaction products were resolved and reported.

1. Introduction

The facile interconversion between oxidation states, the peculiarity of the chemistry and stability of the Pd(II) and Pd(0) complexes have imposed the palladium derivatives among the most versatile and used catalysts [1]. In particular, the Pd(0) derivatives are often employed in oxidative addition involving organic halides which represents the first step of important cross coupling processes [2]. The reactivity of the organic halides toward Pd(0) complexes was widely studied as a function of their nature and structure [1a] but their influence on the intimate mechanism is still a matter of discussion [3,4]. In this respect, we have recently published a paper in which we discussed some aspects of the preferential formation of allenyl or propargyl tautomeric derivatives when propargyl halides react with some dimethylfumarate (dmfu) stabilized Pd(0) complexes bearing thioetheric or diphenyl phosphine quinoline-based ancillary ligands. We were able to isolate the reaction products, resolve the solid state structure of some of them and surmise a plausible mechanism on the basis of some computational and kinetic studies [5].

For the sake of completeness, we have now undertaken a new study in which a wider selection of organic halides were used as oxidants of novel and known Pd(0) dmfu complexes bearing spectator ligands based on the quinoline frame. It is worth nothing that dmfu represents the best compromise between the stability imparted and the reactivity of its palladium(0) olefin derivatives as was clearly established [6] and reviewed [7], whereas ligands based on the quinoline frame are very interesting compounds since they can promote isomerization [8], insertion [9] and cyclometalation reactions [10] in their palladium derivatives.

In order to investigate how the steric and electronic characteristics of the phospho- and thio-quinoline ligands affect the reactivity toward oxidative addition of palladium complexes bearing dimethylfumarate, we have synthesized the related Pd(0) complexes and tested their reactivity with four organic halides in CD_2Cl_2 and CD_3CN. The ligands, the investigated complexes, the organic halides and the products of the reactions are drawn in Scheme 1.

2. Results and discussion

2.1. General considerations

The ligands DPPQ [11], Me-DPPQ [12], T*t*BQ and TMQ [5], Me-T*t*BQ [13], Me-TMQ [10], and of the complexes **1**, **4** [8] and **2**, **3**

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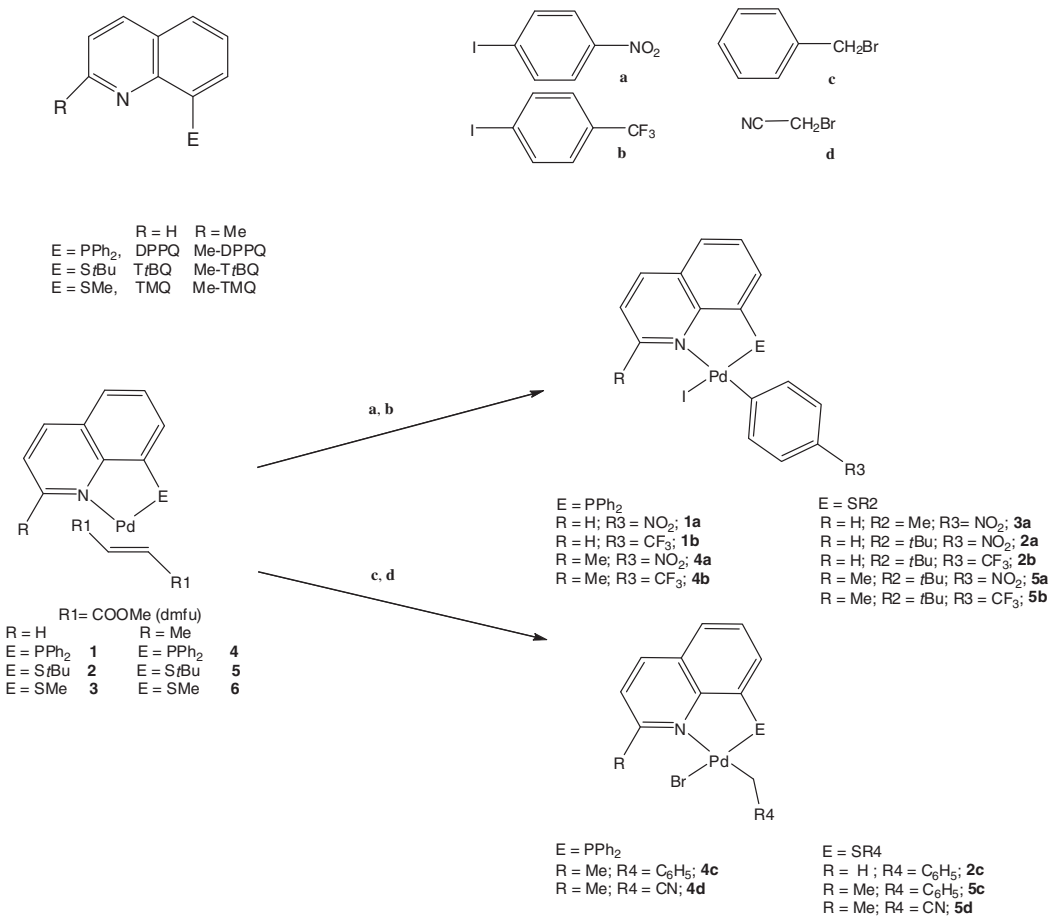


Scheme 1. Ligands, organic halides, starting complexes and reaction products.

[5] were obtained according to published protocols, whereas the complexes **5** and **6** are newly synthesized compounds.

Addition of a stoichiometric amount of the ligands Me-T*t*BQ or Me-TMQ to a solution of the complex $Pd_2(DBA)_3$. $CHCl_3$ in acetone in the presence of a slight excess of dmfu (3:1) under inert atmosphere (Ar) yields the complexes **5** and **6** as stable pale-yellow and yellow precipitates, respectively.

The ^1H and ^{13}C NMR spectra and the elemental analysis are in accord with the formulated structure. In particular, all the signals belonging to the spectator ligands are detected at different fields from those of the free ligands, whereas the protons and carbons of the olefin shift significantly up-field upon coordination ($\Delta\delta_H = 3$, $\Delta\delta_C = 90$ ppm) [7a].

Moreover, at 298 K in CD_2Cl_2 the olefin and carboxylate signals of the complex **5** split into two different groups of signals whereas complex **6** displays well separated peaks only at 233 K.

The temperature dependent splitting of the signals is due to the ditopicity of the spectator ligands which in the case of complex **6** is somehow thwarted by the fluxional movement known as apparent olefin rotation. Such a fluxionality, which is favored by the coordinative capability of the solvent, is due to de-coordination of nitrogen, subsequent rotation about the Pd–S bond and re-coordination of the ancillary ligand at the opposite molecular side of the complex.

At variance with complex **6**, the spectra of complex **5** display only some sort of residual fluxionality at RT, the olefin apparent rotation being easier in the case of the less hindered ligand Me-TMQ and more difficult with the bulky Me-TBQ (see Fig. 1 SM, Supplementary material).

2.2. Reactivity of Pd(0) complexes with aryl iodides

The complexes **1**–**6** were reacted with *p*-I-$C_6H_4NO_2$ and *p*-I-$C_6H_4CF_3$ to give the corresponding iodo-aryl derivatives under standard conditions ($[Complex]_0 \approx 1.2 \times 10^{-3}$ M; [Ar–I]/[Complex] = 4) in CD_3CN or CD_2Cl_2 at 298 K. In Fig. 2 SM (Supplementary Material) the ^1H NMR spectra of the reaction between complex **2** and *p*-I-$C_6H_4NO_2$ carried out in CD_3CN is reported whereas a survey of the results obtained is summarized in Table 1 entries (i) and (ii).

From an inspection of the data in Table 1 (entries (i) and (ii)) it is possible to state the following:

(a) The thioquinoline derivatives **2**, **3** and **5** are more reactive than the phosphoquinoline complex **4** and among the formers, the less encumbered species **3** shows by far the highest reactivity. We have carried out these experiments in CD_3CN since in this solvent we have the highest available reactivity data. Unfortunately, despite their high reactivity complexes **3** and **6** decompose and only 30% of the pure aryl iodide derivative together with a large excess of free ligand, DMFU and metallic palladium can at the best be obtained in the case of complex **3**. Summing up, the best starting species for the reaction under study are the S-*t*-Bu derivatives **2** and **5** which yield the aryl iodide complexes as a consequence of a smooth and selective reaction carried out under very mild conditions.

(b) According to the Hammett parameter *p*-I-$C_6H_4NO_2$ ($\sigma_p = +0.78$) displays a slightly enhanced reactivity with respect to *p*-I-$C_6H_4CF_3$ ($\sigma_p = +0.54$) [14].

Table 1
Half-life ($t_{1/2}$) as reactivity index for the reactions of oxidative addition of *p*-substituted aryl iodides *p*-I-C_6H_5X (X = NO_2, CF_3; entries (i) and (ii)) and $BrCH_2Ph$ or $BrCH_2CN$ (entries (iii) and (iv)) on Pd(0) complexes carried out in CD_3CN,[a] CD_2Cl_2,[b] CD_3CN and CD_2Cl_2 with remarkable decomposition.[c]

Entry	Complex Organic halide	**1**	**2**	**3**	**4**	**5**	**6**
(i)	*p*-I-$C_6H_4NO_2$	105 min[b]	20 min[a]	<5 min[a,c]	40 min[a] 75 min[b]	<10 min[a]	
(ii)	*p*-I-$C_6H_4CF_3$	105 min[b]	120 min[a]	<5 min[a,c]	90 min[b]	20 min[a] 7 h[b]	
(iii)	$BrCH_2C_6H_5$		80 min[a]		150 min[b]	120 min[a] 5.5 h[b]	40 min[a]
(iv)	$BrCH_2CN$				4 h[a] 6 min[b]	days[a] 6 h[b]	

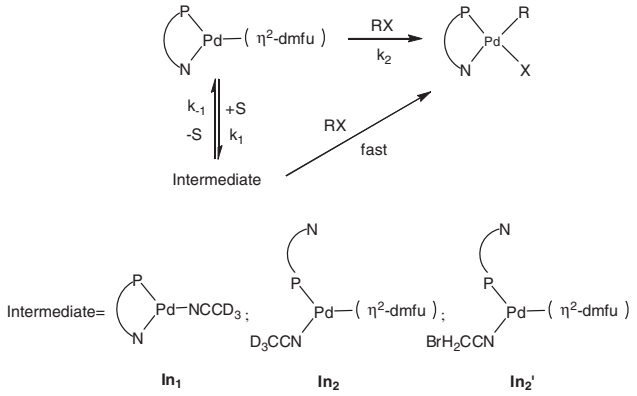
(c) As observed elsewhere, the reactions carried out in CD_3CN are faster than those in CD_2Cl_2 and the mechanism reported in the following Scheme 2 takes into account this experimental observation [6].

The better coordinative capability of CH_3CN favors the solvolytic path thereby increasing the overall reaction rate. Moreover, complex **5** reacts faster than its non methylated analog **2**. Since such a difference in reactivity is essentially due to the distortion imposed to the main coordinative plane of complex **5** by the methyl group in position 2 of the quinoline ring [15], we may advance the hypothesis that in this case $\mathbf{In_2}$ is the most probable intermediate. Such a conclusion was also confirmed by a computational approach based on theoretical calculations carried out with the GAUSSIAN 09 package [16] (see Section 3 for computational details). In this respect, we have calculated the energy values (E) related to the formation of the solvated species ($\mathbf{In_1}$, $\mathbf{In_2}$) involved in the oxidative addition reported in Scheme 2 at 298.15 K and the result is reported in the Scheme 1 SM. The computational response definitely points to the possible formation of intermediate $\mathbf{In_2}$ instead of $\mathbf{In_1}$, the latter being less stable of the former by about 22 kcal.

All the complexes obtained were isolated as stable species in reasonable yield except complex **3a** (complex **3a** in 30% yield). Remarkably, only one of the two possible isomers was always isolated, namely the isomer with the aryl fragment *trans* to the quinoline nitrogen. Such a result, which is not unprecedented, is essentially due to the reduced *trans*-labilizing influence of the nitrogen with respect to the thioetheric sulfur or phosphorus and is clearly apparent in the ^{1}H NMR spectra of the derivatives of the unsubstituted quinoline. In these cases the quinoline proton H^2 resonates as expected at about 10 ppm according with the marked downfield shift induced by the presence of the halogen in *cis* position [8c and refs. therein].

Furthermore, for all these complexes the diagnostic signals of the aromatic carbons bound to the palladium centre resonate at ca. 140 ppm which is 40 ppm down-field from the carbon of the free aryl iodides. (See for instance Figs. 4 SM and 5 SM Supplementary Material). As for the phosphoquinoline derivatives the ^{31}P NMR spectra of the complexes display a singlet at ca. 30 ppm (ca.10 ppm downfield from the Pd(0) complexes), indicating the de-shielding of the phosphorus atom coordinated to a Pd(II) centre and the presence of only one isomer. (See for instance Fig. 6 SM Supplementary Material.)

Finally the elemental analysis (see Section 3), the determination of the solid state structure of complex **2a** (*vide infra*) and the IR spectra (the asymmetric and symmetric stretching ν_{NO2} at ca. 1550 and 1305 cm^{-1} for complexes **1a**–**5a** or the ν_{C-F} stretching at ca. 1150 cm^{-1} for **1b**–**5b**) complete the characterization of these complexes.



Scheme 2. Proposed mechanism involving the solvent intermediacy RX = *p*-I-$C_6H_4NO_2$, *p*-I-$C_6H_4CF_3$, or $BrCH_2C_6H_5$, $BrCH_2CN$.

2.3. Reactivity of Pd(0) complexes with benzyl bromide and bromoacetonitrile

The complexes **2**, **4**–**6** were reacted with $BrCH_2C_6H_5$ to give the corresponding benzyl derivatives under standard conditions ($[Complex]_0 = 1.2 \times 10^{-3}$ M; $[PhCH_2–Br]/[Complex] = 4$) in CD_3CN or CD_2Cl_2 at 298 K whereas only the complexes **4** and **5** were reacted with $BrCH_2CN$ under similar experimental conditions. The $t_{1/2}$ values related to both oxidants are summarized in Table 1 entries (iii) and (iv).

The complexes reacting with benzylbromide which is less reactive than the iodoaryl derivatives, were chosen among the most activated species according to the experimental observations discussed before.

Also in these cases the reactions are faster in CD_3CN than in CD_2Cl_2 and, at variance with the previous results, the most reactive complex **6** does not decompose throughout the reaction progress but rather the reaction product **6c** is markedly instable and cannot be separated from the reaction mixture. Interestingly, the reaction involving complex **2** is faster than that involving complex **4**, indicating a significant involvement of steric factors. Finally, the measurable reactivity of the complex **4** in CD_2Cl_2 allows an otherwise impossible investigation in CD_3CN owing to the precipitation of the reaction product **4c** which is insoluble in the latter solvent.

It is worth noting that the reactivity studies have suggested feasible synthetic protocols characterized by good yields. In particular the reaction of complexes **2** and **5** in CH_3CN with $BrCH_2C_6H_5$ gives the customary isomers bearing the alkyl group *trans* to the quinoline nitrogen, as can be deduced from the ^{1}H NMR significant signals and from the spectrum of complex **2c** in which the quinoline proton H^2 resonates at 9.68 ppm. (See Fig. 7 SM Supplementary Material).

As a decisive test we have carried out a [1H–1H] NOESY experiment (see Fig. 3 SM Supplementary Material) which fully confirms the nature of the isomer in the case of complex **2c** (intense cross peaks between CH_2 benzyl protons and $SC(CH_3)_2$ protons).

By means of the ^1H–^{13}C HMQC spectrum of complexes **2c**, **5c** and **4c** (See for instance Fig. 8 SM Supplementary Material) the Pd–CH_2–Ph signals were identified at 13.3, 15.8 and 23.2 ppm, respectively. Furthermore, complex **4c** was identified by its ^{31}P NMR spectrum in which the phosphorus singlet resonates at 33.6 ppm, which is ca. 10 ppm downfield with respect to the starting Pd(0) complex **4**.

Remarkably, the low coupling constant J_{CP} = 4.6 Hz in the case of complex **4c** confirms the *cis* position of the phosphorus with respect to the alkyl group.

Finally, in the case of complex **5c**, the mutual position of the substituents at the palladium center was univocally determined by means of an X-ray diffraction study (*vide infra*).

The phenomenon of inversion of the sulfur absolute configuration is apparent also in the case of complexes **2c** and **5c**. However, at variance with what observed in the case of the starting olefin substrates, the freezing of sulfur inversion and its consequent acquisition of a specific configuration (S or R) renders the CH_2–Ph protons diastereotopic already at 273 K, thank to the enhanced strength of the Pd(II)–S with respect to the Pd(0)–S bond (See Fig. 9 SM Supplementary Material).

As reported in Table 1 (entry (iv)), complexes **4** and **5** were also reacted with $BrCH_2CN$ and the result was surprisingly discordant with the previous finding. As a matter of fact, both complexes react faster in CD_2Cl_2 than in CD_3CN. For instance, complex **4** reacts completely with $BrCH_2CN$ in CD_2Cl_2 in 30′ ca. whereas the same reaction in CD_3CN took 24 h. This is probably due to the competitive action of CD_3CN toward $BrCH_2CN$. Thus, in analogy to what observed before, we assume that the attack of $BrCH_2CN$ entails the formation of the intermediate **In$_2$**′ (see Scheme 2). The latter should be energetically disfavored with respect to intermediate **In$_2$** owing to the reduced nucleophilicity of $BrCH_2CN$ compared with that of CD_3CN. An appropriate computational study [16] (see Scheme 2 SM Supplementary Material) confirms such a hypothesis suggesting that the intermediate **In$_2$** is more stable than **In$_2$**′ of about 0.9 kcal mol^{-1}.

Therefore, the almost complete formation of the intermediate **In$_2$** induced by its favorable energy and by the presence of a large excess of CD_3CN efficiently contrast the direct attack of the halogenated oxidant $BrCH_2CN$ thereby slowing down the overall rate of the oxidative reaction.[1]

It was therefore noticed that the best protocol for the synthesis of these derivatives requires CH_2Cl_2 as the solvent. Thus, complexes **4d** and **5d** were obtained in such a solvent in good yields and their identification was carried out by means of customary techniques. Particularly diagnostic is the CH_2–Pd signal at −20 ppm ca. and in the case of complex **5d** (Fig. 10 SM Supplementary Material) the presence of the diastereotopic protons CH_2–Pd already at RT, whereas in the ^1H spectrum of **4d** (Fig. 11 SM Supplementary Material) the CH_2–Pd protons resonate as a doublet due to the coupling with the phosphorus in *cis* (J_{P-H} = 3.9 Hz). The IR spectra were also recorded and the $\nu_{C\equiv N}$ at ca. 2200 cm^{-1} can be observed in both cases.

In particular we report (Figs. 10 SM and 11 SM, respectively) the HMQC spectrum of **5d** and the ^1H and ^{31}P spectra of **4d** derivatives.

[1] Taking into account the difference in energy involved in the equilibrium reactions 5 + CD3CN = **In$_2$** (K) and **5** + $BrCH_2CN$ = **In$_2$**′ (K′), it is possible to calculate the ratio K/K′ as $6.2 \times 10^{-3}/1.3 \times 10^{-3} = 4.6$, where $4.6 = \mathbf{In_2} \times [BrCH_2CN]/\mathbf{In_2}' \times [CD_3CN]$, $[BrCH_2CN] = 1 \times 10^{-2}$ M and $[CD_3CN]$ = 19 M (solvent). The ensuing ratio $[\mathbf{In_2}]/[\mathbf{In_2}']$ is 8750. This number clearly testifies the unfavorable concentration of the intermediate **In$_2$**′ as compared to that of **In$_2$**.

2.4. Crystal structure determinations

An ORTEP [17] view of the neutral complex **2a** is shown in Fig. 1. A selection of bond distances and angles is given in the caption of the figure. The geometry around the Pd center is slightly distorted square planar. The four positions around the central Pd are occupied by the carbon C14 of the *p*-nitro benzene ligand, an I^- anion, the N and S atoms of the TTBQ ligand. The maximum deviation from the average basal coordination plane is 0.001(4) Å for C14, while the central Pd1 atom is situated at 0.0207(3) Å above this plane. The Pd1–N1–C5–C6–S1 ring adopts a twisted conformation with the maximum deviations from the mean plane of −0.125(3) Å for N1 and 0.169(4) Å for C6, and its mean plane forms dihedral angles of 3.93(5)° and 9.40(7)° with the coordination and quinoline planes, respectively. The Pd1–I1 of 2.5902(4) Å displays a shortening with respect to the same distances, in the range 2.63–2.64 Å, as found in other similar Pd(II) structures where I is in *trans* position to a S atoms of a thioether group [9a,18,19]. In these compounds the I^- anion exerts a significant *trans* influence on the Pd–S bonds because their distances (in the range 2.31–2.33 Å) are rather longer than those reported in analogous structures where S is in *trans* position to a Cl^- anion (in the range 2.26–2.28 Å) [12,15,20,21].

An ORTEP [17] view of the neutral complex **5c** is shown in Fig 2. A selection of bond distances and angles is given in the caption of the figure. The structure is similar to that of complex **2a** but the presence of the 2-Me substituent on the quinoline ring produces a structural distortion mainly evidenced by the disorder in the orientation of the quinoline moiety. The geometry around the Pd center is distorted square planar toward a tetrahedral arrangement. The four positions around the central Pd are occupied by the sp^3 C15 carbon, a Br^- anion, the N and the S atoms of the Me-TTBQ ligand. The distortion of the square planar geometry is revealed by the arrangement of the four atoms around the Pd1 center. The deviations of the four atoms from the mean basal coordination plane are: −0.0056(9) for Br1, 0.226(6) for N1, −0.017(2) for S1 and 0.404(7) Å for C26, with the Pd1 atom situated at 0.2242(5) Å above the average plane. The Pd1–N1–C5–C6–S1 five membered ring displays a significant twisted conformation with maximum deviations from the mean plane of 0.560(6) Å for N1 and −0.436(6) Å for C6, and forms dihedral angles of 16.0(1)° and 29.3(1)° with the coordination plane and the quinoline moiety, respectively. The Pd1–Br1 bond distance of 2.4882(8) Å displays a slight lengthening with respect to the same distance of 2.4464(6) Å in a similar structure [20]. Because the Pd1–S1 bond exhibits a short distance of 2.277(2) Å it can be concluded that the Br^- anion exerts a *trans* effect comparable to that produced by a Cl^- anion. The longer Pd–C15(sp^3) bond distance of 2.058(7) Å with respect to that of the Pd–C14(sp^2) bond in compound **2a** (1.986(3) Å) can be accounted for by the different hybridisations of the two carbons.

3. Experimental

3.1. 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 stored over silver foil. Anhydrous acetonitrile was as purchased and used under Argon atmosphere. Deuterated solvents and all other chemicals were commercially available grade products and were used as purchased.

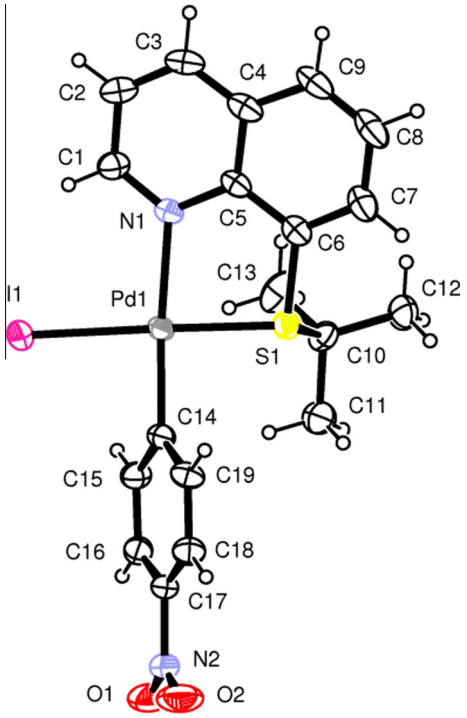


Fig. 1. ORTEP view of complex **2a** showing the thermal ellipsoids at 30% probability level. Selected bond distances (Å): Pd1–I1 = 2.5902(4); Pd1–N1 = 2.158(3); Pd1–S1 = 2.313(1); Pd1–C14 = 1.986(3); S1–C6 = 1.779(4); S1–C10 = 1.887(4). Selected angles (°): I1–Pd1–N1 = 96.84(9); I1–Pd1–S1 = 178.37(3); I1–Pd1–C14 = 87.36(11); N1–Pd1–S1 = 84.46(9); N1–Pd1–C14 = 175.63(14); S1–Pd1–C14 = 91.32(11).

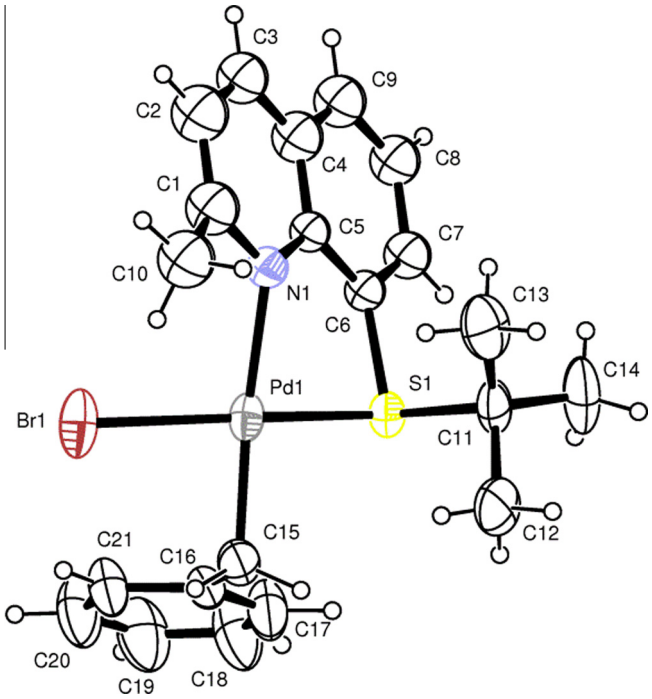


Fig. 2. ORTEP view of complex **5c** showing the thermal ellipsoids at 30% probability level. Selected bond distances (Å): Pd1–Br1 = 2.4882(8); Pd1–N1 = 2.200(5); Pd1–S1 = 2.277(2); Pd1–C15 = 2.058(7); S1–C6 = 1.820(5); S1–C11 = 1.862(6). Selected angles (°): Br1–Pd1–N1 = 92.27(16); Br1–Pd1–S1 = 168.08(5); Br1–Pd1–C15 = 87.2(2); N1–Pd1–S1 = 87.28(15); N1–Pd1–C15 = 174.1(2); S1–Pd1–C15 = 90.3(2).

3.2. IR, NMR and elemental analyses 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. Elemental analyses were carried out using an Elementar C H N "CUBO Micro Vario" analyzer.

3.3. Kinetic measurements by ^{1}H NMR technique

All the reactions were studied by ^{1}H NMR by dissolving the complex under study in 0.6 ml of CD_2Cl_2 ($[Complex]_0 \approx 10^{-2}$ mol dm^{-3}), adding microaliquots of a concentrated CD_2Cl_2 solution of the organic halide under study ($[ArX] \approx 4 \times 10^{-2}$ mol dm^{-3}) and monitoring the signal for the disappearance of the starting complex and the concomitant appearance of the final products. The halftime of each reaction ($t_{1/2}$) was detected and taken as a measure of reactivity.

3.4. Computational details

The geometrical optimization of the complexes was carried out without symmetry constraints, using the hyper-GGA functional MO6 [22,23], in combination with polarized triple-ζ-quality basis sets (LAN2TZ(f)) [24,25] and relativistic pseudopotential for the Pd atoms, a polarized double-ζ-quality basis sets (LANL2DZdp) [26] with diffuse functions for the halogen atoms and a polarized double-ζ-quality basis sets (6-31G(d,p)) for the other elements. Solvent effects (acetonitrile, $\varepsilon = 37.5$) were included using CPCM [27,28].

The "restricted" formalism was applied in all the calculations. By means of the stationary points characterized by IR simulation, the zero-point vibrational energies and thermodynamic parameters were obtained [29].

The software used was GAUSSIAN '09 [16] and all the computational work was carried out on Intel based × 86–64 workstations.

3.5. Crystal structure determination

The crystal data of compounds **2a** and **5c** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation. The data sets were integrated with the DENZO-SMN package [30] and corrected for Lorentz, polarization and absorption effects (SORTAV) [31]. The structures were solved by direct methods using the SIR97 [32] system of programs. The structure **2a** was refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms. The structure **5c** was refined in a similar way, except for the 2-Me-quinoline moiety which was found disordered and refined isotropically over two different positions using some constraints on the bond distances. All calculations were performed using SHELXL-97 [33] and PARST [34] implemented in the WINGX [35] system of programs. The crystal data are given in Supplementary Material Table 1 SM.

3.6. Synthesis of the ligands and complexes

The ligands DPPQ [11], DPPQ-Me [12], T*t*BQ and TMQ [5], Me-T*t*BQ [13], Me-TMQ [10], and of the complexes **1**, **4** [8] and **2**, **3** [5] were synthesized according to published procedures.

3.7. Synthesis of complex *5*

0.1127 g (0.4871 mmol) of Me-T*t*BQ, 0.1755 g (1.218 mmol) of dmfu and 0.2101 g (0.2030 mmol) of $[Pd_2(DBA)_3{\cdot}CHCl_3]$ were dissolved under inert atmosphere (Ar) in 30 ml of anhydrous acetone.

The mixture was stirred for 60 min and eventually treated with active charcoal for 5/10 min and filtered on Celite filter. The resulting yellow solution was dried under vacuum and the residual treated with diethyl ether, filtered off, washed with diethyl ether in excess and dried under vacuum. 0.1452 g (yield 75%) of the title compound was obtained as pale yellow microcrystals.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.34 (s, 9H, ^{t}Bu), 3.09 (s, 3H, quinoline–CH_3), 3.55 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.87, 3.98 (AB system, 2H, J = 9.8 Hz, CH=CH), 7.56 (d, 1H, J = 8.4 Hz, H^3), 7.59 (dd, 1H, J = 8.1, 7.2 Hz, H^6), 7.96 (dd, 1H, J = 8.1, 1.4 Hz, H^5), 8.05 (dd, 1H, J = 7.2, 1.4 Hz, H^7), 8.26 (d, 1H, J = 8.4, Hz, H^4).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 30.7 (CH_3, CMe_3), 30.9 (CH_3, $CH_{3quinoline}$), 45.6 (CH, CH=CH), 46.7 (CH, CH=CH), 50.6 (CH_3, OCH_3), 50.8 (CH_3, OCH_3), 53.9 (C, CMe$_3$), 123.3 (CH, C^3), 125.6 (CH, C^6), 127.9 (C, C^{10}), 130.3 (CH, C^5), 131.4 (C, C^8), 137.8 (CH, C^4), 138.7 (CH, C^7), 149.3 (C, C^9), 163.7 (C, C^2), 174.3 (C, CO), 174.6 (C, CO).

IR (KBr pellets): ν_{CO} 1680 cm^{-1}.

Anal. Calc. for $C_{20}H_{25}NO_4PdS$: C, 49.85; H, 5.23; N, 2.91. Found: C, 49.92; H, 5.18; N, 2.75%.

3.8. Synthesis of complex **6**

The title compound was obtained following the above described procedure using the Me-TMQ ligand. The complex was obtained as yellow microcrystals with 72% yield.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.81 (s, 3H, SCH_3), 3.05 (s, 3H, quinoline–CH_3), 3.62 (s, 6H, OCH_3), 4.00 (bs, 2H, CH=CH), 7.58 (d, 1H, J = 8.4 Hz, H^3), 7.61 (dd, 1H, J = 8.1, 7.3 Hz, H^6), 7.88 (dd, 1H, J = 8.1, 1.3 Hz, H^5), 8.06 (dd, 1H, J = 7.3, 1.3 Hz, H^7), 8.27 (d, 1H, J = 8.4, Hz, H^4).

^{1}H NMR (300 MHz, CD_2Cl_2, T = 233 K, ppm) δ: 2.75 (s, 3H, SCH_3), 2.97 (s, 3H, $CH_{3quinoline}$), 3.58 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.78, 4.07 (AB system, 2H, J = 9.7 Hz, CH=CH), 7.58 (d, 1H, J = 8.4 Hz, H^3), 7.60 (dd, 1H, J = 8.1, 7.3 Hz, H^6), 7.88 (dd, 1H, J = 8.1, 1.3 Hz, H^5), 8.04 (dd, 1H, J = 7.3, 1.3 Hz, H^7), 8.27 (d, 1H, J = 8.4, Hz, H^4).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 253 K, ppm) δ: 25.2 (CH_3, SCH_3), 31.3 (CH_3, $CH_{3quinoline}$), 45.5 (CH, CH=CH), 46.4 (CH, CH=CH), 50.9 (CH_3, OCH_3), 51.1 (CH_3, OCH_3), 123.6 (CH, C^3), 125.3 (CH, C^6), 127.9 (C, C^{10}), 129.1 (CH, C^5), 134.5 (C, C^8), 135.0 (CH, C^7), 138.5 (CH, C^4), 147.1 (C, C^9), 163.8 (C, C^2), 173.6 (C, CO), 173.8 (C, CO).

IR (KBr pellets): ν_{CO} 1684 cm^{-1}.

Anal. Calc. for $C_{17}H_{19}NO_4PdS$: C, 46.42; H, 4.35; N, 3.18. Found: C, 46.39; H, 4.27; N, 3.07%.

3.9. Synthesis of complex **1a**

In a 50 ml two necked flask 0.0640 g (0.1137 mmol) of complex **1** and 0.1132 g (0.4548 mmol) of 1-iodo-4-nitrobenzene were dissolved in 10 ml ca. of anhydrous CH_2Cl_2 under inert atmosphere (Ar). The resulting yellow solution stirred at RT for 5 h turns to red-brown and filtered on a millipore filter to remove metallic palladium. To the clear solution concentrated to small volume under vacuum diethyl ether was added. The dark-red precipitate obtained was filtered off on gooch, washed with diethyl ether and dried under vacuum. 0.0628 g (yield 83%) of the title compound was obtained.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 7.30–7.35 (m, 2H, Ph), 7.39–7.58 (m, 10H, PPh2), 7.59–7.62 (m, 2H, Ph), 7.72–7.80 (m, 2H, H^3, H^6), 8.02 (d,d,d, 1H, J = 9.9, 7.2, 1.3 Hz, H^7), 8.19 (dt, 1H, J = 8.1, 1.4 Hz, H^5), 8.56 (dt, 1H, J = 8.3, 1.7 Hz, H^4), 10.50 (d, 1H, J = 4.8, Hz, H^2). ^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 119.6 (CH, Ph), 123.7 (CH, C^3), 127.9 (d, J_{CP} = 6.8 Hz, CH, C^6), 129.8 (d, J_{CP} = 9.4 Hz, C, C^{10}), 132.5 (CH, C^5), 132.5 (d, J_{CP} = 41.2 Hz, C, C^8), 135.5 (d, J_{CP} = 20.1 Hz, CH, C^7), 138.0 (CH, Ph), 139.2 (CH, C^4), 145.6 (C, Ph), 147.1 (d, J_{CP} = 20,9 Hz, C, C^9), 156.7 (C, Ph), 158.5 (CH, C^2).

^{31}P{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 28.8.

IR (KBr pellets): $\nu_{C=N}$ 1583, ν_{NOas} 1557, ν_{NOs} 1307 cm^{-1}.

Anal. Calc. for $C_{27}H_{20}IN_2O_2PPd$: C, 48.49; H, 3.01; N, 4.19. Found: C, 48.62; H, 3.15; N, 4.04%.

The following complexes were prepared from the appropriate reagents by means of similar protocols as **1a**. Only the reaction time, the color of the products, the yields and the solvent were different. In some cases filtration on millipore or Celite was necessary and when the reaction was carried out in CH_3CN the final precipitation was obtained by dissolving the dried precipitate in small aliquots of CH_2Cl_2 and re-precipitating with diethyl ether and washing with ether or pentane. These parameters will be given for the complexes reported below together with their analytical data.

3.10. Synthesis of complex **1b**

Reaction time = 12 h; color of the complex = pink; yield = 89%; solvent = anhydrous CH_2Cl_2; filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethyl ether.

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 6.98–7.01 (m, 2H, Ph), 7.19–7.62 (m, 2H, Ph), 7.34–7.53 (m, 10H, PPh_2), 7.67–7.75 (m, 2H, H^3, H^6), 7.99 (d,d,d, 1H, J = 9.5, 7.2, 1.3 Hz, H^7), 8.11 (dt, 1H, J = 8.1, 1.3 Hz, H^5), 8.47 (dt, 1H, J = 8.4, 1.6 Hz, H^4), 10.55 (d, 1H, J = 4.9, Hz, H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 122.5 (CH, Ph), 123.6 (CH, C^3), 124.8 (qrt, $^2J_{CF}$ = 31.6 Hz, C, Ph), 125.2 (qrt, $^1J_{CF}$ = 270.0 Hz, CF_3, $PhCF_3$), 127.8 (d, CH, J_{CP} = 6.4 Hz, C^6), 129.7 (d, C, J_{CP} = 9.2 Hz, C^{10}), 132.1 (CH, C^5), 133.8 (d, C, J_{CP} = 41.6 Hz, C^8), 135.5 (d, CH, J_{CP} = 17.8 Hz, C^7), 137.6 (CH, Ph), 138.8 (CH, C^4), 146.6 (C, Ph), 150.7 (d, C, J_{CP} = 20,7 Hz, C^9), 158.4 (CH, C^2).

^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 28.6.

IR (KBr pellets): $\nu_{C=N}$ 1585, ν_{CF} 1151 cm^{-1}.

Anal. Calc. for $C_{28}H_{20}F_3INPPd$: C, 48.62; H, 2.91; N, 2.02. Found: C, 48.78; H, 3.05; N, 1.98%.

3.11. Synthesis of complex **2a**

Reaction time = 2 h; color of the complex = brown; yield = 87%; solvent = anhydrous CH_3CN;filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = yes; washing solvent = diethyl ether.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.24 (s, 9H, ^{t}Bu), 7.69 (dd, 1H, J = 8.3, 4.9 Hz, H^3), 7.74–7.86 (m, 5H, Ph, H^6), 8.11 (dd, 1H, J = 7.4, 1.3 Hz, H^7), 8.15 (dd, 1H, J = 8.2, 1.3 Hz, H^5), 8.51 (dd, 1H, J = 8.3, 1,6 Hz, H^4), 10.15 (dd, 1H, J = 4.9, 1.6 Hz, H^2).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 30.1 (CH_3, CMe_3), 59.4 (C, CMe$_3$), 119.5 (CH, Ph), 123.5 (CH, C^3), 127.2 (CH, C^6), 129.0 (C, C^{10}), 130.2 (C, C^8), 131.6 (CH, C^5), 138.0 (CH, C^7), 139.0 (CH, C^4), 140.0 (CH, Ph), 145.1 (C, Ph), 148.6 (C, C^9), 149.9 (C, Ph), 157.2 (CH, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1587, $\nu_{NO\ as}$ 1557, ν_{NOs} 1304 cm^{-1}.

Anal. Calc. for $C_{19}H_{19}IN_2O_2PdS$: C, 39.84; H, 3.34; N, 4.89. Found: C, 39.96; H, 3.21; N, 4.99%.

3.12. Synthesis of complex **2b**

Reaction time = 12 h; color of the complex = light-brown; yield = 87%; solvent = anhydrous CH_3CN; filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = yes; washing solvent = diethylether.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.24 (s, 9H, ^{t}Bu), 7.25 (d, 2H, J = 7.9 Hz, Ph), 7.64–7.70 (m, 3H, Ph, H^3), 7.84 (dd, 1H, J = 8.4, 7.2 Hz, H^6), 8.09–8.15 (m, 2H, H^7, H^5), 8.49 (dd, 1H, J = 8.3, 1,5 Hz, H^4), 10.14 (dd, 1H, J = 4.9, 1.5 Hz, H^2).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 30.1 (CH_3, CMe_3), 59.2 (C, CMe_3), 122.0 (qrt, $^3J_{CF}$ = 3.6 Hz, CH, Ph), 123.4 (CH, C^3), 124.9 (qrt, $^1J_{CF}$ = 270.0 Hz, CF_3, $PhCF_3$), 125.1 (qrt, $^2J_{CF}$ = 31.5 Hz, C, Ph), 127.1 (CH, C^6), 129.3 (C, C^{10}), 130.1 (C, C^8), 131.5 (CH, C^5), 137.9 (CH, C^7), 138.8 (CH, C^4), 140.0 (CH, Ph), 141.2 (C, Ph), 148.6 (C, C^9), 148.6 (C, Ph), 157.1 (CH, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1586, ν_{CF} 1156 cm^{-1}.

Anal. Calc. for $C_{20}H_{19}F_3INPdS$: C, 40.32; H, 3.21; N, 2.35. Found: C, 40.45; H, 3.39; N, 2.18%.

3.13. Synthesis of complex **2c**

Reaction time = 5 h; color of the complex = yellow; yield = 78%; solvent = anhydrous CH_3CN; filtration = no; re-precipitated from CH_2Cl_2/ether = yes; washing solvent = pentane.

^1H NMR (300 MHz, CD_2Cl_2, T = 273 K, ppm) δ: 1.45 (s, 9H, ^tBu), 3.26 (d, 1H, J = 6.0 Hz, CH_2Pd), 4.19 (d, 1H, J = 6.0 Hz, CH_2Pd), 6.98–7.03 (m, 1H, Ph), 7.08–7.13 (m, 2H, Ph), 7.51 (dd, 1H, J = 8.3, 4.9 Hz, H^3), 7.58–7.65 (m, 3H, Ph, H^6), 7.89 (dd, 1H, J = 8.2, 1.3 Hz, H^5), 7.96 (dd, 1H, J = 7.3, 1.3 Hz, H^7), 8.26 (dd, 1H, J = 8.3, 1,6 Hz, H^4), 9.68 (dd, 1H, J = 4.9, 1.6 Hz, H^2).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, T = 273 K, ppm) δ: 13.3 (CH_2, CH_2Pd), 30.2 (CH_3, CMe_3), 58.3 (C, CMe_3), 122.9 (CH, C^3), 123.5 (CH, Ph), 126.9 (CH, C^6), 128.3 (CH, Ph), 129.2 (C, C^{10}), 129.4 (C, C^8), 130.2 (CH, Ph), 131.5 (CH, C^5), 137.1 (CH, C^7), 138.4 (CH, C^4), 146.2 (C, Ph), 147.8 (C, C^9), 153.5 (CH, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1589 cm^{-1}.

Anal. Calc. for $C_{20}H_{22}BrNPdS$: C, 48.55; H, 4.48; N, 2.83. Found: C, 48.48; H, 4.61; N, 2.97%.

3.14. Synthesis of complex **3a**

Reaction time = 20 min; color of the complex = light-brown; yield = 31%; solvent = anhydrous CH_2Cl_2; filtration in Celite = yes; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethylether.

^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.65 (s, 3H, SCH_3), 7.66–7.69 (m, 2H, Ph), 7.72 (dd, 1H, J = 8.3, 4.9 Hz, H^3), 7.81 (dd, 1H, J = 8.1, 7.3 Hz, H^6), 7.88–7.90 (m, 2H, Ph), 8.10 (dd, 1H, J = 8.1, 1.3 Hz, H^5), 8.16 (dd, 1H, J = 7.3, 1.3 Hz, H^7), 8.52 (dd, 1H, J = 8.3, 1.5 Hz, H^4), 10.14 (dd, 1H, J = 4.9, 1.5 Hz, H^2).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 26.5 (CH_3, SCH_3), 120.1 (CH, Ph), 123.7 (CH, C^3), 128.0 (CH, C^6), 130.5 (C, C^{10}), 130.8 (CH, C^5), 132.5 (C, C^8), 135.5 (CH, C^7), 138.0 (CH, Ph), 139.1 (CH, C^4), 145.5 (C, Ph), 147.1 (C, C^9), 150.1 (C, Ph), 156.9 (CH, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1584, $\nu_{NO\ as}$ 1556, ν_{NOs} 1304 cm^{-1}.

Anal. Calc. for $C_{16}H_{13}IN_2O_2PdS$: C, 36.21; H, 2.47; N, 5.28. Found: C, 36.36; H, 2.59; N, 5.12%.

3.15. Synthesis of complex **4a**

Reaction time = 4 h; color of the complex = red-brown; yield = 89%; solvent = anhydrous CH_2Cl_2; filtration = no; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethylether.

^1H NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 3.48 (s, CH_3, quinoline–CH_3), 7.33–7.55 (m, 15H, PPh_2, Ph, H^3), 7.63 (d,d,d, 1H, J = 8.0, 7.2, 1.2 Hz, H^6), 7.91 (d,d,d, 1H, J = 9.7, 7.2, 1.4 Hz, H^7), 8.01 (dt, 1H, J = 8.0, 1.4 Hz, H^5), 8.22 (dd, 1H, J = 8.5, 1.6 Hz, H^4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 34.6 (CH_3, quinoline–CH_3), 120.1 (CH, Ph), 125.0 (CH, C^3), 126.6 (d, J_{CP} = 6.9 Hz, CH, C^6), 127.7 (d, J_{CP} = 8.3 Hz, C, C^{10}), 131.6 (CH, C^5), 132.9 (d, J_{CP} = 44.5 Hz, C, C^8), 135.2 (CH, C^4), 138.5 (d, J_{CP} = 18.1 Hz, CH, C^7), 136.8 (CH, Ph), 144.1 (C, Ph), 151.3 (d, J_{CP} = 18,7 Hz, C, C^9), 157.5 (C, Ph), 167.1 (C, C^2).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 31.0

IR (KBr pellets): $\nu_{C=N}$ 1601, $\nu_{NO\ as}$ 1554, $\nu_{NO\ s}$ 1307 cm^{-1}.

Anal. Calc. for $C_{28}H_{22}IN_2O_2PPd$: C, 49.25; H, 3.25; N, 4.10. Found: C, 49.17; H, 3.38; N, 3.96%.

3.16. Synthesis of complex **4b**

Reaction time = 4 h; color of the complex = light-brown; yield = 91%; solvent = anhydrous CH_2Cl_2; filtration = no; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethylether.

^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ 6.88–6.90 (m, 2H, Ph), 7.24–7.27 (m, 2H, Ph), 7.36–7.59 (m, 11H, PPh_2, H^3), 7.65 (dd, J = 8.0, 7.2, 1.3 Hz, H^6), 7.96 (d,d,d, 1H, J = 9.3, 7.2, 1.3 Hz, H^7), 8.06 (dt, 1H, J = 8.0, 1.3 Hz, H^5), 8.27 (dt, 1H, J = 8.3, 1.5 Hz, H^4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 34.5 (CH_3, quinoline–CH_3), 122.6 (CH, Ph), 124.2 (qrt, $^2J_{CF}$ = 31.3 Hz, C, Ph), 124.9 (CH, C^3), 126.5 (d, CH, J_{CP} = 6.8 Hz, C^6), 127.7 (d, C, J_{CP} = 8.2 Hz, C^{10}), 131.7 (CH, C^5), 133.3 (d, C, J_{CP} = 42.9 Hz, C^8), 135.0 (CH, C^7), 136.7 (CH, Ph), 138.2 (CH, C^4), 148.5 (C, Ph), 151.3 (d, C, J_{CP} = 18.6 Hz, C^9), 166.9 (C, C^2); $PhCF_3$ not detectable.

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 30.9.

IR (KBr pellets): $\nu_{C=N}$ 1585, ν_{CF} 1153 cm^{-1}.

Anal. Calc. for $C_{29}H_{22}F_3INPPd$: C, 49.35; H, 3.14; N, 1.98. Found: C, 49.24; H, 3.29; N, 2.05%.

3.17. Synthesis of complex **4c**

Reaction time = 4 h; color of the complex = orange; yield = 84%; solvent = anhydrous CH_2Cl_2; filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethylether.

^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 3.19 (s, CH_3, quinoline–CH_3), 3.46 (d, 2H, J_{CP} = 3.7 Hz, CH_2–Pd), 7.07–7.10 (m, 3H, Ph), 7.28–7.30 (m, 2H, Ph), 7.40–7.58 (m, 12H, PPh_2, H^3, H^6), 7.91 (d,d,d, 1H, J = 9.5, 7.2, 1.4 Hz, H^7), 7.95 (dt, 1H, J = 8.0, 1.4 Hz, H^5), 8.16 (dd, 1H, J = 8.5, 1.6 Hz, H^4).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 23.2 (d, J_{CP} = 4.6 Hz, CH_2, CH_2–Pd), 30.1 (CH_3, quinoline–CH_3), 124.0 (CH, Ph), 124.8 (CH, C^3), 126.4 (d, J_{CP} = 6.9 Hz, CH, C^6), 127.2 (d, J_{CP} = 7.7 Hz, C, C^{10}), 127.9 (CH, Ph), 129.2 (CH, Ph), 130.8 (CH, C^5), 133.9 (d, J_{CP} = 18.2 Hz, CH, C^7), 134.6 (d, J_{CP} = 45.6 Hz, C, C^8), 137.6 (CH, C^4), 145.9 (C, Ph), 150.2 (d, J_{CP} = 17,4 Hz, C, C^9), 165.5 (C, C^2).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 33.6.

IR (KBr pellets): $\nu_{C=N}$ 1606 cm^{-1}.

Anal. Calc. for $C_{29}H_{25}BrNPPd$: C, 57.59; H, 4.17; N, 2.32. Found: C, 57.72; H, 4.31; N, 2.18%.

3.18. Synthesis of complex **4d**

Reaction time = 40 min; color of the complex = pale-yellow; yield = 92%; solvent = anhydrous CH_2Cl_2; filtration = no; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethylether.

^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.88 (d, 2H, J_{CP} = 3.8 Hz, CH_2–Pd), 3.31 (s, CH_3, quinoline–CH_3), 1.88 (d, 2H, J_{CP} = 3.8 Hz, CH_2–Pd), 7.50–7.80 (m, 13H, PPh_2, H^3, H^6, H^7), 8.05 (dt, 1H, J = 8.0, 1.4 Hz, H^5), 8.25 (dd, 1H, J = 8.5, 1.8 Hz, H^4).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 40.7.

IR (KBr pellets): $\nu_{C=N}$ 2197, $\nu_{C=N}$ 1606 cm^{-1}.

Anal. Calc. for $C_{24}H_{20}BrN_2PPd$: C, 52.06; H, 3.64; N, 5.06. Found: C, 51.99; H, 3.53; N, 5.13%.

3.19. Synthesis of complex **5a**

Reaction time = 30 min; color of the complex = light-brown; yield = 81%; solvent = anhydrous CH_3CN; filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = yes; washing solvent = diethylether.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.21 (s, 9H, ^{t}Bu), 3.41 (s, CH_3, quinoline–CH_3), 7.54 (d, 1H, J = 8.4 Hz, H^3), 7.65–7.70 (m, 3H, Ph, H^6), 7.83–7.86 (m, 2H, Ph), 8.01 (dd, 1H, J = 7.3, 1.4 Hz, H^7), 8.05 (dd, 1H, J = 8.1, 1.4 Hz, H^5), 8.30 (d, 1H, J = 8.4 Hz, H^4).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 29.8 (CH_3, CMe_3), 33.2 (CH_3, quinoline–CH_3), 58.0 (C, CMe_3), 119.7 (CH, Ph), 124.7 (CH, C^3), 126.2 (CH, C^6), 128.1 (C, C^{10}), 128.8 (C, C^8), 131.4 (CH, C^5), 137.0 (CH, C^7), 138.3 (CH, Ph), 138.6 (CH, C^4), 144.9 (C, Ph), 149.0 (C, C^9), 150.7 (C, Ph), 166.5 (C, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1584, ν_{NOas} 1552, ν_{NOs} 1304 cm^{-1}.

Anal. Calc. for $C_{20}H_{21}IN_2O_2PdS$: C, 40.94; H, 3.61; N, 4.77. Found: C, 40.87; H, 3.74; N, 4.61%.

3.20. Synthesis of complex **5b**

Reaction time = 2 h; color of the complex = dark-yellow; yield = 81%; solvent = anhydrous CH_3CN; filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = yes; washing solvent = diethylether.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.21 (s, 9H, ^{t}Bu), 3.41 (s, CH_3, quinoline–CH_3), 7.23–7.26 (m, 2H, Ph), 7.51–7.57 (m, 3H, Ph, H^6), 7.66 (dd, 1H, J = 8.1, 7.3 Hz, H^6), 8.01 (dd, 1H, J = 7.3, 1.4 Hz, H^7), 8.04 (dd, 1H, J = 8.1, 1.4 Hz, H^5), 8.29 (d, 1H, J = 8.4 Hz, H^4).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 29.8 (CH_3, CMe_3), 33.0 (CH_3, quinoline–CH_3), 57.7 (C, CMe_3), 122.2 (qrt, $^3J_{CF}$ = 3.6 Hz, CH, Ph), 124.7 (CH, C^3), 124.8 (qrt, $^2J_{CF}$ = 31.6 Hz, C, Ph), 124.9 (qrt, $^1J_{CF}$ = 271.2 Hz, CF_3, $PhCF_3$), 126.7 (CH, C^6), 128.0 (C, C^{10}), 129.1 (C, C^8), 131.2 (CH, C^5), 136.9 (CH, C^7), 138.3 (CH, Ph), 138.5 (CH, C^4), 142.1 (C, Ph), 149.0 (C, C^9), 166.3 (C, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1587, ν_{CF} 1152 cm^{-1}.

Anal. Calc. for $C_{21}H_{21}F_3INPdS$: C, 41.36; H, 3.47; N, 2.30. Found: C, 41.51; H, 3.59; N, 2.12%.

3.21. Synthesis of complex **5c**

Reaction time = 12 h; color of the complex = orange; yield = 82%; solvent = anhydrous CH_3CN; filtration on millipore = yes; re-precipitated from CH_2Cl_2/ether = yes; washing solvent = diethylether.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 253 K, ppm) δ: 1.33 (s, 9H, ^{t}Bu), 3.11 (s, CH_3, quinoline–CH_3), 3.36 (d, 1H, J = 5.8 Hz, CH_2Pd), 4.18 (d,1H, J = 5.8 Hz, CH_2Pd), 7.03–7.14 (m, 3H, Ph), 7.23 (d, 1H, J = 8.4, H^3), 7.25 (dd, 1H, J = 8.1, 7.3 Hz, H^6), 7.65–7.75 (m, 4H, Ph, H^7, H^5), 8.01 (d, 1H, J = 8.4, H^4).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 253 K, ppm) δ: 15.8 (CH_2, CH_2Pd), 29.7 (CH_3, CMe_3), 29.8 (CH_3, quinoline–CH_3) 56.8 (C, CMe_3), 124.0 (CH, C^3), 124.5 (CH, Ph), 125.6 (CH, C^6), 127.2 (C, C^{10}), 128.1 (C, C^8), 128.2 (CH, Ph), 129.5 (CH, Ph), 131.4 (CH, C^5), 136.1 (CH, C^7), 138.0 (CH, C^4), 146.4 (C, Ph), 148.3 (C, C^9), 165.1 (C, C^2).

IR (KBr pellets): $\nu_{C=N}$ 1598 cm^{-1}.

Anal. Calc. for $C_{21}H_{24}BrNPdS$: C, 49.57; H, 4.75; N, 2.75. Found: C, 49.41; H, 4.82; N, 2.81%.

3.22. Synthesis of Complex **5d**

Reaction time = 24 h; color of the complex = dark-yellow; yield = 78%; solvent = anhydrous CH_2Cl_2; filtration = no; re-precipitated from CH_2Cl_2/ether = no; washing solvent = diethylether.

^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.39 (s, 9H, ^{t}Bu), 2.13, 2.34 (AB system, 2H, J = 12.4 Hz, CH_2CN), 3.27 (s, 3H, quinoline–CH_3), 7.51 (d, 1H, J = 8.4, H^3), 7.67 (dd, 1H, J = 8.1, 7.4 Hz, H^6), 8.01 (dd, 1H, J = 7.4, 1.3 Hz, H^7), 8.05 (dd, 1H, J = 8.1, 1.3 Hz, H^5), 8.29 (d, 1H, J = 8.4, H^4).

IR (KBr pellets): $\nu_{C=N}$ 2203, $\nu_{C=N}$ 1602 cm^{-1}.

Anal. Calc. for $C_{16}H_{19}BrN_2PdS$: C, 41.98; H, 4.18; N, 6.12. Found: C, 42.07; H, 4.22; N, 6.01%.

4. Conclusion

We have compared the reactivity of six derivatives of palladium(0) stabilized by dimethylfumarate and characterized by spectator ligands based on differently substituted quinoline fragment towards the oxidative addition of four organic halides. The reactions were carried out in CD_3CN and in some selected cases in CD_2Cl_2. All the thioquinoline derivatives and in particular the less hindered complexes display a higher reactivity than the phosphoquinoline complexes although sometimes a massive decomposition prevents any measurement. Among the organic halides p-I-$C_6H_4NO_2$ is the most reactive whereas the reaction rates is usually enhanced in CD_3CN. However, in the case of $BrCH_2CN$ the rate is faster in CD_2Cl_2 due to competition with the solvent CD_3CN. An intimate mechanism was thereby proposed and confirmed by an adequate computational study. Finally the solid state structures of two reaction products were reported.

Appendix A. Supplementary data

CCDC 1404744 and 1404745 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2015.07.049.

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