Polyhedron 144 (2018) 131–143

Contents lists available at ScienceDirect

Polyhedron

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

Synthesis of novel olefin complexes of palladium(0) bearing monodentate NHC, phosphine and isocyanide spectator ligands

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ARTICLE INFO

Article history:
Received 13 November 2017
Accepted 9 January 2018
Available online 31 January 2018

Keywords:
Olefin complexes of palladium(0)
NHC
Phosphine
Isocyanide
Kinetic study

ABSTRACT

We have synthesized and characterized seventeen new bis-NHC, mixed NHC–phosphines or NHC–isocyanides Pd(0) olefin complexes that can potentially act as catalysts. The complexes were characterized by standard spectroscopic methods and elemental analysis and in two cases by SC-XRD technique. We have analyzed with particular care the thermodynamic and kinetic conditions governing the one-pot synthesis of the mixed complexes. In this respect we tried to validate our results by a dedicated computational study on the mutual distribution of the isomers that could be potentially formed. However, the computational result is not clear-cut owing to the not significant value of the calculated ΔG_0. Finally, in one case we have measured the rate of the exchange reaction between not particularly encumbered olefins.

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1. Introduction

Owing to their stability toward heat, moisture and air and their low toxicity [1], NHC ligands have been quite recently recognized as the real alternative to phosphines in the preparation of stable palladium catalysts [2]. Since the discovery [3] and the synthesis of the first stable NHC derivatives [4] the easy tune-up of the steric hindrance of the substituents at the imidazolic nitrogen [5] has allowed their detailed synthetic planning.

In addition, owing to the easy shift between the two reasonably stable oxidation states Pd(0) and Pd(II) [6], the use of palladium derivatives as homogeneous catalysts particularly in the field of the homo- and hetero-cross coupling is widespread [7]. Obviously, the performance of the catalyst can be improved by a wise structural planning which should induce a remarkable reactivity and an adequate stability throughout the turnover processes. A possible solution overcoming these conflicting features might be the synthesis of a Pd(0) pro-catalyst characterized by an easily displaceable olefin and stabilized by strong ligands. In such a way the labile olefin should promote the oxidative addition of organic halides, thereby triggering the overall catalytic process.

The characteristics of the palladium–olefin bond is clearly crucial since it represents a balance between the thermodynamic stability of the catalyst and its reactivity which is often kinetically controlled. [8].

In this respect, we have prepared and fully characterized a number of palladium(0) olefin bis-NHC, mixed NHC-phosphines or NHC-isocyanides derivatives to be tested as catalysts in future investigations. Notably, the one-pot synthesis of complexes bearing two different spectator ligands represents a remarkable and not trivial synthetic challenge, beside allowing the fine tuning of the electronic and steric features of the derivatives which are very important in planning catalysts [9]. We already came across a similar problem in the case of Pd(II) [10] and therefore we decide to extend our investigation to Pd(0) derivatives. In the following Scheme 1 we report the olefins and the starting thiopyridine palladium and silver carbene complexes described in the present paper.

2. Results and discussion

2.1. General remarks

The complexes **1a-d** [11], **1e**, **5a** [12], **3** and **4** [13] were synthesized according to published procedures. The preparation of the imidaziolium salt 1,3-bis(4-methylbenzyl)-2,3-dihydro-1*H*-imidazole bromide and its derivative **2** will be described in Section 4.

2.2. Bis-carbene complexes

In a previous paper [14] we have reported the synthesis and characterization of some palladium (0) bis-carbene complexes stabilized by maleic anhydride. It was apparent that the steric request of the carbene ligands and the nature of the starting palladium

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https://doi.org/10.1016/j.poly.2018.01.010
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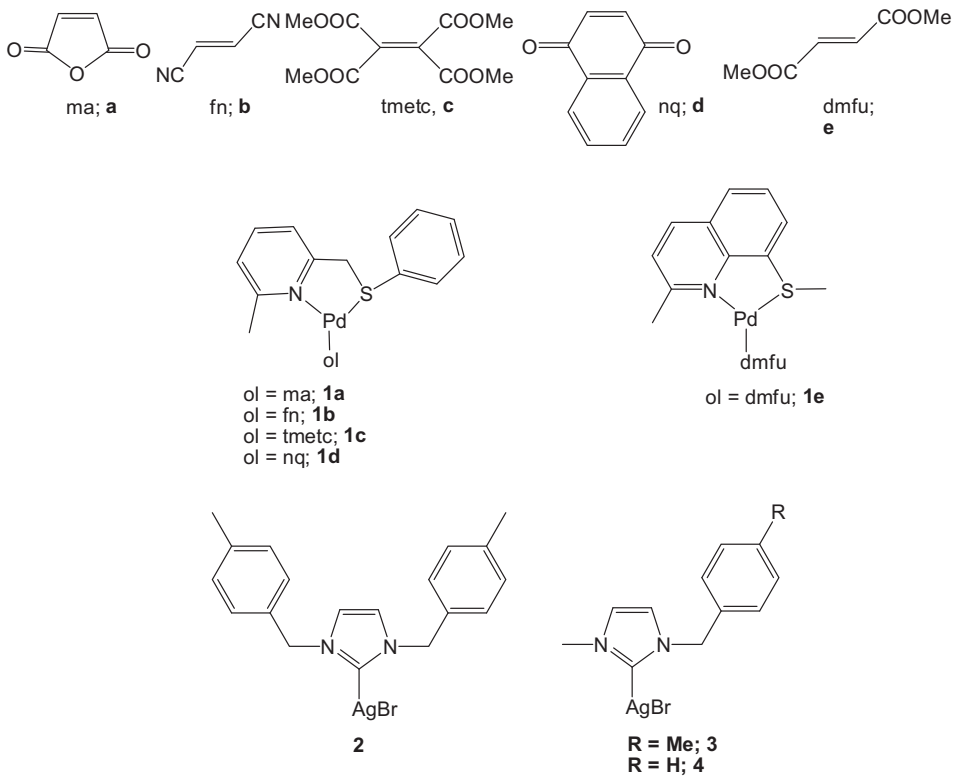


Scheme 1. Starting ligands and silver carbene complexes.

complexes did represent the critical point in the planning of the synthesis [10]. For such a reason, in order to carry out the transmetalation process, we have chosen derivative **2** (^{1}H and ^{13}C{^{1}H} NMR spectrum in Fig. S1, Supplementary Material) and the complexes **1a**–**d** as the palladium reactive species. As a matter of fact, on the basis of our experience, [14] the encumbered complex **2** could still react with derivatives **1a**–**d** characterized by the lability of the 2-methyl-6-(phenylthiomethyl)pyridine ligand to give the bis carbene species **5a**–**d** [15]. The process yielding the derivatives **5b**–**d** is fast (10 min in the case of the most hindered **5c**) and the precipitation of AgBr indicates an almost immediate reaction. The ^{1}H NMR spectra of the complexes clearly point to the coordination of the olefin whose protons resonate as a singlet thanks to the equivalence of the ancillary ligands and at higher field than those of the uncoordinated alkenes. Such a feature is also confirmed by the ^{13}C {^{1}H} NMR spectra of the complexes displaying a marked upfield singlet ($\Delta\delta$ = 70 ÷ 100 ppm) ascribable to the coordinated olefinic carbons. As for the carbene, the AB system related to the C$\underline{H_2}$N and the signals of the coordinated carbon at about 190 ppm are clearly observable. The consistent elemental analysis and the IR spectra complete the characterization of such species (see Section 4 and Fig. S2 in Supplementary Material).

2.3. Mixed complexes, general considerations

The direct synthesis of square planar complexes bearing two different monodentate spectator ligands is not always obvious. In order to obtain pure mixed species not contaminated by derivatives bearing the same two ancillary ligands it is necessary to meet a specific energetic condition. In particular the ΔG° of formation of the heteroleptic species must be reasonably lower than the ΔG° of formation of both the two species bearing the same ligands and therefore the thermodynamics of formation of the heteroleptic complex is crucial. In this respect it was suggested that such a condition can be obtained by the use of strong ligands possibly exerting an extra-stabilizing push and pull effect [9]. However, as was suggested in the case of palladium(II) derivatives, the kinetic aspect of the problem is not always negligible as can be deduced from the reactions describing the whole process [10a] summarized in Scheme 2:

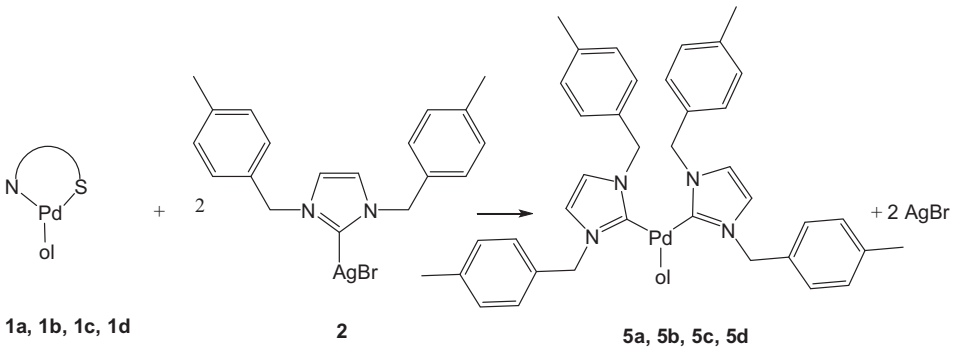
As a matter of fact, under favorable thermodynamic condition we can have different results as a function of different combinations of the rates of the reaction reported in Scheme 2.

In this respect, it is worth noting that the processes involving the complex AgBrNHC are strongly conditioned by the complex nature of the transmetalation reaction [16] and therefore reaction 1, which does not concern the transmetalation process but rather the exchange between ligands, is very probably the fastest one [10a,11a] (see Scheme 3).

Under this hypothesis we can envisage four different possibilities:

(i) Reaction 3 is faster than reaction 2. In this case we will observe the formation of the mixed complex only.
(ii) Reaction 2 is faster than reaction 3 and reaction 4 does not occur. In this case we will obtain the two bis-substituted species [L_2Pd(η^2-ol)] and [$(NHC)_2$Pd(η^2-ol)].
(iii) The rate of reaction 3 is comparable with that of reaction 2 and reaction 4 does not occur. We will obtain all the species, *i.e.* two bis-substituted and one heteroleptic species in variable concentrations.
(iv) *Reaction 4* occurs, the final species obtained will be again the mixed complex only independently of the rate of the reaction.

In order to verify whether the behavior observed in the case of Pd(II) complexes is generally valid, we tried to synthesize by direct



1a, 1b, 1c, 1d 2 5a, 5b, 5c, 5d

Scheme 2. Synthesis of the bis-carbene complexes.

$$[(\text{N-S})\text{Pd}(\eta^2\text{-ol})] + 2\text{L} \longrightarrow [\text{L}_2\text{Pd}(\eta^2\text{-ol})] + \text{N-S} \quad (1)$$

$$[(\text{N-S})\text{Pd}(\eta^2\text{-ol})] + 2\text{AgBrNHC} \longrightarrow [(\text{NHC})_2\text{Pd}(\eta^2\text{-ol})] + \text{L} + 2\text{AgBr} \quad (2)$$

$$[\text{L}_2\text{Pd}(\eta^2\text{-ol})] + \text{AgBrNHC} \longrightarrow [(\text{L})(\text{NHC})\text{Pd}(\eta^2\text{-ol})] + \text{L} + \text{AgBr} \quad (3)$$

$$[\text{L}_2\text{Pd}(\eta^2\text{-ol})] + [(\text{NHC})_2\text{Pd}(\eta^2\text{-ol})] \longrightarrow 2\,[(\text{L})(\text{NHC})\text{Pd}(\eta^2\text{-ol})] \quad (4)$$

N-S = 2-methyl-6-(phenylthiomethyl)pyridine or 2-methyl-8-(methylthio)quinoline

Scheme 3. Reactions involved in the synthesis of mixed NHC-L palladium olefin complexes.

mixing of the reactants some palladium(0) olefin species stabilized by carbene–phosphine or carbene–isocyanide ligands (see Scheme 4).

2.3.1. Mixed triphenyl phosphine–NHC complexes

In this case we have promptly and exclusively obtained the mixed carbene–phosphine palladium olefin derivatives **6a–e**, **9c** and **11c** as a consequence of the concomitant addition of the reactants to the complexes **1a–e**. Therefore, in the light of the above reported considerations we can safely suggest that reactions 1 and 3 are faster than reactions 2 and 4. As for the rate of reaction 4 it is noteworthy that the mixing of the two homogeneously bis-substituted complexes does not yield the mixed derivatives in reasonable time (see Scheme 2).

Since it is not possible to synthesize the dimethylfumarate derivative stabilized by the ligand 2-methyl-6-(phenylthiomethyl)pyridine as starting material [8], in order to extend the range of the coordinated olefins to the labile dimethylfumarate, we have obtained the complex **6e** starting from the complex **1e** which bears the ligand 2-methyl-8-(methylthio)quinoline as spectator [17] (see Scheme 5).

In all cases, the almost immediate precipitation of AgBr indicated that transmetalation had occurred whereas a single peak within 27 ÷ 32 ppm (as a function of the olefin) in the $^{31}P\{^1H\}$ NMR testified the coordination of the phosphine. However, the structural features of these complexes are clearly shown by their ^1H and $^{13}C\{^1H\}$NMR spectra. Thus, all the signals belonging to the carbene are at different chemical shifts with respect to those of the starting silver complex and in particular the diastereotopic Tol-C$\underline{H}_2$-N protons resonate as an AB system or a couple of doublets. Similarly to type **5** complexes the signal of the two olefin protons of complexes **6** shifts downfield ($\Delta\delta \sim 3$–4 ppm) with respect to those of the uncoordinated olefins. Remarkably both protons couple with phosphorus. In particular the proton *trans* to phosphine is characterized by a higher coupling constant. The $^{13}C\{^1H\}$NMR spectra confirm the structures of the complexes synthesized and in particular the carbon resonating at ca. 190 ppm as a doublet owing to the proximity of the phosphorus proves the carbene coordination (see Fig. S3 Supplementary Material) (see Scheme 6).

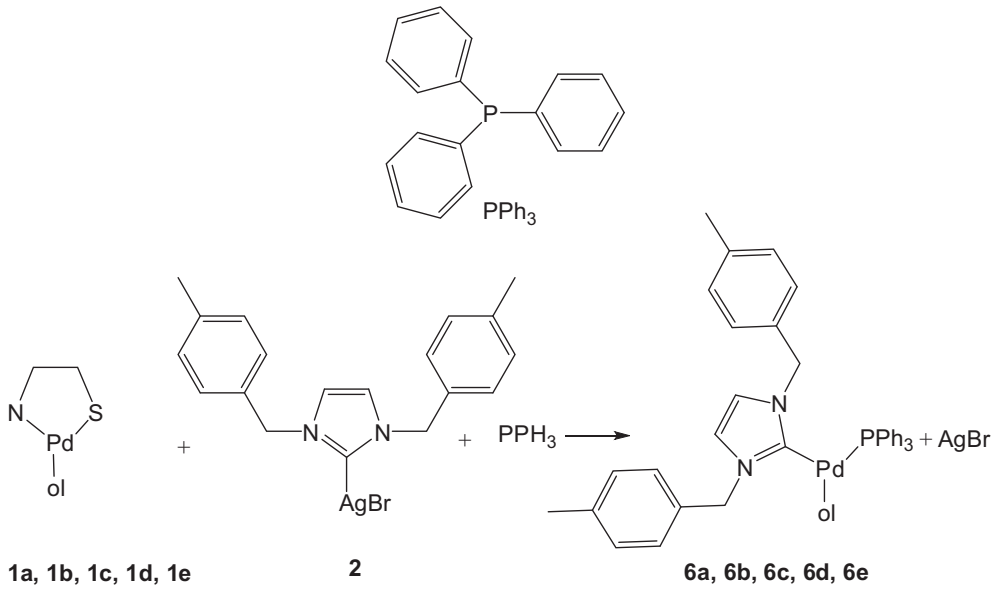
Notably, in the ^1H NMR spectra at temperatures dictated by the nature of the complex under study, the doubling of the signals of the carbenic protons is observed. This fact can be traced back to the freezing of rotation about the Pd-C bond of the carbenic ligand which usually coordinates perpendicularly to the main plane of the complex. The frozen position of the carbene entails the duplication of the signals attributable to the mutual position of the carbenic and olefinic protons above and below the plane of the complex (see Fig. 1 and Fig. S3a,b Supplementary Material).

Not surprisingly, the freezing temperature of the complexes strongly depends on the steric request of the olefin and the presence of the bulky triphenylphosphine. Thus, complex **6d** characterized by the encumbering naphthoquinone freezes at RT whereas a significantly lower temperature is necessary for the less sterically demanding derivatives.

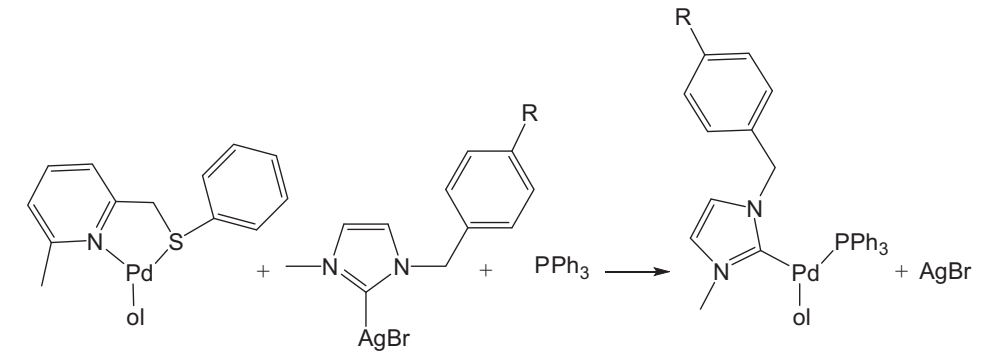
Finally, we have been able to determine the solid state structure of a typical sample of this class of complexes with suitable crystals obtained by the slow freezing of a CH_2Cl_2-diethylether solution of complex **6d**. An ORTEP [18] view of the Pd(0) complexes **6d** is reported in Fig 2. A selection of bond distances and angles is given in Table SM1 (Supplementary Material).

The geometry around the Pd center is formally square planar and can be considered as trigonal planar if one takes the mid-point of the C=C alkene double bond as the third coordination position.

In the complex **6d** the palladium is bonded to the carbene carbon of a symmetrically substituted NHC ligand, the phosphorus of the triphenylphosphine group and μ^2-coordinated to the C20–C21

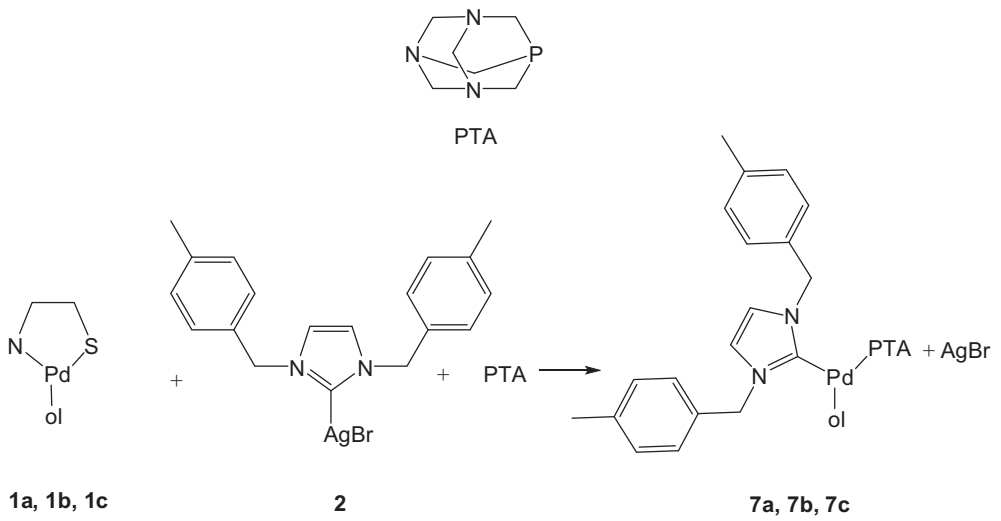


1a, 1b, 1c, 1d, 1e **2** **6a, 6b, 6c, 6d, 6e**



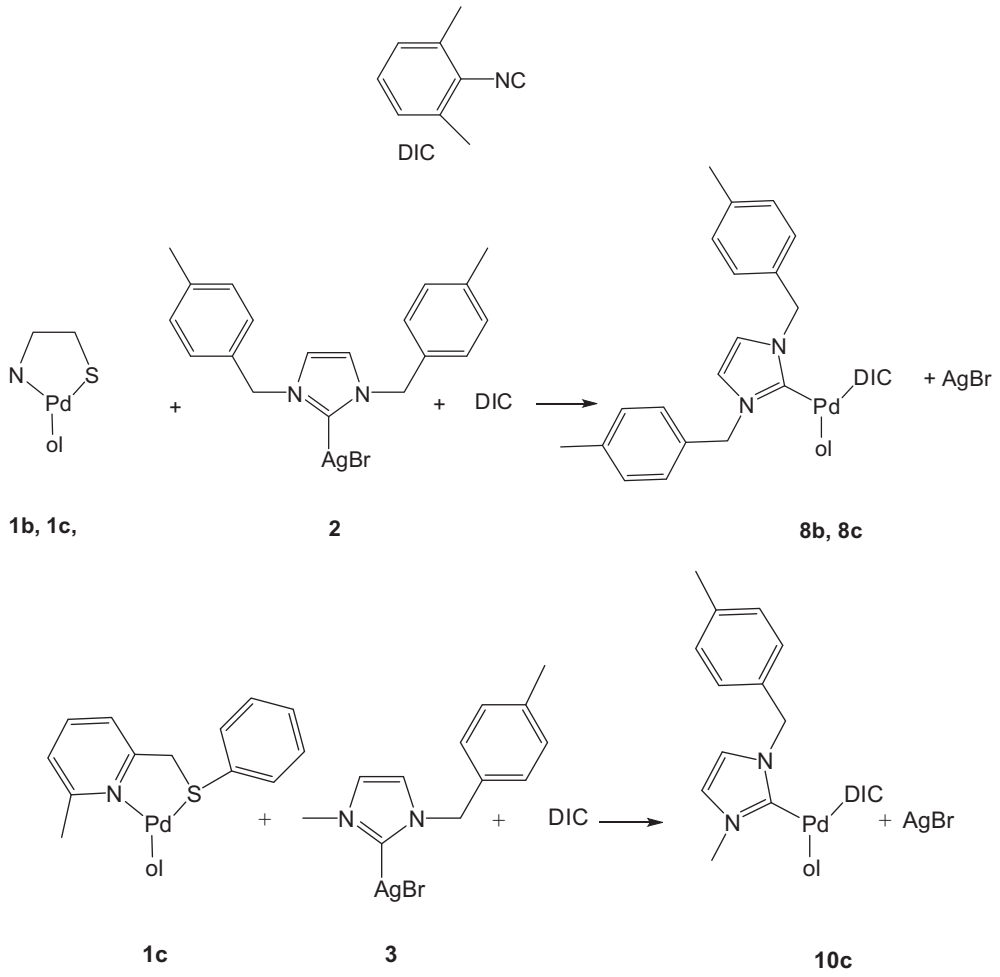
1c **R = Me; 3**
R = H; 4
R = Me; 9c
R = H, 11c

Scheme 4. Synthesis of the mixed NHC-PPH_3 palladium olefin complexes.



1a, 1b, 1c **2** **7a, 7b, 7c**

Scheme 5. Synthesis of the mixed NHC-PTA palladium olefin complexes.



Scheme 6. Synthesis of the mixed NHC-DIC palladium olefin complexes.

double bond of the naphthalene-1,4-dione ligand. The C20═C21 double bond is lengthened to 1.435(3) Å. The mean plane of the naphthalene-1,4-dione is almost perpendicular to the mean coordination plane forming a dihedral angle of 88.68(4)°.

2.3.2. Mixed PTA–NHC complexes

In order to generalize and confirm the feasibility of the one-pot synthesis of mixed carbene–phosphine complexes we have carried out the preparation of palladium(0) olefin complexes bearing one carbene and the phosphine 1,3,5-triaza-7-phospha-adamantane (PTA). Notably, PTA is a water soluble moiety and often its derivatives with the same feature have been used as green catalysts [19]. The synthetic protocol used with the mixed triphenyl phosphine–NHC complexes described above gives super imposable results with complexes **1a-c** whereas the reaction of complexes **1d**–**1e** is characterized by general decomposition. The NMR spectra witness the exclusive formation of the title derivatives and in particular the $^{31}P\{^{1}H\}$ NMR spectra show a singlet in the interval −57 ÷ −62 ppm at ca. 40 ppm downfield of the uncoordinated phosphine. The resonances of the NC$\underline{H}_2$N and NC$\underline{H}_2$P groups of the PTA in the ^{1}H NMR and in general all the signals of the carbene moiety are also characteristic of the coordinated phosphine and carbene which moreover display an AB system related to the diastereotopic Tol-C$\underline{H}_2$N fragments. Remarkably, owing to the reduced bulkiness of PTA with respect of PPh_3 no duplication of such signals is observed, indicating that the fluxionality of the systems cannot be frozen at any feasible temperature. Again, the carbenic carbon resonates in the interval of 187 ÷ 188 ppm as a doublet and the ABX signals of the olefin are observed at lower field than those of the free alkenes (see Fig. S4 Supplementary Material).

2.3.3. Mixed DIC–NHC palladium olefin complexes

According to the hypothesis surmised so far [9] we have also tried to verify the feasibility of the one-pot synthesis of mixed isocyanide–carbene palladium(0) olefin complexes. Thus, we have reacted the derivatives **1a–c** with 2-isocyano-1,3-dimethylbenzene (DIC) and the complexes **2** or **3**. In the case of the reaction of complexes **1a** and **1d** we observed a general decomposition whereas complexes **1b** and **1c** give the mixed DIC-NHC derivatives **8b**, **8c** and **10c**. However, in the case of the reaction of **1b** with an equimolar mixture of DIC and **2**, beside the complex **8b** we noticed the formation of ca. 4% of both the bis-isocyanide species [Pd(η^2-fn)(DIC)$_2$] and **5b** ([Pd(η^2-fn)(NHC)$_2$]). We will discuss this peculiar case in the computational study section. As can be seen in Fig. 3 (See also Fig. S5 in Supplementary material) the structural features of the mixed complexes clearly emerge from the NMR data of the synthesized complex. In particular, the methyl groups of the isocyanide at ca. 2.2 ppm and the AB system of the diastereotopic C$\underline{H}_2$N are apparent in the ^{1}H NMR spectra.

Moreover, the $^{13}C\{^{1}H\}$NMR spectra display weak signals of the coordinated isocyanide and the carbenic carbon at ca. 157 and 187 ppm, which respectively complete the identification of the reaction products. The slow freezing of a CH_2Cl_2–diethylether solution of complex **8b** gave us the opportunity of determining also the solid

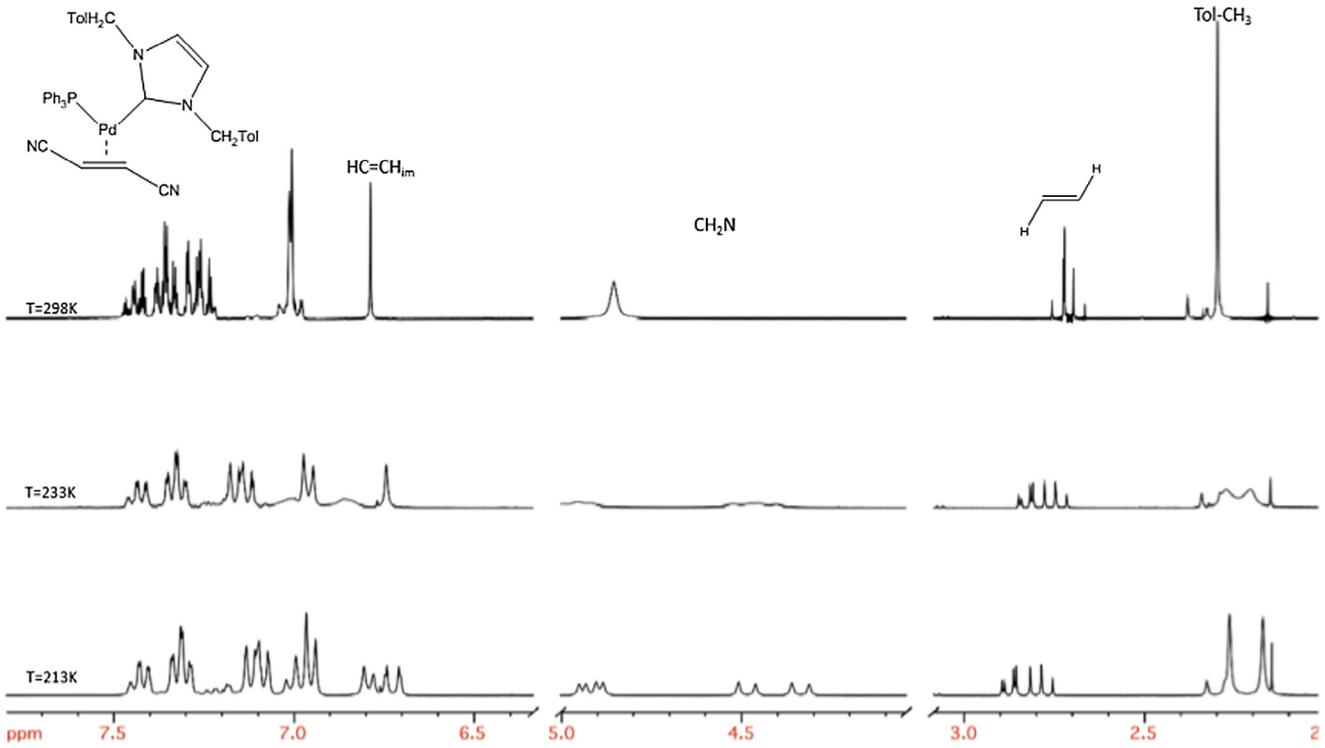


Fig. 1. ^{1}H NMR spectra of complex **6b** in CD_2Cl_2 at different temperatures.

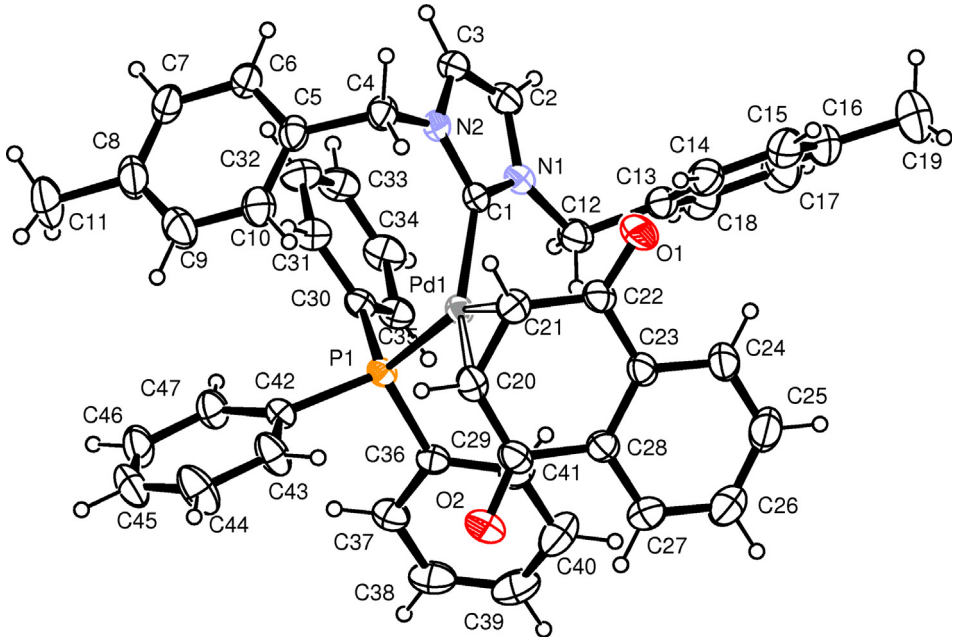


Fig. 2. ORTEP view of cationic complex **6d** showing the thermal ellipsoids at 30% probability level.

state structure of an example of these mixed compounds. Also in this case the geometry around the Pd center is formally square planar and can be considered as trigonal planar if one takes the midpoint of the C=C alkene double bond as the third coordination position. In complex **8b** the palladium is bonded to a symmetrically bis-substituted NHC ligand through the carbene carbon, to the isocyanide carbon of the (2,6-dimethyl-phenyl)-isocyanide ligand and the μ^2-coordinated C20—C21 carbons of the carbene group of 2(*E*)-but-2-ene-dinitrile ligand, thanks to the C=C alkene group. The mean molecular plane of this ligand is rotated by 87.0 (5)° with respect to the Pd coordination plane. The C22—C21—C20—C23 carbon chain is slightly twisted by a torsion angle of −145.4(2)° and the C20=C21 double bond is lengthened to 1.441(3) Å (Fig. 4).

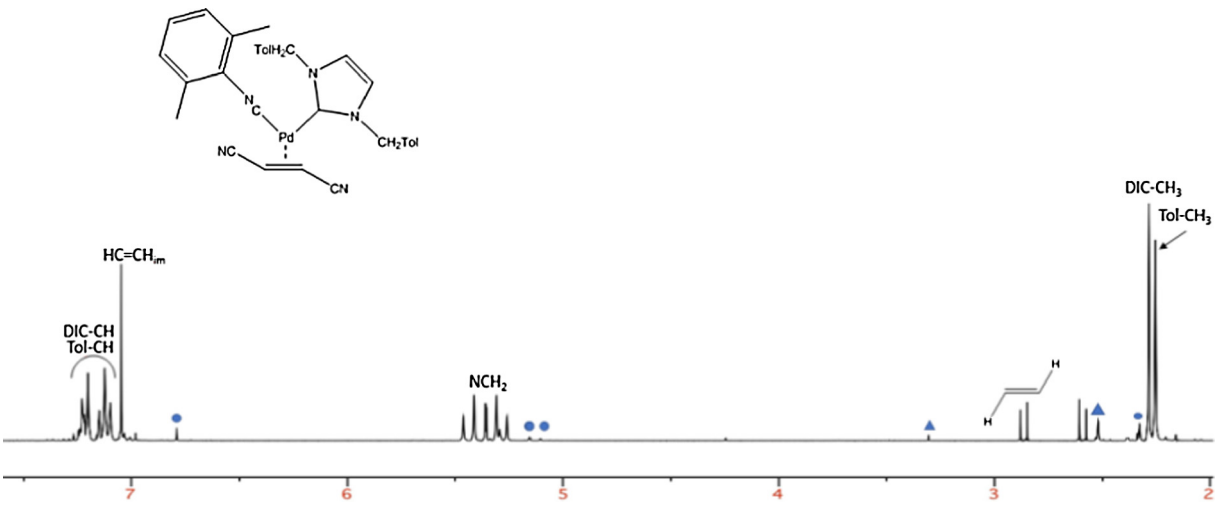


Fig. 3. ^{1}H NMR spectrum of complex **8b** in CD_2Cl_2 at 298 K. ▲ [Pd(η^2–fn)(DIC)$_2$]. ● **5b**: ([Pd(η^2–fn)(NHC)$_2$]).

2.4. Computational study

On the basis of theoretical calculations performed with the Gaussian 09 package [20] (see Section 4 for computational details) we were able to calculate the ΔG_0 values related to the reaction 4 in Scheme 2 with L = PPh_3 and DIC, respectively. The ΔG_0 value was 2.64 (L = PPh_3) and 2.44 kcal/mol (L = DIC)). The positive calculated ΔG_0s, both indicate an unfavourable reaction progress since the formation of the mixed species is about 5 or 6% of the initial concentration of the starting homogeneously bis-substituted species assumed equimolecular (see Eq. (4) in Scheme 2). However, owing to the uncertainty affecting this sort of calculation (almost equivalent in extent to the calculated ΔG_0 values ±2 kcal/mol), no definitive conclusions can be drawn. We can only surmise that when a strong competition among π-electron accepting ligands on palladium(0) complexes (DIC isocyanide and fumaronitrile) a complex distribution among the possible species is probable and possible.

2.5. Kinetic study

In order to assess and confirm the mutual stability between palladium (0) olefin complexes we decided to study kinetically the reaction reported in Scheme 7:

Owing to the unusually slow reaction rate (this sort of reactions entailing the exchange between napthoquinone and maleic anhydride are almost always very fast [11]) we have carried out our investigation by UV–Vis spectrophotometric technique. In our case complex **6d** shows an acceptable solubility and its absorbance principally ascribable to the napthoquinone chromophore provides an adequate absorbance change for the reaction in Scheme 7. Therefore, this study represents the first case of a slow reaction rate involving the exchange between the not particularly hindered olefins maleic anhydride and napthoquinone.

As shown elsewhere by the direct determination of the equilibrium constants by direct titration of the napthoquinone derivatives with maleic anhydride, the latter is a better coordinating moiety toward Pd(0) than napthoquinone. Although their mutual stability (measured as Ke = [maleic anhydride complex][napthoquinone]/[napthoquinone complex][maleic anhydride]) is strongly affected by the nature of the spectator ligands, spanning between 4.5 and 630, [8,21], a favorable concentration ratio between complex **6d** and maleic anhydride (in this case [ma]/[**5d**] ≥ 10) usually ensures the complete displacement of napthoquinone. Moreover, under the adopted experimental conditions the observed changes of absorbance *versus* time obey the monoexponential equation:

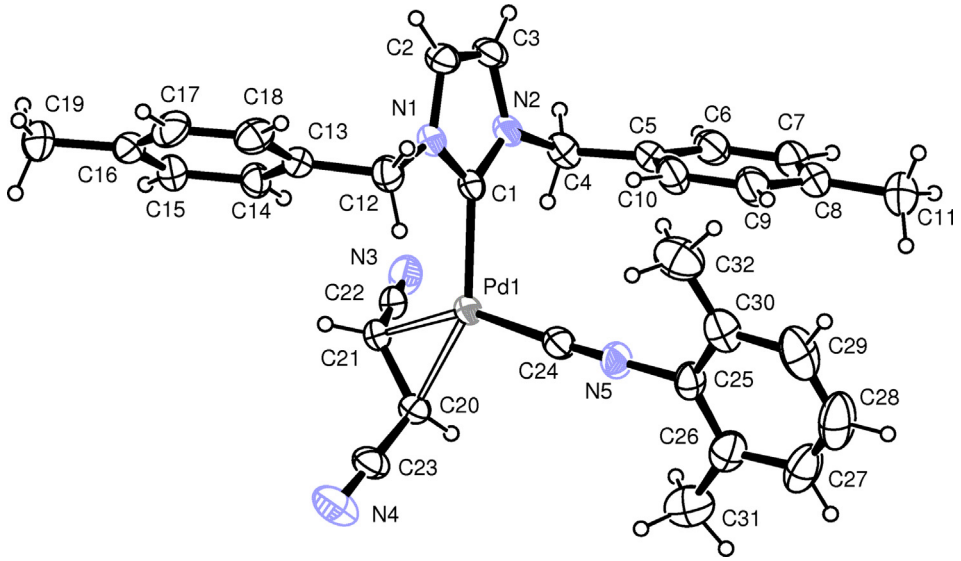
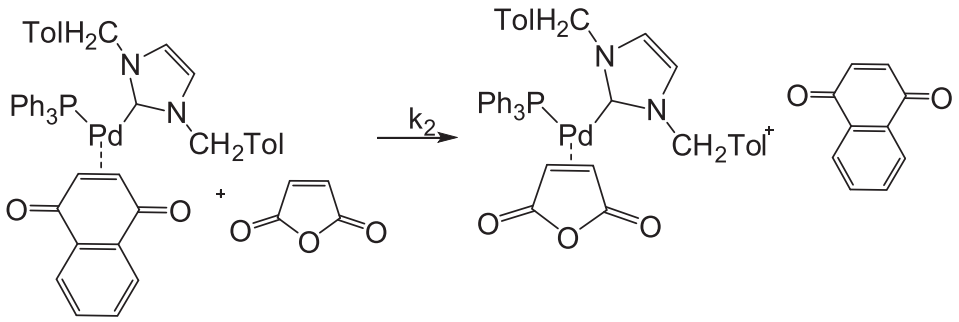


Fig. 4. ORTEP view of cationic complex **8b** showing the thermal ellipsoids at 30% probability level.



Scheme 7. Reaction studied under kinetic conditions.

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

where A_0, A_∞ and A_t represent the initial, the final and absorbance at time t, respectively (Fig. 5).

The monoexponential dependence testifies that the return reaction (with a second order dependence on the displaced napthoquinone concentration) is negligible and that the whole process can be described by the relationship:

$$-d[\mathbf{5d}]/dt = k_2[\mathbf{5d}][ma];\ k_2[ma] = k_{obs}$$

The final spectra of the reactions investigated under the mentioned experimental conditions are coincident with those of the authentic product or mixture of products independently prepared. The calculated k_{obs} represents the pseudo first order rate constant and depends linearly on the concentration of maleic anhydride (Fig. 6).

Linear regression of k_{obs} *versus* [ma] yields the second order rate constant k_2 ($k_2 = 117 \pm 3$ mol^{-2} dm^3 s^{-1}) which is ascribable to a typical associative mechanism involving the formation of a bis-olefinic 18-electron activated state. The adopted methodology is described in details in Section 4 whereas the changes of absorbance at different wavelengths *versus* time, one example of the monoexponential fit of absorbance *versus* time at a fixed wavelength and the linear regression of k_{obs} *versus* [maleic anhydride] are reported in Fig. S6 of Supplementary Material whereas.

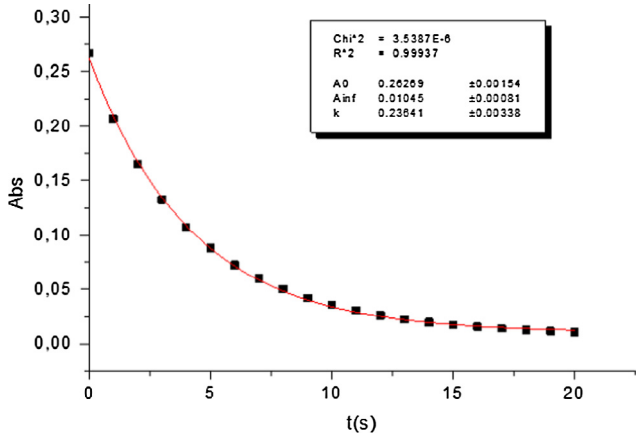


Fig. 5. Absorbance *vs.* time and non linear regression analysis ($\lambda = 416$ nm, $T = 298$ in $CHCl_3$; reaction: **6d** + ma → **6a** + nq; [6d] = 8×10^{-5} mol dm^{-3}, [ma] = 2×10^{-3} mol dm^{-3}).

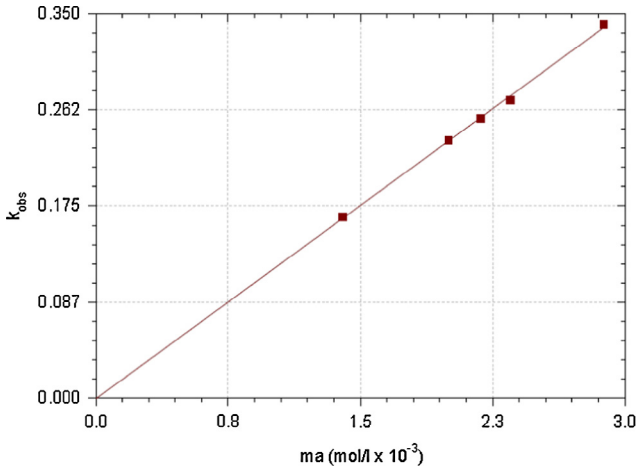


Fig. 6. Linear regression analysis of k_{obs} (s^{-1}) *vs.* [ma] ($\lambda = 416$ nm, $T = 298$ in $CHCl_3$; reaction: **6d** + ma → **6a** + nq).

3. Conclusion

We have synthesized and characterized some novel palladium (0) olefin complexes bearing two NHC as spectator ligands. We have also prepared mixed heteroleptic olefin derivatives bearing NHC and PPh_3, PTA or DIC co-ligands. We have studied the olefin exchange between the coordinated napthoquinone of complex **6d** and maleic anhydride to give **6a**. The second-order rate constant was determined by linear regression of the *pseudo*-first order rate constants measured by UV–Vis spectrophotometry carried out in $CHCl_3$ at 298 K. Such an experimental technique is unusual when the very fast olefin exchange reactions in Pd(0) complexes are studied. In the present case, however, thanks to the steric retard induced by the bulky substituents it was possible to follow the reaction progress. At the best of our knowledge this adds a further item to the few available [11a,21]. Finally, we have carried out the SC-XRD of the complexes **6d** and **8b**.

4. Experimental

4.1. Solvents and reagents

The solvents CH_2Cl_2 and CH_3CN were distilled over CaH_2, acetone was refluxed over **4a** molecular sieves and distilled. All other solvents and chemicals were commercial grade products and used as purchased.

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

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. The UV–Vis spectra were recorded on a l-40 PE spectrofotometer equipped with a Peltier thermostat apparatus.

The elemental analysis of the synthesized complexes was carried out using an Elementar CHN "CUBO micro Vario" analyzer.

4.3. Kinetic measurements

The reaction between complex **6d** and maleic anhydride was at first studied by ^{1}H NMR by dissolving the complex under study in 0.6 ml of $CDCl_3$ ($[Complex]_0 \approx 1.2 \times 10^{-2}$ mol dm^{-3}), adding a microaliquot of a concentrated $CDCl_3$ solution of maleic anhydride ($[ma] \approx 1.1 \times 10^{-1}$ mol dm^{-3}) and monitoring the signal for the disappearance of the starting complex. The reaction was then studied by UV–Vis spectrophotometry by mixing freshly prepared $CHCl_3$ solutions of complex **6d** ($[\mathbf{6d}] = 8 \times 10^{-5}$ mol dm^{-3}) and microaliquots of concentrated solution of maleic anhydride ([ma] = at least 8×10^{-4} mol dm^{-3}) and recording the absorbance changes as a function of time in the 280–560 wavelength interval and at an optimized wavelength.

4.4. Data analysis

Non linear regression analysis of the data related to kinetics measurements was performed by locally adapted routines written in the ORIGIN® 7.5 environment.

4.5. Computational details

Theoretical calculations were performed with the gaussian 09 [20] package using the functional hybrid meta-GGA M06 [22] and the Def2-TZVP basis set [23]. Geometry optimization was performed without any symmetry constraint, followed by analytical frequency calculation to confirm that a minimum had been reached. Solvent effects (CH_2Cl_2, $\varepsilon = 9.93$) were included using CPCM [24].

4.6. Crystal structure determinations

The crystal data of compounds **6d** and **8b** 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 [25] and corrected for Lorentz, polarization and absorption effects (SORTAV) [26]. The structures were solved by direct methods using SIR97 [27] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms.

All calculations were performed using SHELXL-2014/6 [28] and PARST [29] implemented in WINGX [30] system of programs. A selection of bond distances and angles is given in Table SM1 and the crystal data are given in Table SM2 (Supplementary Material).

4.7. Syntesis of the precursors

4.7.1. Synthesis of the 1,3-bis(4-methylbenzyl)-2,3-dihydro-1H-imidazole bromide ligand

3.647 g (0.021 mol) of 1-(4-methylbenzyl)-1*H*-imidazole were dissolved in 50 ml of anhydrous acetonitrile under inert atmosphere (Ar) in a two necked flask. 3.5 g (0.034 mol) of NaBr and 3 ml (0.023 mol) of 1-chloromethyl-4-methylbenzene were successively added to the solution and the resulting mixture was stirred under reflux for 36 h. The unreacted salts were filtered off on a gooch and repeatedly washed with CH_2Cl_2 and the clear solution evaporated under vacuum to small volume. The addition of diethylether to the concentrated solution induces the precipitation of the title product which was repeatedly washed with diethylether and dried under vacuum. 6.62 g (yield 88%) of the imidazolium salt as a white microcrystalline powder were obtained.

^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ: 2.33 (s, 6H, tol-CH_3), 5.50 (s, 4H, N-CH_2), 7.15 (d, $J = 1.6$ Hz, 2H, CH = CH Im), 7,17–7.20 (m, 4H, Ph), 7,33–7.36 (m, 4H, Ph), 10.98 (bt, 1H, NCHN).

$^{13}C\{^{1}H\}$NMR ($CDCl_3$, $T = 298$ K, ppm) δ: 21.1 (CH_3, Ph-CH_3), 53.3 (CH_2, NCH_2), 121.4 (CH, CH = CH Im), 129.0 (CH, Ph *o*-C), 129.5 (C, Ph *i*-C), 130.0 (CH, Ph *m*-C), 139.6 (C, Ph *p*-C), 137.2 (CH, NCHN).

IR (KBr): $\nu_{C=N} = 1557$ cm^{-1}.

Anal. Calc. for $C_{19}H_{21}BrN_2$: C, 63.87; H, 5.92; N, 7.84. Found: C, 63.73; H, 5.81; N, 7.99.

4.7.2. Synthesis of the silver complex 2

To 0.4 g (1.12×10^{-3} mol) of 1,3-bis(4-methylbenzyl)-2,3-dihydro-1*H*-imidazole bromide, dissolved in 30 ml of anhydrous CH_2Cl_2, 0.156 g (6.72×10^{-4} mol) of Ag_2O was added under inert atmosphere (Ar). The resulting mixture was stirred in the dark for 24 h, filtered by means of a millipore apparatus and eventually reduced under vacuum to small volume. Slow addition of diethylether induces the precipitation of a white solid which was repeatedly washed with diethylether and pentane and dried under vacuum. 0.489 g (94% yield) of the title complex was obtained.

^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ: 2.35 (s, 6H, tol-CH_3), 5.25 (s, 4H, N-CH_2), 6.90 (s, 2H, CH = CH Im), 7,16–7.17 (m, 8H, tol-H).

$^{13}C\{^{1}H\}$NMR ($CDCl_3$, $T = 298$ K, ppm) δ: 21.1 (CH_3, Ph-CH_3), 55.5 (CH_2, NCH_2), 121.2 (CH, CH = CH Im), 127.8 (CH, tol *o*-C), 129.7 (CH, tol *m*-C), 132.3 (C, tol *i*-C), 138.5 (C, tol *p*-C), 180.8 (C, NCN).

Anal. Calc. for $C_{19}H_{20}AgBrN_2$: C, 49.17; H, 4.34; N, 6.04. Found: C, 49.22; H, 4.47; N, 5.96.

4.8. Synthesis of bis–NHC complexes

4.8.1. Synthesis of complex 5b

To 0.0724 g (1.808×10^{-4} mol) of complex **1b** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.1678 g (3.616×10^{-4} mol) of **2** dissolved in 5 ml of anhydrous CH_2Cl_2 was added under inert atmosphere (Ar). The mixture was stirred for 15 m and then the AgBr was filtered off with a millipore apparatus. The clear solution was evaporated to dryness and the residue treated with diethylether The precipitate was filtered off on a gooch and washed several times with diethylether and pentane and dried under vacuum. 0.1108 g (83% yield) of the title compound was obtained as a white powder.

^{1}H NMR (CD_2Cl_2, $T = 298$ K, ppm) δ: 2.32 (s, 12H, tol-CH_3), 2.33 (s, 2H, CH = CH), 5.12, 5.30 (AB system, $J = 14.7$ Hz, 8H, N-CH_2), 6.79 (s, 4H, CH = CH Im), 7.00–7.12 (m, 16H, tol-H). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, $T = 298$ K, ppm) δ: 13.9 (CH, CH = CH), 20.8 (CH_3, tol-CH_3), 54.2 (CH_2, NCH_2), 120.9 (CH, CH = CH Im), 123.8 (C, CN), 127.6 (CH, tol *o*-C), 129.3 (CH, tol *m*-C), 133.8 (C, tol *i*-C), 137.7 (C, tol *p*-C), 190.3 (C, NCN).

IR (KBr): $\nu_{CN} = 2190$ cm^{-1}.

Anal. Calc. for $C_{42}H_{42}N_6Pd$: C, 68.42; H, 5.74; N, 11.40. Found: C, 68.57; H, 5.71; N, 11.27.

Derivatives **5c** and **5d** were prepared in a similar way using the appropriate reactants.

4.8.2. Synthesis of complex 5c

Whitish microcrystals; Yield 94%.

^{1}H NMR ($CDCl_3$, $T = 298$ K, ppm) δ: 2.33 (s, 3H, tolyl-CH_3), 3.47 (s, 12H, OCH_3), 5.27 (s, 4H, N-CH_2), 6.58 (s, 2H, CH = CH Im), 6.87–6.90 (m, 2H, tolyl *m*-H), 7.06–7.09 (m, 2H, tolyl *o*-H). ^{13}C

{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.5 (CH_3, Ph-CH_3), 51.9 (CH_3, OCH_3), 54.2 (CH_2, NCH_2), 120.9 (CH, CH = CH Im), 128.2 (CH, tolyl *o*-C), 129.6 (CH, tolyl *m*-C), 134.3 (C, tolyl *i*-C), 137.7 (C, tolyl *p*-C), 172.1 (C,CO), 188.7 (C, NCN). IR (KBr): $\nu_{C=O}$ = 1686, 1706 cm^{-1}.

Anal. Calc. for $C_{48}H_{52}N_4O_8Pd$: C, 62.71; H, 5.70; N, 6.09. Found: C, 62.57; H, 5.78; N, 5.96.

4.8.3. Synthesis of complex **5d**

Orange microcrystals; Yield 68%.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.34 (s, 12H, tol-CH_3), 4.66 (s, 2H, CH = CH), 5.00, 4.96 (AB system, J = 14.8 Hz, 8H, N-CH_2), 6.64 (s, 4H, CH = CH Im), 6.88–7.11 (m, 16H, tol-H), 7.37–7.40 (m, 2H, nq-H), 7.94–7.97 (m, 2H, nq-H), ^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.8 (CH_3, tol-CH_3), 54.4 (CH_2, NCH_2), 60.4 (CH, CH = CH), 120.9 (CH, CH = CH Im), 124.6 (CH, nq-CH), 127.7 (CH, tol *o*-C), 129.2 (CH, tol *m*-C), 129.5 (CH, nq-CH), 129.9 (C, nq-CH), 133.4 (C, tol *i*-C), 137.6 (C, tol *p*-C), 137.7 (C, nq-CH), 181.8 (C, CO), 188.8 (C, NCN).

IR (KBr): $\nu_{C=O}$ = 1619 cm^{-1}.

Anal. Calc. for $C_{48}H_{46}N_4O_2Pd$: C, 70.54; H, 5.67; N, 6.85. Found: C, 70.41; H, 5.73; N, 6.89.

4.9. Mixed triphenyl phosphine–NHC complexes

4.9.1. Synthesis of complex **6a**

To 0.080 g (1.906×10^{-4} mol) of complex **1a** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.0885 g (1.906×10^{-4} mol) of **2** and 0.050 g (1.906×10^{-4}) of PPh_3 dissolved together in 5 ml of anhydrous CH_2Cl_2 were added under inert atmosphere (Ar). The mixture was stirred for 15 m and then AgBr was filtered off with a millipore apparatus. The clear solution was evaporated to small volume under vacuum and treated with diethylether. The pale yellow precipitate was filtered off in a gooch and washed with diethylether and pentane and dried under vacuum. 0.1217 g (86% yield) of the title compound was obtained.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.27 (s, 6H, tol-CH_3), 3.80 (dd, J_{HH} = 3.9 Hz, J_{HP} = 2.8 Hz, 1H, CH = CH *trans*-C), 4.03 (dd, J_{HP} = 10.3 Hz, J_{HH} = 3.9 Hz, 1H, CH = CH *trans*-P), 4.50 (bs, 2H, N-CH_2), 4.88 (bd, 2H, N-CH_2), 6.68 (s, 2H, CH = CH Im), 6.89–6.94 (bm, 8H, tol-H), 7.11–7.42 (m, 15H, PPh_3).

^{1}H NMR (CD_2Cl_2, T = 213 K, ppm) δ: 2.17 (s, 3H, tol-CH_3), 2.44 (s, 3H, tol-CH_3), 3.88 (dd, J_{HH} = 3.9 Hz, J_{HP} = 2.8 Hz, 1H, CH = CH *trans*-C), 4.03 (dd, J_{HP} = 10.3 Hz, J_{HH} = 3.9 Hz, 1H, CH = CH *trans*-P), 4.04 (d, J = 14.4 Hz, 1H, N-CH_2), 4.53 (d, J = 14.2 Hz, 1H, N-CH_2), 4.70 (d, J = 14.4 Hz, 1H, N-CH_2), 4.86 (d, J = 14.2 Hz, 1H, N-CH_2), 6.70 (d, J = 1.7 Hz, 1H, CH = CH Im), 6.74 (d, J = 1.7 Hz, 1H, CH = CH Im), 6.76–6.86 (m, 4H, tol-H), 6.97–7.45 (m, 19H, tol-H PPh_3).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.7 (CH_3, tol-CH_3), 45.2 (CH, CH = CH *trans*-C), 47.0 (d, CH, J_{CP} = 30.0 Hz, CH = CH *trans*-P), 54.3 (CH_2, NCH_2), 121.0 (CH, CH = CH Im), 128.4 (CH, tol *o*-C), 129.7 (CH, tol *m*-C), 133.5 (C, tol *i*-C), 172.5 (C, CO trans-C), 172.6 (C, d, J_{CP} = 5.4. Hz, CO *trans*-P), 188.2 (C, d, J_{CP} = 14.4 Hz, NCN). ^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 29.9.

IR (KBr): $\nu_{C=O}$ = 1717, 1784 cm^{-1}.

Anal. Calc. for $C_{41}H_{37}N_2O_3PPd$: C, 66.18; H, 5.15; N, 3.76. Found: C, 66.03; H, 5.22; N, 3.65.

Derivatives **6b-d**, were prepared in a similar way using the appropriate reactants.

4.9.2. Synthesis of complex **6b**

Yellow microcrystals; Yield 83%.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.29 (s, 6H, tol-CH_3), 2.66–2.76 (m, 4.25, 2H, CH = CH, *trans*-C and *trans*-P), 4.84 (bs, 4H, N-CH_2), 6.78 (s, 2H, CH = CH Im), 6.97–7.03 (m, 8H, tol-H), 7.21–7.46 (m, 15H, PPh_3).

^{1}H NMR (CD_2Cl_2, T = 213 K, ppm) δ: 2.17 (s, 3H, tol-CH_3), 2.27 (s, 3H, tol-CH_3),), 2.79 (ABX system (A), J_{HP} = 12.7 Hz, J_{HH} = 12.5 Hz, 1H, CH = CH *trans*-P), 2.87 (ABX system (B), J_{HH} = 12.7 Hz, J_{HP} = 2.7 Hz, 1H, CH = CH *trans*-C), 4.34 (d, J = 14.4 Hz, 1H, N-CH_2), 4.48 (d, J = 14.1 Hz, 1H, N-CH_2), 4.91 (d, J = 14.4 Hz, 1H, N-CH_2), 4.93 (d, J = 14.1 Hz, 1H, N-CH_2), 6.71 (d, J = 1.6 Hz, 1H, CH = CH Im), 6.74 (d, J = 1.6 Hz, 1H, CH = CH Im), 6.79 (d, J = 7.8 Hz, 2H, tol-H), 6.95 (d, J = 7.8 Hz, 2H, tol-H), 6.94–7.02 (b AB system, 4H, tol-H), 7.07–7.46 (m, 15H, PPh_3).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.8 (CH_3, tol-CH_3), 21.3 (d, CH, J_{CP} = 3.0 Hz, CH = CH *trans*-C), 22.3 (d, CH, J_{CP} = 40.7 Hz, CH = CH *trans*-P), 54.3 (CH_2, NCH_2), 120.9 (CH, CH = CH Im), 123.7 (C, CN *trans*-C), 123.7 (d, C, J_{CP} = 7.6 Hz, CN *trans*-P), 128.4 (CH, tol *o*-C), 129.3 (CH, tol *m*-C), 133.1 (C, tol *i*-C), 137.9 (C, tol *p*-C), 188.5 (C, d, J_{CP} = 12.0 Hz, NCN). ^{31}P{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 27.5.

IR (KBr): ν_{CN} = 2196 cm^{-1}.

Anal. Calc. for $C_{41}H_{37}N_4PPd$: C, 68.00; H, 5.29; N, 7.74. Found: C, 68.12; H, 5.33; N, 7.65.

4.9.3. Synthesis of complex **6c**

White microcrystals; Yield 98%.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.26 (s, 6H, tol-CH_3), 3.30 (s, 6H, OCH_3), 3.55 (s, 6H, OCH_3), 4.63 (d, J = 14.4 Hz, 2H, N-CH_2), 5.19 (d, J = 14.4 Hz, 2H, N-CH_2), 6.57 (s, 2H, CH = CH Im), 6.88–6.95 (m, 8H, tol *m*-H, tol *o*-H), 7.13–7.38 (m, 15H, PPh_3).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.5 (CH_3, Ph-CH_3), 51.7 (CH_3, OCH_3), 52.2 (CH_3, OCH_3), 54.4 (CH_2, NCH_2), 120.7 (CH, CH = CH Im), 129.3 (CH, tol *o*-C), 129.6 (CH, tol *m*-C), 133.5 (C, tol *i*-C), 137.9 (C, tol *p*-C), 170.9 (C,CO), 171.2 (C, d, J_{CP} = 4.3 Hz, CO), 187.5 (C, d, J_{CP} = 17.7 Hz, NCN).

^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 29.9.

IR (KBr): $\nu_{C=O}$ = 1713, 1681 cm^{-1}.

Anal. Calc. for $C_{47}H_{47}N_2O_8PPd$: C, 62.29; H, 5.34; N, 3.09. Found: C, 62.38; H, 5.44; N, 2.99.

4.9.4. Synthesis of complex **6d**

Yellow microcrystals; Yield 86%.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.27 (s, 3H, tol-CH_3), 2.34 (s, 3H, tol-CH_3), 4.25 (d, J = 14.6 Hz, 1H, N-CH_2), 4.43 (d, J = 14.6 Hz, 1H, N-CH_2), 4.61 (dd, J_{HH} = 7.3 Hz, 1H, CH = CH *trans*-C), 4.65 (d, J = 14.5 Hz, 1H, N-CH_2), 4.83 (dd, J_{HP} = 9.8 Hz, J_{HH} = 7.3 Hz, 1H, CH = CH *trans*-P), 5.13 (d, J = 14.5 Hz, 1H, N-CH_2), 6.54 (d, J = 7.9 Hz, 2H, tol-H), 6.59 (d, J = 1.8 Hz, 1H, CH = CH Im), 6.73 (d, J = 1.8 Hz, 1H, CH = CH Im), 6.90 (d, J = 7.9 Hz, 2H, tol-H), 6.89–7.56 (m, 21H, nq-H, tol-H, PPh_3), 7.90–7.97 (m, 2H, nq-H).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.7 (CH_3, tol-CH_3), 20.8 (CH_3, tol-CH_3), 63.6 (CH, CH = CH *trans*-C), 65.6 (d, CH, J_{CP} = 19.0 Hz, CH = CH *trans*-P), 54.0 (CH_2, NCH_2), 54.4 (CH_2, NCH_2), 120.9 (CH, CH = CH Im), 125.0 (CH, nq-CH), 125.6 (CH, nq-CH), 128.0 (CH, tol *o*-C), 128.1 (CH, tol *o*-C), 129.1 (CH, tol *m*-C), 129.3 (CH, tol *m*-C), 130.6 (CH, nq-CH), 130.7 (CH, nq-CH), 132.7 (C, tol *i*-C), 133.3 (C, tol *i*-C), 136.8 (C, nq-CH), 137.0 (C, nq-CH), 137.6 (C, tol *p*-C), 138.0 (C, tol *p*-C), 183.3 (C, d, J_{CP} = 7.1. Hz, CO *trans*-P), 183.4 (C,CO *trans*-C), 189.0 (C, d, J_{CP} = 21 Hz, NCN). ^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 32.0.

IR (KBr): $\nu_{C=O}$ = 1619 cm^{-1}.

Anal. Calc. for $C_{47}H_{41}N_2O_2PPd$: C, 70.19; H, 5.26; N, 3.48. Found: C, 70.21; H, 5.24; N, 3.41.

4.9.5. Synthesis of complex **6e**

To 0.080 g (1.819×10^{-4} mol) of complex **1e** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.0844 g (1.819×10^{-4} mol) of **2** and 0.047 g (1.819×10^{-4} mol) of PPh_3 dissolved together in 5 ml of anhydrous CH_2Cl_2 were added under inert atmosphere (Ar). The mixture was stirred for 15 m and then AgBr was filtered off with a millipore

apparatus. The clear solution was evaporated to small volume under vacuum and treated with diethylether. The brown precipitate was filtered off on a gooch and washed with diethylether and pentane and dried under vacuum. 0.1053 g (73% yield) of the title compound was obtained.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.29 (s, 6H, tol-CH_3), 2.66–2.76 (m, 4.25, 2H, CH = CH, *trans*-C and *trans*-P), 4.84 (bs, 4H, N-CH_2), 6.78 (s, 2H, CH = CH Im), 6.97–7.03 (m, 8H, tol-H), 7.21–7.46 (m, 15H, PPh_3). ^{1}H NMR (CD_2Cl_2, T = 213 K, ppm) δ: 2.17 (s, 3H, tol-CH_3), 2.27 (s, 3H, tol-CH_3),), 2.79 (ABX system(A), J_{HP} = 12.7 Hz, J_{HH} = 12.5 Hz, 1H, CH = CH *trans*-P), 2.87 (ABX system (B), J_{HH} = 12.7 Hz, J_{HP} = 2.7 Hz, 1H, CH = CH *trans*-C), 4.34 (d, J = 14.4 Hz, 1H, N-CH_2), 4.48 (d, J = 14.1 Hz, 1H, N-CH_2), 4.91 (d, J = 14.4 Hz, 1H, N-CH_2), 4.93 (d, J = 14.1 Hz, 1H, N-CH_2), 6.71 (d, J = 1.6 Hz, 1H, CH = CH Im), 6.74 (d, J = 1.6 Hz, 1H, CH = CH Im), 6.79 (d, J = 7.8 Hz, 2H, tol-H), 6.95 (d, J = 7.8 Hz, 2H, tol-H), 6.94–7.02 (b AB system, 4H, tol-H), 7.07–7.46 (m, 15H, PPh_3).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.8 (CH_3, tol-CH_3), 21.3 (d, CH, J_{CP} = 3.0 Hz, CH = CH *trans*-C), 22.3 (d, CH, J_{CP} = 40.7 Hz, CH = CH *trans*-P), 54.3 (CH_2, NCH_2), 120.9 (CH, CH = CH Im), 123.7 (C, CN *trans*-C), 123.7 (d, C, J_{CP} = 7.6 Hz, CN *trans*-P), 128.4 (CH, tol *o*-C), 129.3 (CH, tol *m*-C), 133.1 (C, tol *i*-C), 137.9 (C, tol *p*-C), 188.5 (C, d, J_{CP} = 12.0 Hz, NCN). ^{31}P{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 27.5.

IR (KBr): ν_{CN} = 2196 cm^{-1}.

Anal. Calc. for $C_{43}H_{43}N_2O_4PPd$: C, 65.36; H, 5.61; N, 3.55. Found: C, 65.49; H, 5.73; N, 3.61.

4.9.6. Synthesis of complex **9c**

To 0.064 g (1.10 × 10^{-4} mol) of complex **1c** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.0411 g (1.10 × 10^{-4} mol) of **3** and 0.0288 g (1.10 × 10^{-4} mol) of PPh_3 dissolved in 5 ml of anhydrous CH_2Cl_2 were added under inert atmosphere (Ar). The mixture was stirred for 15 m and then AgBr was filtered off with a millipore apparatus. The clear solution was evaporated to dryness under vacuum and the residue treated with diethylether. The whitish compound was filtered off on a gooch and washed with diethylether and pentane and dried under vacuum. 0.0741 g (83% yield) of the title compound was obtained.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.24 (s, 3H, OCH_3), 3.32 (s, 3H, OCH_3), 3.34 (s, 3H, NCH_3), 3.44 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 4.83 (d, J = 14.4 Hz, 1H, N-CH_2), 5.067 (d, J = 14.4 Hz, 1H, N-CH_2), 6.65 (s, 2H, CH = CH Im), 6.85, 6.95 (AB system, J = 8.1 Hz, 4H, tol *m*-H, tol *o*-H,) 7.18–7.37 (m, 15H, PPh_3).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 21.5 (CH_3, tol-CH_3), 37.6 (CH_3, NCH_3), 51.6 (CH_3, OCH_3), 51.9 (CH_3, OCH_3), 52.2 (CH_3, OCH_3), 52.3 (CH_3, OCH_3), 54.4 (CH_2, NCH_2), 120.6 (CH, CH = CH Im), 122.2 (CH, CH = CH Im), 129.3 (CH, tol *o*-C), 129.6 (CH, tol *m*-C), 133.5 (C, tol *i*-C), 137.9 (C, tol *p*-C), 170.7 (C,CO), 170.9 (C, d, J_{CP} = 4.8 Hz, CO), 171.0 (C, CO), 171.3 (C, d, J_{CP} = 4.4 Hz, CO), 187.4 (C, d, J_{CP} = 16.7 Hz, NCN).

^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.0.

IR (KBr): $\nu_{C=O}$ = 1731, 1711, 1692, 1675 cm^{-1}.

Anal. Calc. for $C_{40}H_{41}N_2O_8PPd$: C, 58.86; H, 5.19; N, 3.43. Found: C, 59.02; H, 5.21; N, 3.32.

4.9.7. Synthesis of complex **11c**

To 0.064 g (1.10 × 10^{-4} mol) of complex **1c** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.0396 g (1.10 × 10^{-4} mol) of **4** and 0.0288 g (1.10 × 10^{-4} mol) of PPh_3 dissolved in 5 ml of anhydrous CH_2Cl_2 were added under inert atmosphere (Ar). The mixture was stirred for 15 m and then AgBr was filtered off with a millipore apparatus. The clear solution was evaporated to dryness under vacuum and the residue treated with diethylether. The whitish compound was filtered off on a gooch and washed with diethylether and pentane and dried under vacuum. 0.0741 g (83% yield) of the title compound was obtained.

^{1}H NMR ($CDCl_3$, T = 298 K, ppm) δ: 3.31 (s, 3H, OCH_3), 3.36 (s, 3H, NCH_3), 3.43 (s, 3H, OCH_3), 3.53 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 4.86 (d, J = 14.4 Hz, 1H, N-CH_2), 5.14 (d, J = 14.4 Hz, 1H, N-CH_2), 6.65,6.67 (AB system, J = 1.8 Hz, 2H, CH = CH Im), 7.03–7.36 (m, 20H, Ph *m*-H, Ph *o*-H, Ph *p*-H, PPh_3).

^{13}C{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 37.6 (CH_3, NCH_3), 51.6 (CH_3, OCH_3), 51.8 (CH_3, OCH_3), 52.2 (CH_3, OCH_3), 52.3 (CH_3, OCH_3), 54.7 (CH_2, NCH_2), 120.6 (CH, CH = CH Im), 122.3 (CH, CH = CH Im), 128.2 (CH, Ph *p*-C), 129.0 (CH, Ph *m*-C), 129.3 (CH, Ph *o*-C), 136.5 (C, Ph *i*-C), 170.7 (C,CO), 170.9 (C, d, J_{CP} = 4.6 Hz, CO), 171.0 (C, CO), 171.1 (C, d, J_{CP} = 4.3 Hz, CO), 187.7 (C, d, J_{CP} = 16.3 Hz, NCN).

^{31}P{^{1}H} NMR ($CDCl_3$, T = 298 K, ppm) δ: 30.0.

IR (KBr): $\nu_{C=O}$ = 1711, 1681 cm^{-1}.

Anal. Calc. for $C_{39}H_{39}N_2O_8PPd$: C, 58.40; H, 5.03; N, 3.49. Found: C, 58.51; H, 5.12; N, 3.47.

4.10. Mixed PTA–NHC complexes

4.10.1. Synthesis of complex **7a**

To 0.062 g (1.548 × 10^{-4} mol) of complex **1a** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.0719 g (1.548 × 10^{-4} mol) of **2** and 0.0243 g (1.548 × 10^{-4} mol) of PTA suspended in 5 ml of anhydrous CH_2Cl_2 were added under inert atmosphere (Ar). The mixture was stirred for 15 m and then AgBr was filtered off with a millipore apparatus. The clear solution was evaporated to dryness under vacuum and the residue treated with diethylether. The whitish compound was filtered off on a gooch and washed with diethylether and pentane and dried under vacuum. 0.0801 g (81% yield) of the title compound was obtained.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.37 (s, 6H, tol-CH_3), 3.73–3.79 (m, 4.25, 2H, CH = CH, *trans*-C and *trans*-P), 3.59 (d, J = 2.7 Hz, 6H, NCH_2P), 4,27, 4.40 (AB system, J = 13.0 Hz, 6H, NCH_2N), 5,07, 5.11 (AB system, J = 15.0 Hz, 4H, NCH_2), 7.10 (s, 2H, CH = CH Im), 7.12–7.26 (m, 8H, tol-H).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.8 (CH_3, tol-CH_3), 42.7 (CH, CH = CH *trans*-C), 45.4 (CH, d, J_{CP} = 28.6 Hz, CH = CH *trans*-P), 52.3 (CH_2, d, J = 6.7 Hz, NCH_2P), 54.5 (CH_2, NCH_2), 73.1 (CH_2, d, J_{CP} = 5.6 Hz, NCH_2N,) 121.8 (CH, CH = CH Im), 127.7 (CH, tol *o*-C), 129.5 (CH, tol *m*-C), 134.0 (C, tol *i*-C), 138.0 (C, tol *p*-C), 188.8 (C, d, J_{CP} = 14.2 Hz, NCN).

^{31}P{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: −60.4.

IR (KBr): $\nu_{C=O}$ = 1781–1717 cm^{-1}.

Anal. Calc. for $C_{29}H_{34}N_5O_3PPd$: C, 54.51; H, 5.52; N, 10.96. Found: C, 54.63; H, 5.47; N, 11.05.

Derivatives **7b-c**, were prepared in a similar way using the appropriate reactants.

4.10.2. Synthesis of complex **7b**

Whitish microcrystals: Yield 83%.

^{1}H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.38 (s, 6H, tol-CH_3), 2.51 (dd, J_{HP} = 9.7 Hz, J_{HH} = 9.7 Hz, 1H, CH = CH *trans*-P), 2.66 (dd, J_{HH} = 9.9 Hz, J_{HP} = 3.9 Hz, 1H, CH = CH *trans*-C), 3.69 (d, J = 2.9 Hz, 6H, NCH_2P), 4,32, 4.44 (AB system, J = 13.0 Hz, 6H, NCH_2N), 5,15, 4.23 (AB system, J = 14.9 Hz, 4H, NCH_2), 7.11 (s, 2H, CH = CH Im), 7.16–7.27 (m, 8H, tol-H).

^{13}C{^{1}H} NMR (CD_2Cl_2, T = 298 K, ppm) δ: 18.2 (d, CH, J_{CP} = 3.6 Hz, CH = CH *trans*-C), 20.8 (CH_3, tol-CH_3), 20.3 (CH, d, J_{CP} = 39.6 Hz, CH = CH *trans*-P), 52.6 partially obscured by CD_2Cl_2 (CH_2, NCH_2-P), 54.5 (CH_2, NCH_2), 73.1 (CH_2, d, J_{CP} = 5.6 Hz, NCH_2N), 121.7 (CH, CH = CH Im), 123.2 (C, J_{CP} = 2.7 Hz, CN *trans*-C), 124.2 (d, C, J_{CP} = 8.1 Hz, CN *trans*-P), 127.7 (CH, tol *o*-C), 129.5 (CH, tol *m*-C), 134.1 (C, tol *i*-C), 138.0 (C, tol *p*-C), 172.5 (C, d, J_{CP} = 5.1 Hz, CO CO *trans*-P), 172.8 (C, CO *trans*-C), 188.4 (C, d, J_{CP} = 11.3 Hz, NCN).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: −62.0.

IR (KBr): ν_{CN} = 2190 cm^{-1}.

Anal. Calc. for $C_{29}H_{34}N_7PPd$: C, 56.27; H, 5.70; N, 15.84. Found: C, 56.13; H, 5.82; N, 15.71.

*4.10.3. Synthesis of complex **7c***

Whitish microcrystals: Yield 92%.

^1H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.38 (s, 6H, tol-CH_3), 3.37 (d, J = 1.9 Hz, 6H, NCH_2P) 3.56 (s, 6H, OCH_3), 3.70 (s, 6H, OCH_3), 4,12, 4.32 (AB system, J = 13.0 Hz, 6H, NCH_2N) 5.09 (d, J = 15.0 Hz, 2H, N-CH_2), 5.35 (d, J = 15.0 Hz, 2H, N-CH_2), 7.11 (s, 2H, CH = CH Im), 7.19–7.26 (m, 8H, tol-H).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 20.8 (CH_3, tol-CH_3), 51.6 (CH_3, OCH_3), 51.7 (CH_3, OCH_3), 51.9 (CH_2, d, J_{CP} = 7.3 Hz, NCH_2-P), 54.0 (CH_2, NCH_2), 72.9 (CH_2, d, J_{CP} = 5.8 Hz, NCH_2N) 121.6 (CH, CH = CH Im), 128.0 (CH, tol *o*-C), 129.4 (CH, tol *m*-C), 134.3 (C, tol *i*-C), 137.8 (C, tol *p*-C), 170.0 (C, d, J_{CP} = 4.9 Hz, CO CO *trans*-P), 170.2 (C, CO *trans*-C), 187.2 (C, d, J_{CP} = 16.0 Hz, NCN).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: −57.7.

IR (KBr): $\nu_{C=O}$ = 1720–1678 cm^{-1}.

Anal. Calc. for $C_{35}H_{44}N_5O_8PPd$: C, 52.47; H, 5.66; N, 8.74. Found: C, 52.36; H, 5.61; N, 8.84.

4.11. Mixed DIC–NHC complexes

*4.11.1. Synthesis of complex **8b***

To 0.080 g (1.997 × 10^{-4} mol) of complex **1b** dissolved in 10 ml of anhydrous CH_2Cl_2, 0.0927 g (1.997 × 10^{-4} mol) of **2** and 0.0262 g (1.997 × 10^{-4} mol) of DIC dissolved together in 5 ml of anhydrous CH_2Cl_2 were added under inert atmosphere (Ar). The mixture was stirred for 15 m and then AgBr was filtered off with a millipore apparatus. The clear solution was evaporated to dryness under vacuum and the residue treated with diethylether. The white compound was filtered off on a gooch and washed with diethylether and pentane and dried under vacuum. 0.1058 g (90% yield) of the title compound was obtained.

^1H NMR (CD_2Cl_2, T = 298 K, ppm) δ: 2.25 (s, 6H, tol-CH_3), 2.28 (s, 6H, DIC-CH_3), 2.59 (d, J = 9.4 Hz, 1H, CH = CH), 2.86 (d, J = 9.4 Hz, 1H, CH = CH), 5.29, 5.43 (AB system, J = 14.9 Hz, 4H, N-CH_2), 7.05 (s, 2H, CH = CH Im), 7.10–7.25 (m, 16H, tol-H, DIC-H).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, T = 298 K, ppm) δ: 18.4 (CH_3, DIC-CH_3), 19.0 (CH, CH = CH), 20.4 (CH, CH = CH), 20.7 (CH_3, tol-CH_3), 54.5 (CH_2, NCH_2), 121.5 (CH, CH = CH Im), 123.4 (C, CN), 123.6 (C, CN), 127.7 (CH, tol *o*-C), 127.7 (CH, *m*-DIC), 128.7 (CH, *p*-DIC), 129.3 (CH, tol *m*-C), 133.9 (C, tol *i*-C), 134.8 (C, *o*-DIC), 137.8 (C, tol *p*-C), 187.5 (C, NCN).

IR (KBr): ν_{CN} = 2196–2134 cm^{-1}.

Anal. Calc. for $C_{32}H_{31}N_5Pd$: C, 64.92; H, 5.28; N, 11.83. Found: C, 65.10; H, 5.31; N, 11.99.

Derivatives **8c** and **10c** were prepared in a similar way using the appropriate reactants.

*4.11.2. Synthesis of complex **8c***

Whitish microcrystals; Yield 93%.

^1H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.12 (bs, 12H, tolyl-CH_3, aryl-CH_3), 3.63 (s, 6H, OCH_3), 3.71 (s, 6H, OCH_3), 4.63 (s, 4H, N-CH_2), 6.92 (s, 2H, CH = CH Im), 6.99 (d, J = 7.8 Hz, 2H, tolyl *m*-H), 7.04 (d, J = 7.5 Hz, 2H, aryl *m*-H), 7.13–7.18 (m, 3H, tolyl *o*-H, aryl *p*-H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 18.8 (CH_3, aryl-CH_3), 21.3 (CH_3, Ph-CH_3), 52.3 (CH_3, OCH_3), 52.4 (CH_3, OCH_3), 54.8 (CH_2, NCH_2), 121.5 (CH, CH = CH Im), 127.9 (CH, aryl *m*-C), 128.6 (CH, tolyl *o*-C), 128.9 (CH, aryl *p*-C), 129.4 (CH, tolyl *m*-C), 134.6 (C, tolyl *i*-C), 135.4 (C, aryl *o*-C), 137.8 (C, tolyl *p*-C), 157.3 (C, CN), 170.6 (C, CO), 170.9 (C, CO), 186.7 (C, NCN).

IR (KBr): $\nu_{C=O}$ = 1685, 1706, 1725 cm^{-1}, ν_{CN} = 2141 cm^{-1}.

Anal. Calc. for $C_{38}H_{41}N_3O_8Pd$: C, 58.95; H, 5.34; N, 5.43. Found: C, 59.07; H, 5.51; N, 5.36.

*4.11.3. Synthesis of complex **10c***

Whitish microcrystals; Yield 73%.

^1H NMR ($CDCl_3$, T = 298 K, ppm) δ: 2.13 (s, 3H, tolyl-CH_3), 2.34 (s, 6H, aryl-CH_3), 3.63 (s, 6H, OCH_3), 3.70 (s, 6H, OCH_3), 3.82 (s, 3H, N-CH_3), 5.32 (s, 2H, N-CH_2), 6.91 (d, J = 1.8 Hz, 1H, CH = CH Im), 6.94 (d, J = 1.8 Hz, 1H, CH = CH Im), 6.98 (d, J = 7.8 Hz, 2H, tolyl *m*-H), 7.06 (d, J = 7.8 Hz, 2H, aryl *m*-H), 7.15–7.17 (m, 3H, tolyl *o*-H, aryl *p*-H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm) δ: 18.9 (CH_3, aryl-CH_3), 21.3 (CH_3, Ph-CH_3), 38.3 (CH_3, NCH_3) 52.3 (CH_3, OCH_3), 52.3 (CH_3, OCH_3), 54.6 (CH_2, NCH_2), 121.3 (CH, CH = CH Im), 122.4 (CH, CH = CH Im), 128.0 (CH, aryl *m*-C), 128.5 (CH, tolyl *o*-C), 129.5 (CH, aryl *p*-C), 129.6 (CH, tolyl *m*-C), 134.6 (C, tolyl *i*-C), 135.3 (C, aryl *o*-C), 137.8 (C, tolyl *p*-C), 157.5 (C, CN), 170.6 (C,CO), 170.8 (C, CO), 186.5 (C, NCN).

IR (KBr): $\nu_{C=O}$ = 1689, 1723 cm^{-1}, ν_{CN} = 2137 cm^{-1}.

Anal. Calc. for $C_{31}H_{35}N_3O_8Pd$: C, 54.43; H, 5.16; N, 6.14. Found: C, 54.35; H, 5.27; N, 6.12.

Appendix A. Supplementary data

CCDC 1581529 and 1581530 contains 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 https://doi.org/10.1016/j.poly.2018.01.010.

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