Substitution reactions between bis-chelate ligands in palladium(II) alkenyl complexes: an unusual way to form unstable *trans*-P complexes. A study on the isomerization mechanism†

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The substitution reactions between asymmetric bis-chelate ligands and alkenyl chloro derivatives of palladium(II) of the type [Pd(L–L′)(Rx)Cl] (L–L′ = 2-phenylsulfanylmethyl-pyridine (HN–SPh), 2-methyl-6-phenylsulfanylmethyl-pyridine (MeN–SPh), 2,2′-bipyridinyl (BiPy), Rx = –CCOOMe=CMeCOOMe (Ra), –CCOOEt=CMeCOOEt (Rb), –CCOO*t*-Bu=CMeCOO*t*-Bu (Rc), –(CCOOMe=CCOOMe)$_2$Me (Rd)) with phosphoquinoline moieties (8-diphenylphosphanyl-quinoline (DPPQ), 8-diphenylphosphanyl-2-methyl-quinoline (DPPQ-Me)) usually leads to the formation of the stable geometrical isomer bearing these groups in the *cis* position thanks to the mutual *trans* influence of the alkenyl and phosphine groups. However, when the leaving group MeN–SPh and the entering ligand DPPQ are involved, the fast and quantitative substitution reaction leads to the formation of a couple of geometrical isomers [Pd(DPPQ)(Rx)Cl]-*trans* P and [Pd(DPPQ)(Rx)Cl]-*cis* P (Rx = Ra, Rb, Rc, Rd) in which the alkenyl and the phosphine groups are in mutual *trans* or *cis* position. The substrate [Pd(DPPQ)(Rx)Cl]-*trans* P (Rx = Ra, Rb, Rc) slowly interconverts into its thermodynamically stable -*cis* P counterpart while the bulky [Pd(DPPQ)(Rd)Cl]-*trans* P displays no tendency to isomerize, thereby allowing separation of the two geometrical forms. Also, the ligand DPPQ-Me induces the formation of the -*trans* P geometrical isomer which is only detectable at low temperature since it rapidly interconverts into the -*cis* P derivative at RT. The kinetics of the interconversion process, a reasonable explanation of the observed phenomenon based on theoretical calculations, and eventually an unequivocal structure determination of the stable [Pd(DPPQ)(Rx)Cl]-*cis* P substrate are reported in the present paper.

Introduction

An impressive number of papers dealing with nucleophilic substitution on planar tetracoordinate complexes in d^8 metals have hitherto been published and the inherent theoretical and applicative aspects of such investigations have been exhaustively reviewed.[1] According to the well established mechanism, the substitution reaction proceeds *via* retention of configuration unless isomerization takes place. Isomerization itself represents a well developed field of interest which is still deeply investigated.[2] In this context, when Pd(II) or Ni(II) complexes are used as catalysts the nature of the geometrical isomer could be very important. As a matter of fact, it was noticed that in the olefin polymerization and copolymerization the *cis* isomers derived from symmetric chelating ligands (P–P or N–N) is the more productive catalyst.[3]

With planar tetracoordinate compounds derived from symmetric bidentate ligands, the complexes originate from mixed chelate ligands (P–N, N–S), and two other unequal substituents may exist as a couple of isomers. It was noticed that palladium complexes of mixed P–N ligands displayed a reduced catalytic activity towards olefin polymerization. Therefore such derivatives did not get much attention[4] although it was stated that different isomers could impart different reactivity to the catalysts.[5] Moreover, the exchange reactions in which bidentate ligands act as entering groups substituting another chelating moiety were not exhaustively investigated from the mechanistic point of view.[2] Notably, the interplay between the nucleophilic power of the different entering atoms and the entropically modulated chelating effect could play an unpredictable role. Quite recently we have proposed a new approach to the syntheses of complexes [Pd(L–L′)(Rx)X] [L–L′ = diphenylphosphinoethane (DPPE), 2,2′-bipyridine (BiPy), 8-diphenylphosphanyl-2-methylquinoline (DPPQ-Me); Rx = ZC=CZMe, (ZC=CZ)$_2$Me (Z = COOMe, COOEt, COO*t*-Bu); X = Cl, I] based on the metathetic ligand exchange between the complex [Pd(MeN–SPh)(R)Cl] (MeN–SPh = 2-methylthiophenyl-6-methylpyridine, R = methyl, vinyl, butadienyl) and the appropriate ligand L–L′.[6] On the basis of such a protocol we have now carried out the synthesis and studied the reactivity related to the substitution reactions yielding the derivatives reported in Scheme 1.

Apparently, addition of an asymmetric phosphorus–nitrogen ligand (DPPQ, DPPQ-Me) (DPPQ = 8-diphenylphosphanylquinoline; DPPQ-Me = 8-diphenylphosphanyl-2-methyl-quinoline) to the complexes [Pd(L–L′)(Rx)Cl] should in principle generate a couple of isomers (namely [Pd(P–N)(Rx)Cl]-*trans* P and

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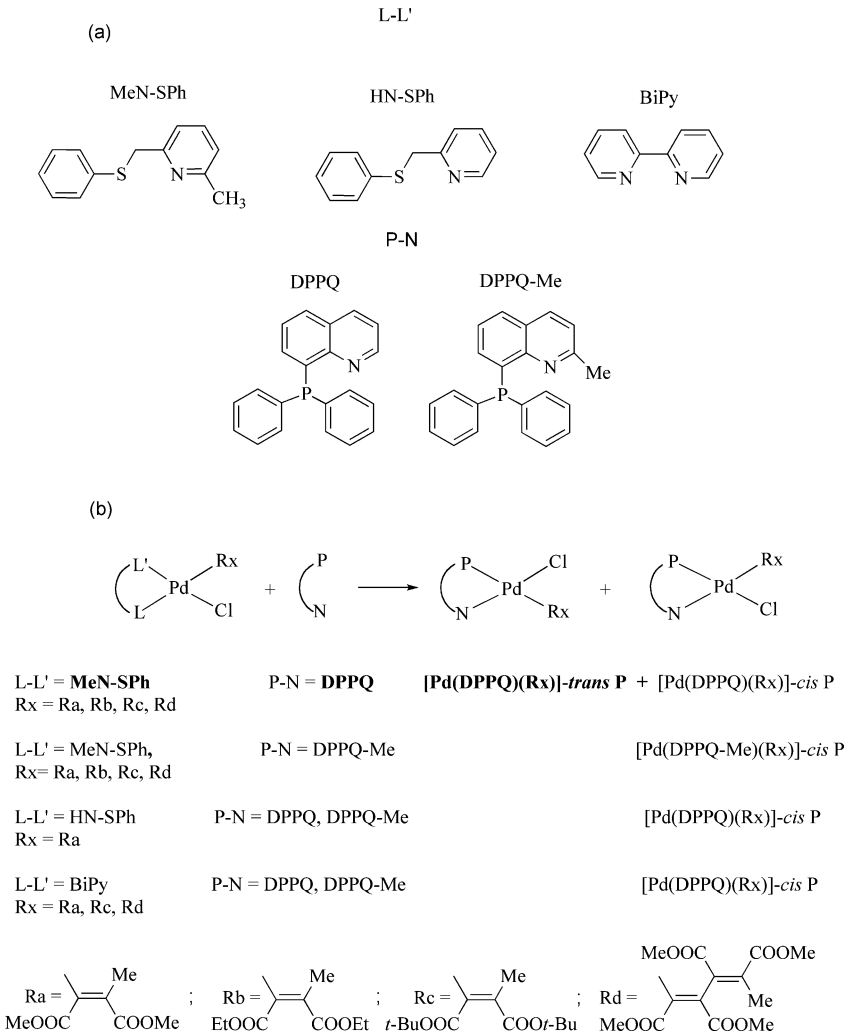


Scheme 1 Ligands (a) and complexes involved in the ligand substitution reaction (b).

[Pd(P–N)(Rx)Cl]-*cis* P in Scheme 1 bearing Rx in the *trans* or *cis* position with respect to the phosphorus atom, respectively) independently of the starting complex. It was instead noticed that only the ligand DPPQ when reacting with the complexes [Pd(MeN–SPh)(Rx)Cl] (which are present in solution only as [Pd(MeN–SPh)(Rx)Cl]-*cis* S isomer), yields a mixture of both [Pd(DPPQ)(Rx)Cl]-*trans* P and [Pd(DPPQ)(Rx)Cl]-*cis* P species in the approximate ratio -*trans* P : -*cis* P = 7 : 1. It is noteworthy that the complexes bearing P–N or S–N chelate ligands and R groups were hitherto obtained mostly as *cis* isomers,[7a-7g] and to the best of our knowledge only in one case as -*trans* P species.[7h] Therefore, the substitution reactions between the complexes [Pd(MeN–SPh)(Rx)Cl] and the ligand DPPQ yielding both the isomeric species represent a remarkable opportunity to be exploited. Moreover, in some cases the kinetics of isomerization can be studied by conventional techniques allowing an in-depth insight into the intimate mechanism governing such a geometrical transformation. The intimate mechanism and the speculative analysis of the overall general rules governing this sort of reactions are the matter of the present paper.

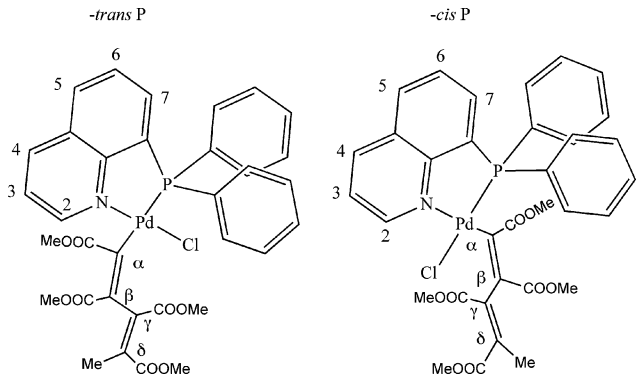
Results

General remarks on the substitution reactions between ligands

Addition under inert atmosphere (N_2) of ligands DPPQ or DPPQ-Me to a solution of the complexes [Pd(L–L′)(Rx)Cl] (L–L′ = HN–SPh, BiPy; Rx = Ra, Rb, Rc, Rd) in CH_2Cl_2 or $CHCl_3$ at RT yields immediately and quantitatively the corresponding complexes [Pd(DPPQ)(Rx)Cl]-*cis* P and [Pd(DPPQ-Me)(Rx)Cl]-*cis* P. However, when complexes [Pd(MeN–SPh)(Rx)Cl], (Rx = Ra, Rb, Rc, Rd) react with ligand DPPQ it is apparent from ^{1}H and ^{31}P NMR experiments that the fast and quantitative MeN–SPh ligand displacement yields a mixture of both [Pd(DPPQ)(Rx)Cl]-*trans* P and [Pd(DPPQ)(Rx)Cl]-*cis* P isomers. In the case of the butadienyl derivative complex (Rx = Rd) no isomerization reaction is observed. Conversely, the [Pd(DPPQ)(Rx)Cl]-*trans* P vinyl derivatives (Rx = Ra, Rb, Rc) undergo isomerization even in the solid state.[8] Taking advantage of this situation and on the basis of the peculiar NMR features, we were able to assign the geometrical configuration to each complex under study, as can be deduced from the Scheme 2 and Table 1.

Table 1 Selected ^{1}H NMR signals characterizing the isomers under study.

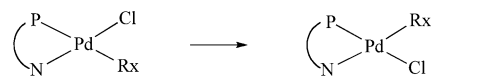
[Pd(DPPQ)(Rx)Cl)]-*trans* P		[Pd(DPPQ)(Rx)Cl)]-*cis* P
Cross peaks		
Rd	COOMe (α) H^2	COOMe (α) Ph, P
	COOMe (γ) H^2, H^4, H^3	COOMe (β) Ph, P
	Me H^2	COOMe (γ) Ph, P
		Me Ph, P
^{1}H NMR (ppm)		
Rd	Me 2.14	Me 1.54
	H^2 9.78	H^2 10.25
Ra	Me 2.54	Me 1.60
	H^2 9.73	H^2 10.20
Rb	Me 2.46	Me 1.60
	H^2 9.73	H^2 10.24
Rc	Me 2.35	Me 1.46
	H^2 9.69	H^2 10.21
^{31}P NMR (ppm)		
Rd	26.2	37.6
Ra	23.6	37.7
Rb	23.3	38.0
Rc	22.2	37.6



Scheme 2 Geometrical configuration of the isomers.

Isomerization reactions

(A). Owing to the remarkable *trans*-influence exerted by the phosphine and the vinyl group and the consequent induced mutual labilization between the groups themselves, the transformation of the complex [Pd(DPPQ)(Rx)Cl]-*trans* P into its more stable isomer [Pd(DPPQ)(Rx)Cl]-*cis* P (Rx = Ra, Rb, Rc) was observed (Scheme 3).



[Pd(DPPQ)(Rx)]-*trans* P [Pd(DPPQ)(Rx)]-*cis* P

Rx = Ra, Rb, Rc

Scheme 3 The isomerization reaction.

The kinetic studies by ^{1}H NMR were carried out by adding the appropriate amount of DPPQ ligand to a pre-thermostated solution of the complexes [Pd(MeN–SPh)(Rx)Cl] (see Scheme 1(b)). The immediate formation of a mixture of both isomers [Pd(DPPQ)(Rx)Cl]-*trans* P and [Pd(DPPQ)(Rx)Cl]-*cis* P was observed followed by isomerization of [Pd(DPPQ)(Rx)Cl]-*trans* P into its -*cis* P counterpart. When the amount of DPPQ was higher than the stoichiometric quantity (the exchange between ligands is in any case quantitative irrespective of the vinyl substituent Rx = Ra, Rc) the ensuing isomerization reaction can be treated by non-linear regression of data to the mono-exponential function (eqn (1)):

$$[[Pd(DPPQ)(Rx)Cl]\text{-}cis\ P]_t = [[Pd(DPPQ)(Rx)Cl]\text{-}trans\ P]_0(1-\exp(-k_{obs}t)) + [[Pd(DPPQ)(Rx)Cl]\text{-}cis\ P]_0 \quad (1)$$

where $[[Pd(DPPQ)(Rx)Cl]\text{-}cis\ P]_0$ and $[[Pd(DPPQ)(Rx)Cl]\text{-}trans\ P]_0$ represent the concentrations of the isomers in the initial mixture at time $t = 0$, whereas $[[Pd(DPPQ)(Rx)Cl]\text{-}cis\ P]_t$ is the concentration of the *cis* isomer at time *t*. $[[Pd(DPPQ)(Rx)Cl]\text{-}trans\ P]_0$ and k_{obs} are the parameters to be optimized in the refinement process. A typical ^{1}H NMR experiment together with the related numerical analysis is shown in Fig. 1.

The plot of the resulting k_{obs} constants *vs.* the $[DPPQ]_0$ (DPPQ concentration in excess at $t = 0$) is described by the following eqn (2):

$$k_{obs} = k_1 + k_2[DPPQ]_0 \quad (2)$$

in which k_1 represents the monomolecular and k_2 the bimolecular path to the [Pd(DPPQ)(Rx)Cl]-*cis* P isomer.

The linear regression plots of rates *vs.* the concentration of free DPPQ ligand, are summarized in Table 2, and shown in Fig. 2.

The ensuing k_2 and k_1 values are $(5.1 \pm 0.6) \times 10^{-2}$, $(1.39 \pm 0.06) \times 10^{-2}$ mol^{-1} dm^3 s^{-1} and $(1 \pm 8) \times 10^{-5}$, $(2 \pm 2) \times 10^{-5}$ s^{-1} for the complexes [Pd(DPPQ)(Rx)Cl], Rx = Ra and Rx = Rc, respectively.

The k_1 values can also be measured from the isomerization reactions triggered by the addition of the ligand DPPQ in slightly stoichiometric defect relative to the complex [Pd(MeN–SPh)(Rx)Cl]. The -*trans* P to -*cis* P isomerization reaction of the immediately formed mixture of [Pd(DPPQ)(Rx)Cl]-*trans* P and [Pd(DPPQ)(Rx)Cl]-*cis* P in the absence of free DPPQ ($[DPPQ]_0 = 0$) was observed. The corresponding k_1 values are reported in Table 3.

Table 2 Rate constants (s^{-1}) for the isomerization reaction of the complex [Pd(DPPQ)(Rx)Cl]-*trans* P to [Pd(DPPQ)(Rx)Cl]-*cis* P (Rx = Ra, Rc) in $CDCl_3$ at 25 °C determined by ^{1}H NMR

$[Pd(DPPQ)(Ra)Cl]_0$[a]	$[DPPQ]_0$[b]	k_{obs}/s^{-1}
2×10^{-2}	0.27×10^{-2}	$(1.88 \pm 0.01) \times 10^{-4}$
2×10^{-2}	1×10^{-2}	$(5.10 \pm 0.06) \times 10^{-4}$
2×10^{-2}	1.31×10^{-2}	$(5.9 \pm 0.1) \times 10^{-4}$
2×10^{-2}	2×10^{-2}	$(1.09 \pm 0.05) \times 10^{-3}$
$[Pd(DPPQ)(Rc)Cl]_0$		
2×10^{-2}	1.2×10^{-2}	$(1.91 \pm 0.01) \times 10^{-4}$
2×10^{-2}	2×10^{-2}	$(2.88 \pm 0.03) \times 10^{-4}$
2×10^{-2}	3×10^{-2}	$(4.52 \pm 0.02) \times 10^{-4}$
2×10^{-2}	4×10^{-2}	$(5.71 \pm 0.03) \times 10^{-4}$

[a] The concentrations reported in Table 2 (mol dm^{-3}) represent the total concentration of the complex extant in solution at $t = 0$ ($[Pd(DPPQ)(Rx)Cl]_0 = [[Pd(DPPQ)(Rx)Cl]\text{-}trans\ P]_0 + [[Pd(DPPQ)(Rx)Cl]\text{-}cis\ P]_0$). [b] The concentration of DPPQ ligand reported in Table 2 represents the concentration of the free DPPQ in solution at $t = 0$ ($[DPPQ]_0 = [DPPQ]_{TOT} - [Pd(DPPQ)(Rx)Cl]_0$; $[DPPQ]_{TOT}$ = total concentration of the ligand added to the initial solution of the starting complex [Pd(MeN–SPh)(Rx)Cl].

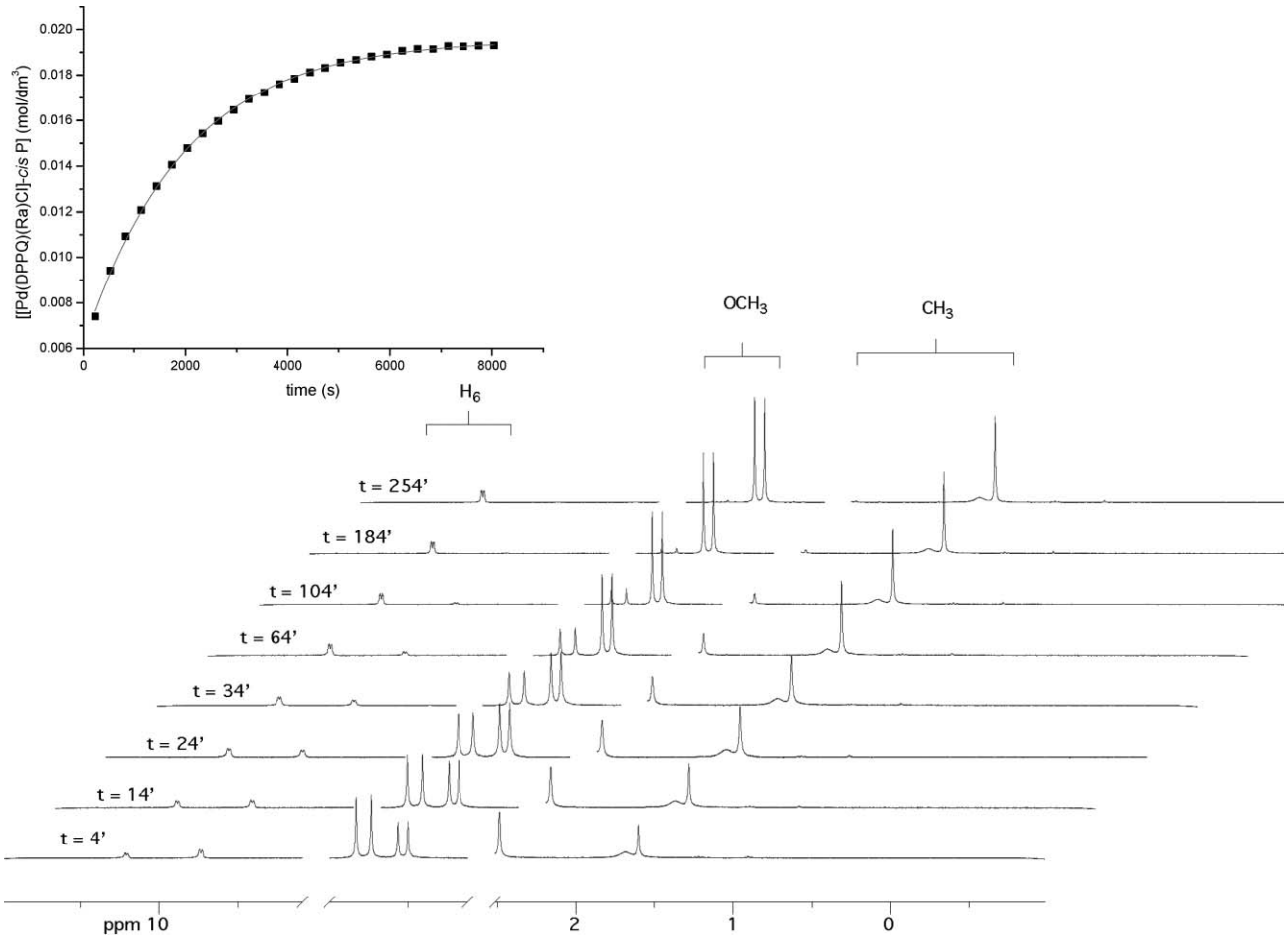


Fig. 1 Selected ^{1}H NMR signals related to the isomerization reaction of the complex [Pd(DPPQ)(Ra)Cl]-*trans* P in CD_3Cl at 298 K. Top insert: non-linear regression analysis according to eqn (1)). $[[Pd(DPPQ)(Ra)Cl]]_0 = 2 \times 10^{-2}$ (mol dm^{-3}); $[DPPQ]_0 = 1 \times 10^{-2}$ (mol dm^{-3}).

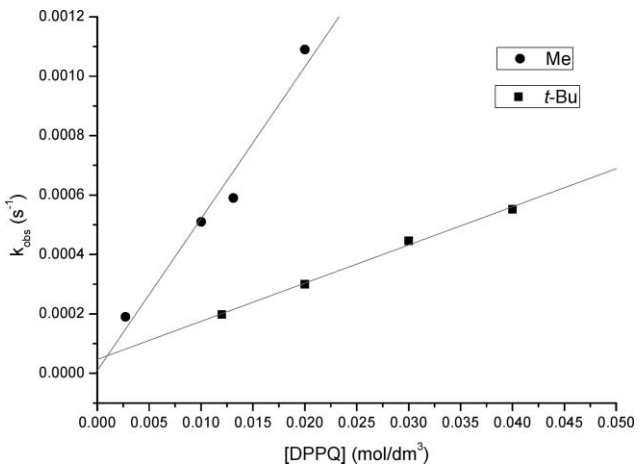


Fig. 2 Linear regression of the rate constants of isomerization measured at 25 °C in $CDCl_3$ for the complexes [Pd(DPPQ)(Rx)Cl]-*trans* P (Rx = Ra, Rc) *vs.* the concentration of free DPPQ.

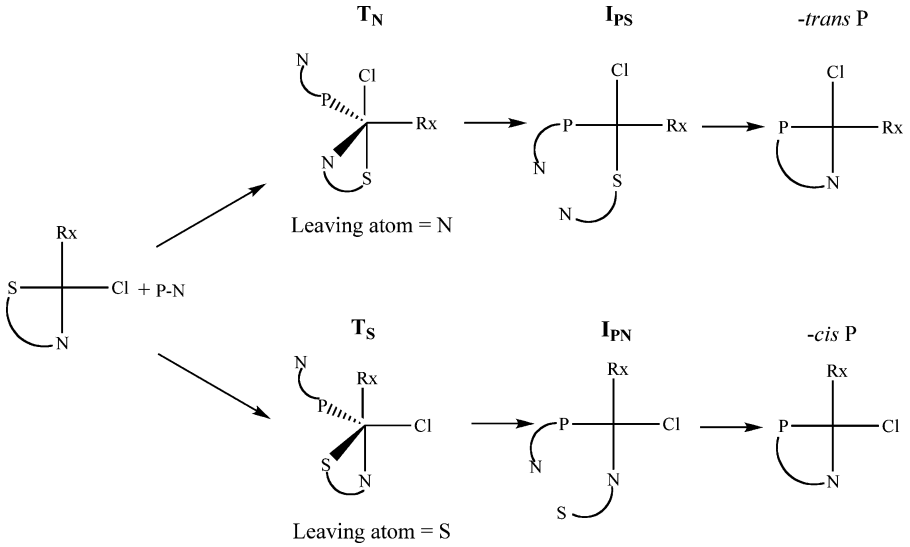
The isomeric mixtures obtained by the substitution reactions among the complexes [Pd(MeN–SPh)(Rx)Cl] and DPPQ can be isolated by removing the solvent at low temperature (250 K). These mixtures, when dissolved in $CDCl_3$ at RT, display the same isomerization rates (coincident k_1 values) as those of the related mixtures produced *in situ* by addition of DPPQ in stoichiometric defect with respect to the complexes [Pd(MeN–SPh)(Rx)Cl].

Table 3 k_1 values for the isomerization reaction obtained by addition of DPPQ in stoichiometric defect in $CDCl_3$, and determined by the initial rate approximation[9]

Complex	k_1/s^{-1}
[Pd(DPPQ)(Ra)Cl]-*trans* P	$(4.9 \pm 0.3) \times 10^{-6}$
[Pd(DPPQ)(Rb)Cl]-*trans* P	$(1.13 \pm 0.02 \times 10^{-5}$
[Pd(DPPQ)(Rc)Cl]-*trans* P	$(7.43 \pm 0.04) \times 10^{-6}$

(B). Addition of DPPQ to a solution of the butadienyl derivative [Pd(MeN–SPh)(Rd)Cl] in $CDCl_3$ induces the immediate formation of an isomeric mixture containing [Pd(DPPQ)(Rd)Cl]-*trans* P and [Pd(DPPQ)(Rd)Cl]-*cis* P in the approximate ratio of 1 : 1.6. However, the isomer [Pd(DPPQ)(Rd)Cl]-*trans* P does not convert into its thermodynamically favoured *cis* counterpart. This fact allows the separation of the two species by fractionated crystallization.

(C). As already stated, addition at RT of the ligand DPPQ-Me in excess or in defect to the complexes [Pd(MeN–SPh)(Rx)Cl] does not induce formation of both isomers. Only formation of the thermodynamically favoured [Pd(DPPQ)(Rx)Cl]-*cis* P was



Scheme 4 Reaction paths yielding the isomers.

observed. However, we were able to produce a highly reactive isomeric mixture by working at low temperature (263 K), with the ligand DPPQ-Me in defect and by taking advantage of the inertness of the *trans* isomer induced by the bulky butadienyl substituent Rd. In this case, at variance with the other cases involving vinyl substituents, it was possible to detect the fast substitution reaction between the ligands MeN–SPh and DPPQ-Me and the slower subsequent isomerization process. Unfortunately, in this case the reaction rates could not be determined owing to the simultaneous presence of several different species ([Pd(MeN–SPh)(Rd)Cl], [Pd(DPPQ-Me)(Rd)Cl]-*cis* P, [Pd(DPPQ-Me)(Rd)Cl]-*trans* P, uncoordinated DPPQ-Me and MeN–SPh). Increasing the temperature (298 K) induces the fast isomerization process yielding the thermodynamically stable [Pd(DPPQ-Me)(Rd)Cl]-*cis* P species. It is however apparent that the isomer ratio is kinetically controlled since the rate of substitution between ligands in this case and in those concerning the vinyl derivatives is faster than that of the subsequent isomerisation. No reactive [Pd(DPPQ)(Rx)Cl]-*trans* P isomers would ever have been otherwise produced upon addition of DPPQ to the complex [Pd(MeN–SPh)(Rx)Cl].

(D). When the unreactive isomeric mixture of [Pd(DPPQ)-(Rd)Cl]-*trans* P and [Pd(DPPQ)(Rd)Cl]-*cis* P undergoes the transmetalation reaction with tributyl-phenylethynyl-stannane in the presence of the stabilizing and accelerating olefin maleic anhydride[10] to give the coupling product (2*Z*,4*Z*)-tetramethyl-7-phenylhepta-2,4-dien-6-yne-2,3,4,5-tetracarboxylate, it was noticed that the more stable isomer [Pd(DPPQ)(Rd)Cl]-*cis* P is indeed the more reactive species. As a matter of fact, the transmetalation reaction undergone by the complex [Pd(DPPQ)(Rd)Cl]-*cis* P is immediate whereas that undergone by [Pd(DPPQ)(Rd)Cl]-*trans* P takes several hours.

Theoretical calculations

The substitution reaction of MeN–SPh with DPPQ yielding both isomers [Pd(DPPQ)(Rx)Cl]-*trans* P and [Pd(DPPQ)(Rx)Cl]-*cis* P should probably proceed *via* attack of the phosphorus to the palladium center, thanks to its well known considerably high nucleophilic capability which is associated with a high *trans* effect.[11] Under this reasonable hypothesis, the incoming transition state and the resulting isomer would depend on the nature of the leaving atom of the MeN–SPh ligand as described in Scheme 4. It is worth noting that Scheme 4 is drawn on the basis of the well established and accepted mechanism governing the nucleophilic substitution reactions in planar tetracoordinate complexes which proceeds with retention of configuration.[1] In this respect, the displacement of pyridine nitrogen or thioetheric sulfur represents the key step in the formation of the -*trans* P or -*cis* P isomer, respectively.

With the aim of clarifying the mechanism involving the two different intermediates, we resorted to a theoretical calculation based on the density functional theory (DFT).[12-14] The energy differences (ΔE) between the two transition states $\mathbf{T_N}$ and $\mathbf{T_S}$ and between the final complexes [Pd(DPPQ)(Ra)Cl]-*trans* P and [Pd(DPPQ)(Ra)Cl]-*cis* P were computed when the DPPQ displaces MeN–SPh or the chelating HN–SPh from the complexes [Pd(N–S)(Rx)Cl]-*cis* S. The schematic energy profiles are shown in Fig. 3(a) and 3(b) respectively and the most relevant results are summarized in Table 4.

X-Ray crystal structure†

The crystal structure for the complex [Pd(DPPQ)(Ra)Cl]-*cis* P together with the relevant and selected bond lengths and angles are reported in Fig. 4 and Table 5, respectively.

Further details are reported in the ESI.†

Discussion

The most intriguing experimental result emerging from the present study is represented by the unequivocal formation of the thermodynamically unstable [Pd(DPPQ)(Rx)Cl]-*trans* P derivatives (together with [Pd(DPPQ)(Rx)Cl]-*cis* P in a lesser amount). This only occurs when the ligand MeN–SPh is displaced from the complexes [Pd(MeN–SPh)(Rx)Cl] by the DPPQ moiety. We

Table 4 Computed energies (Kcal mol^{-1}) and bond lengths (Å) related to the species involved in the formation of the isomeric mixture [Pd(DPPQ)(Ra)Cl]-*trans* P and [Pd(DPPQ)(Ra)Cl]-*cis* P from the reaction of [Pd(N–S)(Ra)Cl], (N–S = MeN–SPh, HN–SPh) with DPPQ (also see Fig. 3)

	ΔE/Kcal mol^{-1}		Selected bond lengths/Å	
	N–S = HN–SPh	N–S = MeN–SPh	N–S = HN–SPh	N–S = MeN–SPh
Ground state for complexes [Pd(N–S)(Ra)Cl]	0.0	0.0	Pd–N = 2.23 Pd–S = 2.42	Pd–N = 2.34 Pd–S = 2.42
$\mathbf{T_S}$ (*cis* path)	9.8	7.2		
$\mathbf{T_N}$ (*trans* path)	8.7	3.1		
$\mathbf{I_{P\text{–}N}}$ (*cis* path)	–5.2	–8.3	Pd–N = 2.31 Pd–P = 2.39	Pd–N = 2.30 Pd–P = 2.41
$\mathbf{I_{P\text{–}S}}$ (*trans* path)	1.7	–6.8	Pd–S = 2.43 Pd–P = 2.50	Pd–S = 2.43 Pd–P = 2.51
[Pd(DPPQ)(Ra)Cl]-*cis* P + N–S	–17.9	–23.1		
[Pd(DPPQ)(Ra)Cl]-*trans* P + N–S	–13.2	–18.4		

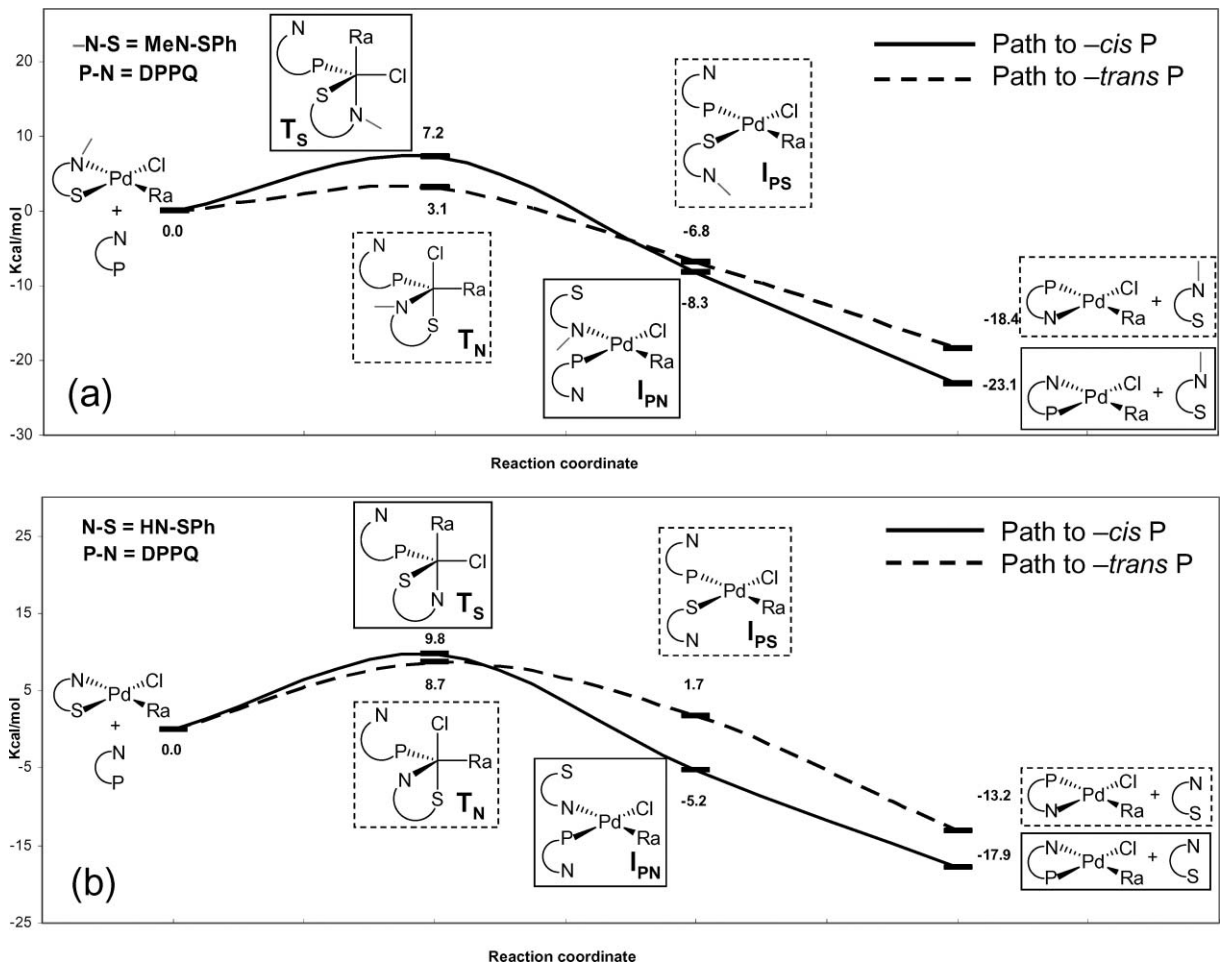


Fig. 3 Calculated energy profiles for the exchange reaction between ligands and the formation of the final isomeric mixture for the reactions (also see Table 4): [Pd(N–S)(Ra)(Cl] + DPPQ → [Pd(DPPQ)(Ra)Cl]-*trans* P + N–S [Pd(N–S)(Ra)(Cl] + DPPQ → [Pd(DPPQ)(Ra)Cl]-*cis* P + N–S N–S = MeN–SPh (Fig. 3(a)) N–S = HN–SPh (Fig. 3(b)).

have firstly assigned the geometrical structure to each isomer and secondly we have undertaken the theoretical study whose conclusions are reported further on. The [Pd(DPPQ)(Rd)Cl]-*cis* P isomer is characterized by the cross-peaks in NOESY spectra between the α, γ, δ COOCH_3 and the protons of the phenyl groups bound to phosphorus. The butadienyl terminal substituent CH_3 also interacts with the phenyl protons indicating the proximity of these groups with the phosphine moiety, no cross-peaks are detectable between the COOCH_3 and the CH_3 with quinoline protons. On the contrary, the [Pd(DPPQ)(Rd)Cl]-*trans* P isomer displays cross-peaks among α and γ COOCH_3 and CH_3 with the quinoline protons (mainly H^2). The characterization of the stable isomers allows the subsequent identification of the reacting ones. Such an identification was carried out by comparison of

Table 5 Selected bond lengths (Å) and angles (°) for [Pd(DPPQ)(Ra)Cl]-*cis* P

Pd–Cl	2.334 (1)	N–C(6)	1.313 (6)
Pd–P	2.201 (1)	N–C(14)	1.381 (6)
Pd–N	2.135 (4)	P–C(13)	1.816 (4)
Pd–C(1)	2.006 (4)	P–C(15)	1.806 (4)
		C(1)–C(3)	1.320 (6)
Cl–Pd–P	177.0 (1)	Pd–N–C(6)	124.7 (3)
Cl–Pd–N	93.4 (1)	Pd–N–C(14)	116.6 (3)
Cl–Pd–C(1)	90.9 (1)	Pd–P–C(13)	101.2 (1)
P–Pd–N	84.7 (1)	Pd–P–C(15)	117.4 (1)
P–Pd–C(1)	91.0 (1)	Pd–C(1)–C(3)	123.2 (3)
N–Pd–C(1)	174.5 (2)	C(2)–C(1)–C(3)	123.6 (4)

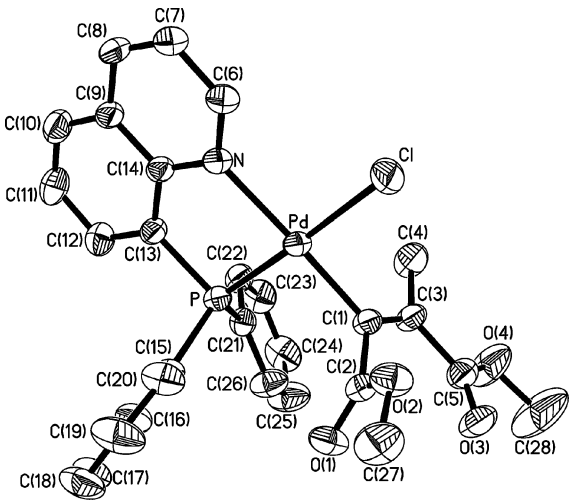


Fig. 4 ORTEP[15] view of the complex [Pd(DPPQ)(Ra)Cl]-*cis* P, together with the numbering scheme. Thermal ellipsoids drawn at the 40% probability level; hydrogen atoms have been omitted.

the proton and phosphorus chemical shifts. It is apparent that the analogy among the chemical shifts related to ^{31}P and ^{1}H (CH_3, H^2) signals belonging to different complexes is to be traced back to an identical geometrical distribution. Thus, for instance, the downfield shift (37.6 ppm) of the phosphorus of the [Pd(DPPQ)(Rd)Cl]-*cis* P complex and the highfield shift (26.2) of its -*trans* P counterpart allows the identification of all the other parent compounds (*cf.* Table 1). Moreover, the nature of the complex [Pd(DPPQ)(Ra)(Cl)]-*cis* P was also confirmed by the ^{31}P and ^{1}H NMR spectra of part of the crop subsequently used for the X-ray structural characterization.

Theoretical calculations

From Fig. 3(a), (b) and Table 4 it is apparent that:

(i) The difference in energy between the final complexes [Pd(DPPQ)(Ra)Cl]-*trans* P and [Pd(DPPQ)(Ra)Cl]-*cis* P is $\Delta E_{(transP-cisP)} = 4.7$ Kcal mol^{-1}); the [Pd(DPPQ)(Ra)Cl]-*cis* P derivative being the more stable, as expected.

(ii) The energies of the starting complexes [Pd(MeN–SPh)(Ra)Cl] and [Pd(HN–SPh)(Ra)Cl] are different; the complex [Pd(MeN–SPh)(Ra)Cl] being the less stable as can be deduced from the superimposition of the energy levels determined in both cases for the final complexes which are obviously the same ($E_{[Pd(MeN-SPh)(Ra)Cl]} - E_{[Pd(HN-SPh)(Ra)Cl]} \approx 5$ Kcal mol^{-1}). This fact is somehow confirmed by the calculated Pd–N length which is longer in the case of [Pd(MeN–SPh)(Ra)Cl] than in the case of [Pd(HN–SPh)(Ra)Cl] (2.34 *vs.* 2.23 Å).

(iii) When the complex [Pd(MeN–SPh)(Ra)Cl] is taken into consideration, the energy of the transition state $\mathbf{T_N}$ is lower than that of $\mathbf{T_S}$ (3.1 *vs.* 7.2 Kcal mol^{-1}; $\Delta E_{(TS-TN)} = 4.1$ Kcal mol^{-1}).

(iv) The transition states $\mathbf{T_N}$ and $\mathbf{T_S}$ for the complex [Pd(HN–SPh)(Ra)Cl], although displaying the same trend, are at considerably higher energy (8.7 *vs.* 9.8 Kcal mol^{-1}) with respect to the transition states involved in the previously considered case. Moreover, the corresponding values are very near ($\Delta E_{(TS-TN)}$= 1.1 Kcal mol^{-1}).

(v) The differences in energy between the $\mathbf{I_{PS}}$ and $\mathbf{I_{PN}}$ intermediates are very low in the case of the ligand MeN–SPh ($\Delta E_{(IPS-IPN)} =$ 1.5 Kcal mol^{-1}) and markedly higher in the case of HN–SPh ($\Delta E_{(IPS-IPN)} = 6.9$ Kcal mol^{-1}).

(vi) The energy level of the intermediate $\mathbf{I_{PS}}$ in the case of the ligand HN–SPh is higher than that of the related starting complex [Pd(HN–SPh)(Ra)Cl] ($\Delta E = 1.7$ Kcal mol^{-1}).

Point (i) confirms the experimental observation that the -*cis* P isomer represents the final product of any exchange reaction, whereas point (ii) indicates that the complex [Pd(MeN–SPh)(Ra)Cl]—thanks to the distortion at the main coordination plane—is energetically closer to the pentacoordinate transition state and therefore more prone to nucleophilic substitution than the complex [Pd(HN–SPh)(Ra)Cl].[7f,7g,16,17] The high energy barrier to $\mathbf{T_S}$ and $\mathbf{T_N}$ in the case of [Pd(HN–SPh)(Ra)Cl] and the energy level referred to the intermediate $\mathbf{I_{PS}}$ (points (iv) and (vi)) justify in the authors' opinion two experimental results. Firstly, the aromatic nitrogen, irrespective of its reduced kinetic *trans* effect and influence as compared with that of the thioetheric sulfur,[18] displays the same remarkable coordinating capability and this fact suggests that some sort of π back donation from palladium to the quinoline (or pyridine) ring stabilizing the Pd–N bond would be operative in the absence of distortion. Secondly, the similar energy barriers for $\mathbf{T_N}$ and $\mathbf{T_S}$ ($\Delta E_{(TS-TN)} = 1.1$ Kcal mol^{-1}) coupled with the high energy of the intermediate $\mathbf{I_{PS}}$ (1.7 Kcal mol^{-1}; $\Delta E_{(IPS-IPN)} =$ 6.9 Kcal mol^{-1}) could eventually explain why no -*trans* P isomer is experimentally observed in the case involving the starting complex [Pd(HN–SPh)(Ra)Cl].

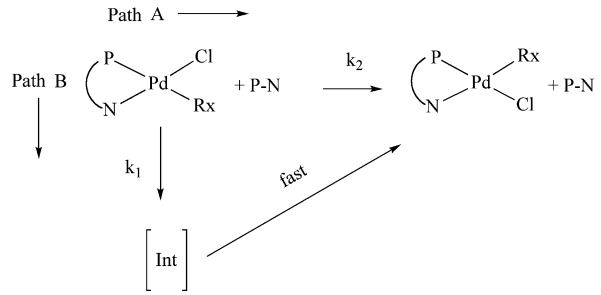
When the ligand MeN–SPh is involved, the intermediate $\mathbf{I_{PN}}$ is somewhat destabilized by the steric hindrance exerted by the methyl substituent in position 2 of the coordinating pyridine (point (v)). Therefore, at variance with the previous case, the path through $\mathbf{I_{PN}}$ does not represent a particularly advantageous way to the final products so that the unstable -*trans* P species can be formed. Moreover, the lowered energy barrier related to the transition state $\mathbf{T_N}$ (3.1 Kcal mol^{-1}) kinetically favours the formation of the -*trans* P isomer.

Notably, when the substituted chelate ligand is the symmetric BiPy, the reaction proceeds with the formation of the more stable -*cis* P isomer only. In this case, in the absence of alternative paths, the substitution reaction of the symmetric chelate ligand yields only the thermodynamically favored derivative.

Isomerization reactions

(A). It is worthy to remember that the formation of the -*trans* P species (and its -*cis* P counterpart) takes place *in situ*

by adding an adequate amount of the ligand DPPQ to a solution of [Pd(MeN–SPh)(Rx)Cl] complex. Under these circumstances, formation of the thermodynamically unstable vinyl derivatives [Pd(DPPQ)(Rx)Cl]-*trans* P (Rx = Ra, Rb, Rc) represents an unusually favourable case which allows a detailed study of the isomerization reactions of substrates bearing chelate ligands. In this case it is apparent that the stepwise mechanism reported in Scheme 5 is operative.



Scheme 5 Isomerization mechanism.

Path A is a bimolecular associative isomerization process,[1e,1d,19] in which the free ligand phosphanylquinoline, present in stoichiometric excess, attacks the complex [Pd(P–N)(Rx)Cl]-*trans* P inducing the rearrangement to its -*cis* P counterpart. Coordination of the phosphine of the free P–N ligand, the ring opening at the quinoline nitrogen of the coordinate P–N moiety, the subsequent ring closure of the incoming ligand and the consequent displacement of the leaving P–N would describe the observed isomerization in which P–N acts as a concentration-constant promoter of the reaction.[20] Such a step is clearly influenced by the steric requirement of the Rx groups (Ra: $k_2 = (5.1 \pm 0.4) \times 10^{-2}$, Rc: $k_2 = (1.34 \pm 0.06) \times 10^{-2}$ mol^{-1} dm^3 s^{-1}) as would be expected in case of associative reactions.[1d] Path A represents an efficient process so that a slight DPPQ excess warrants a quantitative isomerization reaction. Independently of the DPPQ excess the reactions were always described by a monoexponential relationship (see results).

Path B (k_1) represents the monomolecular way to isomerization which can also be observed in the absence of DPPQ in excess. In this respect it is worth noting that the presence of the displaced ligand MeN–SPh in the isomeric mixture does not alter the overall rate of the isomerization process, and the calculated rate constants (k_1) were coincident with those determined from the isomerization reaction of the isolated pure mixture of the -*trans* P and -*cis* P complexes. Notably, path B is not affected by the steric nature of the complexes involved (the measured k_1 values are substantially independent of the nature of Rx: Table 3). Moreover, such an isomerization process is also observed in the solid state. The isolated and purified isomeric mixture within a few days displays the complete disappearance of the -*trans* P species. Apparently, under the mutual *trans* influence exerted by the alkenyl and the phosphine groups, isomerization probably takes place *via* a T-shaped structure leading to a Y-shaped intermediate which eventually converts into the thermodynamically stable -*cis* P species.[21]

(B). In our opinion the behaviour of the complex [Pd(DPPQ)-(Rd)Cl]-*trans* P which does not undergo isomerization in the solid state nor in solution is surprising.

The inertness of such a species could be explained by the bulkiness of the substituents and by some sort of stabilizing intramolecular interaction between the butadienyl fragment and the ligand DPPQ hindering the transition states of the dissociative and associative paths. Unfortunately, several attempts at producing crystals suitable for diffractometric studies aimed at a better understanding of this problem were unsuccessful.

(C). The introduction of the methyl group on position 2 of the quinoline ring seems to remove the stabilization previously discussed (B) and the presence of the thermodynamically unstable [Pd(DPPQ-Me)(Rd)Cl]-*trans* P isomer can only be observed at low temperature

The methyl group, while enhancing the basicity of the quinoline nitrogen, induces an intrinsic instability on the ensuing complexes, forcing them into a distorted geometry thanks to its steric hindrance. This fact, which is not unprecedented, generally favours the reactivity of the involved species as has been shown for allene insertion on complexes of the type [Pd(R′N–SPh)(Me)Cl] (R′ = H, Me, Cl) or transmetalation reactions.[7f,7g,10,16,17]

Notably, the general destabilization and the consequent enhanced reactivity of such a derivative if compared with that of undistorted analogs was also apparent when the energies of the complexes [Pd(HN–SPh)(Rx)Cl] and [Pd(MeN–SPh)(Rx)Cl] were compared, as appears in the theoretical calculations section.

(D). In a former study dealing with transmetalation reactions the mechanism proposed by some of us, suggested that the lability of the nitrogen of the chelate P–N ligand would have enhanced the overall reactivity of the complex involved in the transmetalation processes.[10] We therefore surmise that the lower reactivity of the thermodynamically unstable [Pd(DPPQ)(Rd)Cl]-*trans* P can be traced back to the scarce *trans* effect of the chlorine group which does not induce a consistent labilization of the quinoline nitrogen. On the contrary, in the [Pd(DPPQ)(Rd)Cl]-*cis* P complex the quinoline nitrogen in *trans* position to the butadienyl moiety easily undergoes destabilization. Thus, the labilization of the quinoline nitrogen in *trans* position to the *trans* labilizing Rd group favours the olefin pre-coordination which was supposed to be the key step to the subsequent fast transmetalation process.[10]

Conclusion

The present work examines the results of the exchange reactions between bidentate asymmetric ligands in planar tetracoordinate Pd(II) complexes of general formula [Pd(L-L′)(Rx)Cl]. The most important issue is the possibility of determining the nature of the geometrical isomers taking advantage of the features of the leaving ligand only. Thus, the alkenyl palladium derivatives bearing the pyridylthioether ligand MeN–SPh when reacting with the phosphoquinoline DPPQ moiety, leads to the formation of both the isomers [Pd(DPPQ)(Rx)Cl]-*cis* P and the quite rare and thermodynamically unstable [Pd(DPPQ)(Rx)Cl]-*trans* P, in significant quantity. When the alkenyl group is the butadienyl derivative Rd, the ligand exchange reaction produces a stable isomeric mixture whose composition does not change with time allowing the quantitative separation of the isomers. On the contrary when Rx = Ra, Rb and Rc (vinyl residue) a slow isomerization is observed. The detailed study of such isomerization in the case of Rx = Ra, Rc was carried out and two mechanistic steps (associative and

dissociative) to the stable -*cis* P isomer were highlighted. When the ligand DPPQ-Me is used the isomerization at RT turns out to be immediate and in this case the unstable -*trans* P derivative can only be observed at low temperature. The structure of the complex [Pd(DPPQ)(Ra)Cl]-*cis* P which represents the thermodynamically stable isomerization product was unequivocally determined by an X-ray diffractometric study.

Experimental

Computational details

Calculations were performed with the ADF2007[12] package at the BLYP[13] level using DZP basis set in the frozen core approximation. Scalar relativistic effects were taken into account by the zeroth-order regular approximation (ZORA).[14] The geometry optimizations were performed without any symmetry constraint, followed by analytical frequency calculations to confirm that a minimum or a transition state had been reached. Cartesian coordinates and energies of stationary points are reported in the ESI.†

Materials

Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were purified by standard procedures and distilled under argon immediately prior to use. 1D- and 2D-NMR spectra were recorded using a Bruker 300 Avance spectrometer. Chemical shifts (ppm) are given relative to TMS (^{1}H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR).

Peaks are labelled as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). The proton and carbon assignment was performed by ^{1}H–2D COSY, ^{1}H–2D NOESY, ^{1}H–^{13}C HMQC and HMBC experiments.

IR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer.

DPPQ,[22] DPPQ-Me,[16] and complexes [Pd(MeN–SPh)(Rx)Cl][16] (Rx = Ra, Rb, Rc), [Pd(HN–SPh)(Ra)Cl],[16] [Pd(DPPQ-Me)(Ra)Cl],[16] [Pd(BiPy)(Ra)Cl],[16] [Pd(MeN–SPh)(Rd)Cl],[16] [Pd(DPPQ-Me)(Rd)Cl][16] were prepared following literature procedures. All other chemicals were commercial grade and were used without further purification.

^{1}H NMR kinetic measurements

In a typical NMR experiment 1.2×10^{-2} mmol of the complex under study ([Pd(MeN–SPh)(Rx)Cl)] Rx = Ra, Rc) was dissolved in 0.6 ml of CD_2Cl_2 and the appropriate weighed amount of DPPQ ligand was added in order to produce the molar ratio required by the particular process The reaction progress was followed at 298 K by recording selected integrated signals of the reactants and products. The ensuing rate constants were computed from non-linear regression of the concentration profiles *vs.* time according to the first order rate law (eqn (1)) (see results session).

Synthesis of the complexes

[Pd(DPPQ)(Ra)Cl]-*cis* P. 0.095 g (0.303 mmol) of the bidentate ligand DPPQ was added in one portion to a solution of [Pd(MeN–SPh)(Ra)Cl] (0.120 g, 0.233 mmol) in 10 ml of freshly distilled dichloromethane. The reaction mixture was stirred for 6 h at room temperature. The resulting clear yellow solution was concentrated at reduced pressure and the title complex was precipitated by addition of diethyl ether. The clear yellow powder was filtered off, washed with small aliquots of diethyl ether and *n*-pentane, and vacuum dried (0.131 g, yield 92%). Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the complex.

^{1}H NMR ($CDCl_3$, 298 K): δ 1.60 (s, 3H, =CCH_3), 3.50 (s, 3H, α-$COOCH_3$), 3.56 (s, 3H, β-$COOCH_3$), 7.39–7.48 (m, 5H, PPh_2), 7.56–7.66 (m, 3H, PPh_2), 7.70–7.76 (m, 2H, H^3, H^6), 7.81–7.88 (m, 2H, PPh_2), 7.99 (ddd, 1H, J = 9.9 Hz; 7.2 Hz; 1.1 Hz, H^7), 8.11 (dt, 1H, J = 8.1 Hz; 1.1 Hz, H^5), 8.48 (dt, 1H, J =8.4 Hz; 1.6 Hz, H^4), 10.20 (dd, 1H, J =5.0 Hz; 1.6 Hz, H^2).

^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 37.7.

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 21.1 (CH_3, =CCH_3), 51.1 (CH_3, α-OCH_3), 51.3 (CH_3, β-OCH_3), 123.1 (CH, C^3), 128.0 (d, C, J_{CP} = 7.2 Hz, α-C=C), 129.9 (d, C, J_{CP} = 48.6 Hz, C^8), 131.4 (CH, C^6), 132.0 (CH, C^5), 137.1 (CH, C^7), 139.1 (CH, C^4), 150.4 (C, C^{10}), 150.6 (C, C^9), 154.2 (CH, C^2), 155.8 (C, β-C=C), 164.2 (CO, β-CO), 171.9 (d, CO, J_{CP} = 4 Hz, α-CO).

IR (KBr pellet) ν = 1696 cm^{-1} (C=O); 1599 cm^{-1} (C=N).

Anal. Calcd for $C_{28}H_{25}ClNO_4PPd$: C, 54.92; H, 4.12; N, 2.29. Found: C, 54.82; H, 4.21; N, 2.36%.

[Pd(DPPQ)(Rb)Cl]-*cis* P. 0.094 g (0.300 mmol) of DPPQ was added in one portion to a solution of [Pd(MeN–SPh)(Rb)Cl] (0.120 g, 0.222 mmol) in 10 ml of freshly distilled dichloromethane. The reaction mixture was stirred for 24 h at room temperature. The resulting clear yellow solution was concentrated under reduced pressure and addition of diethyl ether gave the product as a microcrystalline clear yellow solid. It was filtered through a sintered glass-filter, washed with small aliquots of diethyl ether and *n*-pentane, and dried under vacuum. (0.132 g, yield 93%).

^{1}H NMR ($CDCl_3$, 298 K): δ 1.09 (t, 3H, J = 7.1 Hz, α-CH_2CH_3), 1.18 (t, 3H, J = 7.1 Hz, β-CH_2CH_3), 1.60 (s, 3H, =CCH_3), 3.77–3.88 (m, 1H, α-CH_2CH_3), 4,21 (qd, 2H, J = 7.1 Hz; J = 2.6 Hz, β-CH_2CH_3) 4.04–4.15 (m, 1H, α-CH_2CH_3), 7.37–7.49 (m, 5H, PPh_2), 7.55–7.76 (m, 5H, PPh_2, H^3,H^6), 7.85–7.92 (m, 2H, PPh_2), 8.00 (ddd, 1H, J = 9.9 Hz; 7.2 Hz; 1.1 Hz, H^7), 8.10 (dt, 1H, J =8.1 Hz; 1.1 Hz, H^5), 8.46 (dt, 1H, J =8.4 Hz; 1.6 Hz, H^4), 10.21 (dd, 1H, J = 5.0 Hz; 1.6 Hz, H^2).

^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 38.0.

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 13.9 (CH_3, α-CH_2CH_3), 14.1 (CH_3, β-CH_2CH_3), 21.2 (CH_3, =CCH_3), 59.8 (CH_2, α-CH_2CH_3), 59.9 (CH_2, β-CH_2CH_3), 123.1 (CH, C^3), 127.9 (d, C, J_{CP} = 7.2 Hz, α-C=C), 130.4 (d, C, J_{CP} = 55.3 Hz, C^8), 131.4 (CH, C^6), 131.9 (CH, C^5), 136.9 (CH, C^7), 139.0 (CH, C^4), 150.0 (C, C^{10}), 150.6 (C, C^9), 154.2 (CH, C^2), 155.6 (C, β-C=C), 163.7 (CO, β-CO), 171.5 (d, CO, J_{CP} = 4 Hz, α CO).

IR (KBr pellet) ν = 1697 cm^{-1} (C=O); 1603 cm^{-1} (C=N).

Anal. Calcd for $C_{30}H_{29}ClNO_4PPd$: C, 56.26; H, 4.56; N, 2.19. Found: C, 56.12; H, 4.50; N, 2.30%.

[Pd(DPPQ)(Rc)Cl]-*cis* P. 0.094 g (0.300 mmol) of DPPQ was added to a solution of [Pd(MeN–SPh)(Rc)Cl] (0.120 g, 0.200 mmol) in 10 ml of freshly distilled dichloromethane. The reaction mixture was stirred for 24 h at room temperature. The resulting clear yellow solution was concentrated under reduced pressure and the title complex was precipitated by addition of

diethyl ether. The clear yellow powder was filtered off, washed with small aliquots of diethyl ether and *n*-pentane, and vacuum dried (0.134 g, yield 96%).

^{1}H NMR ($CDCl_3$, 298 K): δ 1.37 (s, 9H, α-*t*-Bu), 1.46 (s, 3H, =CCH_3), 1.51 (s, 9H, β-*t*-Bu), 7.33–7.42 (m, 5H, PPh_2), 7.54–7.60 (m, 1H, PPh_2), 7.67–7.74 (m, 4H, PPh_2, H^3, H^6), 7.83–7.90 (m, 2H, PPh_2), 8.03 (ddd, 1H, J =9.9 Hz; 7.2 Hz; 1.1 Hz, H^7), 8.06 (dt, 1H, J = 8.1 Hz; 1.1 Hz, H^5), 8.44 (dt, 1H, J = 8.4 Hz; 1.6 Hz, H^4), 10.2 (dd, 1H, J =5.0 Hz; 1.6 Hz, H^2).

^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 37.6.

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 21.2 (CH_3, =CCH_3), 28.1 (CH_3, α-OC(CH_3)$_3$, 28.4 (CH_3, β-OC(CH_3)$_3$, 78.8 (C, α-OC(CH_3)$_3$, 79.6 (C, β-OC(CH_3)$_3$, 123.1 (CH, C^3), 127.9 (d, C, J_{CP} = 7.5 Hz, α-C=C), 130.0 (d, C, J_{CP} = 55.9 Hz, C^8), 130.9 (CH, C^6), 131.7 (CH, C^5), 137.1 (CH, C^7), 138.9 (CH, C^4), 150.3 (C, C^{10}), 150.5 (C, C^9), 154.1 (CH, C^2), 156.4 (C, β-C=C), 162.6 (CO, β-CO), 171.0 (d, CO, J_{CP} = 3.7 Hz, α-CO).

IR (KBr pellet) ν = 1697 cm^{-1} (C=O); 1601 cm^{-1} (C=N).

Anal. Calcd for $C_{34}H_{37}ClNO_4PPd$: C, 58.63; H, 5.35; N, 2.01. Found: C, 58.64 H, 5.39; N, 2.08%.

[Pd(BiPy)(Rc)Cl]. 0.038 g (0.241 mmol) of BiPy was added to a solution of [Pd(MeN–SPh)(Rc)Cl] (0.120 g, 0.200 mmol) in 10 ml of dichloromethane. The reaction mixture was stirred for 15 min at room temperature. Then, the clear yellow solution was concentrated *in vacuo* and addition of diethyl ether gave the product as a white powder. It was filtered through a sintered glass filter, washed with small aliquots of diethyl ether and *n*-pentane, and dried under vacuum (0.102 g, yield 93%).

^{1}H NMR ($CDCl_3$, 298 K): δ 1.51 (s, 9H, α-*t*-Bu), 1.59 (s, 9H, β-*t*-Bu), 2.39 (s, 3H, =CCH_3), 7.44–7.54 (m, 2H, H^5, $H^{5'}$), 8.00 (td, 1H, J = 7.9 Hz; J = 1.4 Hz, H^3), 8.07 (td, 1H, J = 7.9 Hz; J = 1.4 Hz, $H^{3'}$), 8.08–8.16 (m, 2H, H^4, $H^{4'}$), 8.91 (d, 1H, J =5.7 Hz, H^2), 9.14 (d, 1H, J =5.7 Hz, $H^{2'}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 21.2 (CH_3, =CCH_3), 28.2 (CH_3, α-OC(CH_3)$_3$, 28.3 (CH_3, β-OC(CH_3)$_3$, 79.8 (C, α-OC(CH_3)$_3$, 80.0 (C, β-OC(CH_3)$_3$, 121.5 (CH, $C^{3'}$), 122.1 (CH, C^3), 126.2 (CH, $C^{5'}$), 126.9 (CH, C^5), 127.6 (C, J_{CP} = 7.5 Hz, α-C=C), 138.7 (CH, $C^{4'}$), 139.5 (CH, C^4), 149.3 (CH, $C^{6'}$), 153.1 (CH, C^6), 153.5 (C, $C^{2'}$), 155.7 (C, C^2), 158.8 (C, β-C=C), 163.1 (CO, β-CO), 172.2 (d, CO, α-CO).

IR (KBr pellet) ν = 1697 cm^{-1} (C=O); 1602 cm^{-1} (C=N).

Anal. Calcd for $C_{23}H_{29}ClN_2O_4Pd$: C, 51.22; H, 5.42; N, 5.19. Found: C, 51.34 H, 5.36; N, 5.12%.

[Pd(DPPQ-Me)(Rc)Cl]-*cis* P. 0.072 g (0.22 mmol) of DPPQ-Me was added to a solution of [Pd(MeN–SPh)(Rc)Cl] (0.120 g, 0.200 mmol) in 10 ml of freshly distilled dichloromethane. The reaction mixture was stirred for 15 min at room temperature. The resulting clear yellow solution was concentrated under reduced pressure and the title complex was precipitated by addition of diethyl ether. The clear yellow powder was filtered off, washed with small aliquots of diethyl ether and *n*-pentane, and vacuum dried (0.134 g, yield 94%).

^{1}H NMR ($CDCl_3$, 298 K): δ 1.30 (s, 9H, α-*t*-Bu), 1.59 (s, 9H, β-*t*-Bu), 1.67 (s, 3H, =CCH_3), 3.41 (CH_3, 3H, quinoline-CH_3), 7.33–7.46 (m, 5H, PPh_2), 7.46 (d, CH, J =8.4 Hz, 1H, H^3), 7.51–7.62 (m, 2H, PPh_2, H^6), 7.90–7.97 (m, 3H, PPh_2, H^5), 8.04 (ddd, 1H, J =9.9 Hz; 7.2 Hz; 1.1 Hz, H^7), 8.16 (dt, 1H, J =8.4 Hz; 1.6 Hz, H^4).

^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 37.3.

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 22.2 (CH_3, =CCH_3), 28.0 (CH_3, α-OC(CH_3)$_3$, 28.6 (CH_3, β-OC(CH_3)$_3$, 29.4 (CH_3, quinoline-CH_3), 78.9 (C, α-OC(CH_3)$_3$), 79.7 (C, β-OC(CH_3)$_3$), 125.4 (CH, C^3), 126.6 (CH, C^6), 126.7 (d, C, J_{CP} = 7.7 Hz, α-C=C), 130.4 (d, C, J_{CP} = 52.2 Hz, C^8), 131.2 (CH, C^5), 134.0 (CH, C^7), 138.0 (CH, C^4), 150.8 (C, C^{10}), 151.0 (C, C^9), 167.1 (C, C^2), 156.3 (C, β-C=C), 162.6 (CO, β-CO), 167.1 (C, C^2), 170.4 (d, CO, J_{CP} = 5.5 Hz, α-CO).

IR (KBr pellet) ν = 1698 cm^{-1} (C=O); 1610 cm^{-1} (C=N).

Anal. Calcd for $C_{35}H_{39}ClNO_4PPd$: C, 59.16; H, 5.53; N, 1.97. Found: C, 59.27 H, 5.50; N, 1.94%.

[Pd(DPPQ)(Rd)Cl]-*cis* P and [Pd(DPPQ)(Rd)Cl]-*trans* P. 0.095 g (0.303 mmol) of the bidentate ligand DPPQ was added to a dichloromethane solution (20 ml) of [Pd(MeN–SPh)(Rd)Cl] (0.140 g, 0.213 mmol). The reaction mixture was stirred for 30 min at room temperature. The resulting clear yellow solution was concentrated to a small volume (2 ml) and the product was precipitated by addition of diethyl ether. The resulting solid was filtered off, washed with small aliquots of diethyl ether and *n*-pentane and finally dried under vacuum to give a clear yellow powder (0.136 g, yield 85%) consisting of a mixture of the two isomers *cis* (55%) and *trans* (45%). The crude solid was redissolved in a 1 : 4 mixture of CH_2Cl_2 : *n*-hexane and cooled to 0 °C for 12 h. This allowed the complete precipitation of the less soluble *trans* isomer as a white microcrystal solid (0.063 g). This product was recovered by filtration through a sintered glass filter. The filtered solution was evaporated to dryness on a rotary evaporator. Addition of a 1 : 4 mixture of diethyl ether : *n*-hexane followed by filtration of the pale-yellow solid afforded 0.064 g of virtually pure *trans* isomer (0.064 g).

***Trans*-isomer.** ^{1}H NMR ($CDCl_3$, 298 K): δ 1.54 (s, 3H, =CCH_3), 3.45 (s, 3H, γ-COOCH_3), 3.46 (s, 3H, α-COOCH_3), 3.60 (s, 3H, β-COOCH_3), 3.69 (s, 3H, δ-COOCH_3), 7.37–7.57 (m, 6H, PPh_2), 7.63–7.71 (m, 2H, H^3, H^6), 7.82–7.94 (m, 5H, PPh_2, H^7), 8.04 (dt, 1H, J = 8.0 Hz; 1.1 Hz, H^5), 8.41 (dt, 1H, J =8.4 Hz; 1.6 Hz, H^4), 10.24 (dd, 1H, J = 5.2 Hz; 1.6 Hz, H^2).

^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 37.6.

^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, ppm): δ 17.6 (CH_3, =CCH_3), 51.2 (CH_3, α-OCH_3), 51.8 (CH_3, γ-OCH_3), 51.9 (CH_3, β-OCH_3), 52.1 (CH_3, δ-OCH_3), 123.1 (CH, C^3), 127.8 (CH, C^6), 129.5 (d, C, J_{CP} = 9.6 Hz, α-C=C), 129.8 (d, C, J_{CP} = 47 Hz, C^8), 131.7 (CH, C^5), 135.3 (γ-C=C,), 136.6 (CH, C^7), 137.1 (δ-C=C,), 139.0 (CH, C^4), 150.0 (C, C^{10}), 150.3 (C, C^9), 154.4 (CH, C^2), 162.1 (β-C=C), 162.7 (CO, β-CO), 167.7 (CO, γ-CO), 169.0 (C, δ-CO), 171.9 (d, CO, J_{CP} = 4 Hz, α-CO).

IR (KBr pellet) ν = 1709, 1683 cm^{-1} (C=O); 1588 cm^{-1} (C=N).

Anal. Calcd for $C_{34}H_{31}ClNO_8PPd$: C, 54.13; H, 4.14; N, 1.86. Found: C, 54.22; H, 4.23; N, 1.82%.

***Cis*-isomer.** ^{1}H NMR ($CDCl_3$, 298 K): δ 2.14 (s, 3H, =CCH_3), 3.00 (s, 3H, γ-COOCH_3), 3.69 (s, 3H, δ-COOCH_3), 3.74 (s, 3H, β-COOCH_3), 3.90 (s, 3H, α-COOCH_3), 7.38–7.64 (m, 9H, PPh_2, H^3) 7.74 (t, 1H, J = 8.0 Hz; H^6), 7.86–8.00 (m, 3H, PPh_2, H^7), 8.07 (dt, 1H, J = 8.0 Hz; 1.1 Hz, H^5), 8.43 (dt, 1H, J = 8.2 Hz; 1.6 Hz, H^4), 9.78 (dd, 1H, J =5.2 Hz; 1.6 Hz, H^2).

^{31}P{^{1}H} NMR ($CDCl_3$, 298 K, ppm):δ 26.2.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298 K, ppm): δ 19.4 (CH_3, $=CCH_3$), 51.2 (CH_3, γ-OCH_3), 51.8 (CH_3, α-OCH_3), 51.9 (CH_3, δ-OCH_3), 52.0 (CH_3, β-OCH_3), 123.3 (CH, C^3), 125.8 (C, γ-C=C), 128.0 (CH, C^6), 132.2 (CH, C^5), 132.3 (d, C, $J_{CP} = 55$ Hz, C^8), 132.8 (d, C, $J_{CP} = 7.0$ Hz, α-C=C), 138.1 (CH, C^7), 138.9 (CH, C^4), 141.6 (C, δ-C=C), 152.6 (C, C^{10}), 153.0 (C, C^9), 159.6 (CH, C^2), 162.6 (β-C=C), 162.8 (CO, β-CO), 167.2 (CO, γ-CO), 170.4 (C, δ-CO), 175.2 (d, CO, $J_{CP} = 4$ Hz, α-CO).

IR (KBr pellet) $\nu = 1711$ cm^{-1} (C=O); 1591 cm^{-1} (C=N).

Anal. Calcd for $C_{34}H_{31}ClNO_8PPd$: C, 54.13; H, 4.14; N, 1.86. Found: C, 54.32; H, 4.20; N, 1.90%.

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