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Facile synthesis and reactivity study of mixed phosphane–isocyanide Pd(II) and Pd(0) complexes

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ABSTRACT

The reaction between an equimolecular mixture of isocyanide CNR (CNR = di-methylphenyl isocyanide (DIC), *tert*-butyl isocyanide (TIC), triphenyl phosphane (PPh_3) and a dechlorinated solution of the palladium allyl dimers $[Pd(\eta^3\text{-allyl})Cl]_2$ (allyl = 2-Meallyl, 1,1-Me_2allyl) in stoichiometric ratio yields the mixed derivative $[Pd(\eta^3\text{-allyl})(CNR)(PPh_3)]$ only. Apparently, the mixed derivative represents the most stable species among all the possible ones that might be formed under those experimental conditions. Theoretical calculations are in agreement with the experimental observation and the energy stabilization of the mixed species with respect to the homoleptic derivatives is traced back to an overall *push–pull* effect exerted by the isocyanide and the phosphane acting synergically. Similar behavior is observed in the case of the synthesis of the palladacyclopentadienyl complexes $[Pd(C_4(COOMe)_4)(CNR)(PPh_3)]$ and of the palladium(0) olefin complexes whose synthesis invariably yields the mixed $[Pd(\eta^2\text{-olefin})(CNR)(PPh_3)]$ derivatives. The paper includes studies on the reactivity toward allylamination in the case of the palladium(II) allyl complexes. A diffractometric investigation on the solid state structures of four different palladium isocyanide–phosphane complexes is also included.

1. Introduction

With the aim of evaluating the electronic characteristics of the spectator ligands from kinetic data, we have been recently involved in a study dealing with the reactivity toward amination of palladium allyl complexes bearing mixed monodentate carbene, phosphite, phosphane and isocyanide ligands. The synthesis of the allyl derivatives bearing phosphanes and isocyanides ($[Pd(\eta^3\text{-allyl})(L')(L'')]ClO_4$), was indeed trivial since the complexes required were obtained by simple addition of equimolecular amounts of phosphane and isocyanide to a CH_2Cl_2 solution of the allyl dimer $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ dechlorinated with $NaClO_4$ [1,2]. We have also noticed that a non statistical mixture of homoleptic and mixed complexes was obtained when equimolecular solutions of different ligands (L′ = phosphites, L″ = isocyanides, and phosphanes) were added to the dechlorinated allyl dimer obtained as previously described.[1] Moreover, simultaneous addition of different isocyanides, namely di-methylphenyl isocyanide (DIC) and *tert*-butyl isocyanide (TIC) again gave rise to the statistical mixture (25%:50%:25%) of all the possible species [3] irrespectively of their remarkable different steric hindrance and electron donating characteristics.

Therefore, among the explored ligands, only the equimolecular mixture of phosphanes (L′) and isocyanides (L″) yields the mixed derivatives $[Pd(\eta^3\text{-allyl})(L')(L'')]ClO_4$ as the sole products of the synthesis. In order to rationalize such a surprising behavior we undertook an accurate literature investigation on complexes of the type *cis*-$[Pd(E\text{-}E)(CNR)(PR'_3)]^{n+}$ ($n = 0, 1$; E–E = generic coordinating systems imposing *cis* geometry) [4]. Some derivatives ($[Pd(CNR)(PR'_3)X_2]$ [5], $[Pd(CNR)(PR'_3)(R'')X]$ [8]) bearing the phosphanes *trans* to isocyanides can also be found in the literature together with complexes of the type *trans*-$[Pd(CNR)_2(PR'_3)_2]$ [4h,6].

From such an investigation it was clear that the mixed complexes were synthesized by means of different synthetic protocols and with different stoichiometric ratios among phosphanes, isocyanides and the metal, suggesting that no generalized approaches has in any case been exploited.

Thus, we thought that an understanding of the energetic reasons governing the formation of the mixed (or homoleptic) complexes and consequently the simplest experimental conditions for the achievement of the former was in order. In this respect, we have undertaken a systematic experimental investigation on the facile synthesis of some of the above mentioned mixed complexes of palladium(0) and palladium(II) and a theoretical study of their thermodynamic stability. Moreover, we have also carried

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[1] Remarkably, the obtainment of the allyl complexes bearing mixed L′ (L′ = NHCs) and L″ (L″ = phosphane, phosphite, isocyanide) ligands was strictly governed by the sequence of addition of the monodentate ligands. In this respect, the pure mixed L′–L″ species can only be obtained by the addition *in situ* of the phosphane, phosphite and isocyanide moieties to a dechlorinated CH_2Cl_2 solution of the previously synthesized $[Pd(\eta^3\text{-allyl})(NHC)Cl]$ derivatives. Apparently, the added L″ ligands, although very efficient, cannot displace the NHC fragment probably for kinetic reasons (see Section 2).

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out a diffractometric study on some of these substrates and investigation on the reactivity of the palladium(II) mixed allyl derivatives toward amination.

2. Result and discussion

The species and the complexes involved in the present study are summarized in Scheme 1.

2.1. Synthesis of $[Pd(\eta^3\text{-allyl})(PPh_3)(CNR)]ClO_4$ complexes (allyl = 2-Meallyl; 1,1-Me_2allyl; CNR = DIC, TIC)

Addition of an equimolecular mixture of CNR (CNR = DIC, **a**; TIC, **b**) and PR'_3 (**c**) (Pd: CNR: PPh_3 = 1:1:1) to a solution of the allyl dimer $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$ (allyl = 2-Meallyl (**1**), 1,1-Me_2-allyl (**2**)) and $NaClO_4$ in CH_2Cl_2:MeOH (3:1 v:v) yields the mixed allyl palladium(II) complexes $[Pd(\eta^3\text{-allyl})(DIC)(PPh_3)]^+$ (**1a**, **2a**) or $[Pd(\eta^3\text{-allyl})(TIC)(PPh_3)]^+$ (**1b**, **2b**) *only* after the precipitation of NaCl. The ensuing complexes are stable in the solid and in solution of chloridated solvents and their characterization is easily obtained by means of ^1H, ^{31}P and ^{13}C NMR. In the cases of the complexes bearing the symmetric allyl fragment 2-Meallyl, (**1a**, **1b**) four signals due to the *anti* and *syn* allyl protons are detectable. The *syn* proton *trans* to phosphorus resonates as a pseudo triplet ($^3J_{P-H} \approx {}^4J_{H-H} \approx 5$ Hz) at the lowest field with respect to the other allyl protons, while the *anti* proton *trans* to phosphorus resonates as a doublet ($^3J_{P-H}$ = 10 Hz). The signals of the methyl protons of CNR and of the phenyl groups of PPh_3 belonging to the pure mixed complexes are also detectable at high and low field, respectively, confirming that no homoleptic species are present in solution. Notably, both the mixed derivatives of the asymmetric 1,1-Me_2allyl (**2a**, **2b**) are detectable only as the unique isomers bearing the bis-substituted allyl carbon *trans* to phosphorus. As a matter of fact, the protons of the anti methyl substituents at the terminal allyl carbon (CH_{3anti}) resonate as doublets at higher field with respect to the *syn* (CH_{3syn}) whereas, only the couplings with the central proton (two doublets) are detectable in the case of the terminal *anti* and *syn* allyl protons (*trans* to CNR). All the NMR experiments (^1H, ^{31}P, ^{13}C NMR, HMQC and HMBC) are in accord with the proposed formulation. In particular the ^{13}C NMR spectra clearly display three different signals for the allyl carbons in both cases. The allyl carbons *trans* to phosphorus in any case resonate as a doublet at the lowest field ($^3J_{P-C} \approx 24$–27 Hz). Moreover, the ^{31}P NMR spectra display a unique singlet (between 26 and 28 ppm) in all the allyl complexes synthesized, thereby confirming the presence in solution of the sole isomer previously described in the case of complexes **2a** and **2b** [1] (see Section 4 and Supporting Information for a selection of NMR spectra).

2.2. Synthesis of $[Pd(C_4(COOMe)_4)(PPh_3)(CNR)]$ complexes (CNR = DIC, TIC)

The palladacyclopentadienyl complexes of the type $[Pd(C_4(COOMe)_4)(CNR)(PPh_3)]$, (**3**) cannot be synthesized from the usual polymeric starting substrate $[Pd(C_4(COOMe)_4)]_n$ [7] upon addition of CNR and PPh_3, since the formation of a mixture of not easily identifiable species was observed in those cases, probably due to the low solubility of the polymeric precursor. Since the alternative procedure based on the oxidative coupling of dimethyl-2-butynedioate (dma) of a mixed CNR–PPh_3 palladium(0) substrate gave no appreciable result, we have adopted a tailored approach derived from a synthetic protocol we proposed elsewhere [8], consisting in the reaction of the labile 6-methyl-2-phenylthiomethylpyridine (MeN-SPh) ligand with the polymer $[Pd(C_4(COOMe)_4)]_n$ yielding the complex $[Pd(C_4(COOMe)_4)(MeN\text{-}SPh)]$. Simultaneous addition of an equimolecular solution of DIC or TIC and PR'_3 to the latter gave rise to the mixed $[Pd(CNR)(PR'_3)(C_4(COOMe)_4)]$ complexes (**3a**, **3b**) as the only products. The ^1H and ^{13}C NMR spectra display four different groups of signals ascribable to the four magnetically non equivalents $-OCH_3$ fragments. The structural distribution of the ligands can also be determined from the ^1H and ^{13}C signals due to phosphane and isocyanide groups which clearly indicate the concomitant presence of only one phosphane and one isocyanide and from the ^{31}P spectra displaying only one singlet ascribable to the phosphorus atom in both cases (~26 ppm) (see Section 4 and Supporting Information for a selection of NMR spectra).

2.3. Synthesis of $[Pd(\eta^2\text{-olefin})(PPh_3)(CNR)]$ complexes (CNR= DIC, TIC)

The synthesis of the complexes of palladium(0) of the type $[Pd(\eta^2\text{-olefin})(CNR)(PR'_3)]$ was also achieved taking advantage of the lability of the ligand MeN-SPh since the direct "classical" addition of equimolecular amounts of CNR and PR'_3 to the complex $[Pd_2(DBA)_3{\cdot}CHCl_3]$ in the presence of the olefin induces a massive formation of metallic palladium along with the wanted complex. We have therefore synthesized the complexes $[Pd(\eta^2\text{-olefin})(MeN\text{-}SPh)]$ [9] (olefin = ma, **4**; nq, **5**; tmetc, **6**; fn, **7**; *cis*-SO_2-tol, **8**; *trans*-SO_2-tol, **9**) which were reacted with the usual equimolecular mixture of CNR (CNR = DIC, **a**; TIC, **b**) and PR'_3. The expected mixed complexes **4a**, **5a**, **6a**, **7a, 8a**, **9a** and **4b**, **5b**, **6b** were obtained. All the ensuing derivatives were stable in the solid and in solution and the presence of homoleptic complexes was never detected, as confirmed by their ^{31}P NMR spectra which always display only one singlet between 26.0 and 29.4 ppm.

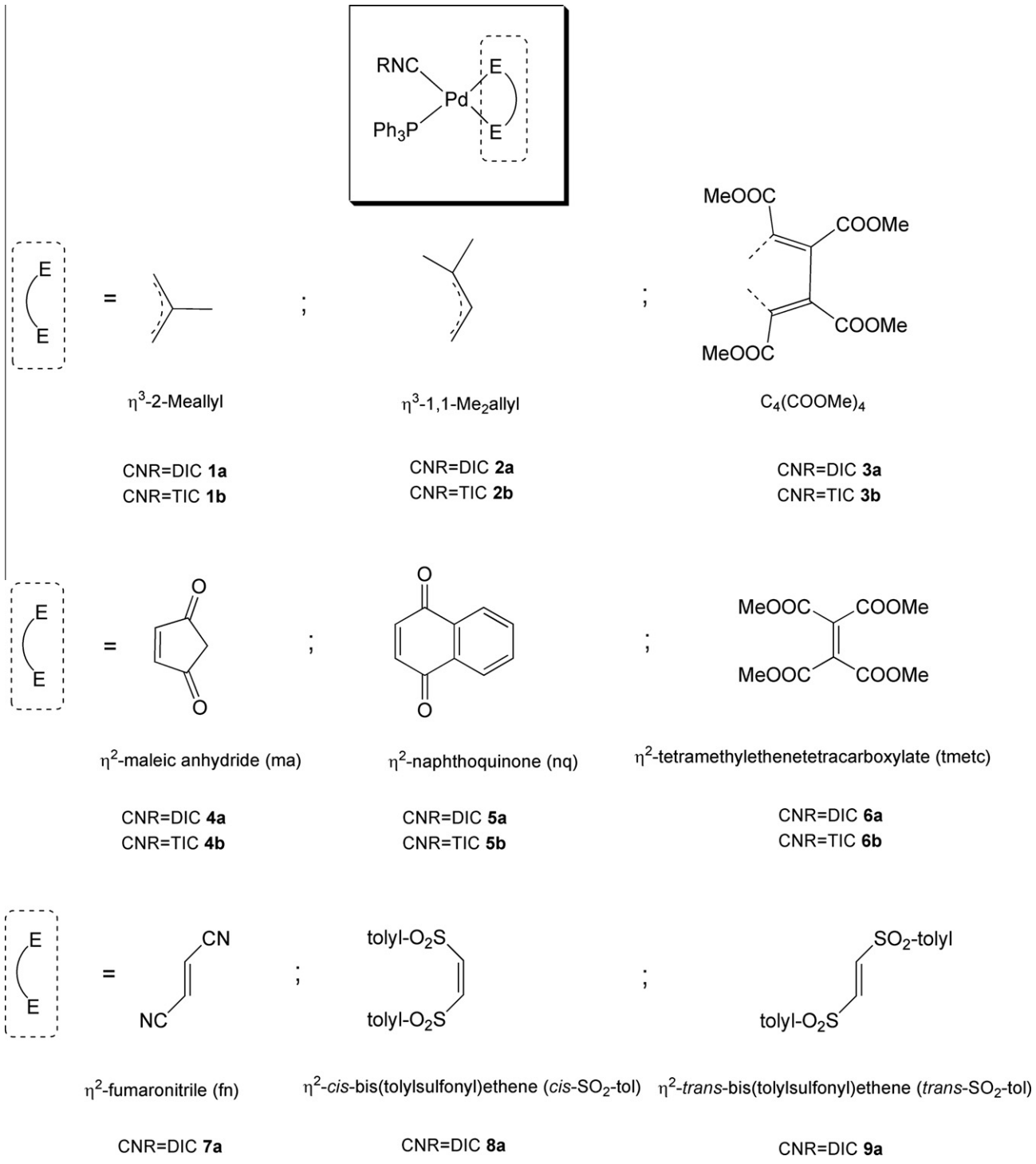
The spectator ligands CNR and PR'_3 were also detected by means of ^1H, ^{13}C and ^{31}P NMR spectra displaying all the expected signals. The coordinated olefins are also detectable by NMR techniques and their coordination is characterized by a high field shift of the olefin protons and carbons ($\leqslant$3, $\leqslant$80 ppm, respectively) with respect to those of the uncoordinated ones. Moreover, the complex asymmetry and the presence of the NMR active phosphorus allow a prompt identification of the olefin protons and carbons. As an example, the proton of maleic anhydride *cis* to phosphorus in the complex **4b** resonates as a *pseudo* triplet ($J_{P-H} \approx J_{H-H} \approx 4.1$ Hz) at 3.94 ppm whereas the signal of the *trans* proton at 4.73 ppm resonates as a doublet of doublets (J_{P-H} = 9.8 Hz). Similar behavior can be observed in the case of the olefin carbons (50.1 ppm *cis* to P and 50.9, *trans* to P, J_{P-C} = 26.3 Hz) and generally speaking in all the palladium(0) olefin derivatives. In agreement with the general behavior the complexes of the symmetric olefin tmetc **6a** and **6b** display only two singlets related to the two different olefin methyl substituents (3.27 ppm *cis* to P and 3.73 *trans* to P) (see Section 4 and Supporting Information for a selection of NMR spectra).

2.4. Crystal structure determinations

At the best of our knowledge the crystal structures reported in this paper represent the first diffractometric study on complexes of palladium(0) olefin complexes, allyl palladium(II) and palladacyclopentadiene derivatives bearing mixed phosphane and isocyanide as spectator ligands.

ORTEP [10] views of the allyl cationic complexes **2a** and **2b** are shown in Figs. 1 and 2. Selected bond distances and angles are given in Table 1.

In these two complexes the palladium atom, bound to one triphenylphosphane group, one isocyanide carbon and two η^3-allylic terminal carbon atoms, shows distorted square-planar coordination. In both **2a** and **2b** complexes the C3 terminal carbon bearing the dimethyl substituents is *trans* to the thriphenylphosphane



Scheme 1. Ligands and complexes synthesized and studied.

group. The *trans* influence exerted by the phosphane is evidenced by the lengthening of Pd–C3 (allyl) bond distances, ranging from 2.265(5) to 2.293(5) Å, if compared with the Pd–C1 ones, *trans* to isocyanide carbon atoms, which are in the range 2.114(6)–2.143(6) Å. Apparently the substituents are involved in Pd–C bond lengthening as observed also in other [Pd(η^3-substituted-allyl)(C,P)] complexes where Pd–C(*trans* to P) distances become longer upon terminal substitution from 2.18(2) to 2.28(2) Å (on average) [11]. The η^3-allyl fragments are obliquely placed with respect to the metal square coordination plane and form with the same plane dihedral angles of 65.1(8)° and 58.6(6)°, for the two complexes, **2a** and **2b**, respectively. The central C2 atoms of the η^3-allyl groups are situated above the mean coordination plane by 0.47(1) and 0.623(6) Å, respectively (Figs. 1s, 2s Supporting Information).

An ORTEP view of the neutral palladacyclopentadiene complex **3a** is shown in Fig. 3 and selected bond distances and angles are reported in Table 2. The geometry around the palladium center is distorted square planar. The four positions around the central palladium are occupied by the 1,4 carbon atoms of the 1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-diene-1,4-diyl anionic ligand, one triphenylphosphane and one isocyanide carbon atom. The

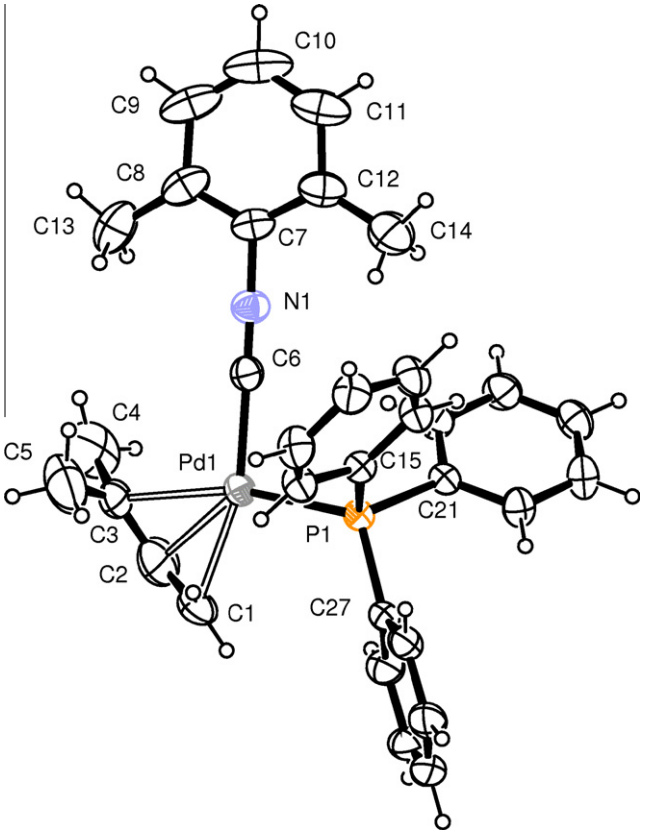


Fig. 1. An ORTEP view of complex **2a** showing the thermal elipsoides at 30% probability level. (For the sake of clarity the perchlorate anion was omitted.)

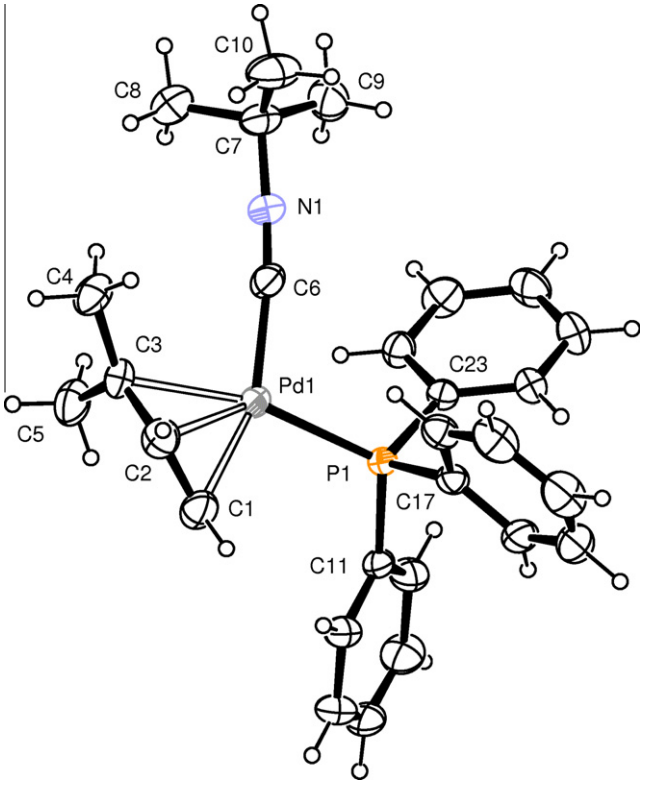


Fig. 2. An ORTEP view of complex **2b** showing the thermal elipsoides at 30% probability level. (For the sake of clarity the perchlorate anion was omitted.)

Table 1
Selected bond distances and angles (Å and °) for compounds **2a** and **2b**.

	2a	2b
Pd1–P1	2.324(1)	2.322(1)
Pd1–C1	2.143(5)	2.114(6)
Pd1–C2	2.156(7)	2.144(5)
Pd1–C3	2.293(5)	2.265(5)
Pd1–C6	2.002(5)	2.001(5)
C1–C2	1.453(12)	1.394(9)
C2–C3	1.330(10)	1.387(8)
P1–Pd1–C1	97.6(2)	99.0(2)
P1–Pd1–C2	132.9(3)	133.4(2)
P1–Pd1–C3	164.5(1)	165.2(2)
P1–Pd1–C6	97.6(1)	102.4(2)
C6–Pd1–C1	163.8(2)	158.5(2)
C6–Pd1–C2	127.7(3)	121.2(2)
C6–Pd1–C3	97.2(2)	91.4(2)
C1–C2–C3	123.9(9)	121.9(5)
P1,Pd1,C6^C1,C2,C3	65.1(8)	68.4(6)

^ = Dihedral angle.

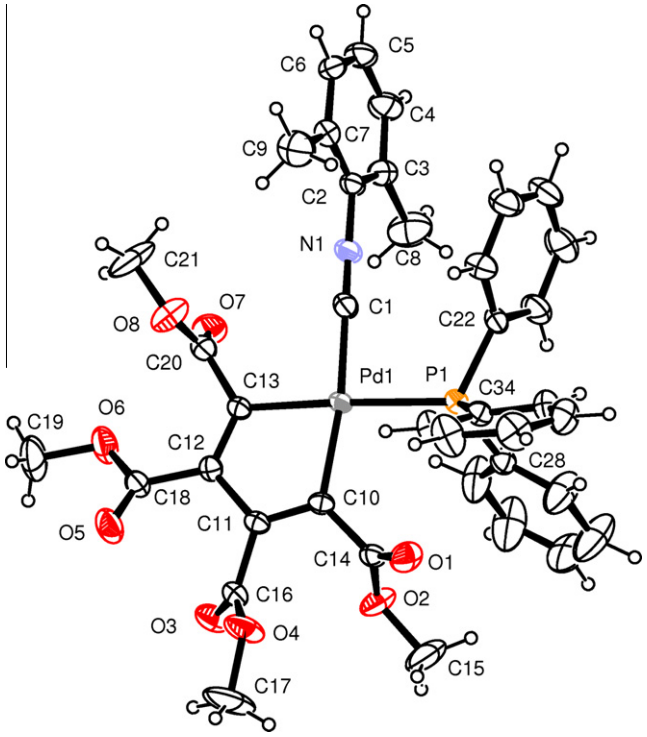


Fig. 3. An ORTEP view of complex **3a** showing the thermal ellipsoids at 30% probability level.

maximum deviation from the basal plane is 0.078(3) Å for the isocyanide carbon C1. The palladacyclopentadiene ring is approximately planar with maximum deviations from the mean plane for C12 and C13 atoms of −0.022(3) and 0.023(3) Å, respectively, and forms an angle of only 1.42(7)° with the coordination plane. The Pd1–C10 and Pd1–C13 bonds display distances of 2.067(3) and 2.073(3) Å longer than analogous distances in similar compounds, with a Pd–C average bond length of 2.02(2) Å, where the carbon atoms are in *trans* positions to nitrogen or sulphur atoms, showing that the triphenylphosphane and isocyanide groups exert a comparably slight *trans* influence on Pd–C(diene) distances. [12]

An ORTEP view of complex [Pd(η^2-ma)(TIC)(PPh_3)] (**4b**) is shown in Fig. 4. A selection of bond distances and angles is given in Table 3. The palladium is bound to one isocyanide carbon atom, one triphenylphosphane group and η^2-coordinated to the C=C double bond of the maleic anhydride. The structure shows that

Table 2
Selected bond distances and angles (Å and °) for compound **3a**.

Pd1–P1	2.3627(8)	C10–C11	1.347(4)
Pd1–C1	1.991(4)	C11–C12	1.480(4)
Pd1–C10	2.067(3)	C12–C13	1.336(4)
Pd1–C13	2.073(3)		
P1–Pd1–C1	90.8(1)	C1–Pd1–C13	91.7(1)
P1–Pd1–C10	98.0(1)	C10–Pd1–C13	79.4(1)
P1–Pd1–C13	177.1(1)	Pd1–C10–C11	114.2(2)
C1–Pd1–C10	170.4(1)	Pd1–C13–C12	114.9(2)

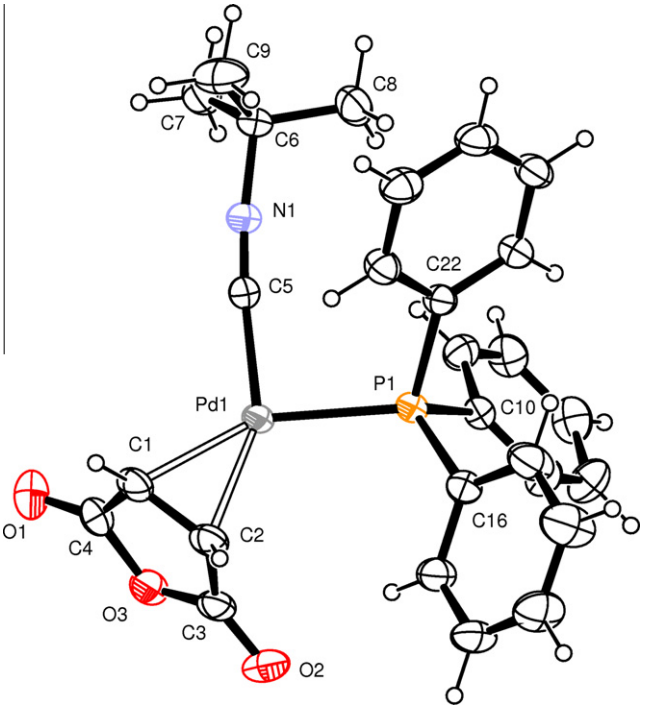


Fig. 4. An ORTEP view of complex **4b** showing the thermal ellipsoids at 30% probability level.

the palladium center is trigonal planar, as expected for zero-valent complexes of the type [Pd(η^2-olefin)(L′)(L″)]. Pd1–C1 and Pd1–C2 bond distances of 2.126(2) and 2.095(2) Å are in perfect agreement with the Pd(0)–C distances in other similar complexes of Pd(0) with maleic anhydride. [13] The C1═C2 alkene bond length of 1.425(4) Å is 0.093 Å longer than in the free alkene and is consistent with π-back bonding from Pd(0). The maleic anhydride moiety forms an angle of 68.42(6)° with the Pd1–P1–C5 coordination plane (Fig. 3s, Supporting Information).

2.5. Formation of the mixed complexes

Substitution among ligands in the case of palladium derivatives is generally fast so that, the ratios among the ensuing products are under thermodynamic control. It would hence be important to stress that when we talk of equimolecular conditions we mean that the synthesis of the complexes is carried out by mixing equal concentrations of all the involved species ([starting complex]$_0$ = [CNR]$_0$ = [PPh_3]$_0$) since such a stoichiometric constraint plays a fundamental role in the reaction economy. However, even under such a condition the formation of mixed species *only* occurs rarely, the formation of all the possible complexes (one mixed and two homoleptic) being the most frequent event. This fact is governed by the mutual stability (stability constants) of the ensuing species

Table 3
Selected bond distances and angles (Å and degrees) for compound **4b**.

Pd1–P1	2.3387(5)	C2–C3	1.467(3)
Pd1–C1	2.126(2)	C3–O3	1.407(2)
Pd1–C2	2.095(2)	C4–O3	1.394(3)
Pd1–C5	2.012(5)	C1–C4	1.452(3)
C1–C2	1.425(3)		
P1–Pd1–C1	149.35(6)	Pd1–C2–C1	71.5(1)
P1–Pd1–C2	110.96(6)	Pd1–C1–C4	110.1(1)
P1–Pd1–C5	94.68(5)	Pd1–C2–C3	107.8(1)
Pd1–C1–C2	69.1(1)		
Pd1,C1,C5 ^C1,C2,C3,C4,O3	68.42(6)		

^ = Dihedral angle.

which obviously depends on the chemical characteristics of the added ligands, other things being equal. Thus a similar stability among complexes yields an almost statistical distribution of the derivatives (25%:50%:25%) [3]. Intuitively, in the case of a different stability between the two homoleptic complexes, the mixed species will generally have a stability intermediate between those of the formers. Such a situation is the most usual and experimentally verified and gives rise to a distribution of the species governed by the mutual equilibrium constants. In order to rationalize these observations let us first suppose that the addition of equimolecular amounts of the ligands A and B to a generic species ML_2 ([A]$_0$ = [B]$_0$ = [ML_2]$_0$; L = labile ligand; M = metal) yields the mixed species MAB only according to the reaction:

$$ML_2 + A + B \rightarrow MAB + 2L \tag{1}$$

Also, consider the reactions that the mixed species undergoes when reacting with the ligands A or B to give the homoleptic derivatives.

$$MAB + A = MAA + B \quad K_1 = \frac{[MAA][B]}{[MAB][A]}; \quad \Delta G_1^0 \tag{2}$$

$$MAB + B = MBB + A \quad K_2 = \frac{[MBB][A]}{[MAB][B]}; \quad \Delta G_2^0 \tag{3}$$

The mixed complex MAB may also react to give the homoleptic complexes according to reaction (4) where the condition [M]$_0$ = [A]$_0$ = [B]$_0$ is implicit:

$$2MAB = MAA + MBB \quad K_3 = \frac{[MAA][MBB]}{[MAB]^2};$$
$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0 \tag{4}$$

Obviously, the stability of complex MAB is governed by the magnitude of K_3 and in particular the degree of advancement of reaction (5) is:

$$\xi_3 = \frac{[MAB]_0 \cdot \sqrt{K_3}}{2\sqrt{K_3} + 1}; \quad K_3 = e^{-\frac{\Delta G_3^0}{RT}} \tag{5}$$

where [MAB]$_0$ represents the starting concentration of the mixed complex (see Eq. (1)).[2] A very small equilibrium constant K_3 ($\Delta G_3^0 \gg 0$) renders the degree of advancement negligible and consequently the mixed derivative the most prominent species. Apparently, the stability of the mixed complex MAB with respect to the combination of the stabilities of the homoleptic species ($\Delta G_1^0 + \Delta G_2^0 = \Delta G_3^0$) is the sole condition required in order to enrich the reaction mixture in the mixed derivative. The formation of only the mixed complexes [Pd(η^3-allyl)(L)(X)] (L = neutral ligand, X^- = halide) is often observed when the allyl-halide palladium dimer is reacted with the stoichiometric amount of L in chloridated solvents. On the contrary, mixed complexes bearing neutral molecules as spectator ligands are less frequent and are observed when

[2] Under non equimolecular conditions such a conclusion will no longer be valid.

the two neutral ligands are weak (CH_3CN, pyridine) and strong ($P(OR)_3$, PR_3) [2] coordinating species, respectively.[3] Apparently, the condition expressed by Eq. (5) can also be achieved when only one of the homoleptic derivatives is very unstable, the equilibrium constant being modulated only by the ΔG_3^0 value. Obviously, in that case the stoichiometric equivalence among concentrations and consequently the degree of advancement is an essential prerequisite. However, in our case both the homoleptic species ([Pd(η^3-allyl)$(CNR)_2$]ClO_4, [Pd(η^3-allyl)$(PPh_3)_2$]ClO_4), are very stable complexes since both phosphane and isocyanide are strong ligands. Therefore, the formation of only the mixed derivative was somewhat unexpected. Remarkably, we have experimentally shown that the use of equimolecular amount of triphenylphosphane and isocyanide induces the formation of the mixed derivatives only, also when different substrates of Pd(II) or Pd(0) are used.

In order to rationalize the problem we have resorted to a theoretical investigation by means of the functional hybrid meta-GGA M06 software [14]. The results for the allyl (C_3H_5) Pd(II) and the maleic anhydride Pd(0) derivatives with DIC and PPh_3 are reported in Scheme 2

The equilibrium constants derived from the ΔG_3^0 and ΔG_6^0 values are $K_3 = 9.5 \times 10^{-9}$ and $K_6 = 4.2 \times 10^{-6}$ and the corresponding degrees of advancement ξ_3=[[Pd(η^3-C_3H_5)(DIC)(PR′$_3$)] ClO_4]$_0 \times 9.7 \times 10^{-5}$ and ξ_6 = [Pd(η^2-ma)(DIC)(PPh_3)]$_0 \times 2.1 \times 10^{-3}$, respectively, indicating that in any case the mixed species hardly revert into their homoleptic precursors (Eq. (5)). We crosschecked this theoretical result by mixing equimolecular amounts of the homoleptic complexes [Pd(η^3-C_3H_5)$(DIC)_2$]ClO_4 and [Pd(η^3-C_3H_5)(PR'$_3)_2$]ClO_4 in $CDCl_3$. As expected, the subsequent fast reaction yielded *only* the mixed [Pd(η^3-C_3H_5)(DIC)(PR′$_3$)]ClO_4 derivative. At the best of our knowledge only the use of isocyanides and posphanes induces the formation of mixed complexes. Apparently, phosphanes and isocyanides act synergically probably thanks to a *push–pull* global effect strongly stabilizing their derivatives. Similar stabilization might also be achieved with ligand mixtures that we have not investigated yet, such as carbenes/isocyanides or carbenes/phosphanes, as at least one paper in the literature seems to indicate [15].

2.6. Reactivity of the allyl complexes toward amination

As a part of an ongoing study carried out in our laboratory [16] we have also investigated the allylamination of the CNR/PPh_3 mixed allyl complexes with piperidine whose remarkable basicity (p*K*a = 11.12) coupled with a reduced steric hindrance renders the reaction rate easily accessible. Preliminary studies were carried out in $CDCl_3$ by ^1H and ^{31}P NMR experiments whereas the reaction rates were measured by UV–Vis techniques. Amination of the complexes bearing the symmetric allyl fragment **1a** and **1b** in the presence of dimethylfumarate (dmfu) as stabilizing olefin yields 1-(2-methylallyl)piperidine only and the complex [Pd(η^2-dmfu)(CNR)(PPh_3)] as can be deduced from the NMR spectra of the reaction mixture (see Section 4). On the contrary, the derivatives **2a** and **2b** according to the asymmetric nature of the allyl fragment give the two allylpiperidine regioisomers, namely 1-(1,1-Me_2allyl)piperidine (**R_A**) and 1-(3,3-Me_2allyl)piperidine (**R_B**) (Scheme 3):

Notably, the regioisomer **R_A** is significantly less stable than **R_B**. Nevertheless it represents the species that is formed in excess. In order to minimize the rearrangement of **R_A** into **R_B** we have monitored the amine attack at the allyl fragment of homoleptic and mixed complexes by NMR experiments at 273 K. At this temperature the amine attack is still fast whereas the subsequent isomerization is remarkably slower. The regioisomer distribution is reported in the following Table 4.

In any case, the bis-substituted allyl carbon is far more prone to nucleophilic attack by piperidine than its un-substituted analog probably due to the stabilization exerted by the two methyl groups of the incipient cation formed upon the amine attack to the coordinated allyl fragment (Scheme 4). [1,16] Moreover such an effect is somewhat enhanced by the presence of a phosphorus atom *trans* to the bis-substituted allyl carbon (entries 3, 4, 5 versus 1, 2 in Table 4), probably thanks to the weakening of the Pd–$C_{trans\text{-}P}$ bond, as pointed out by the crystallographic data (*vide supra*). Consequently, the mixed PPh_3/CNR 1,1-Me_2allyl complexes display a selectivity comparable to that of the bis-phosphane derivative **$2P_2$**.

We have carried out a detailed kinetic study whose results based on reaction Scheme 4 [1,16] are reported in Table 5. It is evident that complexes bearing the 1,1-Me_2allyl fragment (**2a**, **2b**) react faster than those bearing the less hindered 2-Me-allyl despite their steric hindrance, in agreement with the stabilizing effect induced by the two methyl substituents on the η^2-allylamonium intermediate (Fig. 4s, Supporting Information).[4]

For the sake of clarity in Scheme 4 we have reported only the attack at the most substituted carbon. However, the attack at the less substituted allyl termini is also possible (see Table 4; ratio = 5:95). Since the ratio between products is equal to the ratio between second order rate constants it is evident that the attack at the most substituted carbon is more than one order of magnitude faster than that occurring at the unsubstituted allyl termini (~20:1). The difference in reactivity between complexes bearing different isocyanides (Table 5) is easily interpreted on the basis of the different inductive effect of the two isocyanides.

2.7. Reaction of complex 5b with dimethyl-2-butynedioate (dma)

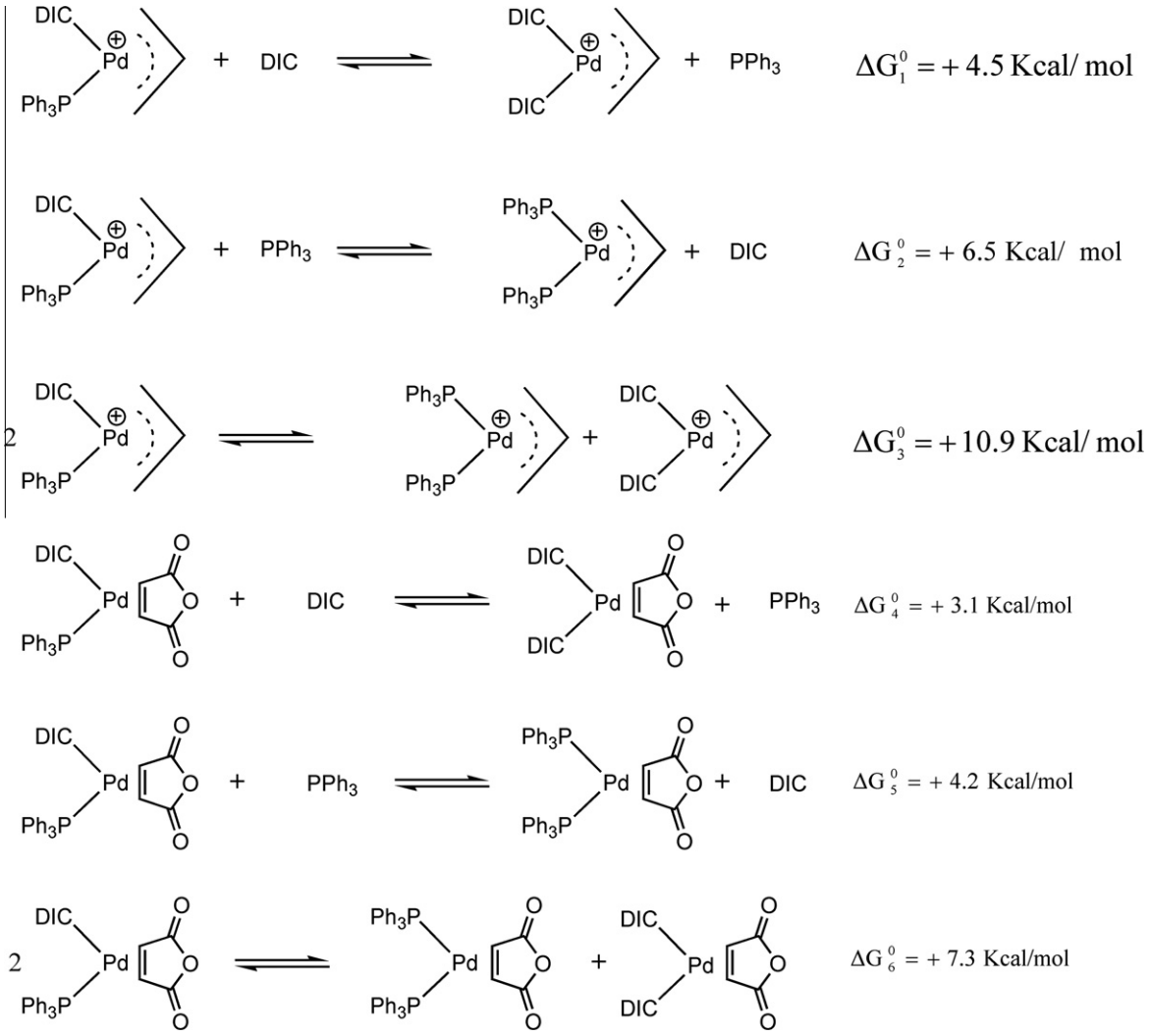
As already stated, the mixed palladacyclopentadienyl derivatives can be obtained neither by reacting the [Pd(C_4(COOMe)$_4$)] polymer with CNR and PPh_3 nor by oxidative coupling [8b,17] of complexes of the type [Pd(η^2-olefin)(CNR)(PPh_3)] with dimethyl-2-butynedioate (dma) since both these approaches yielded several not easily identifiable decomposition products. Thus, in order to obtain some more information we have undertaken an NMR study of the reaction of the complexes [Pd(η^2-nq)(TIC)(PPh_3)] (**5b**) with dma at reduced temperature (253 K). The formation in solution of the complexes [Pd(η^2-dma)(TIC)(PPh_3)] was observed as indicated by the signals attributable to the protons of the ester groups –COOC*H*$_3$ at 3.33 and 3.85 ppm of the coordinated dma and by the ^{31}P signal at 31.1 ppm with respect to 29.2 ppm of the starting complexes. These derivatives are quite rare and stabilized by a limited number of bulky spectator ligands [9a,18] (Section 4).

3. Conclusion

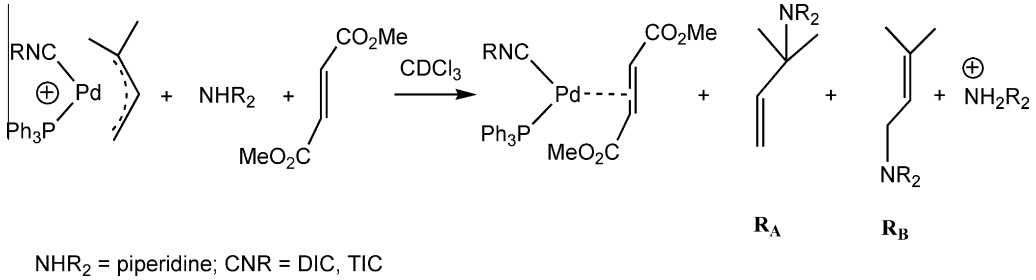
We have prepared some new mixed complexes of palladium in different oxidation states bearing isocyanides and triphenylphosphane as mixed spectator ligands. The synthetic protocol was based on the reaction with strictly stoichiometric ratios of all the

[3] A positive ΔG_3 can also be obtained from the combination of a highly positive ΔG_1 (or ΔG_2) and a negative value of $\Delta G_2'$ (or $\Delta G_1'$). This situation is verified when the homoleptic complex MAA (or MBB) is much more unstable than the other, as probably is the case of the complexes [Pd(η^3-allyl)$(CH_3CN)_2$]$^+$ or [Pd(η^3-allyl)$(py)_2$]$^+$ with respect to [Pd(η^3-allyl)$(P(OR)_3)_2$]$^+$ and [Pd(η^3-allyl)$(PR_3)_2$]$^+$. The stoichiometric constraint ([A]$_0$ = [B]$_0$ = [ML_2]$_0$) causes the formation of the mixed derivative only.

[4] From Scheme 4 the observed rate constants are of the type $k_{obs} = k_2 \cdot [PIP]_0$ and were obtained by non linear regression analysis of the monoexponential function $(D_t - D_\infty = (D_0 - D_\infty \cdot \exp(-k_{obs} \cdot t)$ recorded from the UV–Vis experiments obtained at suitable wavelengths and at various [PIP]$_0$ concentrations. D_t, D_0 and D_∞ represent the optical density at time *t*, at the beginning and at the end of reaction, respectively. The second order k_2 constants were calculated from linear regression analysis of the k_{obs} versus piperidine concentration data (see as an example Fig. 4s, Supporting Information).



Scheme 2. Calculated DG_f^0 for homoleptic and mixed palladium(II) and palladium(0) complexes.

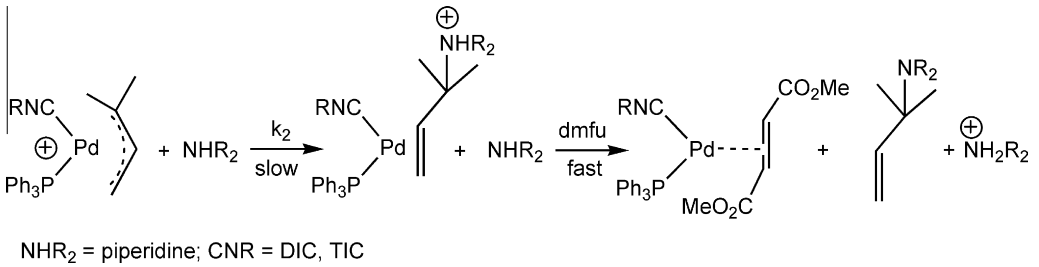


Scheme 3. Amination reaction of palladium allyl derivatives bearing mixed ligands.

Table 4
Regioisomer distribution upon the piperidine attack at 273 K on the complexes in column 2.

Entries	Complex	% $\mathbf{R_A}$	% $\mathbf{R_B}$
1	[Pd(η^3-1,1-Me_2allyl)$(DIC)_2$]ClO_4 (**2a$_2$**)	66	34
2	[Pd(η^3-1,1-Me_2allyl)$(TIC)_2$]ClO_4 (**2b$_2$**)	67	33
3	[Pd(η^3-1,1-Me_2allyl)$(PPh_3)_2$]ClO_4 (**2P$_2$**)	93	7
4	[Pd(η^3-1,1-Me_2allyl)(DIC)(PPh_3)]ClO_4 (**2ac**)	95	5
5	[Pd(η^3-1,1-Me_2allyl)(TIC)(PPh_3)]ClO_4 (**2bc**)	95	5

reactants involved and was traced back to the considerable stability imparted to the resulting mixed complexes by the synergic *push–pull* effect exerted by the concomitant presence of one isocyanide and one phosphane group. Notably such a result can also be achieved by mixing equimolecular amounts of the two homoleptic complexes which rapidly and completely revert to the mixed substrate. We have furthermore studied the reactivity of the mixed species by means of some standard reactions (*i.e.* allyl amination and olefin exchange in the case of Pd(II) allyl or Pd(0) olefin



Scheme 4. Detailed mechanism for the allyl amination reaction of palladium allyl derivatives.

Table 5
Second order rate constants at 298 K in $CHCl_3$.

Complex	k_2 ($dm^3 mol^{-1} s^{-1}$)
[Pd(η^3-1,1-Me_2allyl)(DIC)(PPh_3)]ClO_4 (**2a**)	5.15 ± 0.24
[Pd(η^3-1,1-Me_2allyl)(TIC)(PPh_3)]ClO_4 (**2b**)	0.89 ± 0.07
[Pd(η^3-2-Me-allyl)(DIC)(PPh_3)]ClO_4 (**1a**)	1.72 ± 0.07
[Pd(η^3-2-Me-allyl)(TIC)(PPh_3)]ClO_4 (**1b**)	0.41 ± 0.02

derivatives, respectively). For the sake of completeness we have carried out the X-ray structural determination of four novel isocyanide–phosphane substrates.

4. Experimental

4.1. Materials

All solvents were purified by standard procedures and distilled under argon immediately prior to use. Fumaronitrile was purified by sublimation under vacuum and piperidine distilled over NaOH. 1D- and 2D-NMR spectra were recorded using a Bruker 300 Avance spectrometer. Chemical shifts (ppm) are given relative to TMS (^1H and ^{13}C NMR) and 85% H_3PO_4 (^{31}P NMR). UV–Vis spectra were recorded on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP 6 (Peltier temperature programmer) apparatus. IR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer.

4.2. Crystal structure determinations

The crystal data of compounds **2a**, **2b**, **3a**, and **4b** 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 [19] and corrected for Lorentz, polarization and absorption effects (SORTAV) [20]. The structures were solved by direct methods using SIR97 [21] 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. In complex **4b** the disordered $C21H_3$ methyl of the methoxy carbonyl group bonded to C13 was refined over two positions with occupancies of 0.60 and 0.40, respectively.

All calculations were performed using SHELXL-97 [22] and PARST [23] implemented in WINGX [24] system of programs. The crystal data are given in Table 1s (Supporting Information).

4.3. Computational details

Theoretical calculations were performed with the GAUSSIAN 09 [25] package using the functional hybrid meta-GGA M06 [14] and the Def2-TZVP basis set [26]. The geometry optimization was performed without any symmetry constraint, followed by analytical frequency calculation to confirm that a minimum had been reached.

4.4. Preliminary NMR studies and kinetic measurements

The kinetics of attack of piperidine on allyl palladium complexes were carried out by means of ^1H or ^{31}P NMR techniques at 298 K by dissolving the complex under study in 0.8 ml of $CDCl_3$ in the presence of dimethylfumarate ($[dmfu]_0 = 2.7 \times 10^{-2}$, $[complex]_0 = 1.8 \times 10^{-2}$ mol dm^{-3}, [complex] = **1a**, **2a**, **1b**, **2b**, **2a$_2$**, **2b$_2$**, **2P$_2$**). An appropriate aliquot of piperidine was added ($[pip]_0 = 9 \times 10^{-2}$ mol dm^{-3}) and the reactions were followed to completion by monitoring the disappearance of the starting complexes and the concomitant appearance of the Pd(0) olefin complex.

4.5. Spectrophotometric kinetic measurements

A UV–Vis preliminary investigation was carried out in order to determine the wavelength of the highest absorbance change. Thus, 3 mL of freshly distilled $CHCl_3$ solution of the complex under study ($[complex]_0 \approx 1 \times 10^{-4}$ mol dm^{-3}) in the presence of dimethylfumarate ($[dmfu]_0 \approx 3 \times 10^{-4}$ mol dm^{-3}) was placed in the thermostatted (298 K) cell compartment of the UV–Vis spectrophotometer. Adequate aliquots of a concentrated solution of piperidine were then added ($[pip]_0 \geqslant 10 \times [complex]_0$) by means of a micropipette. The reaction was monitored by recording the UV–Vis spectra as a function of time corresponding to the largest absorbance change in the 260–400 nm wavelength intervals. The kinetics of nucleophilic attack at a fixed wavelength were recorded under *pseudo*-first order conditions at 310 nm. The piperidine concentrations were within the 1×10^{-3}–1×10^{-2} mol dm^{-3} interval and were obtained by adding known aliquots of the mother solution of piperidine (0.1–0.3 mol dm^{-3}) to a solution of the complex under study dissolved in 3 mL of freshly distilled $CHCl_3$ ($[complex]_0 \approx 1 \times 10^{-4}$ mol dm^{-3}) in the presence of dimethylfumarate ($[dmfu]_0 \approx 3 \times 10^{-4}$ mol dm^{-3}).

4.6. NMR studies on the exchange reaction of naphthoquinone in complex 5b with dimethyl-2-butynedioate (dma)

Complex [Pd(η^2-nq)(TIC)(PPh_3)] (**5b**) (6.4 mg, 1.05×10^{-2} mmol) were dissolved in 0.8 ml of $CDCl_3$ at 253 K. Dimethyl-2-butynedioate (dma) (4.5 mg, 3.2×10^{-2} mmol) were added. The reaction went to completion in few minutes.

4.7. Synthesis of the precursors, Intermediates and complexes *2* and *2b*

The synthesis of the precursors bis-[Pd(η^3-1,1-Me_2allyl)Cl]$_2$, bis-[Pd(η^3-2-Meallyl)Cl]$_2$ [27], [Pd_2(DBA)$_3$·$CHCl_3$] [28], [Pd(C_4(COOMe)$_4$)]$_n$ [29] and of the intermediates [Pd(C_4(COOMe)$_4$)(MeN-SPh)] [8b], [Pd(η^2-ma)(MeN-SPh)], [Pd(η^2-nq)(MeN-SPh)], [Pd(η^2-tmetc)(MeN-SPh)], [Pd(η^2-fn)(MeN-SPh)], [Pd(η^2-*cis*-SO_2-tol)(MeN-SPh)] and [Pd(η^2-*trans*-SO_2-tol)(MeN-SPh)] [9b] (MeN-SPh = 6-methyl-2-phenylthiomethylpyridine) [16e] was carried out according to published procedures. Complexes **2a** and **2b** were synthesized as reported in Ref. [1].

*4.8. Synthesis of the complex [Pd(η^3-2-Meallyl)(DIC)(PPh_3)]ClO_4 (**1a**)*

To 0.0821 g (0.21 mmol) of the allyl dimer [Pd(η^3-2-Meallyl)Cl]$_2$ dissolved in 7 ml of CH_2Cl_2 were added in sequence 0.0547 g (0.42 mmol) of DIC dissolved in 4 ml of CH_2Cl_2, 0.1169 g (0.83 mmol) of $NaClO_4{\cdot}H_2O$ dissolved in 5 ml of MeOH and 0.1092 g (0.42 mmol) of PPh_3. The cloudy solution (NaCl) was stirred for 30 m and eventually dried under reduced pressure. The residue was dissolved in CH_2Cl_2 (10 ml), treated with activated carbon and filtered by means of a celite filter. The resulting clear solution concentrated under reduced pressure yields the title complex as white solid (0.254 g, 0.39 mmol, yield 94%) upon addition of diethyl ether.

Notably, this complex can also be obtained by mixing equimolecular amounts of [Pd(η^3-2-Meallyl)(DIC)$_2$]ClO_4 and [Pd(η^3-2-Meallyl)(PPh_3)$_2$]ClO_4 in $CDCl_3$. The ^{1}H and ^{13}C NMR spectra of the reaction product is virtually undistinguishable from those of an authentic sample of the title complex.

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 1.99 (s, 3H, CH_{3allyl}), 2.13 (s, 6H, CH_{3dic}) 3.46 (bs, 1H, allyl $H_{anti\ trans\text{-}C}$), 3.73 (bs, 1H, allyl $H_{syn\ trans\text{-}C}$), 3.91 (d, 1H, J = 9.9 Hz, allyl $H_{anti\ trans\text{-}P}$), 4.99 (q, 1H, J = 3.9 Hz allyl $H_{syn\ trans\text{-}P}$), 7.07 (d, 2H, J = 7.5 Hz, H^c), 7.24 (t, 1H, J = 7.5 Hz, H^d), 7.51 (m, 15H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 18.4 (CH_3, $(CH_3)_{2dic}$), 23.8 (CH_3, CH_{3allyl}), 72.4 (CH_2, allyl $CH_{2trans\text{-}C}$), 74.6 (d, CH_2, J_{CP} = 26.9 Hz, allyl $CH_{2trans\text{-}P}$), 128 (CH, C^c), 130.3 (CH, C^d), 135.7 (C, C^b), 138.4 (d, C, J_{CP} = 5.5 Hz, allyl $C_{central}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 25.8.

IR (KBr pellets, cm^{-1}): $\nu_{C\equiv N}$ 2169, ν_{ClO} 1094, δ_{ClO} 622.

The following complexes were obtained in an analogous way using the appropriate isocyanide and allyl fragment.

*4.9. [Pd(η^3-2-Meallyl)(TIC)(PPh_3)]ClO_4 (**1b**)*

(White micro crystals, 94 % yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 1.33 (s, 9H, t-Bu), 1.95 (s, 3H, CH_{3allyl}), 3.18 (bs, 1H, allyl $H_{anti\ trans\text{-}C}$), 3.65 (d, 1H, J_{HP} = 9.2 Hz allyl $H_{anti\ trans\text{-}P}$), 3.66 (s, 1H, allyl $H_{syn\ trans\text{-}C}$), 4.94 (dd, 1H, $J_{HP} \sim J_{HH}$ = 4.5 Hz allyl $H_{syn\ trans\text{-}P}$), 7.48 (m, 15H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 23.6 (CH_3, CH_{3allyl}), 29.6 (CH_3, t-Bu), 58.9 (C, $C(CH_3)_3$), 70.5 (CH_2, allyl $CH_{2\ trans\text{-}C}$), 74.4 (d, CH_2, J_{CP} = 27.1 Hz, allyl $CH_{2trans\text{-}P}$), 135.3 (C, CN), 138.2 (d, C, J_{CP} = 5.4 Hz, allyl $C_{central}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 26.

IR (KBr pellets, cm^{-1}): $\nu_{C\equiv N}$ 2216, ν_{ClO} 1091, δ_{ClO} 623.

*4.10. [Pd(C_4(COOMe)$_4$)(DIC)(PPh_3)] (**3a**)*

To 0.07 g (0.12 mmol) of the intermediate [Pd(C_4(COOMe)$_4$)(MeN-SPh))] dissolved in anhydrous CH_2Cl_2 were added in sequence and under inert atmosphere (Ar) 0.0152 g (0.12 mmol) of DIC and 0.034 g (0.12 mmol) of PPh_3. The resulting yellow solution was stirred for 45 m and eventually treated with activated carbon. The mixture was then filtered on a celite filter and the clear yellow solution concentrated under reduced pressure. Addition of diethyl ether induces the precipitation of 0.0757 g (0.10 mmol, yield 84%) of the title compound as pale yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 2.03 (s, 6H, CH_3), 2.66 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 6.99 (d, 2H, J = 7.8 Hz, H^c), 7.16 (t, 1H, J = 7.8 Hz, H^d), 7.34 (m, 9H, Ph), 7.61 (m, 6H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 18.1 (CH_3, $(CH_3)_{dic}$), 50.1 (CH_3, OCH_3), 50.8 (CH_3, OCH_3), 51.2 (CH_3, OCH_3), 51.4 (CH_3, OCH_3), 125.5 (C, C^a), 128.2 (CH, C^c), 131.2 (CH, C^d), 134.8 (C, C^b), 151.5 (C, C_{cyclo}), 161.7 (d, C, J = 9.6 Hz, C_{cyclo}), 163.6 (d, C, J = 8.4 Hz, CO), 165.8 (C, C_{cyclo}), 170.3 (C, CO), 171.7 (C, C_{cyclo}), 172.6 (d, C, J = 6.8 Hz, CO), 174.9 (d, C, J = 5.4 Hz, CO).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 26.2.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1700, $\nu_{C\equiv N}$ 2183.

The following complex was obtained in an analogous way using the appropriate intermediate.

*4.11. [Pd (C_4(COOMe)$_4$)(TIC)(PPh_3)] (**3b**)*

(Pale yellow micro crystals, 84 % yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 1.12 (s, 9H, t-Bu), 2.56 (s, 3H, OCH_3), 3.59 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 7.42 (m, 9H, Ph), 7.59 (m, 6H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 29.4 (CH_3, t-Bu), 50.0 (CH_3, OCH_3), 50.5 (CH_3, OCH_3) 51.1 (CH_3, OCH_3) 51.2 (CH_3, OCH_3), 57.6 (C, $\underline{C}(CH_3)_3$), 150.5 (C, C_{cyclo}), 162.6 (d, C, J = 9.5 Hz, C_{cyclo}), 164 (C, CO), 165.6 (C, CO), 168.8 (C, C_{cyclo}), 170.2 (C, C_{cyclo}), 172.6 (d, C, J = 6.4 Hz, CO), 174.8 (d, C, J = 6.4 Hz, CO).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 25.6.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1700, $\nu_{C\equiv N}$ 2203.

*4.12. [Pd(η^2-ma)(DIC)(PPh_3)] (**4a**)*

To 0.0715 g (0.17 mmol) of the intermediate [Pd(η^2-ma)(MeN-SPh)] dissolved in 10 ml of anhydrous CH_2Cl_2 under inert atmosphere (Ar), 0.0223 g (0.17 mmol) of DIC and 0.0448 g (0.17 mmol) of PPh_3 were added in sequence. The resulting stirred yellow solution in 45 m decolorates to pale yellow. Addition of activated carbon, filtration through celite filter, reduction to small volume under reduced pressure and eventually addition of diethyl ether yield the title compound as pale yellow solid. 0.0827 g (0.12 mmol, yield = 81%) of the complex was obtained after washing the precipitate with diethyl ether and pentane.

^{1}H NMR (300 MHz, $CDCl_3$, T = 278 K, δ(ppm)): 2.14 (s, 6H, CH_3), 4.05 (bs, 1H, $H_{trans\text{-}C}$), 4.54 (bs, 1H, $H_{trans\text{-}P}$), 7.05 (d, 2H, J = 7.8 Hz, H^c), 7.19 (t, 1H, J = 7.8 Hz, H^d), 7.46 (m, 15H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 278 K, δ(ppm)): 18.5 (CH_3, $(CH_3)_{dic}$), 51.1 (CH, $C_{olefin\ trans\text{-}C}$), 51.6 (d, CH, J_{CP} = 30.3 Hz, $C_{olefin\ trans\text{-}P}$), 126.5 (C, C^a), 127.8 (CH, C^c), 129.2 (CH, C^d), 135.2 (C, C^b), 156.3 (C, CN), 171.2 (C, $CO_{trans\text{-}N}$), 171.4 (d, C, J_{CP} = 6.3 Hz, $CO_{trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 28.1.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1734, $\nu_{C=O}$ 1799, $\nu_{C\equiv N}$ 2150.

The following complexes were obtained in an analogous way using the appropriate intermediate and isocyanide. In the case of partial or remarkable solubility of the complexes in diethyl ether, the reaction mixture was evaporated to dryness under reduced pressure, recovered by diethyl ether or pentane and washed by pentane only.

*4.13. [Pd(η^2-nq)(DIC)(PPh_3)] (**5a**)*

(Dark yellow micro crystals, 75 % yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 278 K, δ(ppm)): 2.10 (s, 6H, CH_3), 4.83 (d, 1H, J = 8.0 Hz, $H_{trans\text{-}C}$), 5.15 (dd, 1H, J_{HH} = 8.0, J_{HP} = 7.5 Hz, $H_{trans\text{-}P}$), 7.02 (d, 2H, J = 7.5 Hz, H^c), 7.16 (t, 1H, J = 7.5 Hz, H^d), 7.34 (m, 16H, H_{nq}, Ph), 7.55 (m, 2H, H_{nq}), 8.05 (d, 1H, J = 9.0, H_{nq}).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 278 K, δ(ppm)): 18.5 (CH_3, $(CH_3)_{dic}$), 67.0 (CH, $\underline{C}_{olefin\ trans\text{-}C}$), 68.2 (d, CH, J_{CP} = 16.8 Hz, $\underline{C}_{olefin\ trans\text{-}P}$), 124.9 (CH, CH_{nq}), 125.6 (CH, CH_{nq}), 126.3 (C, C^a), 127.7 (CH, C^c), 128.9 (CH, C^d), 131.4 (CH, $(CH_{nq})_2$), 135.1 (C, C^b), 184.9 (C, $CO_{trans\text{-}C}$), 185 (d, C, J_{CP} = 6.3 Hz, $CO_{trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 28.7.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1591, $\nu_{C=O}$ 1636, $\nu_{C\equiv N}$ 2132.

*4.14. [Pd(η^2-tmetc)(DIC)(PPh_3)] (**6a**)*

(Partially soluble in diethyl ether, white micro crystals, 77% yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 2.07 (s, 6H, CH_{3dic}), 3.28 (s, 6H, $CH_{3olefin\ trans\text{-}C}$), 3.72 (s, 6H, $CH_{3olefin\ trans\text{-}P}$), 7.01 (d, 2H, J = 7.8 Hz, H^c), 7.15 (d, 1H, J = 7.8 Hz, H^d), 7.52 (m, 15H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 18.4 (CH_3, $(CH_3)_{dic}$), 51.8 (CH_3, OCH_3 *trans*-C), 52.4 (CH_3, OCH_3 *trans*-P), 66.5 (C, $C_{olefin\ trans\text{-}C}$), 67.4 (d, C, J_{CP} = 33.7 Hz, $C_{olefin\ trans\text{-}P}$), 126.2 (C, C^a), 127.8 (CH, C^c), 129.1 (CH, C^d), 135.5 (C, C^b), 169.0 (C, $CO_{trans\text{-}C}$) 169.3 (d, C, J_{CP} = 4.6 Hz, $CO_{trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 26.4.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1695, $\nu_{C=O}$ 1730, $\nu_{C\equiv N}$ 2142.

*4.15. [Pd(η^2-fn)(DIC)(PPh_3)] (**7a**)*

(White micro crystals, 85% yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 2.20 (s, 6H, CH_3), 3.02 (dd, 1H, J = 10.0, J = 3.9 Hz, $H_{olefin\ trans\text{-}C}$), 3.41 (dd, 1H, $J_{HH} = J_{HP}$ = 10.0 Hz, $H_{olefin\ trans\text{-}P}$), 7.07 (d, 2H, J = 7.5 Hz, H^c), 7.21 (t, 1H, J = 7.5 Hz, H^d), 7.48 (m, 15H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 278 K, δ(ppm)): 18.6 (CH_3, $(CH_3)_{dic}$), 28.0 (d, CH, J_{CP} = 34.8 Hz, $CH_{olefin\ trans\text{-}P}$), 28.5 (CH, $\underline{CH}_{olefin\ trans\text{-}C}$), 121.4 (C, $CN_{trans\text{-}C}$), 122.1 (d, C, J_{CP} = 7.6 Hz, $CN_{trans\text{-}P}$), 126.5 (C, C^a), 127.9 (CH, C^c), 129.3 (CH, C^d), 135.1 (C, C^b).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 26.0.

IR (KBr pellets, cm^{-1}): $\nu_{C\equiv N}$ 2134, $\nu_{C\equiv N}$ 2203.

*4.16. [Pd(η^2-cis-SO_2-tol)(DIC)(PPh_3)] (**8a**)*

(White micro crystals, 84% yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 2.11 (s, 6H, $(CH_3)_{dic}$), 2.30 (s, 3H, 3 CH_{3tol}), 2.31 (s, 3H, 3 CH_{3tol}), 4.27 (m(ABC system), 2H, J_{HH} = 9.7, J_{HP} = 7.2, J_{HP} = 3.5 Hz, H_{olefin}), 7.01 (m, 6H, H^c, H_{tol}), 7.14 (t, 1H, J = 7.5 Hz, H^d), 7.36 (m, 9H, Ph), 7.49 (d, 2H, J = 8.2 Hz, H_{tol}), 7.57 (m, 6H, Ph), 7.75 (d, 2H, J = 8.2 Hz, H_{tol}).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 18.4 (CH_3, $(CH_3)_{dic}$), 21.3 (CH_3, $(CH_3)_{tol}$), 21.4 (CH_3, $(CH_3)_{tol}$), 65.4 (CH, $CH_{olefin\ trans\text{-}C}$), 66.6 (d, CH, J_{CP} = 39.8 Hz, $CH_{olefin\ trans\text{-}P}$), 126.4 (s, C, J_{CP} = 5.4 Hz, C^a), 127.5 (CH, C^c), 128.7 (CH, C^d), 135.5 (C, C^b), 141.3 (C, $CSO_{2olefin\ trans\text{-}C}$), 141.8 (d, C, J_{CP} = 6.7 Hz, $CSO_{2olefin\ trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 26.7.

IR (KBr pellets, cm^{-1}): $\nu_{S=O}$ 1142, $\nu_{S=O}$ 1299, $\nu_{C\equiv N}$ 2151.

*4.17. [Pd(η^2-trans-SO_2-tol)(DIC)(PPh_3)] (**9a**)*

(White micro crystals, 83% yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 2.19 (s, 6H, $(CH_3)_{dic}$), 2.36 (s, 6H, $(CH_3)_{tol}$), 4.31 (dd, 1H, J = 9.3 Hz, J = 2.7 Hz, $H_{olefin\ trans\text{-}C}$), 4.51 (t, 1H, J = 9.3 Hz, $H_{olefin\ trans\text{-}P}$), 6.93 (m, 4H, m, H_{tol}), 7.05 (d, 2H, J = 7.8 Hz, H^c), 7.16 (t, 1H, J = 7.8 Hz, H^d), 7.32 (d, 2H, J = 8.1 Hz, H_{tol}), 7.40 (m, 11H, Ph, H_{tol}), 7.65 (m, 6H, H_{tol}).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 18.5 (CH_3, $(CH_3)_{dic}$), 21.4 (CH_3, $(CH_3)_{tol}$), 65.5 (CH, $CH_{olefin\ trans\text{-}C}$), 66.8 (d, CH, J_{CP} = 41.4 Hz, $CH_{olefin\ trans\text{-}P}$), 127.6 (CH, C^c), 128.6 (C, C^a), 128.8 (CH, C^d), 135.37 (C, C^b), 140.1 (C, $CSO_{2olefin\ trans\text{-}C}$), 141.7 (d, C, J_{CP} = 8.1 Hz, $CSO_{2olefin\ trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 27.6.

IR (KBr pellets, cm^{-1}): $\nu_{S=O}$ 1155, $\nu_{S=O}$ 1304, $\nu_{C\equiv N}$ 2142.

*4.18. [Pd(η^2-ma)(TIC)(PPh_3)] (**4b**)*

(Soluble in diethyl ether, pale yellow micro crystals, 83% yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 1.26 (s, 9H, *t*-Bu), 3.94 (t, 1H, $J_{HH} = J_{PH}$ = 4.2 Hz, $H_{trans\text{-}C}$), 4.38 (dd, 1H, J_{PH} = 9.7 Hz, J_{HH} = 4.2 Hz, $H_{trans\text{-}P}$), 7.44 (m,15H, Ph).

^{13}C {^{1}H} NMR: (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 30 (CH_3, *t*-Bu), 50.1 (CH, $CH_{olefin\ trans\text{-}C}$), 50.9 (d, CH, J_{CP} = 26.3 Hz, $CH_{olefin\ trans\text{-}P}$), 56.9 (C, $C(CH_3)_3$), 171.3 (CO, $C_{trans\text{-}C}$), 171.5 (CO, $C_{trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 28.2.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1731, $\nu_{C=O}$ 1800, $\nu_{C\equiv N}$ 2171.

*4.19. [Pd(η^2-nq)(TIC)(PPh_3)] (**5b**)*

(Soluble in diethyl ether, orange micro crystals, 81% yield).

^{1}H NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 1.25 (s, 9H, *t*-Bu), 4.74 (d, 1H, J = 7.6 Hz, $H_{trans\text{-}C}$), 5.02 (dd,1H, J_{HP} = 9.1 Hz, J_{HH} = 7.6 Hz, $H_{trans\text{-}P}$), 7.37 (m,15H, Ph, 1H, H_{nq}), 7.59 (m, 2H, H_{nq}), 8.07 (d, 1H, J = 7.7 Hz, H_{nq}).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 30.0 (CH_3, *t*-Bu), 56.5 (C, $C(CH_3)_3$), 66.2 (CH, $CH_{olefin\ trans\text{-}C}$), 67.5 (d, CH, J_{CP} = 13.0 Hz, $CH_{olefin\ trans\text{-}P}$), 124.8 (CH, CH_{nq}), 125.5 (CH, CH_{nq}), 131.0 (CH, CH_{nq}), 134.0 (CH, CH_{nq}), 136.1 (C, C_{nq}), 136.2 (C, C_{nq}) 184.5 (C, $CO_{trans\text{-}C}$), 184.6 (d, C, J_{CP} = 6.3 Hz, $CO_{trans\text{-}p}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 29.4.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1630, $\nu_{C=O}$1640 $\nu_{C\equiv N}$ 2166.

*4.20. [Pd(η^2-tmetc)(TIC)(PPh_3)] (**6b**)*

(Pale yellow micro crystals, 81% yield). **^{1}H NMR** (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 1.26 (s, 9H, *t*-Bu), 3.27 (s, 6H, $OCH_{3\ trans\text{-}C}$), 3.73 (s, 6H, $OCH_{3\ trans\text{-}P}$), 7.37 (m, 9H, Ph), 7.48 (m, 6H, Ph).

^{13}C {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 30 (CH_3, *t*-Bu), 51.5 (CH_3, $OCH_{3\ trans\text{-}C}$), 52.0 (CH_3, $OCH_{3trans\text{-}P}$), 56.5 (C, $C_{olefin\ trans\text{-}C}$), 66.2 (d, C, J_{CP} = 36.3 Hz, $C_{olefin\ trans\text{-}P}$), 56.3 (C, $C(CH_3)_3$), 168.9 (C, $CO_{trans\text{-}C}$), 169.0 (d, C, J_{CP} = 4.6 Hz, $CO_{trans\text{-}P}$).

^{31}P {^{1}H} NMR (300 MHz, $CDCl_3$, T = 298 K, δ(ppm)): 27.4.

IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1695, $\nu_{C=O}$1726 $\nu_{C\equiv N}$ 2176.

Appendix A. Supplementary material

CCDC 825710 (2a), 825711 (2b), 25712 (3a), 825713 (4b) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.09.006.

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