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Insertion of Isocyanides across the Pd−C Bond of Phosphinoquinoline Allyl Palladium Complexes Bearing η^1- and η^3-Coordinated Allyl Groups. A Synthetic and Mechanistic Study

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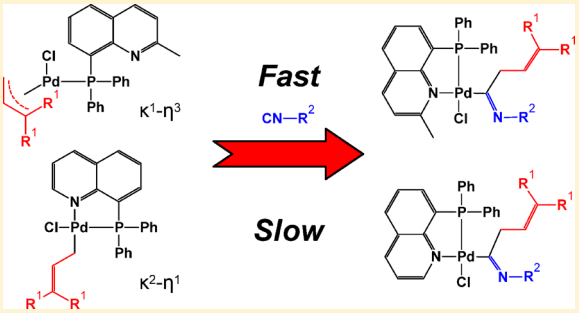
Supporting Information

ABSTRACT: We undertook an exhaustive study on the structural characteristics and reactivity toward the insertion of isocyanides across the Pd−C bond of palladium complexes bearing coordinated chloride, bidentate phosphoquinolines as spectator ligands, and differently substituted allyl groups. It was shown that the allyl hapticity is influenced not only by the nature of the spectator ligand but also by the position of the methyl substituents on the allyl fragment. Thus, in the presence of chloride, the κ^1-η^3 configuration is always assumed when the distorted 8-(diphenylphosphino)-2-methyl quinoline (DPPQ-Me) acts as ancillary ligand, whereas the unsubstituted 8-(diphenylphosphino)quinoline ligand (DPPQ) generally favors the κ^2-η^1 configuration with the exception of the complex with the 2-methyl-substituted allyl fragment, which adopts the κ^2-η^3 configuration with chloride as the counterion. We have determined the reactivity toward the insertion of the isocyanide on the Pd−C bond, and we have observed decidedly different rate laws when η^3- or η^1-allyl complexes were investigated. In particular, the rate law of the reaction involving the η^1-allyl derivatives displays a second-order dependence on complex and isocyanide concentration, whereas the insertion on η^3-allyl complexes is better described by a first-order process. We have interpreted such experimental results on the basis of a general pre-equilibrium mechanism in which the observed rates of the studied reactions are governed by the magnitude of the equilibrium constant. Finally, we have determined the solid-state structure of the insertion product palladium(chloro)(8-(diphenylphosphino)quinoline)(2,6-dimethyl-*N*-(4-methylpent-3-enylidene)benzenamine) (complex **1Bd**).



INTRODUCTION

Metal-mediated organic synthesis is a widely studied topic, and in particular the insertion of unsaturated molecules across the palladium−carbon bond probably represents one of the most investigated fields.[1,2] Unsaturated molecules such as alkynes,[3] alkenes,[4] allenes,[5] carbon monoxide,[6] and isocyanides[7] were employed as inserting moieties across the metal−carbon bond in alkyl, aryl, and acyl palladium complexes.[5−8] However, the insertion of isocyanides across the palladium allyl bond was comparatively less studied,[7v,9] although the allyl fragment represents an interesting theoretical challenge and might give different attractive insertion products owing to its propensity to adopt different hapticities. As a matter of fact, it is well known that the allyl fragment in the presence of strong nucleophiles or chelating spectator ligands can drop its customary η^3-coordinative mode to assume the monohapto configuration[7v,10] and therefore to give nontrivial organic derivatives as a consequence of insertion reactions.[11] Recently, our group studied the amination reaction of phosphinoquinoline allyl complexes of palladium and found that the hapticity of the allyl group strongly affects the reactivity of the complexes and in part the regioselectivity of the amine attack.[12] We have therefore undertaken a further study in which two differently characterized isocyanides react with some palladium phosphinoquinoline allyl complexes. Taking advantage of previous findings,[7e,v,12] we have chosen the palladium substrates on the basis of the hapticity of the allyl group and the governing difference in the electronic and steric characteristics of the inserting isocyanides. The allyl complexes, the isocyanides employed, and the ensuing insertion products together with their numbering scheme are reported in Scheme 1.

RESULT AND DISCUSSION

Starting Complexes. The reaction in chlorinated solvents of the dimers $[Pd(\mu\text{-}Cl)(\eta^3\text{-allyl})]_2$ and $[Pd(\mu\text{-}Cl)(\eta^3\text{-}1,1\text{-}Me_2\text{-allyl})]_2$ with two equivalents of the ligands 8-(diphenylphosphino)quinoline (DPPQ) or 8-(diphenylphosphino)-2-methylquinoline (DPPQ-Me) yields the neutral complexes **1A,B** and **2A,B**, respectively. The hapticity of the allyl group is dictated by the nature of the spectator ligand since in the presence of coordinated chloride DPPQ-Me favors η^3-

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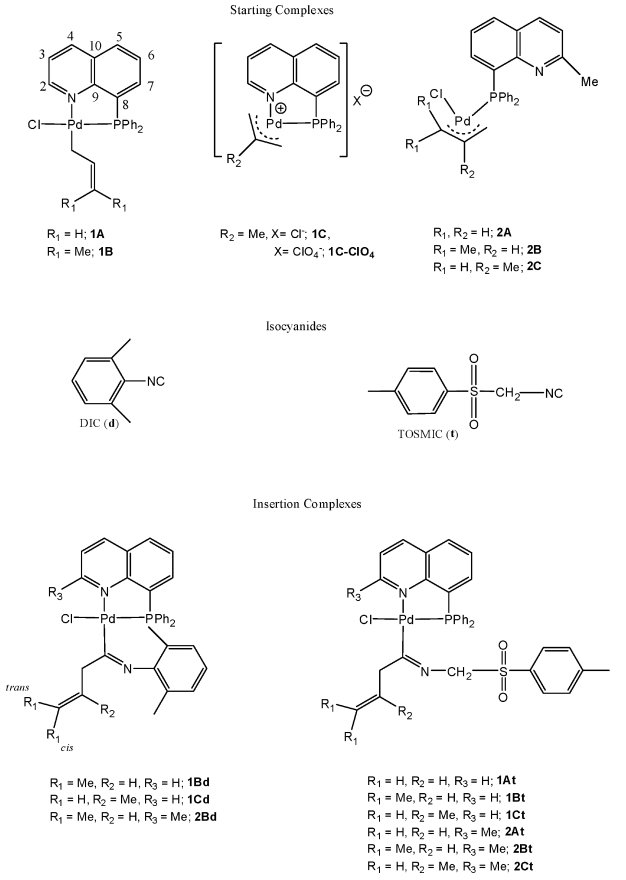
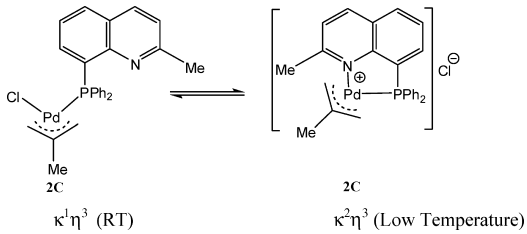
Scheme 1. Starting Substrates and Complexes Obtained from the Isocyanide Insertion Reaction



coordination (**2A**, **2B**), whereas the unsubstituted DPPQ induces the monohapticity of the allyl group (**1A**, **1B**). These complexes were synthesized and characterized elsewhere, and their ^{1}H and ^{13}C NMR spectra allowed unequivocal identification of the hapticity of the allyl fragment, which was definitely established by the crystal structure determination of complex **1A** in the case of the η^1 derivatives.[12] Interestingly, at variance with the complexes **1A** and **1B**, derivative **1C** displays the 2-methylallyl group η^3-coordinated with the chloride acting as the counterion. As a matter of fact, the ^{1}H NMR spectrum of complex **1C** recorded at 223 K (in order to minimize $\eta^3-\eta^1-\eta^3$ fluxionality) does not differ from the spectrum of the cationic complex **1C-ClO$_4$**, which was synthesized in mixed solvents (CH_2Cl_2−MeOH) in the presence of $NaClO_4$ acting as a dechlorinating agent.[13] In particular, the RT ^{1}H NMR spectrum of complex **1C** displays a broad singlet at 3.67 ppm ascribable to all the allyl protons, which at low temperature (223 K) split into a couple of doublets traceable back to the *syn* and *anti* protons *trans* to phosphorus (H_{syn} = 5.02 ppm; H_{anti} = 4.18 ppm) and a signal ascribable to the *syn* and *anti* protons *trans* to nitrogen at 3.32 ppm resonating as a broad singlet due to the residual selective $\eta^3-\eta^1-\eta^3$ isomerization still operative even at 223 K.[12] Remarkably, the high-field position of such a singlet rules out the possible presence of chloride in *trans* position (see later). In the case of complex **1C-ClO$_4$**, owing to the absence of chloride,[14] no fluxional rearrangements are observed, and its RT ^{1}H NMR spectrum is almost coincident with that of **1C** recorded at low temperature, apart from the splitting of the allyl protons (*syn* and *anti*) *trans* to nitrogen into a couple of signals (see Supporting Information: Figure S1). Finally, the allyl carbons in the ^{13}C NMR spectra are compatible with the η^3-κ^2 structure reported in Scheme 1 with the carbon *trans* to phosphorus and the one *trans* to nitrogen resonating at ca. 80 and 50 ppm, respectively. Moreover, the ^{31}P NMR data confirm the κ^2-coordination of the DPPQ ligand since the signal of phosphorus resonates at ca. 35 ppm, whereas in the case of complexes with the allyl group η^3 and the DPPQ-Me ligand κ^1-coordinated via phosphorus and the chloride bound to palladium (**2A**, **2B**, **2C**) the same signal shifts about 10 ppm upfield of the complexes. The ensuing result, which is evidently imposed by the nature of the allyl fragment bearing a methyl group in position 2, is unexpected.[15]

The DPPQ-Me ligand displays a reduced coordinative capability of the nitrogen donor with respect to DPPQ due to the distortion induced on the scaffold of the complex by the methyl substituent, as observed elsewhere in the case of palladium complexes bearing pyridylthioether ligands.[8a,b] Therefore, the reaction of the complex $[Pd(\eta^3\text{-}C_3H_4Me)(\mu\text{-}Cl)]_2$ with DPPQ-Me yields the complex **2C**. In this respect, the ^{1}H and ^{13}C NMR spectra of complex **2C** do not substantially differ from those of the complexes **2A** and **2B** already published.[12] Moreover, in the case of the latter compounds, an NMR investigation at variable temperature shows that the general fluxionality observed at RT (which is caused by nucleophilic interaction of the free chloride with the complexes) slows down at low temperature, indicating that the cationic κ^2-η^3 configuration is predominant. Complex **2C** displays similar behavior and the κ^1-η^3 ↔ κ^2-η^3 temperature-modulated equilibrium position can be observed also in this case (Scheme 2).

Scheme 2. Temperature-Dependent Hapticity of Complex 2C



Characterization of the Insertion Products. All the insertion reactions were followed by NMR technique before any synthetic attempt was tried. The reactions were carried out under almost stoichiometric conditions, and the ensuing stable imino derivatives are represented in Scheme 1. Remarkably, only the monoinsertion products were observed in our cases, although isocyanides sometime can give polyinsertion.[16] The monoinsertion observed in our case is probably due to the steric hindrance and the reduced nucleophilicity of the monoinserted imino fragment, which severely hampers any further attack of the isocyanide, which moreover is only in slight excess with respect to the allyl complex.

Among all the possible products of the 2,6-dimethylphenyl isocyanide (DIC) insertion, only the complexes **1Bd**, **2Bd**, and **1Cd** were stable enough to be isolated and characterized. As a matter of fact, DIC insertion on the complexes **1A** and **2A** proceeds smoothly, taking some hours or a few minutes, respectively, but the reaction products undergo massive decomposition and cannot be separated pure, although they

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can be identified in solution. Conversely, all the 1-(isocyanomethylsulfonyl)-4-methyl benzene (TOSMIC) derivatives were stable compounds.

It is worth noting that the signals of the inserted isocyanides resonate at significantly different frequencies with respect to those of the free molecules. Thus, the ^{1}H NMR spectra of the DIC derivatives are characterized by the presence of up-field shifts of the signals of the inserted isocyanide (inserted DIC, $\underline{H}^c$, $\underline{H}^d$ within 6.5−7 ppm, $C\underline{H}_3$ 1.8−2 ppm; free DIC $\underline{H}^c$, $\underline{H}^d$ 7.1, 7.2 ppm, $C\underline{H}_3$ 2.44 ppm), whereas the TOSMIC complexes are identified by the diastereotopicity of the $C\underline{H}_2$-SO_2 protons (see later). Moreover, in the ^{13}C NMR spectra the peak of the iminic functional group of the insertion products is always observed at ca. 180 and 190 ppm in the case of DIC and TOSMIC derivatives, respectively. As for the IR spectra, the imine stretchings $\nu_{C=N}$ are observed at ca. 1600 cm^{-1}. No hints of signals at ca. 2100 cm^{-1} are detected, so the mere coordination of the isocyanide to palladium can be safely ruled out.

Furthermore, the NMR spectra of the inserted complexes are characterized by the presence of all the signals belonging to the spectator ligands resonating at different frequencies from those of the allyl precursors. In particular the ^{31}P NMR spectra of the inserted complexes display the phosphorus signal within 23 and 28 ppm.

As for the allyl fragments we have observed that the alkyl protons $C\underline{H}_2CN$ of the DIC derivatives, owing to the deshielding induced by the iminic group, resonate as a doublet at ca. 3 ppm, whereas in the case of the TOSMIC complexes the $C\underline{H}_2CN$ protons resonate as a couple of doublets due to their diastereotopicity.

The $\underline{C}H_2CN$ carbons are in any case observed within 43−54 ppm, and these signals appear as doublets owing to the long-range coupling with phosphorus ($J_{CP} \approx 10$ Hz).

The olefinic protons resonate within 4.5 and 6 ppm, and the observed multiplicity is in any case consistent with the structure of the allyl group. The corresponding olefinic carbons appear within 110 and 145 ppm with the central carbons resonating at higher field. The full description of the NMR spectra of all the new complexes is given in detail in the Experimental Section.

The diastereotopicity of the $C\underline{H}_2CN$ and $C\underline{H}_2SO_2$ protons in the TOSMIC complexes is probably due to hindered rotation about the Pd−C bond. As a matter of fact, the NOESY spectra of the TOSMIC derivatives display an intense cross-peak among one of the $C\underline{H}_2SO_2$ protons and some aromatic protons of the phenyl substituents on phosphorus. Such an experimental evidence suggests that the $CH_2SO_2C_6H_4$-Me fragment *cis* to the palladium center is sterically engaged with the phenyl substituents on phosphorus (see Supporting Information: Figures S2 and S3).

Mechanistic Investigation. In order to rationalize the reactivity of the isocyanides across the palladium−carbon bond, we decided to investigate in detail the mechanism of insertion of DIC and TOSMIC across the Pd−C bond in palladium complexes bearing the allyl groups with different hapticity. A preliminary study was carried out by monitoring the ^{1}H and when possible the ^{31}P NMR spectra of solutions obtained by mixing almost equimolecular solutions (~1.6 × 10^{-2} mol dm^{-3}) of the complex and the isocyanide under study in CD_2Cl_2 at 298 K. The ensuing results are summarized in Table 1.

From the preliminary results it was possible to deduce the following general conclusions:

Table 1. Reaction Times Determined by Preliminary NMR Investigations Carried out in CD_2Cl_2 at 298 K for the Reaction: Complex + Isocyanide → Insertion Product

	isocyanides	
complex	TOSMIC (min)	DIC (min)
1A	35	240[b]
1B	18	60
1C	<8[a]	60
2A	<8[a]	40[b]
2B	<8[a]	<8[a]
2C	<8[a]	240[b]

[a]Reactions too fast to be recorded by NMR technique. [b]Reactions proceeding with decomposition of the products.

(1) In reactions between the same complex and different isocyanides, TOSMIC is always more reactive than DIC thanks to its higher electrophilicity and reduced steric hindrance at carbon.
(2) In the case of neutral η^1-complexes, the reactivity of the 3,3′-Me_2-allyl derivative **1B** is higher than that of complex **1A** owing to the enhanced nucleophilicity of the dimethylated allyl fragment. Consequently, it is possible to state that the hindrance of the peripheral methyl groups probably does not interfere with the intimate insertion mechanism.
(3) A comparison of the reactivity of neutral complexes bearing the η^3-coordinated allyl groups **2A**, **2B**, and **2C**, while confirming the highest reactivity of the complex bearing the 3,3-disubstituted allyl group, highlights the marked reduction of reaction rate of complex **2C**. Apparently, the methyl group at position 2 of the allyl fragment heavily interferes with the inserting isocyanide. Unfortunately, owing to the observed high rates, such a hypothesis could not be verified in the case of the reactions with TOSMIC.
(4) The complex **2C** is less reactive than the cationic complex **1C**. Reasonably, the positive charge on palladium increases the electrophilicity of the precoordinated isocyanide and renders nucleophilic attack of the allyl fragment easier.
(5) Finally, the neutral complexes bearing the allyl group η^1-coordinated (**1A** and **1B**) are less reactive than those with the allyl group η^3-coordinated (**2A** and **2B**).

We have therefore undertaken a detailed kinetic investigation in order to assess the intimate mechanism of the isocyanide insertion on different allyl fragments coordinated to the palladium center with different hapticity. We have chosen as a spot check the reactions yielding stable products and displaying an amenable rate under NMR conditions, and in this respect we decided to lower the experimental temperature to 288.15 K.

First of all, we have investigated the reaction of the complex **1B** with DIC and TOSMIC isocyanides by means of ^{1}H NMR technique in CD_2Cl_2. The concentration profiles detected as the integration areas of the feasible NMR signals of the starting complex and product versus time for both the reactions carried out under almost equimolecular conditions for the complex and the isocyanide are described by a second-order rate law of the type

$$\text{rate} = -\text{d[complex]}/\text{d}t = k_2[\text{complex}][\text{isocyanide}] \quad (1)$$

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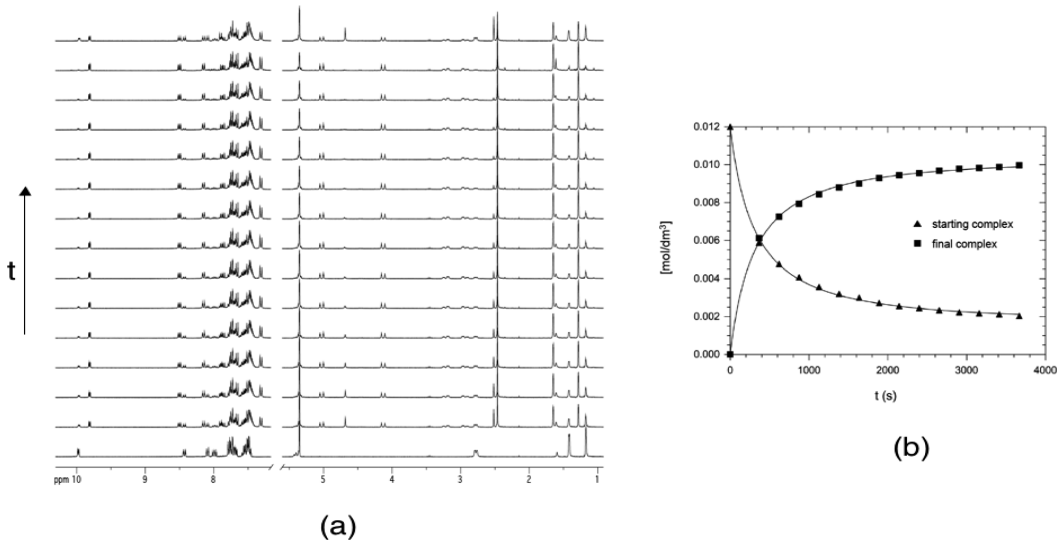

Figure 1. (a) ^{1}H NMR spectra in CD_2Cl_2 recorded at 288.15 K and (b) the corresponding best fits of the concentrations of the complexes **1B** (■) ($[\mathbf{1B}]_0 = 1.2 \times 10^{-2}$; $[\text{TOSMIC}]_0 = 1 \times 10^{-2}$ mol L^{-1}) and **1Bt** (▲) vs time for the reaction **1B** + TOSMIC → **1Bt**.

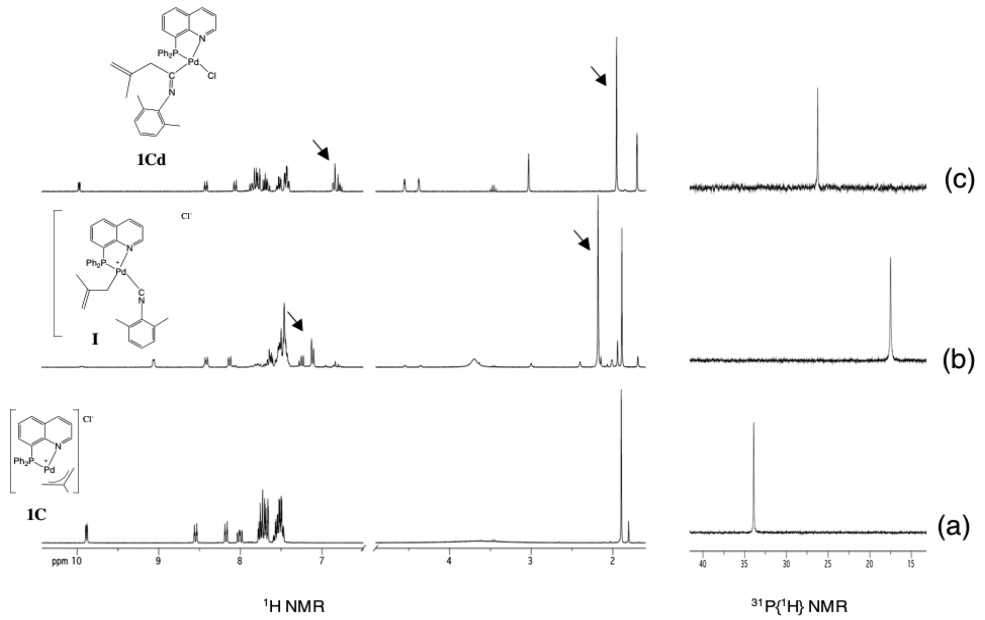

Figure 2. ^{1}H (left) and ^{31}P{^{1}H} NMR (right) spectra for the reaction **1C** + DIC → **1Cd** in CD_2Cl_2 recorded at 288 and 223 K, respectively. (a) NMR spectra of the starting complex **1C**. (b) NMR spectra of the starting complex **1C** immediately after the addition of DIC; the signals of the coordinated DIC in the intermediate are indicated by the arrows. (c) NMR spectra of the final product. The inserted DIC is indicated by the arrows.

Regression analysis of the concentration versus time data yields the second-order rate constants for both the isocyanides (k_2 = 0.287 ± 0.006 in the case of TOSMIC and $k_2 = (3.21 \pm 0.02) \times 10^{-2}$ L mol^{-1} s^{-1} for DIC, respectively). Notably, these values agree with the qualitative data of Table 1 and with the general remarks reported above (see point 1).

The ^{1}H NMR spectra and the best fits of the concentration versus time data for the reaction between complex **1B** and TOSMIC are reported in Figure 1a,b.

In order to verify the second relevant point of the comments raised before, we have studied the reaction between the complex **1A** and the isocyanide TOSMIC. The regression analysis, while confirming the rate law governing the insertion mechanism on η^1-derivatives, allows the determination of the related second-order rate constant k_2. In particular, the rate constant value ($k_2 = (5.64 \pm 0.08) \times 10^{-2}$ L mol^{-1} s^{-1}) proves the lower nucleophilicity and consequently the reduced reactivity of the unsubstituted allyl fragment (see Supporting Information, Figure S4; in Figure S5 we report the regression analysis for the reaction of **1B** with DIC under similar experimental conditions). Notably, complex **1C** behaves differently from the η^1-derivatives. As can be seen in Figure 2 the ^{1}H NMR spectra of the reaction of complex **1C** with DIC clearly show the immediate and quantitative formation of an intermediate species that slowly rearranges to the reaction product.

In this case, the reaction progress (Figure 3) is conveniently interpreted as a first-order monoexponential decay of the type

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$$\text{rate} = -\text{d}[\text{intermediate}]/\text{d}t = \text{d}[\text{inserted product}]/\text{d}t = k_1[\text{intermediate}] \quad (2)$$

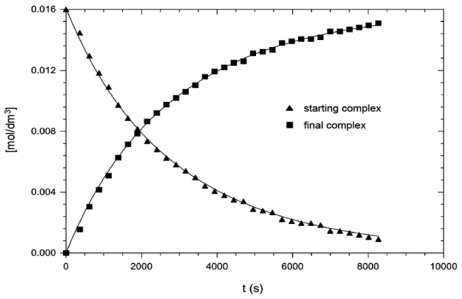


Figure 3. Best fit of the concentrations of the complexes **1C** and **1Cd** ($[\mathbf{1C}]_0 = 1.2 \times 10^{-2}$; $[\text{DIC}] = 2.0 \times 10^{-2}$ mol L^{-1}) vs time for the reaction **1C** + DIC → **1Cd**.

We think that these experimental results can be interpreted on the basis of the general mechanism reported in Scheme 3.

The first step of this scheme involves the fast and reversible formation of the ion-pair intermediate **I** bearing the η^1-allyl group *cis* to the isocyanide, which slowly evolves into the reaction products.[17] In the case of complexes **1A** and **1B**, for which no intermediates were observed, the value of the equilibrium constant K_e ought to be small. Thus, the reaction rate takes the experimentally observed form

$$\text{d}[\text{product}]/\text{d}t = -\text{d}[\text{complex}]/\text{d}t = k_2[\text{complex}][\text{DIC}] \quad (3)$$

where $k_2 = K_e k_{ins}$, the latter constants not being independently accessible.

On the contrary, in the case of complex **1C** the immediate and quantitative formation of a transient species **I** is observed (see Figure 2). Apparently, the K_e value is high and the formation of the final product **P** proceeds smoothly via the intramolecular insertion with a rate described by the relationship

$$\text{d}[\text{product}]/\text{d}t = -\text{d}[\mathbf{I}]/\text{d}t = k_{ins}[\mathbf{I}] \quad (4)$$

which is coincident with the experimentally observed rate law and provides the true value of the insertion rate constant.

Some features related to the nature of intermediate **I** can be deduced from the analysis of the NMR spectra in Figure 2b. In particular signals due to the coordinated isocyanide are detectable at higher field with respect to the free and at lower field to the inserted one, respectively, and significant shifts for the signals of the spectator ligand DPPQ are observed in both the ^{1}H and ^{31}P NMR spectra. Unfortunately, the allyl fragment undergoes a fluxional rearrangement at any safely attainable temperature (down to 188 K), probably triggered by the chloride counterion, and therefore its hapticity cannot be established.[18]

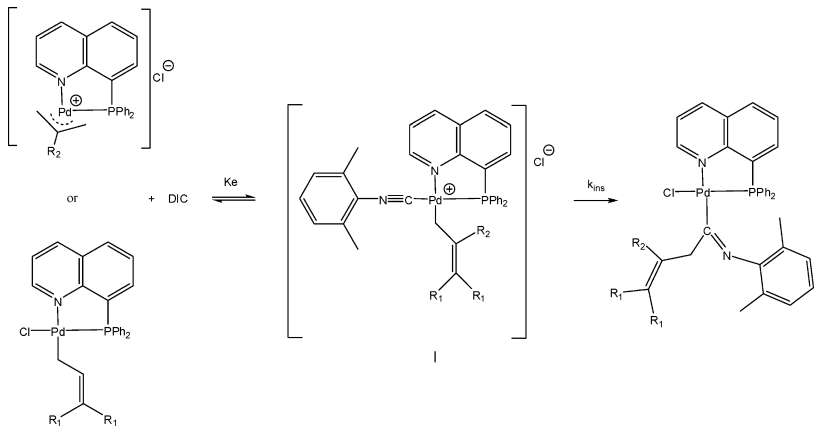
Furthermore, the formation of an intermediate bearing the isocyanide coordinated to palladium is also suggested by the IR spectrum of a CH_2Cl_2 solution of an almost equimolecular mixture of **1C** and DIC ($[\mathbf{1C}] \approx [\text{DIC}] \approx 1.8 \times 10^{-2}$ mol L^{-1}) recorded immediately after mixing. The ν_{CN} at 2124 cm^{-1} of the uncoordinated isocyanide shifts to 2181 cm^{-1} (see Supporting Information, Figure S6), which represents the typical frequency of a coordinated isocyanide in cationic palladium complexes.[7v] Such a signal disappears with time with a rate comparable with that determined by the temperature-controlled ^{1}H NMR experiment (see above).

Crystal Structure Determination. In order to assess unambiguously the structure of the insertion products, we have carried out the diffractometric determination of the solid-state structure of complex **1Bd**.

An ORTEP[19] view of complex **1Bd** is shown in Figure 4. The Pd(II) exhibits square-planar coordination with Cl and P *trans* to each other and an imino group *trans* to the nitrogen N1 of the quinoline moiety. The compound exhibits a slight distortion from planarity at the Pd center, with the largest deviation from the coordination plane Pd1/P1/N1/Cl1/C22 of 0.015(2) Å for the imine C22 atom. The quinoline ligand is rotated with respect to the Pd coordination plane by 17.52(4)°.

The Pd1−N1 bond length of 2.180(2) Å is in agreement with Pd−N(sp^2) distances in the range 2.13−2.18 Å of complexes having similar square-planar coordination arrangements.[12,20−22] These bonds are relatively long compared to the mean distance of 2.06(2) Å in [Pd(P−N)Cl_2] complexes where the nitrogen is *trans* to a Cl, showing that the C(sp^2) carbon determines a *trans* influence on N greater than the Cl atom. The plane of the imino group (N2═C22−C23) makes a dihedral angle of 69.9(2)° with the mean Pd coordination plane.

Scheme 3. Insertion of Isocyanides on η^1- or η^3-Allyl Palladium Phosphoquinoline Complexes: General Mechanism



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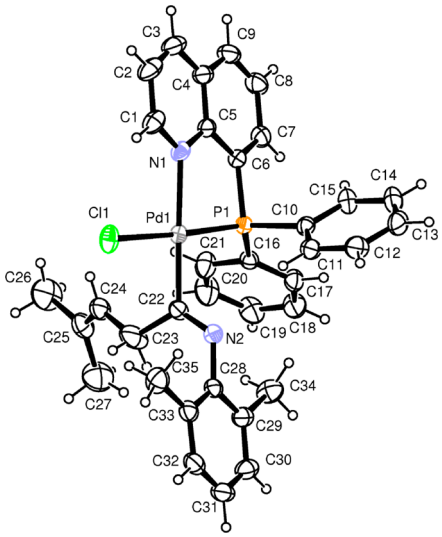

Figure 4. ORTEP view of the complex **1Bd** showing thermal ellipsoids at the 30% probability level.

The crystal data are given in Table S1. Selected bond distances and angles are given in Table 2.

Table 2. Selected Bond Distances and Angles (Å and deg) of 1Bd

Distances	
Pd1−N1	2.180(2)
Pd1−P1	2.2191(5)
Pd1−Cl1	2.3554(6)
Pd1−C22	1.993(2)
C22−N2	1.254(2)
C22−C23	1.516(3)
Angles	
P1−Pd1−N1	82.62(5)
P1−Pd1−Cl1	176.78(2)
N1−Pd1−Cl1	94.18(5)
C22−Pd1−Cl1	88.28(6)
P1−Pd1−C22	94.93(6)
N1−Pd1−C22	177.44(7)
Pd1−C22−N2	118.6(1)
Pd1−C22−C23	118.6(2)
N2−C22−C23	122.4(2)

CONCLUSION

We have synthesized some palladium phosphoquinoline chloro complexes bearing unsubstituted and substituted allyl groups. The hapticity of the allyl group is governed by an interplay of the structural and electronic features of the allyl itself and the spectator ligands. In this respect, the palladium derivatives of DPPQ always display a chelate spectator ligand P−N independently of the hapticity of the allyl fragment. Thus, the allyl and 3,3-dimethylallyl derivatives adopt the κ^2-η^1 configuration, whereas the 2-Me-allyl derivative **1C** prefers the κ^2-η^3 arrangement with the Cl^- forced out of the coordination sphere and acting as a counterion.

Conversely, DPPQ-Me favors the formation of κ^1-η^3 derivatives with the quinoline nitrogen uncoordinated and the chloride occupying the fourth coordination position.

The rate of insertion reactions of isocyanides on the palladium allyl complexes is governed by the hapticity of the allyl group. Thus, the monohapto allyl derivatives react following a second-order rate law, whereas the trihapto complex displays a first-order rate. The experimental results were interpreted on the basis of a common mechanism involving a pre-equilibrium reaction, in which the value of the pre-equilibrium constant determines the observed rate law.

We have eventually determined the solid-state structure of complex **1Bd**.

EXPERIMENTAL SECTION

Materials. All solvents were purified by standard procedures and distilled under argon immediately before 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 labeled 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.

The ligands DPPQ[23] and DPPQ-Me,[3] the starting complexes $[Pd(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)]_2$,[24] $[Pd(\mu\text{-Cl})(\eta^3\text{-}1,1\text{-}Me_2C_3H_3)]_2$, and $[Pd(\mu\text{-Cl})(\eta^3\text{-}2\text{-Me-}C_3H_4)]_2$,[16] and the derivatives **1A**, **1B**, **2A**, and **2B**[12] were prepared following literature procedures. All other chemicals were commercial grade and were used without further purification.

Synthesis of Complex 1C. A mixture of 75.5 mg (0.192 mmol) of the complex $[Pd(\mu\text{-Cl})(\eta^3\text{-}2\text{-Me-}C_3H_4)]_2$ and 125.2 mg (0.399 mmol) of DPPQ dissolved in 20 mL of anhydrous CH_2Cl_2 was stirred under inert atmosphere (Ar) for 20 min. Evaporation under vacuum to a small volume and addition of diethyl ether yields 174.4 mg of the title complex as a dark yellow solid. Yield: 89%. ^{1}H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.91 (s, 3H, allyl−CH_3), 3.67 (bs, 4H, allyl−H), 7.47−7.79 (m, 12H, H^3, H^6, PPh_2), 8.00 (m, 1H, H^7), 8.17 (dt, 1H, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ =1.2 Hz, H^5), 8.54 (dt, 1H, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ 1.7 Hz, H^4), 9.89 (dd, 1H, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ 1.6 Hz, H^2). ^{1}H NMR (300 MHz, $CDCl_3$, T = 223 K, ppm) δ: 2.14 (s, 3H, CH_3−allyl), 3.32 (bs, 2H, allyl−H_{syn}, allyl H_{anti} *trans*-N), 4.18 (bd, 1H, $^3J_{H,H}$ = 9.0 Hz, allyl H_{anti} *trans*-P), 5.02 (bd, 1H, $^3J_{H,H}$ = 4.8 Hz, allyl−H_{syn}, *trans*-P), 7.47−7.60 (m, 10H, PPh_2), 7.88 (t, 1H, $^3J_{H,H}$ = 8.1 Hz, H^6), 7.99−8.07 (m, 2H, H^3, H^7), 8.38 (d, 1H, $^3J_{H,H}$ = 8.1 Hz, H^5), 8.84 (d, 1H, $^3J_{H,H}$ = 8.4 Hz, H^4), 9.82 (d, 1H, $^3J_{H,H}$ = 4.7 Hz, H^2). ^{13}C{^{1}H} NMR ($CDCl_3$, T = 223 K, ppm) δ: 24.8 (CH_3, CH_3−allyl), 50.6 (CH_2, allyl−CH_2 *trans*-N), 83.4 (d, CH_2, $^2J_{P,C}$ = 28.8 Hz, allyl−CH_2 *trans*-P), 124.8 (CH, C^7), 128.7 (d, CH, $^3J_{P,C}$ = 6.4 Hz, C^6), 133.6 (CH, C^5), 138.6 (CH, C^3), 141.1 (CH, C^4), 150.7 (C, C^{10}), 151.0 (C, C^9), 160.3 (CH, C^2). ^{31}P{1H} NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 35.5. IR (KBr pellets): ν_{CN} 1607, 1593, 1569 cm^{-1}. Anal. Calcd for $C_{25}H_{23}ClNPPd$: C, 58.84; H, 4.54; N, 2.74. Found: C,58.61; H, 4.63; N, 2.97.

Synthesis of Complex 1C-ClO_4. A mixture of 75.5 mg (0.192 mmol) of the complex $[Pd(\mu\text{-Cl})(\eta^3\text{-}2\text{-Me-}C_3H_4)]_2$ and 125.2 mg (0.399 mmol) of DPPQ dissolved in 20 mL of anhydrous CH_2Cl_2 was stirred under an inert atmosphere (Ar) for 20 m. To the resulting yellow solution was added 52 mg (0.37 mmol) of $NaClO_4.H_2O$ dissolved in 2.5 mL of MeOH. A cloudy suspension of NaCl immediately formed. The mixture was stirred for a further 30 m, dried under vacuum, and redissolved in CH_2Cl_2 in the presence of activated charcoal. The suspension containing NaCl and $NaClO_4$ in excess was filterd off on a Celite filter, and the resulting clear solution concentrated under vacuum. Addition of diethyl ether induces the precipitation of 91.5 mg of the title complex as a yellow solid, which was dried under vacuum. Yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$, T = 223 K, ppm) δ: 2.14 (s, 3H, CH_3−allyl), 2.90 (s, 1H, H_{anti} *trans*-N), 3.79 (s, 1H, H_{syn} *trans*-N), 4.27 (d, 1H, $^3J_{H,H}$ = 9.5 Hz, allyl H_{anti} *trans*-P), 5.02 (m, 1H,allyl−H_{syn}, *trans*-P), 7.49−7.60 (m, 10H, PPh_2), 7.83

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(t, 1H, $^3J_{H,H}$ = 8.1 Hz, H^6), 7.96 (m, 1H, H^7), 8.24 (m, 1H, H^3), 8.34 (d, 1H, $^3J_{H,H}$ = 8.1,Hz, H^5), 8.64 (d, 1H, $^3J_{H,H}$ = 8.3 Hz, H^4), 9.74 (d, 1H, $^3J_{H,H}$ = 5.0 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 223 K, ppm) δ: 24.1(CH_3, CH_3−allyl), 52.5 (d, CH_2, $^2J_{P,C}$ = 2.3 Hz, allyl−CH_2 *trans*-N), 82.0 (d, CH_2, $^2J_{P,C}$ = 28.8 Hz, allyl−CH_2 *trans*-P), 124.6 (CH, C^7), 128.4 (d, CH, $^3J_{P,C}$ = 6.3 Hz, C^6), 133.2 (CH, C^5), 138.4 (CH, C^3), 140.5 (CH, C^4), 150.8 (C, C^{10}), 151.1 (C, C^9), 160.8 (CH, C^2). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$, T = 298 K, ppm) δ: 32.391. IR (KBr pellets): ν_{CN} 1593, 1571 cm^{-1}. Anal. Calcd for $C_{25}H_{23}ClNO_4PPd$: C, 52.28; H, 4.04; N, 2.44. Found: C, 52.57; H, 4.29; N, 2.37.

Synthesis of Complex 2C. The title complex was synthesized following the same procedure as complex **1C** using DPPQ-Me as spectator ligand. Pale yellow microcrystals. Yield: 83%. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.91 (s, 3H, allyl−CH_3), 2.71 (s, 3H, CH_3−quinoline), 3.50 (bs, 4H, allyl−H), 7.40−7.69 (m, 12H, H^3, H^6, H^7, PPh_2), 8.04 (d, 1H, $^3J_{H,H}$ = 8.0, H^5), 8.29 (dd, 1H, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ =1.7 Hz, H^4). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 23.5. ^1H NMR (300 MHz, CD_2Cl_2, T = 213 K, ppm)[25] δ: 1.99 (s, 3H, CH_3−allyl), 2,99 (s, 3H, CH_3−quinoline), 3.23 (bs, 2H, allyl−H_{syn}, allyl H_{anti} *trans*-N), 3.85 (bd, 1H, $^3J_{H,H}$ = 10.0 Hz, allyl H_{anti} *trans*-P), 5.02 (bd, 1H, $^3J_{H,H}$ = 5.4 Hz, allyl−H_{syn}, *trans*-P), 7.44−7.59 (m, 10H, PPh_2), 7.70−7.80 (m, 3H, H^6, H^3, H^7), 8.22 (d, 1H, $^3J_{H,H}$ = 7.0 Hz, H^5), 8.54 (d, 1H, $^3J_{H,H}$ = 8.4 Hz, H^4). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 213 K, ppm) δ: 32.08. IR (KBr pellets): ν_{CN} 1635, 1607, 1558 cm^{-1}. Anal. Calcd for $C_{26}H_{25}ClNPPd$: C, 59.56; H, 4.81; N, 2.67. Found: C, 59.71; H, 4.98; N, 2.51.

Synthesis of Complex 1Bd. A mixture of 60 mg (0.114 mmol) of complex **1B** and 16.5 mg (0.126 mmol) of 2,6-dimethyl phenyl isocyanide dissolved in 6 mL of anhydrous CH_2Cl_2 was stirred under inert atmosphere (Ar) for ca. 60 min. Evaporation of the dark yellow solution under vacuum to a small volume and addition of diethyl ether yields 51.5 mg of the title complex as a dark yellow solid. Yield: 70%. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.16 (s, 3H, $CH_{3\ cis}$), 1.42 (s, 3H, $CH_{3\ trans}$), 1.87 (s, 6H, Ph−CH_3), 2.92 (d, 2H, $^3J_{H,H}$ = 7.1 Hz, CH_2−CH), 5.30 (m, 1H, CH=CH_2), 6.73 (t, 1H, $^3J_{H,H}$ = 7.8 Hz, H−Ph_{ortho}), 6.86 (d, 2H, $^3J_{H,H}$ = 7.8 Hz, H−Ph_{meta}), 7.43−7.56 (m, 6H, PPh_2), 7.67−7.75 (m, 2H, H^3, H^6), 7.83−7.90 (m, 5H, H^7, PPh_2), 8.10 (dt, 1H, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ =1.3 Hz, H^5), 8.46 (dt, 1H, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.7 Hz, H^4), 9.99 (dd, 1H, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 1.6 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 18.0 (CH_3, $CH_{3\ cis}$), 19.5 (CH_3, Ph−CH_3), 26.4 (CH_3, $CH_{3\ trans}$), 43.0 (d, CH_2, $^3J_{P,C}$ = 10.7 Hz, CH_2−CH), 119.3 (CH, CH=CH_2), 122.0 (CH, CH−Ph_{para}), 126.8 (C, C−Ph_{ortho}), 127.8 (CH, CH−Ph_{meta}), 131.8 (CH, C^5), 132.7 (C, $C(CH_3)_2$), 136.8 (CH, C^7), 139.1 (CH, C^4), 149.9 (C, C^{10}), 150.2 (C, C^9), 150.3 (C, C−Ph_{ipso}), 154.0 (CH, C^2), 181.4 (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 23.3. IR (KBr pellets): ν_{CN} = 1605 cm^{-1}. Anal. Calcd for $C_{35}H_{34}ClN_2PPd$: C, 64.13; H, 5.23; N, 4.27. Found: C, 64.49; H, 5.04; N, 4.52.

The following complexes were synthesized by a similar procedure using the appropriate allyl complexes and isocyanides. The color of the ensuing insertion products, the yield, the reaction time previously determined by NMR experiments, and the spectrometric data are indicated in sequence.

Complex 1Cd. Dark yellow solid. Yield: 81%, 90 min. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.70 (s, 3H, C−CH_3), 2.95 (s, 6H, Ph−CH_3), 3.03 (s, 1H, CH_2−C), 4.37 (m, 1H, CH_2=C_{cis}), 4.55 (m, 1H, CH_2=C_{trans}), 6.78 (m, H−Ph_{ortho}), 6.85 (m, 2H, H−Ph_{meta}) 7.39−7.56 (m, 6H, PPh_2), 7.64−7.72 (m, 2H, H^3, H^6), 7.76−7.89 (m, 5H, H^7, PPh_2) 8.07 (dt, 1H, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2 Hz, H^5), 8.42 (dt, 1H, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.7 Hz, H^4), 9.98 (dd, 1H, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 1.6 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 19.5 (CH_3, Ph−CH_3), 24.1 (CH_3, CH_3−C), 51.3 (bs, CH_2, CH_2−C), 113.7 (CH_2, CH_2=C), 123.1 (CH, CH−Ph_{para}), 127.6 (C, C−Ph_{ortho}), 131.4 (CH, C^5), 135.9 (CH, C^7), 138.6 (CH, C^4), 142.5 (C, C=CH_2), 149.0 (C, C^{10}), 149.3 (C, C^9), 153.7 (CH, C^2), 178.9. (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 26.2. IR (KBr pellets): ν_{CN} = 1602 cm^{-1}. Anal. Calcd for $C_{34}H_{32}ClN_2PPd$: C, 63.66; H, 5.03; N, 4.37. Found: C, 63.77; H, 5.21; N, 4.18.

Complex 2Bd. Dark yellow solid. Yield: 78%, 20 min. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.14 (s, 3H, CH_{3cis}), 1.57 (s, 3H, CH_{3trans}), 2.00 (s, 6H, Ph−CH_3), 3.13 (s, 3H, $CH_{3quinoline}$), 3.33 (d, 2H, $^3J_{H,H}$ = 6.6 Hz, CH_2−CH), 5.30 (m, 1H, CH=CH_2), 6.92 (m, 3H, H−Ph_{ortho}, H−Ph_{meta}), 7.34−7.60 (m, 13H, H^3, H^6, H^7, PPh_2), 7.93 (d, 1H, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.3 Hz, H^5), 8.15 (dd, 1H, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.5 Hz, H^4). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 27.6. IR (KBr pellets): ν_{CN} =1650 cm^{-1}. Anal. Calcd for $C_{36}H_{36}ClN_2PPd$: C, 64.58; H, 5.42; N, 4.18. Found: C, 64.91; H, 5.71; N, 4.29.

Complex 1At. Yellow solid. Yield: 84%, 35 min. In order to avoid decomposition, the following reaction mixtures were thermally quenched at 0 °C (ice bath) at the end of the reaction and before reduction to a small volume. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.47 (s, 3H, Ph−CH_3), 2.96 (dd, 1H, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ =7.2 Hz, CH_2−CH), 3.22 (dd, 1H, $^2J_{H,H}$ = 17.0, $^3J_{H,H}$ = 7.2 Hz, CH_2−CH), 4.22 (d, 1H, $^2J_{H,H}$ = 14.9 Hz, CH_2SO_2), 4.61 (dm, 1H, $^3J_{H,H}$ = 17.2, CH_2=CH_{cis}), 4.86 (dm, 1H, $^3J_{H,H}$ = 10.1, CH_2=CH_{trans}), 5.04 (d, 1H, $^2J_{H,H}$ = 14.9 Hz, CH_2SO_2), 5.97 (m, 1H, CH=CH_2), 7.31 (d, 2H, $^3J_{H,H}$ = 7.9 Hz, H−Ph_{ortho}), 7.43−7.70 (m, 14H, H−Ph_{meta}, H^3, H^6, PPh_2), 7.89 (m, 1H, H^7), 8.15 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, H^5), 8.50 (dt, 1H, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.8 Hz, H^4), 9.82 (dd, 1H, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 1.6 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 21.9 (CH_3, Ph−CH_3), 49.6 (d, CH_2, $^3J_{P,C}$ = 10.2 Hz, CH_2−CH), 77.0 (CH_2, CH_2SO_2), 115.1 (CH_2, CH_2=CH), 129.2 (CH, CH−Ph), 129.3 (CH, CH−Ph), 132.4 (CH, C^5), 135.7 (CH, CH=CH_2), 137.4 (CH, C^7), 139.2 (CH, C^4), 144.2 (C, C−Ph_{para}), 149.4 (C, C^{10}), 149.7 (C, C^9), 153.1 (CH, C^2), 192.8 (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 28.5. IR (KBr pellets): ν_{CN} = 1615, δ_{SO2} = 1314, 1137, 562 cm^{-1}. Anal. Calcd for $C_{33}H_{30}ClN_2O_2PPdS$: C, 57.32; H, 4.37; N, 4.05. Found: C, 57.13; H, 4.45; N, 4.23.

Complex 1Bt. Yellow solid. Yield: 90%, 20 min. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.30 (s, 3H, CH_{3cis}), 1.65 (s, 3H, CH_{3trans}), 2.47 (s, 3H, Ph−CH_3), 2.92 (dd, 1H, $^2J_{H,H}$ = 18.1, $^3J_{H,H}$ = 6.9 Hz, CH_2−CH), 3.22 (dd, 1H, $^2J_{H,H}$ = 18.1, $^3J_{H,H}$ = 6.9 Hz, CH_2−CH), 4.16 (d, 1H, $^2J_{H,H}$ = 14.8 Hz, CH_2SO_2), 5.04 (d, 1H, $^2J_{H,H}$ = 14.8 Hz, CH_2SO_2), 5.36 (m, 1H, CH=CH_2), 7.31 (d, 2H, $^3J_{H,H}$ = 7.8 Hz, H−Ph_{ortho}), 7.43−7.67 (m, 14H, H−Ph_{meta}, H^3, H^6, PPh_2), 7.84 (m, 1H, H^7), 8.15 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, H^5), 8.50 (dt, 1H, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.7 Hz, H^4), 9.83 (dd, 1H, $^3J_{H,H}$ = 4.8, $^4J_{H,H}$ = 1.6 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 18.0 (CH_3, $CH_{3\ cis}$), 21.9 (CH_3, Ph−CH_3), 25.8 (CH_3, $CH_{3\ trans}$), 44.5 (d, CH_2, $^3J_{P,C}$ = 10.9 Hz, CH_2−CH), 76.7 (CH_2, CH_2SO_2), 120.9 (CH, CH=CH_2), 129.1 (CH, CH−Ph), 129.4 (CH, CH−Ph), 131.5 (C, $C(CH_3)_2$), 132.3 (CH, C^5), 137.5 (CH, C^7), 139.1 (CH, C^4), 144.1 (C, C−Ph_{para}), 149.4 (C, C^{10}), 149.7 (C, C^9), 153.1 (CH, C^2), 193.1 (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 28.1. IR (KBr pellets): ν_{CN} = 1620, δ_{SO2} = 1315, 1152, 1134, 570 cm^{-1}. Anal. Calcd for $C_{35}H_{34}ClN_2O_2PPdS$: C, 58.42; H, 4.76; N, 3.89. Found: C, 58.73; H, 4.57; N, 3.91.

Complex 1Ct. Yellow solid. Yield: 84%, 15 min. In order to avoid decomposition, the following complexes were obtained by reduction under vacuum of the volume of the reaction mixtures immediately after the predetermined reaction time. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.51 (s, 3H, C−CH_3), 2.45 (s, 3H, Ph−CH_3), 2.91 (d, 1H, $^2J_{H,H}$ = 16.8 Hz, CH_2−C), 3.27 (d, 1H, $^2J_{H,H}$ = 16.8 Hz, CH_2−C), 4.17 (d, 1H, $^2J_{H,H}$ = 14.8 Hz, CH_2SO_2), 4.39 (m, 1H, CH_2=C_{cis}), 4.66 (m, 1H, CH_2=C_{trans}), 5.09 (d, 1H, $^2J_{H,H}$ = 14.8 Hz, CH_2SO_2), 7.29 (d, 2H, $^3J_{H,H}$ = 8.0 Hz, H−Ph_{ortho}), 7.43−7.80 (m, 14H, H−Ph_{meta}, H^3, H^6, PPh_2), 7.89 (m, 1H, H^7), 8.15 (dt, 1H, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.3 Hz, H^5), 8.50 (dt, 1H, $^3J_{H,H}$ = 8.3, $^4J_{H,H}$ = 1.7 Hz, H^4), 9.84 (dd, 1H, $^3J_{H,H}$ = 4.9, $^4J_{H,H}$ = 1.6 Hz, H^2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 21.9 (CH_3, Ph−CH_3), 22.6 (CH_3, CH_3−C), 53.8 (d, CH_2, $^3J_{P,C}$ = 10.7 Hz, CH_2−C), 76.6 (CH_2, CH_2SO_2), 112.9 (CH_2; CH_2=C), 129.2 (CH, CH−Ph), 129.3 (CH, CH−Ph), 132.3 (CH, C^5), 137.4 (CH, C^7), 139.2 (CH, C^4), 143.5 (C, C=CH_2), 144.1 (C, C−Ph_{para}), 149.4 (C, C^{10}), 149.7 (C, C^9), 153.1 (CH, C^2), 192.0 (C, C=

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N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 28.3. IR (KBr pellets): ν_{CN} = 1628, δ_{SO2} = 1310, 1159, 1139, 564 cm^{-1}. Anal. Calcd for $C_{34}H_{32}ClN_2O_2PPdS$: C, 57.88; H, 4.57; N, 3.97. Found: C, 58.07; H, 4.65; N, 4.12.

Complex 2At. Yellow solid. Yield: 77%, 15 min. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 2.46 (s, 3H, Ph−CH_3), 2.73 (dd, 1H, $^2J_{H,H}$ = 17.2, $^3J_{H,H}$ = 6.3 Hz, C$\underline{H}_2$−CH), 3.21 (dd, 1H, $^2J_{H,H}$ = 17.2, $^3J_{H,H}$ = 6.3 Hz, C$\underline{H}_2$−CH), 3.28 (s, 3H, $CH_{3quinoline}$), 4.57 (dm, 1H, $^3J_{H,H}$ = 17.2, C$\underline{H}_2$=CH_{cis}), 4.79 (dm, 1H, $^3J_{H,H}$ = 10.1, C$\underline{H}_2$=CH_{trans}), 4.85 (d, 1H, $^2J_{H,H}$ = 14.8 Hz, CH_2SO_2), 5.14 (d, 1H, $^2J_{H,H}$ = 14.8 Hz, CH_2SO_2), 5.74 (m, 1H, C$\underline{H}$=CH_2), 7.28 (d, 2H, $^3J_{H,H}$ = 7.9 Hz, H−Ph_{ortho}), 7.45−7.74 (m, 14H, H−Ph_{meta}, H^3, H^6, PPh_2), 7.88 (m, 1H, H^7), 8.02 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, H^5), 8.24 (dd, 1H, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ = 1.6 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 21.9 (CH_3, Ph−CH_3), 29,0 (CH_3, $CH_{3quinoline}$) 48.8 (d, CH_2, $^3J_{P,C}$ = 10.6 Hz, $\underline{C}H_2$−CH), 77.2 (CH_2, CH_2SO_2), 114.8 (CH_2, CH_2=CH), 129.1 (CH, CH−Ph), 129.4 (CH, CH−Ph), 131.9 (CH, C^5), 135.9 (CH, $\underline{C}H$=CH_2), 138.3 (CH, C^7), 138.3 (CH, C^4), 144.2 (C, C−Ph_{para}), 149.9 (C, C^{10}), 150.1 (C, C^9), 166.3 (C, C^2), 189.7 (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 28.2. IR (KBr pellets): ν_{CN} = 1633, δ_{SO2} = 1312, 1156, 1136, 557 cm^{-1}. Anal. Calcd for $C_{34}H_{32}ClN_2O_2PPdS$: C, 57.88; H, 4.57; N, 3.97. Found: C, 57.71; H, 4.72; N, 3.72.

Complex 2Bt. Yellow solid. Yield: 91%, 50 min. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.31 (s, 3H, CH_{3cis}),1.61 (s, 3H, CH_{3trans}), 2.46 (s, 3H, Ph−CH_3), 2.76 (dd, 1H, $^2J_{H,H}$ = 17.5, $^3J_{H,H}$ = 7.1 Hz, C$\underline{H}_2$−CH), 3.21 (dd, 1H, $^2J_{H,H}$ = 17.5, $^3J_{H,H}$ = 7.1 Hz, C_{H2}−CH), 3.27 (s, 3H, $CH_{3quinoline}$) 4.78 (d, 1H, $^2J_{H,H}$ = 14.6 Hz, CH_2SO_2), 5.15 (d, 1H, $^2J_{H,H}$ = 14.6 Hz, CH_2SO_2), 5.15 (m, 1H, C$\underline{H}$=CH_2), 7.29 (d, 2H, $^3J_{H,H}$ = 7.9 Hz, H−Ph_{ortho}), 7.45−7.75 (m, 14H, H−Ph_{meta}, H^3, H^6, PPh_2), 7.83 (m, 1H, H^7), 8.01 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, H^5), 8.23 (dd, 1H, $^3J_{H,H}$ = 8.4, $^4J_{H,H}$ = 1.7 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 246 K, ppm) δ: 18.1 (CH_3, CH_{3cis}), 21.9 (CH_3, Ph−CH_3), 25.7 (CH_3, CH_{3trans}), 29.0 (CH_3, $CH_{3quinoline}$), 43.9 (d, CH_2, $^3J_{P,C}$ = 11.7 Hz, CH_2−CH), 76.8 (CH_2, CH_2SO_2), 120.9 (CH; CH=CH_2), 129.1 (CH, CH−Ph), 129.4 (CH, CH−Ph), 131.5 (CH, C^5), 132.4 (C, $C(CH_3)_2$), 134.9 (CH, C^7), 138.3 (CH, C^4), 144.2 (C, C−Ph_{para}), 149.8 (C, C^{10}), 150.1 (C, C^9), 166.2 (C, C^2), 190.2 (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 27.6. IR (KBr pellets): ν_{CN} = 1639, δ_{SO2} = 1313, 1134, 558 cm^{-1}. Anal. Calcd for $C_{36}H_{36}ClN_2O_2PPdS$: C, 58.94; H, 4.95; N, 3.82. Found: C, 59.14; H, 5.07; N, 3.56.

Complex 2Ct. Yellow solid. Yield: 85%, 15 min. ^1H NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 1.37 (s, 3H, C−CH_3), 2.45 (s, 3H, Ph−CH_3), 2.72 (d, 1H, $^2J_{H,H}$ = 16.5 Hz, CH_2−C), 3.16 (s, 3H, $CH_{3quinoline}$), 3.34 (d, 1H, $^2J_{H,H}$ = 16.5 Hz, CH_2−C), 4.35 (m, 1H, CH_2=C_{cis}), 4.61 (m, 1H, CH_2=C_{trans}), 4.80 (d, 1H, $^2J_{H,H}$ = 14.9 Hz, CH_2SO_2), 5.18 (d, 1H, $^2J_{H,H}$ = 14.9 Hz, CH_2SO_2), 7.27 (d, 2H, $^3J_{H,H}$ = 7.9 Hz, H−Ph_{ortho}), 7.46−7.80 (m, 14H, H−Ph_{meta}, H^3, H^6, PPh_2), 7.85 (m, 1H, H^7), 8.02 (dt, 1H, $^3J_{H,H}$ = 8.0, $^4J_{H,H}$ 1.2 Hz, H^5), 8.23 (dd, 1H, $^3J_{H,H}$ = 8.5, $^4J_{H,H}$ =1.6 Hz, H^4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 243 K, ppm) δ: 21.9 (CH_3, Ph−CH_3), 22.4 (CH_3, CH_3−C), 28.9 (CH_3, $CH_{3quinoline}$), 53.6 (d, CH_2, $^3J_{P,C}$ = 12.1 Hz, CH_2−C), 76.7 (CH_2, CH_2SO_2), 112.2 (CH_2, CH_2=C), 129.1 (CH, CH−Ph), 129.4 (CH, CH−Ph), 131.8 (CH, C^5), 134.6 (CH, C^7), 138.3 (CH, C^4), 143.6 (C, $\underline{C}$=CH_2), 144.1(C, C−Ph_{para}), 149.8 (C, C^{10}), 150.0 (C, C^9), 166.2 (C, C^2), 188.3 (C, C=N). $^{31}P\{^1H\}$ NMR (300 MHz, CD_2Cl_2, T = 298 K, ppm) δ: 28.3. IR (KBr pellets): ν_{CN} = 1640, δ_{SO2} = 1311, 1155, 1133, 567 cm^{-1}. Anal. Calcd for $C_{35}H_{34}ClN_2O_2PPdS$: C, 58.42; H, 4.76; N, 3.89. Found: C, 58.31; H, 4.95; N, 3.61.

Preliminary Reactivity Study and Kinetic Measurements. In order to assess the reaction time of the reaction under study (which is a crucial parameter to avoid decomposition), we have carried out some NMR preliminary investigations. In a typical experiment 16 mmol of the starting allyl complex was mixed into an NMR tube with 19 mmol of isocyanide, and the reaction mixture was monitored with time up to the disappearance of the starting material.

The kinetic measurements were based on a similar experimental approach carried out at 288.15 K in CD_2Cl_2 after the preliminary determination of the suitable substrates, isocyanides, and reagent concentrations.

The formation of intermediate **I** was observed in an IR experiment in which a concentrated solution of DIC was added by means of a micropipet to a solution of complex **1C** in CH_2Cl_2. The IR spectrum between 2260 and 2000 cm^{-1} was recorded immediately after mixing in a liquid cell with NaCl windows (d = 0.5 mm).

Computational Details. DFT calculations were performed with the DMol[315a,b] program; geometries of the compounds were optimized at the DFT PBE[15c] level using the double numerical polarized basis set (DNP).[15d] Relativistic effects of core electrons were computed using DFT semi-core pseudopotentials;[15e] the conductor-like screening model[15f,g] (COSMO) was used to simulate a solvent environment for the calculation.

The mathematical treatment of the experimental kinetic data was carried out in Origin or Scientist environments.

Crystal Structure Determination. The crystal data of compound **1Bd** 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[26] and corrected for Lorentz, polarization, and absorption effects (SORTAV).[27] The structure was solved by direct methods using the SIR97[28] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms.

All calculations were performed using SHELXL-97[29] and PARST[30] implemented in the WINGX[31] system of programs (CCDC 982379).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Further details of the structure determination, final coordinates, bond distances and bond angles for **1Bd**, NMR and IR spectra, and concentration vs time profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) It is noteworthy that complex **1A** also displays a temperature-dependent fluxionality, which at variance with the present case was interpreted as a $\eta^1-\eta^3-\eta^1$ isomerism since the low-temperature NMR spectra point to the monohapticity of the allyl fragment (see ref 12).

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(15) We tried to confirm the experimental finding by means of a computational approach (see references below (a−g)). However, the computational response is not in accord with the experimentally observed coordinative choice of the allyl group. The most stable computed species is in fact the κ^2-η^1 complex (with structure similar to those of **1A** and **1B** in Scheme1), whereas the κ^2-η^3 we experimentally found as predominant is the less energetically favored ($\Delta E \approx 3.6$ and 4.5 kcal mol^{-1} at 298 and 225 K, respectively, when compared with the κ^2-η^1 structure). Finally the structure of the type κ^1-η^3 (similar to the structure shown by the DPPQ-Me derivatives **2A**, **2B**, and **2C** in Scheme1) is characterized by an intermediate stability ($\Delta E \approx 1.5$ and 2 kcal mol^{-1} at 298 and 225 K, respectively, when compared with the κ^2-η^1 structure). Apparently, due to the small difference in energy among the possible limiting structures, the similar steric and electronic features, and the solvent interactions among neutral or ionic species, the final coordinative choice of the allyl and the spectator group ligand could not be safely predicted. In other words, the computational comparison of neutral and/or ionic complex when interaction with an even weakly polarized solvent is present is not justified. (a) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508−517. (b) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756−7764. (c) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868. (d) Delley, B. *J. Phys. Chem. A* **2006**, *110*, 13632−13639. (e) Delley, B. *Phys. Rev. B* **2002**, *66*, 155125/1−155125/9. (f) Klamt, A.; Schürmann, G. *J. Chem. Soc., Perkin Trans.* **1993**, *2*, 799−805. (g) Delley, B. *Mol. Simul.* **2006**, *32*, 117−123.

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