6762 *Organometallics* **2009,** *28,* 6762–6770
DOI: 10.1021/om900786e

ORGANOMETALLICS
Article

Migratory Insertion of Allyl Groups across the Pd−C Bond in Palladium(II) Isocyanide Complexes. The Fundamental Interplay between Temperature and Allyl Hapticity

Luciano Canovese,* Fabiano Visentin, Claudio Santo, and Carlo Levi

Dipartimento di Chimica, Università Ca' Foscari, Venice, Italy

Received September 9, 2009

The 2,6-dimethylphenyl- and *tert*-butylisocyanides (DIC and TIC, respectively) react in chlorinated solvents with the allyl dimers $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_3Me_2)]_2$ and $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$, giving the insertion products *trans*-$[Pd(DIC)_2(C{=}N(2,6\text{-}Me_2C_6H_3)CH_2CHCMe_2)Cl]$, *trans*-$[Pd(TIC)_2(C{=}N(CMe_3)CH_2CHCMe_2)Cl]$, and *trans*-$[Pd(DIC)_2(C{=}N(2,6\text{-}Me_2C_6H_3)CH_2CHCH_2)Cl]$, respectively. In particular, the reaction between the complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_3Me_2)]_2$ and DIC was studied in detail, and a number of different species involved in the insertion process were identified. A mechanistic network taking into account all the involved derivatives was proposed on the basis of independently measured equilibrium and rate constants.

In this respect, two independent equilibria, both involving the formation of η^1-allyl intermediates, were detected and the related constants determined. The formation of such intermediates bearing the η^1-allyl fragment in *cis* position to the isocyanide is crucial when the subsequent insertion is considered. The intermediates, however, do not display the same reactivity owing to the different thermodynamic parameters governing their formation. In particular the formation of $[Pd(\eta^1\text{-}C_3H_3Me_2)(DIC)_2Cl]$ (**MD2Cl**) represents the privileged path to the product *trans*-$[Pd(DIC)_2(C{=}N(2,6\text{-}Me_2C_6H_3)CH_2CHCMe_2)Cl]$ (**P**) when the insertion process is carried out at RT. The alternative intermediate $[Pd(\eta^1\text{-}C_3H_3Me_2)(DIC)_3]^+Cl^-$ (**MD3**) hardly contributes to the formation of the product **P** since it is disfavored by increasing the temperature.

Introduction

Palladium-catalyzed nucleophilic substitution on allyl substrates represents an important and versatile methodology that has attracted a great deal of interest for its potential applications in organic synthesis.[1] Generally, when nucleophiles such as amines or carbanions are employed, the nucleophilic attack occurs at the terminal carbon of the allyl moiety, although alternative mechanisms were proposed.[2] However, the propensity of the allyl moiety to assume the monohapto configuration under the attack of strong or chelating nucleophiles is well known,[3] and therefore, in the presence of an adequate unsaturated moiety an insertion reaction yielding new interesting organic or organometallic fragments might occur.[4] Isocyanides (CNR) represent a favorable alternative to the isoelectronic carbon monoxide, owing to their high reactivity, the easy handling, and their chemical and steric characteristics, which can be widely modulated by the appropriate choice of the substituent R.[5] However, in spite of the great number of reported isocyanide insertions into the Pd−C bond[6] and at variance with carbon monoxide,[7] to the best of our knowledge they were occasionally employed as reactants toward palladium allyl derivatives.[8] Moreover, the mechanism involved in this sort of reactions was never determined. Recently, we have noticed that the product of insertion of isocyanide CNR across the Pd−R′ bond was markedly influenced by both the nature of R and R′ and the molar ratio between the complex and the isocyanide.[6r,9] Thus, the reaction of the complexes $[Pd(L{-}L')(R')X)]$ (L−L′ = pyridyl thioether, diphenyl phosphanylquinoline ligands, X = Cl, I; R′ = Me, C_6H_4-Me-4) with an equimolecular amount of 2,6-dimethylphenyl isocyanide (DIC) yielded quantitatively the monoinserted derivative $[Pd(L{-}L')(C(Me){=}NC_6H_3Me)_2X]$. On the other hand, addition of DIC in a 2:1 ratio to a solution of the tolyl derivatives $[Pd(L{-}L')(C_6H_4\text{-}Me\text{-}4)X]$ gave rise to an

*Corresponding author. E-mail: cano@unive.it.

(1) (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173–1192. (b) Godlesky, S. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelbach M. F., Eds.; Pergamon: Oxford, U.K., 1991; Vol. *4*, p 585. (c) Tsuji, J. In *Palladium and Catalysts Innovation in Organic Synthesis*; Wiley: Chichester, U.K. 1995; p 290. (d) *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; Wiley: New York, 2002. (e) *Metal-catalyzed Cross-coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004.

(2) (a) Trost, B. M.; Keinam, E. *J. Am. Chem. Soc.* **1978**, *100*, 7779–7781. (b) Trost, B. M.; Verhoeven, T. B. *J. Am. Chem. Soc.* **1980**, *102*, 4730–4743. (c) Granberg, K. L.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6858–6863.

(3) (a) Jutand, A. *Appl. Organomet. Chem.* **2004**, *18*, 574−582, and references therein. (b) Garcia-Iglesias, M.; Buñuel, E.; Cárdenas, D. J. *Organometallics* **2006**, *25*, 3611−3618, and references therein. (c) Aydin, J.; Szabó K. J. *Org. Lett.* **2008**, *10*, 2881−2884, and references therein.

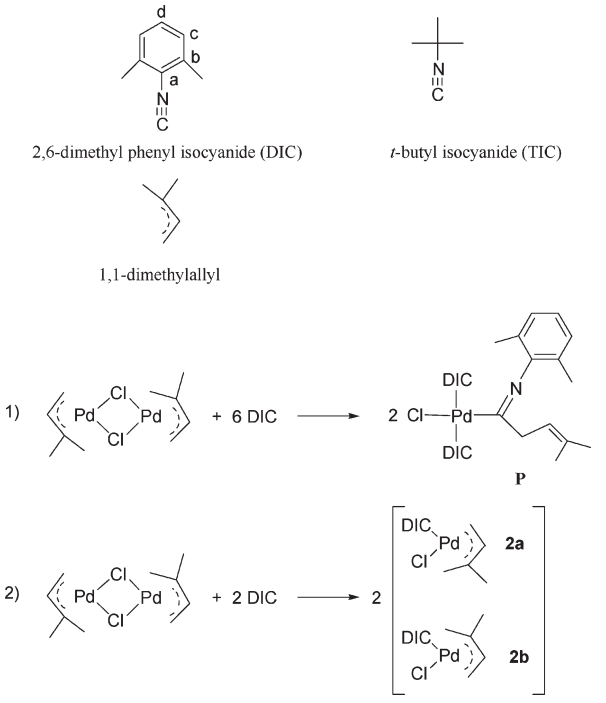
(4) Cucciolito, M. E.; Vitagliano, A. *Organometallics* **2008**, *27*, 6360–6363.

(5) Crociani, B. In *Reactions of Coordinated Ligands*; Plenum: New York, Vol. *1*, 1982; p 553, and references therein.

 Published on Web 11/06/2009

equimolecular mixture of *trans*-[Pd(DIC)$_2$(C(C$_6$H$_4$Me-4)=NC$_6$H$_3$(Me)$_2$)X] and the unreacted starting complexes.[6n,r] The imidoyl dimeric complex [Pd(CNC$_6$H$_3$Me$_2$)(C(Me)=NC$_6$H$_3$Me$_2$)Cl]$_2$ was instead obtained under similar experimental conditions when the methyl complexes [Pd(L−L′)(Me)X)] were used as starting substrates. In their early studies Tsuji and Crociani[8a,b] claimed that dimeric μ-Cl species were obtained when the complexes [Pd(η^3-C$_3$H$_5$)(CNR)Cl] (CNR = cyclohexyl, phenyl, and *p*-nitrophenyl isocyanide) were reacted with one further molecule of isocyanide. In an attempt to obtain similar complexes containing the DIC isocyanide we observed that a completely different and far more complicated reaction took place. Therefore, since no further papers have hitherto appeared, with the aim of investigating in detail the reactivity toward the palladium allyl complexes of the isocyanide derivatives, we have undertaken an exhaustive study on the compounds and reactions summarized in Scheme 1. The results are reported in the present paper.

Scheme 1. Isocyanides and Complexes Involved in the Migratory Allyl Insertion



Results and Discussion

When the dimer [Pd(μ-Cl)(η^3-C$_3$H$_3$Me$_2$)]$_2$ reacts at RT in chlorinated solvents with six equivalents of DIC isocyanide, the almost immediate formation of complex **P** takes place, which represents the product of an allyl migratory insertion. (reaction 1 in Scheme 1). No hints of the dimeric complexes described by Crociani and Tsuji are detectable under our experimental conditions. Such a reaction seems to be of general application since similar insertion products are observed when the dimer [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ reacts with DIC or when the dimer [Pd(μ-Cl)(η^3-C$_3$H$_3$Me$_2$)]$_2$ reacts with the more hindered TIC (the reaction in the latter case takes, however, a longer time, i.e. ∼60 min).

However, an accurate insight into reaction 1 allows a more detailed picture of the whole mechanism. A stepwise addition of DIC to a solution of the dimer [Pd(μ-Cl)(η^3-C$_3$H$_3$Me$_2$)]$_2$ yields different species as a function of the molar ratio between the starting complex and the isocyanide. Thus, the ratio [DIC]/[[Pd(μ-Cl)(η^3-C$_3$H$_3$Me$_2$)]$_2$] = 2:1 yields the isomeric mixture of complexes **2a** and **2b** (reaction 2 in Scheme 1), which can be easily isolated and unambiguously characterized. The assignment of the structures of the two isomers was obtained by phase-sensitive NOESY and stems from the key interligand cross-peaks between the *syn* allyl protons and the C$\underline{H}_3$ protons of the coordinated DIC in isomer **2a**. The distribution between isomers is **2a**/**2b** = 5:1.

Upon addition at RT of *only* one equivalent of DIC to a chlorinated solvent solution of the complexes **2** (**2a** + **2b**), an equimolecular mixture of the product **P** and the unreacted **2** isomers in rapid interconversion was produced. Dechlorination of this solution by addition of a methanol solution of NaClO$_4$ yields the easily separable cationic complex [Pd(η^3-C$_3$H$_3$Me$_2$)(DIC)$_2$]ClO$_4$ as an air-stable single product, which was completely characterized (see Experimental Section). Remarkably, removal of the chloride from complex **P** causes the elimination of the inserted isocyanide. As will be discussed later, the presence or the absence of chloride in solution is of paramount importance in governing the migratory insertion reactions.

In an attempt at determining the key species involved in the overall reaction yielding product **P**, we carried out a detailed NMR study at low temperature. Thus, we preliminarily added two equivalents of DIC to a solution of the complexes **2** at 203 K in CD_2Cl_2. No formation of the product **P** was observed in that case. On the contrary, some different species were detectable, none of which turned into complex **P** at that temperature even after a long time.

A subsequent detailed analysis of the system allows the identification of all the species and their role in the insertion process (*vide post*). Scheme 2 anticipates the results of such an analysis. The species relevant to the calculation procedures are indicated with the abbreviations used in the numerical refinement processes.

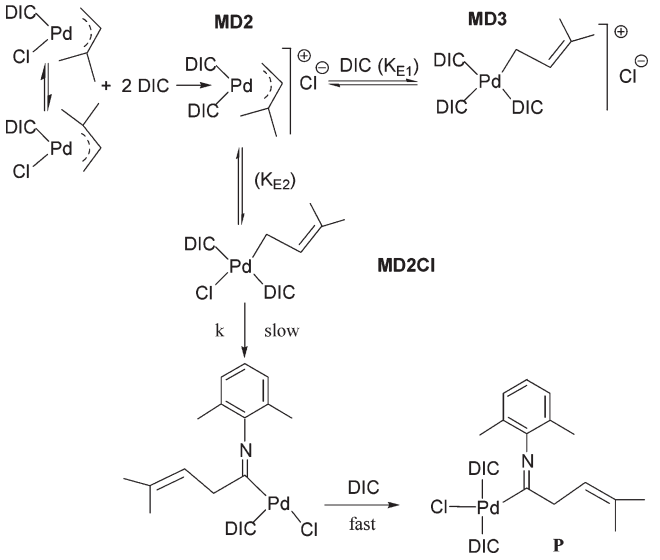
(6) (a) Dupont, J.; Pffefer, M.; Daran, J. C.; Jeannin, Y. *Organometallics* **1987**, *6*, 899–901. (b) Zografidis, A.; Polborn, K.; Beck, W.; Markies, B. A.; van Koten, G. *Z. Naturforsch., B: Chem. Sci.* **1994**, *49*, 1494–1498. (c) Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 433–446. (d) Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917–927. (e) Delis, J. G. P.; Aubel, P. G.; Vrieze, K.; van Leeuwen, P. W. N. M.; Veldman, N.; Speck, A. L.; van Neer, F. J. R. *Organometallics* **1997**, *16*, 2948–2957. (f) Vicente, J.; Abad, J. A.; Shaw, K. F.; Gil-Rubio, J.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **1997**, *16*, 4557–4566. (g) Böhm, A.; Polborn, K.; Sünkel, K.; Beck, W. *Z. Naturforsch., B: Chem. Sci.* **1998**, *53*, 448–458. (h) Lin, Y.-S.; Yamamoto, A. *Organometallics* **1998**, *17*, 3466–3478. (i) Vicente, J.; Saura-Llamas, I.; Turpin, J.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **1999**, *18*, 2683–2693. (j) Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1027–1038. (k) Saluste, C. G.; Whitby, R. J.; Furber, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4156–4158. (l) Vicente, J.; Abad, J. A.; Frankland, A. D.; Lopez-Serrano, J.; Ramirez de Arellano, M. C.; Jones, P. G. *Organometallics* **2002**, *21*, 272–282. (m) Onitsuka, K.; Yamamoto, M.; Suzuki, S.; Takahashi, S. *Organometallics* **2002**, *21*, 581–583. (n) Vicente, J.; Abad, J.-A.; Martinez-Viviente, E.; Jones, P. G. *Organometallics* **2002**, *21*, 4454–4467. (o) Curran, D. P.; Du, W. *Org. Lett.* **2002**, *4*, 3215–3218. (p) Kim, Y. J.; Chang, X. H.; Han, J. T.; Lim, M. S.; Lee, S. W. *Dalton Trans.* **2004**, 3699–3708. (q) Albert, J.; D'Andrea, L.; Granell, J.; Zafrilla, J.; Font-Bardia, M.; Solans, X. *J. Organomet. Chem.* **2007**, *692*, 4895–4902. (r) Canovese, L.; Visentin, F.; Santo, C.; Levi, C.; Dolmella, A. *Organometallics* **2007**, *26*, 5590–5601. (s) Bortoluzzi, M.; Paolucci, G.; Pitteri, B.; Vavasori, A.; Bertolasi, V. *Organometallics* **2009**, *28*, 3247–3255.

(7) Zhang, J.; Braunstein, P.; Welter, R. *Inorg. Chem.* **2004**, *43*, 4172−4177, and references therein.

(8) (a) Kajimoto, T; Takahashi, H.; Tsuji, J. *J. Organomet. Chem.* **1970**, *23*, 275–280. (b) Boschi, T.; Crociani, B. *Inorg. Chim. Acta* **1971**, *5*, 477–480. (c) Scrivanti, A.; Carturan, G.; Crociani, B. *Organometallics* **1983**, *2*, 1612–1617.

(9) Gambino, G. "Thesis", Università Ca' Foscari, Venice, 2006.

Scheme 2. Mechanism of the Migratory Allyl Insertion



The validation of Scheme 2 was achieved by determining independently the equilibrium constants K_{E1} and K_{E2} and the rate constant k.

Determination of the Equilibrium Constant K_{E1}. As already stated, dechlorination of complex **2** and the subsequent addition of an equimolecular amount of DIC yields the complex $[Pd(\eta^3\text{-}C_3H_3Me_2)(DIC)_2]ClO_4$ (the cationic complex $[Pd(\eta^3\text{-}C_3H_3Me_2)(DIC)_2]^+$ is always indicated as **MD2** independently of the counterion). A further addition of two equivalents of DIC at RT does not induce any insertion process. On the contrary, only a fast (on the NMR time scale) $\eta^3-\eta^1$ selective allyl isomerization process takes place (see Figure 1).

As a matter of fact, upon DIC addition the RT ^{1}H NMR spectrum displays the collapse of the two original doublets at ~4.6 and ~3.5 ppm, ascribable to the allyl H_{syn} and H_{anti} protons into a doublet centered at ~4.0 ppm, and the original doublet of doublets centered at ~5.5 ppm related to the central allyl proton reverts into a triplet at the same chemical shift. The Me_{syn} and Me_{anti}, on the contrary, are hardly affected by DIC addition. Such a process is clearly a regioselective $\eta^3-\eta^1$ fluxional phenomenon in which the monohapto allyl fragment coordinated to the palladium center via the unsubstituted carbon terminus represents a less energy demanding path to the rearrangement than its analogue with the allyl fragment coordinated via the 1,1-bis-substituted carbon.[10] No insertion processes are observable in this case within some hours (Figure 1a).

Surprisingly, decreasing the temperature of the solution previously studied to 213 K induces a dramatic effect on the ^{1}H NMR spectrum. The triplet at ~5.5 ppm undergoes no marked transformation, whereas the doublet related to the protons of the unsubstituted allyl terminus ($Me_2C\text{-}CH\text{-}C\underline{H}_2$) shifts upfield by ~3.5 ppm and the signals due to the methyl protons bound to the other allyl terminus resonate as two singlets at ~1.9 and ~1.6 ppm (Figure 1b). The difference in the chemical shifts of the methyl substituents is in this case markedly reduced if compared with that of the starting complex.

(10) Canovese, L.; Visentin, F.; Uguagliati, P.; Bandoli, G. *Inorg. Chim. Acta* **1988**, *277*, 247–252.

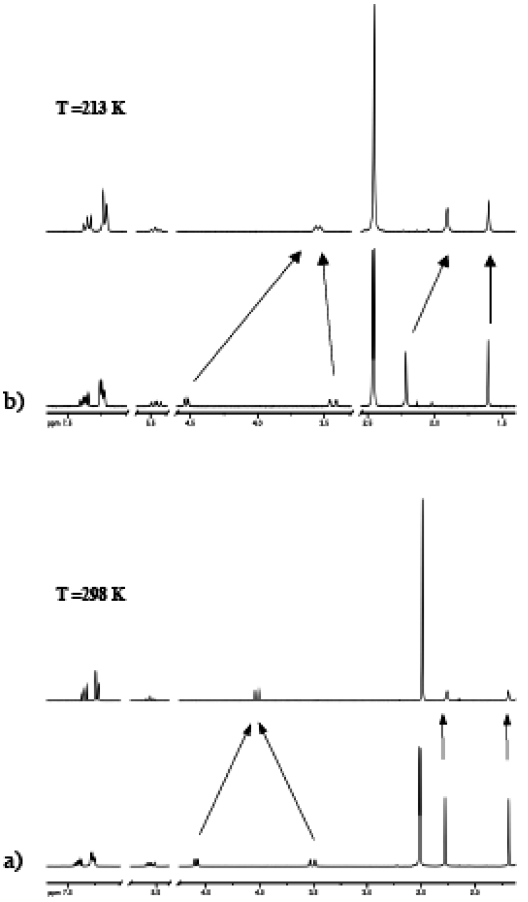


Figure 1. Fluxional $\eta^3-\eta^1$ rearrangement induced upon addition of DIC in excess to a solution of $[Pd(\eta^3\text{-}C_3H_3Me_2)(DIC)_2]ClO_4$ in CD_2Cl_2 at different temperatures.

The upfield shift of the $Me_2C\text{-}CH\text{-}C\underline{H}_2$ protons but especially the ensuing proximity of the methyl signals represents clear evidence of the presence in solution of species bearing an η^1-allyl fragment bound to palladium via the unsubstituted terminal carbon. As a matter of fact, the independently synthesized and characterized complex **P**, which bears a structurally comparable allyl fragment, displays similar behavior with close methyl group signals ($\Delta\delta$ = 0.03 ppm).

At fixed temperature these two effects are magnified upon increasing the concentration of added DIC (see Scheme 2 and Figure 2).

These spectral features suggest a rapid interconversion (on the NMR time scale) between the two complexes **MD2** ($[Pd(\eta^3\text{-}C_3H_3Me_2)(DIC)_2]^+$) and **MD3** ($[Pd(\eta^1\text{-}C_3H_3Me_2)(DIC)_3]^+$), which bear a differently coordinated allyl fragment. At fixed DIC concentration the ratio between complexes **MD2** and **MD3** is also markedly influenced by temperature changes.

We therefore decided to study the reaction between the complexes **MD2** and **MD3** by adding successive aliquots of DIC to a solution of **MD2** in CD_2Cl_2. The titrations were repeated at five different temperatures in the interval 193−233 K, and within this range no decomposition processes nor reactions yielding byproduct were observed. The reaction appeared to be reversible and can be described by eq 1.

$$\mathbf{MD2} + \mathrm{DIC} = \mathbf{MD3} \qquad (1)$$

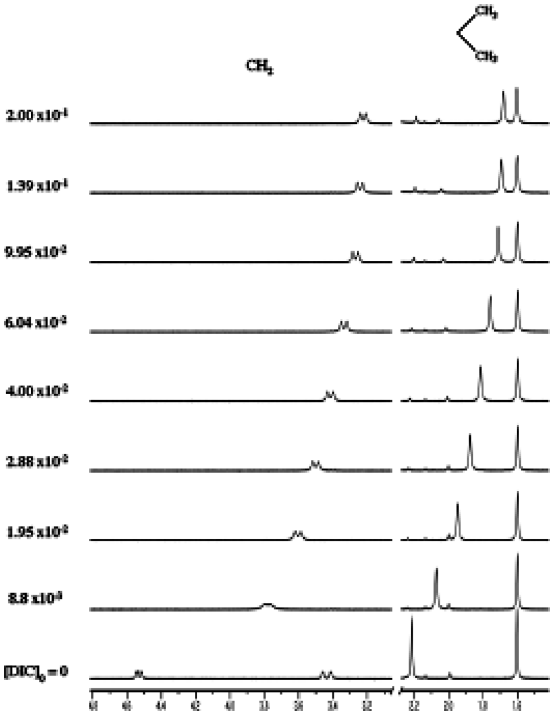


Figure 2. Resulting ^{1}H NMR spectra when increasing amounts of DIC are added to a CD_2Cl_2 solution of the complex [Pd(η^3-$C_3H_3Me_2$)(DIC)$_2$]ClO_4 (**MD2**) at 213 K.

In Figure 2 the effect of the titration by DIC on the chemical shifts of the methyl groups of the allyl termini at 213 K is reported. As can be seen, the difference between the chemical shift related to the *syn* and *anti* methyl groups of the trihapto allyl moiety ($\Delta\delta$ = 0.64 ppm) decreases to a lesser extent when the allyl fragment is forced into an η^1 position by the incoming DIC nucleophile (extrapolated $\Delta\delta$ = 0.04 ppm). Notably, the signal due to the protons of the methyl group in *anti* position hardly changes upon DIC addition; therefore only the chemical shift δ related to the *syn* protons can be taken into consideration in the regression analysis (*vide infra*).

Each equilibrium determination at any temperature explored was analyzed by a regression analysis based on the following equations carried out under the SCIENTIST environment.

$$K_{E1} = [\mathbf{MD3}]/([\mathbf{MD2}]_0[\mathbf{MD3}])([\mathrm{DIC}]_0[\mathbf{MD3}]) \quad (2)$$

$$\delta_M = \delta_I - [\mathbf{MD3}](\delta_I - \delta_F)/[\mathbf{MD2}]_0 \quad (3)$$

where $[\mathbf{MD2}]_0$ represents the initial concentration of **MD2**, $[\mathrm{DIC}]_0$ the total concentration of DIC added at every titration interval, [**MD3**] the calculated concentration of **MD3** upon every DIC addition, δ_I the proton chemical shift of the methyl in *anti* position of **MD2** before DIC addition, δ_F the proton chemical shift of the methyl group in η^1 position in **MD3** (chemical shift of the final complex), and δ_M the ensuing value of the chemical shift at every titration interval. Notably, δ_F and δ_I are slightly temperature dependent.

The optimized K_{E1} and δ_F parameters, the almost temperature-independent δ_I, the $[\mathrm{DIC}]_0$ interval, the experimental temperatures T, and $[\mathbf{MD2}]_0$ are summarized in Table 1.

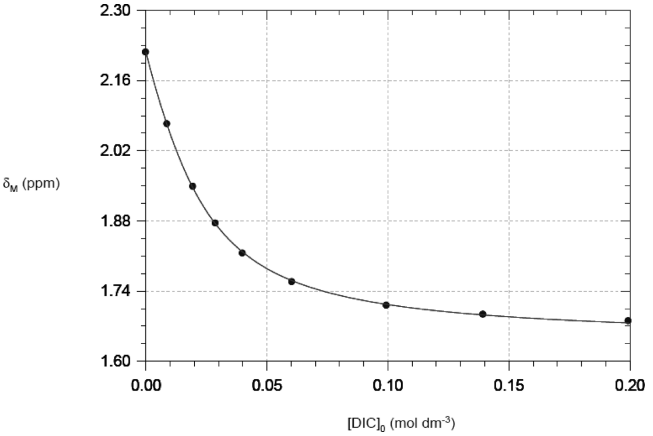


Figure 3. Nonlinear regression analysis for the titration of the complex [Pd(η^3-$C_3H_3Me_2$)(DIC)$_2$]ClO_4 (**MD2**) with DIC in CD_2Cl_2 at 213 K.

Table 1. Initial Concentrations of MD2, Interval of the Used DIC Concentrations, Temperatures, δ_I, and the Determined Parameters δ_F and K_{E1} Related to the Study of Equilibrium 1 in CD_2Cl_2

$[\mathbf{MD2}]_0 \times 10^2$ mol dm^{-3}	$[\mathrm{DIC}]_0 \times 10^1$ mol dm^{-3}	T, K	δ_I, ppm	δ_F, ppm	K_{E1}
1.86	0−1.264	193.1	2.19	1.61 ± 0.01	440 ± 50
1.86	0−1.364	203.1	2.21	1.63 ± 0.01	163 ± 7
1.88	0−1.994	213.1	2.22	1.64 ± 0.01	84 ± 2
1.86	0−1.878	223.1	2.22	1.66 ± 0.01	72 ± 5
1.88	0−3.226	233.1	2.23	1.67 ± 0.01	38 ± 2

In Figure 3 the plot of the regression analysis of the titration carried out at 213 K is reported, whereas the whole set of regression plots are reported in the Supporting Information.

As already noticed, the K_{E1} value considerably decreases with increasing the temperature, thereby suggesting the secondary importance of this equilibrium when the overall mechanism is studied at higher temperatures. We carried out the van't Hoff linear regression of the data reported in Table 1, and the values of $\Delta H^0 = -4.95 \pm 0.5$ kcal mol^{-1} and $\Delta S^0 = -14 \pm 2$ cal mol^{-1} K^{-1} were determined. In particular, the negative ΔS^0 value is in accord with the associative equilibrium process, the total charge of both involved complexes being unchanged. The extrapolated values at 298.15 and 283.15 K for K_{E1} are 3.7 ± 5 and 5.8 ± 8, respectively (to the extent that this extrapolation procedure over such a wide temperature range is warranted, taking into account the change in polar features of the solvent involved).

Determination of the Equilibrium Constant K_{E2}. Upon addition of one equivalent of DIC to the isomeric mixture of **2** in CD_2Cl_2 at 193 K, the formation of the couple of complexes **MD2** and **MD2Cl** is observed (see Scheme 2). In the presence of coordinating chloride and in the absence of free DIC, the amount of **MD3** in solution is negligible.

The equilibrium between the already described **MD2** and the **MD2Cl** substrate is slow with respect to the NMR time scale. Therefore, at variance with the previously discussed case in which only the averaged spectrum of two rapidly interconverting species was observable, in this case both the species were distinguishable. **MD2Cl** is characterized by a difference between the chemical shifts of the methyl

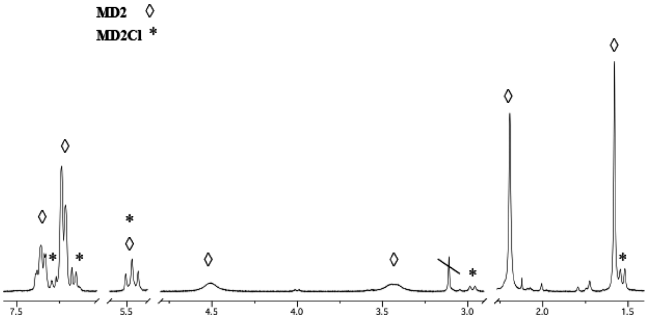


Figure 4. ^{1}H NMR spectrum displaying the equilibrium between the complexes [Pd(η^3-$C_3H_3Me_2$)(DIC)$_2$]Cl (**MD2**) and [Pd(η^1-$C_3H_3Me_2$)(DIC)$_2$Cl] (**MD2Cl**) in CD_2Cl_2 at 213 K.

substituents at the allyl termini (C-(C$\underline{H}_3$)$_2$), considerably smaller than that of the starting complex ($\Delta\delta$ = 0.03 vs 0.64 ppm) and similar to that of the already discussed **MD3** species. Moreover, the C$\underline{H}_2$ allyl terminus coordinated to palladium resonates as a doublet at significantly low chemical shift (~2.97 ppm) (see Figure 4).

All these observations suggest the monohapticity of the allyl fragment via the unsubstituted carbon termini in **MD2Cl**[11] (see Scheme 2).

At variance with the previously described equilibrium (eq 1; K_{E1}) the equilibrium summarized in eq 4 cannot be studied by means of a titration with a soluble organic chloride (e.g., TEBACl; tetrabutylammonium chloride) of the CD_2Cl_2 solution of complexes **MD2** and **MD2Cl**.[12] As a matter of fact, the butyl protons of TEBA obscure a relevant part of the spectrum, and moreover a general fluxionality of the allylic signals take place when nucleophiles or adventitious impurities acting as nucleophiles are added to solutions of palladium allyl derivatives.[13]

$$\mathbf{MD2} + \mathrm{Cl}^- = \mathbf{MD2Cl} \qquad (4)$$

We therefore decided to study equilibrium 4 by determining the concentrations of the complexes involved by a deconvolution process of the methyl signals resonating in the interval 1.45−1.65 ppm recorded at different temperatures in the interval 193−233 K. The equimolecular amount of DIC added to the isomeric mixture of complex **2** induces the formation of only the complexes **MD2** and **MD2Cl**. The equilibrium constants were thereafter calculated by means of eq 5 on the basis of the concentrations of **MD2** and **MD2Cl** determined at any imposed temperature.

$$K_{E2} = [\mathbf{MD2Cl}]/[\mathbf{MD2}]^2 \qquad (5)$$

The recorded spectra are reported in Figure 5, while the one-shot equilibrium constants and the related temperatures are summarized in Table 2. At this juncture a caveat is in order: equilibrium 4 involves the knowledge of *free* ionic species concentrations (**MD2** and Cl^-), which is not warranted in a low-polarity solvent at low temperatures, where ionic pairs cannot be ruled out. However this is a customary, albeit semiquantitative approach in this type of determination.

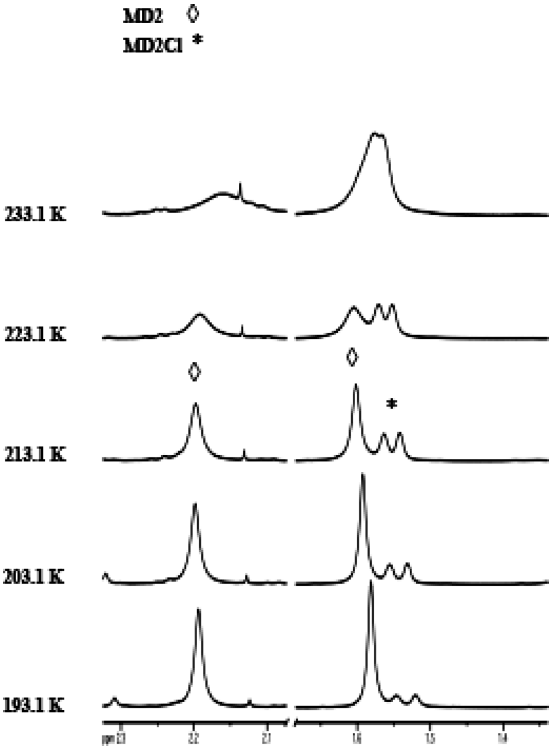


Figure 5. Equilibrium distribution between the complexes **MD2** and **MD2Cl** at different temperatures.

Table 2. Temperatures, Complex Concentrations, and Related Equilibrium Constants Determined by Addition of DIC to an Equimolecular Solution of 2 in CD_2Cl_2 ([DIC]$_0$ = [2]$_0$ = 2.92 × 10^{-2} mol dm^{-3})

T, K	[MD2Cl]$_e$ × 10^3 mol dm^{-3}	([MD2]$_e$; [Cl$^-$]$_e$) × 10^2 mol dm^{-3}	K_{E2}[a]
193.1	2.72	2.65	3.87
203.1	4.48	2.47	7.34
213.1	6.40	2.28	12.3
223.1	8.73	2.05	20.8
233.1	10.3	1.89	28.8

[a] K_{E2} values are reported without uncertainties since they were calculated on the basis of one single measurement. See text.

The van't Hoff linear regression of the ln K_{E2} vs $1/T$ data gives the following result: ΔH^0 = +4.50 ± 0.15 kcal mol^{-1} and ΔS^0 = +26 ± 1 cal mol^{-1} K^{-1}. From the determined parameters within the validity limits pointed to earlier, we can extrapolate the K_{E2} values at 298.15 and 283.15 K, which are 247 ± 112 and 165 ± 98, respectively.

Notably, at variance with the K_{E1} value, K_{E2} increases with increasing temperature. It is therefore possible to push the direction of the migratory insertion by only acting on the reaction temperature. In the case of equilibrium 4, despite the associative nature of the process, a positive value of ΔS^0 is determined. This very fact suggests a massive release of the initially organized molecules of the polarized solvent around the charged [Pd(η^3-$C_3H_3Me_2$)(DIC)$_2$]$^+$Cl$^-$ (**MD2**) molecule when the latter reverts into the neutral [Pd(η^1-$C_3H_3Me_2$)-(DIC)$_2$Cl] (**MD2Cl**). The positive ΔS^0 value along with its

(11) In Scheme 2 the complex **MD2Cl** should display a *cis* structure according to the theory of the nucleophilic substitution in square-planar complexes, which states that any substitution occurs with retention of the initial configuration. We, however, cannot exclude that in the presence of free nucleophile such as chloride and/or DIC an extensive *cis*−*trans* isomerization takes place, as the spectra seem to indicate.

(12) The presence of chloride as counterion of the complex **MD2** induces the formation of the **MD2Cl** derivative at any concentration.

(13) Canovese, L.; Visentin, F.; Uguagliati, P.; Chessa, G.; Pesce, A. *J. Organomet. Chem.* **1998**, *566*, 61–71.

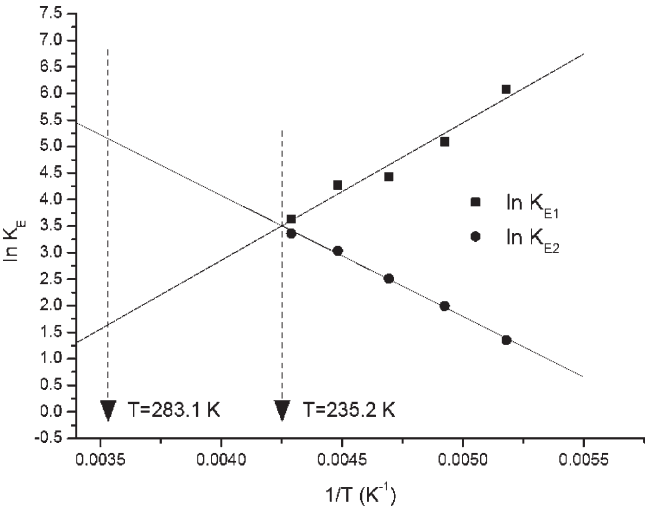


Figure 6. Linear regression plots of the van't Hoff equation for K_{E1} and K_{E2}. The temperatures of inversion and of the kinetic measurements are reported.

related positive ΔH^0 justifies the existence of an inversion temperature (~235.2 K, see Figure 6). Beyond that point, at the kinetic measurement temperature (283.1 K), the K_{E2} value becomes far more important than that of K_{E1}, which is modulated by unfavorable thermodynamic parameters.

Determination of the Rate Constant *k*. Owing to the complexity of Scheme 2, only a stepwise approach to the kinetic problem allows a solution of the mechanistic network. Thus, by means of the independent determination of K_{E1} and K_{E2} and of the subsequent kinetic measurements, the complete disentanglement of the problem by direct determination of the rate constant k was achievable. According to Scheme 2, the ensuing value of k would be independent of DIC concentration. In order to prove it, the reaction was followed at two different DIC concentrations. Unfortunately, the concentration of the reactant cannot be in large excess with respect to the other species under NMR conditions. Thus, the whole process was triggered by setting up a solution obtained by mixing at 283.1 K[14] the isomeric mixture of complex **2** and DIC in the ratios 1:3.6 and 1:2, respectively ($[\mathbf{2}]_0$:$[DIC]_{tot}$ = 0.0317:0.114 and 0.033:0.066 mol dm^{-3}, respectively). The derivative [Pd(η^3-$C_3H_3Me_2$)(DIC)$_2$]Cl (**MD2**) was immediately and quantitatively formed ($[\mathbf{MD2}]_T = [\mathbf{2}]_0$). In the presence of the isocyanide at concentration $[DIC]_0 = [DIC]_{tot} - [\mathbf{2}]_0$ the complex **MD2** undergoes the pre-equilibria previously described (K_{E1}, K_{E2}), giving rise to the equilibrium mixture formed by the species **MD2**, **MD3**, and **MD2Cl**, which eventually evolves into the final complex **P** by the subsequent migratory insertion. The smooth progression of the reaction was followed by recording the decrease of the ^{1}H NMR average signals at 5.52 ppm related to the **S** mixture and the increase of those of complex **P** at 5.74 ppm as a function of time and was analyzed by an iterative process carried out under the SCIENTIST environment based on the following equations:

$$[\mathbf{MD2}]_T = 0.0317 \text{ mol dm}^{-3} \text{ (total metal concentration)}$$

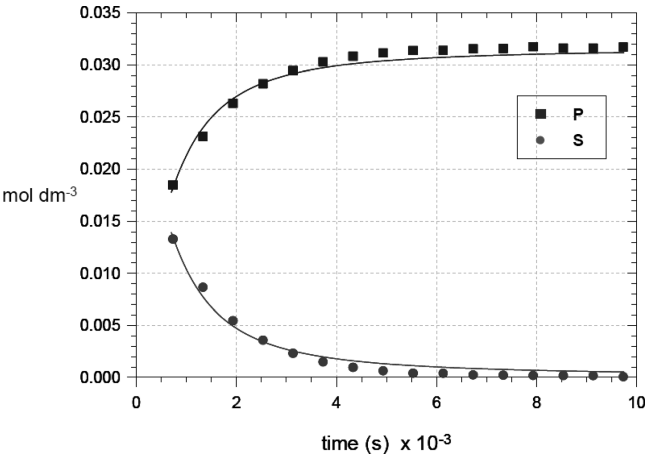


Figure 7. Nonlinear regression analysis of the kinetics of the insertion of DIC across the Pd−C bond of the complex [Pd(η^3-$C_3H_3Me_2$)(DIC)$_2$]Cl (**MD2**) in CD_2Cl_2 at 283.1 K.

$$[DIC]_0 = 0.0823 \text{ mol dm}^{-3}$$

$$K_{E1} = 5.8 \text{ (extrapolated equilibrium constant)}$$

$$K_{E2} = 165 \text{ (extrapolated equilibrium constant)}$$

$$[DIC]_0 = [DIC] + [\mathbf{MD3}] + [\mathbf{P}] \text{ (mass balance)}$$

$$[\mathbf{MD2}]_T = [\mathbf{MD2}] + [\mathbf{MD3}] + [\mathbf{MD2Cl}] + [\mathbf{P}] \quad (6)$$

$$[\mathbf{MD2}]_T = [Cl^-] + [\mathbf{MD2Cl}] + [\mathbf{P}]$$

$$K_{E1} = [\mathbf{MD3}]/[\mathbf{MD2}][DIC]$$

$$K_{E2} = [\mathbf{MD2Cl}]/[\mathbf{MD2}][Cl^-]$$

$$[\mathbf{S}] = [\mathbf{MD2}] + [\mathbf{MD2Cl}] + [\mathbf{MD3}]$$

$$d[\mathbf{P}]/dt = k[\mathbf{MD2Cl}]$$

Under these conditions the ensuing k value was (2.18 ± 0.05) × 10^{-3} s^{-1}, and the related regression analysis is shown in Figure 7.

In the second case the concentration of DIC at time $t = 0$ ($[DIC]_0$) is equal to the concentration of $[\mathbf{MD2}]_T$. Such a concentration, however, albeit sufficient for the quantitative formation of the final product **P**, induces a strong instability in the nonlinear regression procedure since the concentration of complex **MD3**, which represents 5.6% of the total concentration of the starting complexes at time $t = 0$, suddenly drops to a very low value upon consumption of free DIC. The most convenient solution of the problem could be a simplification of the reaction scheme consisting in ignoring the equilibrium described by K_{E1} and treating the whole system as a simple pre-equilibrium between **MD2** and

(14) 283 K represents the optimized temperature for the migratory insertion process, which occurs at a rate compatible with the ^{1}H NMR technique.

Scheme 3. Mechanism for the Migratory Allyl Insertion Carried Out under Equimolecular Conditions ($[\mathbf{MD2}]_T = [\mathbf{DIC}]_0$)

$$\mathbf{MD2} + Cl^- \underset{}{\overset{K_{E2}}{\rightleftharpoons}} \mathbf{MD2Cl} \xrightarrow{k} \mathbf{P}$$

MD2Cl in the presence of equimolecular Cl^-. The complex **MD2Cl** in the presence of free isocyanide (which does not affect the kinetics) gives the product **P** according to Scheme 3:

The numerical regression carried out under the SCIENTIST environment was based on the following equations in which the symbols used and the related meaning are the same as those previously employed:

$$[\mathbf{MD2}]_T = 0.033 \text{ mol dm}^{-3} \text{ (total metal concentration)}$$

$$[\mathbf{DIC}]_0 = 0.033 \text{ mol dm}^{-3} \text{ (initial concentration of DIC)}$$

$$K_{E2} = 165 \text{ (extrapolated equilibrium constant)}$$

$$[\mathbf{MD2}]_T = [\mathbf{MD2}] + [\mathbf{MD2Cl}] + [\mathbf{P}]$$

$$[\mathbf{MD2}]_T = [Cl^-] + [\mathbf{MD2Cl}] + [\mathbf{P}]$$

$$K_{E2} = [\mathbf{MD2Cl}]/[\mathbf{MD2}][Cl^-] \quad (7)$$

$$[\mathbf{S}] = [\mathbf{MD2}] + [\mathbf{MD2Cl}]$$

$$d[\mathbf{P}]/dt = k[\mathbf{MD2Cl}]$$

In this case the ensuing k value was $(2.12 \pm 0.06) \times 10^{-3}$ s^{-1}, which is in very good agreement with the previous determination. The independence of the rate constant k on DIC concentration was therefore demonstrated together with the proposed mechanistic picture.

Conclusion

We were able to resolve the complex mechanism governing the allyl migratory insertion across the Pd−C bond in isocyanide complexes of palladium by means of an accurate kinetic analysis carried out by a stepwise validation of the network proposed in Scheme 2. In particular we have first determined the equilibrium constants related to the formation of different complexes bearing the coordinated isocyanide, chloride, and the tri- or monohapto allyl fragment (eqs 1 and 4). The two independent equilibrium studies carried out at different temperatures and the determination of the thermodynamic parameters of the equilibria allowed the determination of the rate constant k and some general conclusions. The migration of an allyl fragment occurs when the latter is η^1-coordinated. Therefore, in order to obtain the subsequent insertion, a strategy to force the monohapticity of the allyl moiety is necessary. Usually the allyl monohapticity was induced by forcing its coordinating ability by strong tris-chelating ligands[15] or by using tris- or bis-chelating ligands in the presence of chloride.[3a,16] However, although the coordinating capability of chloride toward platinum group metals in nonprotic solvents is well known, no hypothesis on the driving force governing the allyl coordinative choice was advanced. As a matter of fact, only the van't Hoff analysis of the equilibria between the differently coordinated allyl derivatives can provide the correct answer. We were able to establish that in polarized nonprotic solvents the formation of *neutral* complexes containing strong nucleophiles and the η^1-coordinated allyl fragment (**MD2Cl**) is favored by increasing the temperature thanks to the positive ΔH^0 value involved in the equilibrium reaction. The presence of the chloride ion justifies the positive ΔS^0 value of the equilibrium reaction 4, which is probably due to the disorder associated with the release of solvent molecules as a consequence of the formation of the neutral derivative **MD2Cl**.[17] The *ionic* complex **MD3**, albeit containing the η^1-coordinated allyl moiety in the favorable *cis* position with respect to the isocyanide, does not display similar reactivity since the extent of its formation is governed by unfavorable thermodynamic parameters. In this case the negative entropy value is in accord with the associative equilibrium process between substrates bearing the same charge. In other words, complex **MD3** does not give insertion since an increase in temperature (which in principle would induce the increase on reaction rate) disfavors the formation of the complex itself. The nature of the solvent is however crucial. As a matter of fact, in coordinating and polar solvents such as water or alcohols, soluble ionic allyl complexes are very stable and no hints of η^1 neutral species are evident.[18] The migratory insertion rate constant k, which is independent of the isocyanide concentration, was eventually obtained, and the conclusion that such an insertion occurs only when the allyl is η^1-coordinated and in *cis* position to the Pd−C bond can be safely confirmed.

Experimental Section

Materials. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using argon immediately prior to use. 1D- and 2D-NMR spectra were recorded using a Bruker DPX300 spectrometer. Chemical shifts (ppm) are given relative to TMS (^{1}H and ^{13}C NMR).

(15) (a) Rülke, R. E.; Kliphuis, D.; Elsevier, C. J.; Fraanje, J.; Goubitz, K.; van Leeuwen, P. W. N. M.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1817–1819. (b) Wehman, P.; Rülke, R. E.; Kaasjager, V. E.; Kamer, P. C. J.; Kooijman, H.; Spek, A. L.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1995**, 331–332. (c) Rülke, R. E; Kaasjager, V. E.; Vehman, P.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Vrieze, K.; Fraanje, J.; Goubitz, K.; Spek, A. L. *Organometallics* **1996**, *15*, 3022–3031. (d) Byers, P. K.; Canty, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 639–641. (e) Ramdeehul, S.; Barloy, L.; Osborn, J. A.; De Cian, A.; Fisher, J. *Organometallics* **1996**, *15*, 5442–5444. (f) Barloy, L.; Ramdeehul, S.; Osborn, J. A.; Carlotti, C.; Taulelle, F.; De Cian, A.; Fisher, J. *Eur. J. Inorg. Chem.* **2000**, 2523–2532.

(16) (a) Braunstein, P.; Naud, F.; Dedieu, A.; Rohmer, M.-M.; DeCian, A.; Rettig, S. J. *Organometallics* **2001**, *20*, 2966–2981. (b) Kolmar, M.; Helmchen, G. *Organometallics* **2002**, *21*, 4771–4775. (c) Braunstein, P.; Zhang, J.; Welter, R. *J. Chem. Soc., Dalton Trans.* **2003**, 507–509.

(17) It is noteworthy that Braunstein et al. already noticed (see ref 16a) that at low temperature in the presence of chloride the trihapticity of the η^3-allyl coordination is favored even in the presence of potentially terdentate ligands. On increasing the temperature, formation of the neutral η^1-allyl complex bearing the chloride ion coordinated together with the potentially tris-chelating bis(oxazoline) acting as a bis-chelating ligand was observed.

(18) Mesnager, J.; Kuntz, E.; Pinel, C. *J. Organomet. Chem.* **2009**, *694*, 2513–2518.

Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), 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.

$[Pd(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)]_2$[19] and $[Pd(\mu\text{-Cl})(\eta^3\text{-}1,1\text{-}C_3H_3Me_2)]_2$[20] were prepared following literature procedures. All other chemicals were commercial grade and were used without further purification.

Equilibrium and Kinetic Measurements. The equilibrium measurements were analyzed by ^{1}H NMR technique. In the case of equilibrium 1 the complex **MD2** was dissolved in 0.8 mL of CD_2Cl_2 ($[\mathbf{MD2}]_0 = 1.88 \times 10^{-2}$ mol dm^{-3}) and titrated by addition of weighed amounts of solid DIC in the range 1.02×10^{-2} to 0.332 mol dm^{-3}. Any addition was carried out upon freezing the test tube in an acetone/liquid nitrogen mixture. The resulting solution was then taken to the experimental temperature into the NMR probe. The titrations were repeated at five different temperatures in the interval 193−233 K. The equilibrium position was evaluated from the difference between the chemical shifts of the Me substituents of the allyl fragment. In the case of equilibrium 4 the complex **2** (**2a** + **2b**) was dissolved in 0.8 mL of CD_2Cl_2 ($[\mathbf{2}]_0 = 2.92 \times 10^{-2}$ mol dm^{-3}) and frozen at 193 K in an acetone/liquid nitrogen mixture. An equimolecular amount of DIC was then added, and the resulting solution was taken to the experimental temperatures. The equilibrium position was estimated from methyl signal integration carried out at any temperature by peak deconvolution (*vide post*).

The reaction kinetics were followed by integration of the peaks at 5.52 and 5.74 ppm of the solution obtained by dissolving the complex **2** (**2a** + **2b**) with an appropriate amount of DIC ($[\mathbf{2}]_0$:$[DIC]_{tot}$ = 0.0317:0.114 and 0.033:0.066 mol dm^{-3}) in CD_2Cl_2 at 298 K. The uncertainty in the temperature measurements is estimated at ±1 K in any case.

Line-Fitting Analysis. Line-fitting analysis of NMR peaks was performed using the line-fitting module available in MestReC (v 4.9.9.6). Fitting was performed in the interval 1.45−1.65 ppm without any constraint on peak parameters. The default convergence criteria were used.

Synthesis of the Complexes. [Pd(η^3-1,1-$C_3H_3Me_2$)(DIC)Cl]). A 0.100 g (0.762 mmol) amount of 2,6-dimethylphenylisocyanide (DIC) was added as a solid to a solution of $[Pd(\mu\text{-Cl})(\eta^3\text{-}1,1\text{-}C_3H_3Me_2)]_2$ (0.161 g, 0.381 mmol) in dichloromethane (15 mL). The clear solution was stirred at room temperature for 10 min, after which time the solvent was removed under vacuum. The light yellow residue was washed with diethyl ether (3 × 3 mL) and then with *n*-pentane (2 × 3 mL). Finally the resulting solid was dried under vacuum. Yield: 0.231 g (89%).

^{1}H NMR ($CDCl_3$, 298 K): **Isomer 2a** δ 1.44 (s, 3H, allyl CH_{3anti}), 1.86 (s, 3H, allyl CH_{3syn}), 2.46 (s, 6H, DIC CH_3), 3.05 (d, J = 12.8 Hz, 1H, allyl H_{anti} *trans*-Cl), 3.96 (d, J = 7.4 Hz, 1H, allyl H_{syn} *trans*-Cl), 5.13 (dd, J = 12.8 Hz, J = 7.4 Hz 1H, allyl $H_{central}$), 7.13 (d, J = 7.6 Hz, 2H, DIC H^c), 7.25 (t, J = 7.6 Hz, 1H, DIC H^d). **Isomer 2b** δ 1.49 (s, 3H, allyl CH_{3syn}), δ 1.92 (s, 3H, allyl CH_{3anti}), δ 2.46 (s, 6H, DIC CH_3), 3.51 (d, J = 13.4 Hz, 1H, allyl H_{anti} *trans*-DIC), 4.23 (d, J = 7.4 Hz, 1H, allyl H_{syn} *trans*-DIC), 5.36 (dd, J = 13.4 Hz, J = 7.4 Hz 1H, allyl $H_{central}$), 7.13 (d, J=7.6 Hz, 2H, DIC H^c), 7.25 (t, J = 7.6 Hz, 1H, DIC H^d). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): **Isomer 2a** δ 18.8 (CH_3, DIC CH_3), 20.8 (CH_3, allyl CH_{3syn}), 26.3 (CH_3, allyl CH_{3anti}), 50.3 (CH_2, allyl *trans*-Cl), 110.1 (CH, allyl $_{central}$), 127.9 (CH, DIC C^c), 127.9 (C, DIC C^a), 129.6 (CH, DIC C^d), 135.4 (C, DIC C^b), 150.5 (C, DIC CNR) (the quaternary C allyl trans-DIC not detectable). **Isomer 2b** For this isomer only A few signals are detectable and distinguishable: 22.8 (CH_3, allyl CH_{3syn}), 29.0 (CH_3, allyl CH_{3anti}), 94.0 (CH_2, allyl *trans*-DIC), 113.6 (CH, allyl $_{central}$). IR (KBr), cm^{-1}: 2169 ν_{CN}. Anal. Calcd for $C_{14}H_{18}ClNPd$: C, 49.14; H, 5.30; N, 4.09. Found: C, 49.28; H, 5.23; N, 4.18.

[Pd(η^3-C_3H_5)(DIC)Cl]). A 0.100 g (0.762 mmol) sample of 2,6-dimethylphenylisocyanide (DIC) was added as a solid to a solution of $[Pd(\mu\text{-Cl})(\eta^3\text{-}C_3H_5)]_2$ (0.139 g, 0.381 mmol) in dichloromethane (15 mL). The clear solution was stirred at room temperature for 10 min, after which time the solvent was removed under vacuum. The light yellow residue was washed with diethyl ether (3 × 3 mL) and then with *n*-pentane (2 × 3 mL). Finally the resultant solid was dried under vacuum.

Yield: 0.208 g (87%). ^{1}H NMR ($CDCl_3$, 298 K): δ 2.47 (s, 6H, DIC CH_3), 3.00 (d, J = 12.5 Hz, 1H, allyl H_{anti} *trans*-Cl), 3.55 (d, J = 13.3 Hz, 1H, allyl H_{anti} *trans*-DIC), 4.28 (d, J = 7.4 Hz, 1H, allyl H_{syn} *trans*-Cl), 4.58 (d, J = 7.4 Hz, 1H, allyl H_{syn} *trans*-DIC), 5.57 (m, allyl $H_{central}$), 7.14 (d, J = 7.5 Hz, 2H, DIC H^c), 7.27 (t, J = 7.5 Hz, 1H, DIC H^d). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 18.7 (CH_3, DIC CH_3), 58.1 (CH_2, allyl *trans*-Cl), 75.0 (CH_2, allyl *trans*-DIC), 117.4 (CH, allyl $_{central}$), 128.0 (CH, DIC C^c), 128.0 (C, DIC C^a), 129.8 (CH, DIC C^d), 135.6 (C, DIC C^b), 149.2 (C, DIC CNR). IR (KBr), cm^{-1}: 2180 ν_{CN}. Anal. Calcd for $C_{14}H_{18}ClNPd$: C, 45.88; H, 4.49; N, 4.46. Found: C, 45.64; H, 4.39; N, 4.56.

[Pd(η^3-1,1-$C_3H_3Me_2$)(DIC)$_2$]ClO_4. To a solution of $[Pd(\mu\text{-Cl})(\eta^3\text{-}1,1\text{-}C_3H_3Me_2)]_2$ (0.12 g, 0.284 mmol) in CH_2Cl_2 (15 mL) was added DIC (0.149 g, 1.14 mmol) dissolved in 5 mL of the same chlorinated solvent. Addition of $NaClO_4 \cdot H_2O$ (0.184 g, 1.14 mmol) in CH_3OH to the stirred mixture yielded the precipitation of NaCl with the concomitant decoloration of the solution. The reaction mixture was stirred for 30 min, and the solvent was removed under reduced pressure. The resulting sticky solid was dissolved in 20 mL of CH_2Cl_2, treated with activated charcoal, and filtered through Celite. The resulting clear solution, concentrated under reduced pressure, yielded the crude product as an off-white solid upon addition of diethyl ether. Finally the crude product was recrystallized from CH_2Cl_2/diethyl ether. Yield: 0.257 g (84%).

^{1}H NMR ($CDCl_3$, 298 K): δ 1.69 (s, 3H, allyl CH_{3anti}), 2.25 (s, 3H, allyl CH_{3syn}), 2.50 (s, 12H, DIC CH_3), 3.58 (dd, J_3 = 13.8 Hz, J_5 = 1.2 Hz, 2H, allyl H_{anti}), 4.64 (d,d J_3 = 7.9 Hz, J_5 = 1.2 Hz, 2H, allyl), 5.63 (dd, J = 13.8 Hz, J = 7.9 Hz 1H, allyl $H_{central}$), 7.18 (d, J = 7.8 Hz, 2H, DIC H^c), 7.21 (d, J = 7.8 Hz, 2H, DIC H$^{c'}$), 7.32 (t, J = 7.8 Hz, 1H, DIC H^d), 7.34 (t, J = 7.8 Hz DIC, 1H, H$^{d'}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 18.7 (CH_3, DIC CH_3), 22.4 (CH_3, allyl CH_{3syn}), 28.5 (CH_3, allyl CH_{3anti}), 61.6 (CH_2, C^3 allyl), 111.0 (C, C^1 allyl), 116.0 (CH, allyl $_{central}$), 125.4 (C, DIC C^a), 128.2 (CH, DIC C^c), 128.4 (CH, DIC C$^{c'}$), 128.4 (C, DIC C^a), 130.6 (CH, DIC C^d), 130.7 (CH, DIC C$^{d'}$), 135.6 (C, DIC C^b), 135.8 (C, DIC C$^{b'}$), 146.0 (C, DIC CNR), 146.0 (C, DIC CNR′). IR (KBr), cm^{-1}: 2166 ν_{CN}, 1090 ν_{ClO}, 624 δ_{ClO}. Anal. Calcd for $C_{14}H_{18}ClNPd$: C, 49.14; H, 5.30; N, 4.09. Found: C, 49.27; H, 5.36; N, 4.12.

***trans*-[Pd(DIC)$_2$(C=N(2,6-$Me_2C_6H_3$)CH_2CHCMe_2)Cl].** To 0.100 g (2.37 mmol) of $[Pd(\mu\text{-Cl})(\eta^3\text{-}1,1\text{-}C_3H_3Me_2)]_2$ in CH_2Cl_2 (10 mL) was added as a solid 0.187 g (1.42 mmol) of DIC under inert atmosphere (Ar) at 0 °C. The resulting solution was stirred for 15 min and then evaporated under vacuum. The resulting off-white solid was washed with diethyl ether (3 × 3 mL) and with *n*-pentane (2 × 3 mL).

Yield: 0.270 g (94%). The product decomposes in several hours in chlorinated solvent but can be stored as a solid at −18 °C for weeks. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.79 (d, J_5 = 1.4 Hz, 3H, allyl CH_3), 1.82 (d, J_5 = 1.4 Hz, 3H, allyl CH_3), 2.11 (s, 6H, C=N{$C_6H_3(CH_3)_2$}), 2.39 (s, 12H, DIC CH_3), 3.63 (d, J = 7.4 Hz, 2H, allyl H^3), 5.75 (dqn, J_3 = 7.4 Hz, J_5 = 1.4 Hz, 1H, allyl H^2), 6.88 (m, 3H, H$^{c'}$,H$^{d'}$), 7.12 (d, J = 7.7 Hz, 4H, DIC H^c), 7.27 (t, J = 7.7 Hz, 2H, DIC H^d). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 18.5 (CH_3, allyl CH_3), 18.6 (CH_3, DIC CH_3), 18.7 (CH_3, C=N{$C_6H_3(CH_3)_2$}), 25.8 (CH_3, allyl CH_3), 48.5 (CH_2, allyl C^3), 119.4 (CH, C^2 allyl), 123.0 (CH, C$^{d'}$), 125.4

(19) Hartley, F. R.; Jones, S. R. *J. Organomet. Chem.* **1974**, *66*, 465–473.

(20) Auburn, P. R.; Mackenzie, P. B.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2033–2046.

(C, DIC C^{a}), 126.5 (C, $C^{a'}$), 128.0 (CH, DIC C^{c} and $C^{c'}$), 130.0 (CH, DIC C^{d}), 135.8 (C, DIC C^{b}), 144.7 (C, DIC CNR′), 149.1 (C, $C^{b'}$), 177.2 (C, C=N{$C_6H_3(CH_3)_2$}). IR (KBr), cm^{-1}: 2174 ν_{CN}. Anal. Calcd for $C_{32}H_{36}ClN_3Pd$: C, 63.58; H, 6.00; N, 6.95. Found: C, 63.64; H, 6.09; N, 6.88.

***trans*-[Pd(DIC)$_2$(C=N(2,6-Me$_2$C$_6$H$_3$)CH$_2$CHCH$_2$)Cl].** To 0.100 g (2.73 mmol) of [Pd(μ-Cl)(η^3-C_3H_5)]$_2$ in CH_2Cl_2 (10 mL) was added 0.215 g (1.64 mmol) of DIC as a solid under inert atmosphere (Ar) at 0 °C. The resulting solution was stirred for 15 min and then evaporated under vacuum. The resulting off-white solid was washed with diethyl ether (3 × 3 mL) and with *n*-pentane (2 × 3 mL).

Yield: 0.290 g (92%). The product decomposes in several hours in chlorinated solvent but can be stored as a solid at −18 °C for weeks. ^{1}H NMR ($CDCl_3$, 298 K): δ 2.11 (s, 6H, C=N-{$C_6H_3(CH_3)_2$}), 2.40 (s, 12H, DIC CH_3), 3.71 (d, J = 7.2 Hz, 2H, allyl H^3), 5.26 (d, J = 10.0 Hz, 1H, allyl *cis* H^1), 5.34 (d, J = 17.0 Hz, 1H, allyl *trans* H^1), 6.34 (m, 1H, allyl H^2), 6.90 (m, 3H, $H^{c'}$,$H^{d'}$), 7.13 (d, J = 7.5 Hz, 4H, DIC H^c), 7.24 (t, J = 7.5 Hz, 2H, DIC H^d). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 18.8 (CH_3, C=N{$C_6H_3(CH_3)_2$}), 19.0 (CH_3, DIC CH_3), 53.7 (CH_2, allyl C^3), 117.5 (CH_2, C^1 allyl), 123.1 (CH, $C^{d'}$), 127.9 (CH, DIC C^c and $C^{c'}$), 129.6 (CH, DIC C^d), 135.5 (C, DIC C^b), 144.2 (C, DIC CNR′), 149.2 (C, $C^{b'}$), 176.9 (C, C=N{$C_6H_3(CH_3)_2$}). The partial decomposition of the product does not allow a safe assignment of the signals of the quaternary carbons C^a and $C^{a'}$. IR (KBr), cm^{-1}: 2173 ν_{CN}. Anal. Calcd for $C_{30}H_{32}ClN_3Pd$: C, 62.50; H, 5.60; N, 7.29. Found: C, 62.64; H, 5.66; N, 7.39.

***trans*-[Pd(TIC)$_2$(C=N(CMe$_3$)CH$_2$CHC(Me)$_2$)Cl].** An NMR sample of [Pd(μ-Cl)(η^3-1,1-$C_3H_3Me_2$)]$_2$ (0.0082 g in 0.8 mL of $CDCl_3$) was treated with 6 equiv of TIC (13.2 μL). The reaction went to completion in 1 h with formation of one single product. The features of the ^{1}H NMR spectrum were compatible with those of the title compound.

^{1}H NMR ($CDCl_3$, 298 K): δ 1.46−147 (bs, 24H, TIC C(CH_3)$_3$ and allyl CH_3), 1.75 (s, 9H, C=N{C=N(C(CH_3)$_3$)}), 3.20 (d, J = 7.4 Hz, 2H, allyl H^3), 5.38 (dqn, J_3 = 7.4 Hz, J_5 = 1.4 Hz, 1H, allyl H^2). The product decomposes in a few hours in the NMR tube.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.