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Mechanistic and Kinetic Investigation on the Formation of Palladacyclopentadiene Complexes. A Novel Interpretation Involving a Bimolecular Self-Reaction of a Monoalkyne Intermediate

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The stoichiometric reaction between the complex [Pd(η²-dmfu)(BiPy)] (dmfu = dimethylfumarate; BiPy = 2,2’-bipyridine) and the deactivated alkyne dmbd (dimethyl-2-butyne-3-dioate) and pna (methyl (4-nitrophenyl)propynoate), providing the respective palladacyclopentadienes, was investigated. The mechanism leading to the palladacyclopentadiene derivative involves a bimolecular self-rearrangement of the monoalkyne intermediate [Pd(η²-alk)(BiPy)] (alk = dmbd, pna), followed by the customary attack of the free alkyne on the intermediate [Pd(η²-alk)(BiPy)] itself and on the elusive and highly reactive “naked palladium” [Pd(BiPy)(0)] formed. The alkyne pna proved to be less effective in the displacement of dmfu than dmbd. The reaction under stoichiometric equimolar conditions of the latter with [Pd(η²-dmfu)(BiPy)] allows the direct determination of the bimolecular self-reaction rate constant kₙ and consequently the assessment of all the rate constants involved in the overall mechanistic network.

Introduction

The stereospecific synthesis of conjugated dienes is of considerable importance since many natural products and bioactive compounds contain the 1,3-diene unit or even multiple unsaturations with higher degrees of conjugation. For these reasons, transition-metal-mediated conversion of alkynes into polyenes and, more precisely, the development of selective methods for the synthesis of 1,3-dienes have been research areas of interest for many years now. This had led to the development of catalysts based on cobalt,¹ ruthenium,² nickel,³ and palladium⁴ for the double addition of diazo compounds to alkynes or the direct coupling of a stereodefined alkenyl-metallic compound with a stereodefined vinyl electrophile such as a vinyl halide. Other stereoselective methods of diene synthesis based on dyne reduction with a zinc/copper reagent or a sodium—mercury amalgam were also described.⁵

In addition to these approaches, some catalytic processes involving metallacyclopentadiene species as intermediates have been published. However, to the best of our knowledge, the synthesis of conjugated dienes from two molecules of an alkyne via a metallacyclopentadiene is limited to only a few transition metals, such as titanium,⁶ zirconium,⁶ iridium,⁸ and palladium.⁹

However, owing to the complexity of the catalytic cycle, which is often complicated by the presence of several byproducts, few exhaustive mechanistic studies have been carried out. Particularly, the formation of the key intermediate metallacyclopentadiene species has been studied in detail only once.⁹ Nevertheless, identification of the species involved and their reactivity at the very first step of the catalytic cycle seem somehow crucial for the understanding of the whole process. For that reason measurable rates of reaction and mild conditions are necessary for a viable approach so that all possible information could be gathered from the system under investigation. In this respect we have found that the complex [Pd(η²-dmfu)(BiPy)] (dmfu = dimethylfumarate; BiPy = 2,2’-bipyridine) and the alkynes dmbd (dimethyl-2-butyne-3-dioate) and pna (methyl (4-nitrophenyl)propynoate) seem to be tailored for a detailed stoichiometric investigation.

of the reaction yielding the palladacyclopentadienyl derivatives according to Scheme 1.

As a matter of fact, type 2 complexes, which are produced by the equilibrium displacement of an alkene by an activated alkyn, represent a peculiar class of substrates that can accumulate as unreactive species, which, depending on their electronic and steric characteristics, react with an additional molecule of the alkyn to give palladacyclopentadiene derivatives or react with the palladacyclopentadiene itself to yield mellitate derivatives. The understanding of the initial equilibria in the formation of palladacycles is also of crucial importance for a better understanding of the intimate mechanism governing the first step of other catalytic cycles, such as the formation of functional dienes from coupling reactions between alkynes, organic halides, and organotin reagents.9, c, d

Scheme 1

![Scheme 1](image)

2a, 3a: Z≡Z = COOMe
2b, 3b, 3b*: Z = COOMe, Z’ = C₆H₄NO₂

Results and Discussion

Reaction between [Pd(η²-dmfu)(BiPy)] and Dimethyl-2-butyndioate (dmbd). When an equimolar amount of dmbd is added to a solution of [Pd(η²-dmfu)(BiPy)] ([[Pd(η²-dmfu)-(BiPy)]] ≈ 1 × 10⁻² mol dm⁻³), the formation of the cyclopalladate [Pd(BiPy)(C₄(COOMe)₄)] together with unreacted [Pd(η²-dmfu)(BiPy)] is observed by ¹H NMR. The same reaction carried out in the presence of dmbd in 2-fold (or higher) excess ([Pd(η²-dmfu)(BiPy)] ≈ 1 × 10⁻² mol dm⁻³; [dmbd] = (2−3) × 10⁻³ mol dm⁻³) yields the complex [Pd(BiPy)(C₄(COOMe)₄)] and free dmfu (or free dmfu and dmbd in stoichiometric excess). A reasonable reaction scheme that takes all the experimental observations into account is summarized in Scheme 2.

However, Scheme 2 is of considerably complexity. Only a stepwise approach can be adopted in order to solve such a mechanistic network, since multiparametric analysis of kinetic data does not warrant reliable equilibrium and rate constants because of their high correlation. In this respect we first tried determining the value of Kₑ by titration of an [Pd(0)(η²-alkene)] derivative with the alkyn dmbd.

Determination of Kₑ. It was already stated that addition of an equimolar amount of dmbd to a solution of [Pd(η²-dmfu)(BiPy)] at RT yields instantaneously the reaction products. Apparently, the displacement of dmfu by dmbd is energetically favored and therefore quantitative; the use of a Pd(0) derivative bearing a more coordinating alkyn is recommended in order to contrast efficiently the electrophilicity of dmbd and determine the equilibrium constant by direct titration. Moreover, the reactions subsequent to the equilibrium displacement in Scheme 2 need to be quenched; otherwise no equilibrium concentrations could be measured with confidence. Some of us have determined previously the coordinating ability order among deactivated alkynes bonded to Pd(0) complexes, which was often confirmed later. Therefore, the low coordinating capability of dmfu is not surprising since this alkyn is one of the less coordinating among the deactivated ones (maleic anhydride and fumaronitrile being ca. 7900 and 4400 times more effective than dmfu, respectively). We have thus determined the equilibrium constant of the displacement of fn from the complex [Pd(η²-fn)(BiPy)] by titration with dmbd at 213 K, monitored by ¹H NMR. Under these conditions K became easily accessible (K ≈ 0.16 ± 0.01) because of the coordinating ability of fn and the slow rates of subsequent reactions. Figure 1 displays the nonlinear regression fit based on the following relevant relationships (fn = fumaronitrile):

\[
\begin{align*}
\text{[Pd(}\eta^2\text{-fn}(\text{BiPy})\text{)] + dmbd} & \leftrightarrow [\text{Pd(}\eta^2\text{-dmbd}(\text{BiPy})] + \text{fn} ; K
\text{1} K & = [2\text{a}_{\text{eq}}] \left(\frac{[\text{I}_{\text{eq}}]}{[2\text{a}_{\text{eq}}]([\text{dmbd}]_{\text{0}} - [2\text{a}_{\text{eq}}])}\right)
\text{2} [\text{I}_{\text{eq}}] & = 1 \times 10^{-2} \text{ mol dm}^{-3}
\text{3} [\text{dmbd}]_{\text{0}} & \text{ in the range } (1-6.2) \times 10^{-2} \text{ mol dm}^{-3}
\end{align*}
\]

The Kₑ value related to the equilibrium displacement of dmfu by dmbd (equilibrium A in Scheme 2) was then calculated by multiplying K by 4400. The ensuing value (Kₑ ≈ 700) was taken as a reasonable equilibrium constant for the displacement of dmfu by dmbd at 213 K. The value of Kₑ ≈ 70 estimated at 298 K justifies the almost quantitative displacement of dmfu.

Figure 1. Nonlinear regression fit of the equilibrium concentrations determined by $^1$H NMR technique at 213 K for the reaction [Pd($\eta^2$-fn)(BiPy)] + dmdb $\leftrightarrow$ [Pd($\eta^2$-dmdb)(BiPy)] + fn.

when an equimolar amount of dmdb was added to a solution of [Pd($\eta^2$-dmfu)(BiPy)] at 298 K.\(^{(13,14)}\)

Determination of $k_c$. An interpretation of Scheme 2 suggests another route to the analytical solution of the rate constant network. Addition of an equimolar amount of dmdb to a solution of [Pd($\eta^2$-dmfu)(BiPy)] would yield almost quantitatively 2a (path A in Scheme 2);\(^{(15)}\) two molecules of 2a would react with each other to give the palladacyclopentadiene 3a and the so-called naked palladium Pd(0) (path B), which reacts very rapidly with the free dmfu to give the starting complex 1 (path C). Owing to the stoichiometry of the reaction, such an equimolar reaction would therefore yield an equimolar mixture of complexes 1 and 3a (it is noteworthy that $^1$H NMR experiments carried out under equimolar conditions, albeit too fast to be analyzed kinetically, yielded the mixture we expected; see Experimental Section). Therefore, we have determined the $k_c$ value from three independent measurements carried out by UV-vis technique at different concentrations of 1 and dmdb (ratio 1:1; [1] = [dmdb] = 4 x 10^{-4}, 2 x 10^{-4}, 1 x 10^{-4} mol dm^{-3}) by nonlinear regression of the integrated form of the second-order differential equation model given below, with $k_c$ and $\varepsilon_{2a}$ as the parameters to be optimized:

$$[1]_0 = [1] + [2a] + [3a] \text{ (mass balance)}$$

$$-d[2a]/dt = d[Pd]\text{ln}/dt = 2k_c[2a]^2 \quad D = \varepsilon_{2a}[2a] + \varepsilon_{\text{ln}}[Pd]$$

$$([1] + [3a]) = [Pd]_0 ; \varepsilon_{\text{ln}} = \varepsilon_1 + \varepsilon_{3a}$$

$D$ represents the optical density at time $t$, and $\varepsilon_1$, $\varepsilon_{2a}$, and $\varepsilon_{3a}$ are the molar extinction coefficients of 1, 2a, and 3a respectively.

(13) In the case of exchange between alkynes in $\alpha$-diimine derivatives of Pd(0) a value of $\Delta H^\theta = -3.5 \pm 0.5$ kcal mol\(^{-1}\) was determined.\(^{(11)}\) From that value under the reasonable hypothesis that the slope of the van't Hoff relationship does not change considerably on going from the exchange between two alkynes to the exchange of an alkene with an alkyne, the value of $\Delta S_{\text{obs}}$ was calculated from the expression $\Delta S_{\text{obs}} = \Delta S_{\text{in}}(\Delta F^\theta R)/(213-298)/213 \times 298); K_0 = 66$. We consider that approach reliable since we have also studied the RT exchange between maleic anhydride and dmdb in pyridylthioether derivatives of Pd(0)\(^{(19)}\) and the exchange constant between [Pd($\eta^2$-fn)(neoc)] and dmdb.\(^{(14)}\) The equilibrium constants determined in those cases when multiplied by 7900 and 4400 give the values of 110 and 54, respectively, which compare quite well with the value of 66 estimated in the present work. As a matter of fact, such values represent the equilibrium constants for the exchange between dmfu and dmdb in complexes bearing different ancillary ligands. Not surprisingly the $K_0$ value is almost independent of the nature of the ancillary ligand.


(15) With $K_0 = 70$ the formation of complex 2 from an equimolecular addition of dmdb to 1 is about 90% of the initial concentration of [1] (ξ = [1][kt-(K_0)^2]/(K_0-1)).

Figure 2. Linear regression plot of $k_{\text{obs}}$ vs [dmdb] for the reaction of complex 2a with dmdb.

Determination of $k_2$. The value of $k_2$ was also measured by UV-vis technique under pseudo-first-order conditions ([dmdb]$_0 \geq 10$[1]$_0$). The excess of dmdb shifts the equilibrium mixture well over to the right and drives the reaction to completion. Therefore, at the end of the reaction only 3a, excess dmdb, and free dmfu have been detected in solution. The nonlinear regression process was based on the model reported below with the same symbols as above:

$$[1]_0 = [1] + [2a] + [3a] \text{ (mass balance)}$$

$$-d[2a]/dt = k_{\text{obs}}[2a] + 2k_c[2a]^2 - k_{\text{in}}[Pd(0)][dmdb]_0 \quad d[3a]/dt = k_{\text{obs}}[2a] + k_{\text{in}}[2a]^2 \quad D = \varepsilon_{2a}[2a] + \varepsilon_{3a}[3a]$$

$$k_{\text{obs}} = k_2[dmdb]_0; \text{ initial conditions [2a} = [2a]_0, [3a] = 0$$

The regression analysis yields the values for $k_{\text{obs}}$ at four different dmdb concentrations, with $k_c = 44$ and $k_{\text{in}} = 10000$ mol\(^{-1}\) dm\(^{-3}\) s\(^{-1}\) held constant during the refinement process. The linear regression of the $k_{\text{obs}}$ vs [dmdb] yielding $k_2 = 0.79 \pm 0.05$ mol\(^{-1}\) dm\(^{-3}\) s\(^{-1}\) is reported in Figure 2.

Reaction between [Pd($\eta^2$-dmfu)(BiPy)] and Methyl (4-Nitrophenyl)propionate (pna). In analogy with the previous study carried out with dmdb, we tried to determine the reactivity of methyl (4-nitrophenyl)propionate toward palladium(0) dmfu derivatives. Unfortunately, the exchange equilibrium reaction between dmfu and pna

$$[Pd(\eta^2\text{-dmfu})(\text{BiPy})] + \text{pna} \leftrightarrow [Pd(\eta^2\text{-pna})(\text{BiPy})] + \text{dmfu} \quad (K_{E}^\circ)$$

is far from complete, and even at low temperature (213 K in CDCl$_3$) a number of other species are detected in solution. Apparently the palladium(0) alkyne complex 2b, which is produced by the addition of pna to the starting complex [Pd($\eta^2$-dmfu)(BiPy)], is a very reactive species, and the addition (necessarily at RT) of the titrant pna into the NMR tube induces

(16) The $k_{\text{in}}$ value used during the refinement process is an arbitrarily high number related to a very fast reaction, which can be varied from 1000 to 10 000 without affecting the ensuing $k_{\text{obs}}$ value.
the onset of the reaction with the formation of the following species:

1. the complex \([\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]\) (2b);
2. the unreacted \([\text{Pd}(\eta^2\text{-dmfu})(\text{BiPy})]\) (1);
3. the unreacted pna;
4. the free dmfu;
5. the symmetric (3b) and the nonsymmetric (3b') palladium cyclopentadienyl derivatives;
6. the symmetric (4b) and the nonsymmetric mellitate (4b').

In order to evaluate the equilibrium constant \(K_E^*\), we took several independent \(^1\)H NMR spectra of the reaction mixture obtained upon subsequent additions of pna and estimated only the concentrations of the species directly involved in the equilibrium and calculated therefrom the \(K_E^*\) values. The ensuing \(K_E^*\) values were badly determined, thus we decided to follow a different approach to a better evaluation of the equilibrium constant. Thus, we titrated spectrophotometrically at RT a solution of the complex \([\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]\) from the mechanistic network and consider

\[
\begin{align*}
\text{Pd}(0) + \text{pna} & \rightarrow 2 \text{b} (k_{f}) + [\text{Pd}(\eta^2\text{-pna})(\text{BiPy})] \\
\text{Pd}(0) + \text{pna} & \rightarrow 2 \text{b} (k_{f}) + [\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]
\end{align*}
\]

Figure 3. Nonlinear regression fit of the equilibrium determined by UV–vis technique at 298 K for the reaction \([\text{Pd}(\eta^2\text{-dmfu})(\text{neoc})]\) + \text{pna} \leftrightarrow [\text{Pd}(\eta^2\text{-pna})(\text{neoc})] + \text{dmfu}.

The values of \(K_E^*\) for the \(2b\) complex with the \(\text{Pd}(\eta^2\text{-pna})(\text{BiPy})\) as the sole starting material.\(^{18}\)

The results emerging from this kinetic study rationalize the reactivity of the monoalkyn derivative of Pd(0) and indicate

\[
\begin{align*}
\text{Pd}(0) + \text{pna} & \rightarrow 2 \text{b} (k_{f}) + [\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]
\end{align*}
\]


Table 1

<table>
<thead>
<tr>
<th>[pna]_0 (mol dm(^{-3}))</th>
<th>(k_{f}) (random and negligible)</th>
<th>(k_{f}) (mol(^{-1}) dm(^{3}) s(^{-1}))</th>
<th>(k_{f}) (mol(^{-1}) dm(^{3}) s(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>1.48 \times 10^{-2}</td>
<td>negligible</td>
<td>97 \pm 1.5</td>
<td>103 \pm 6</td>
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<tr>
<td>1.98 \times 10^{-2}</td>
<td>negligible</td>
<td>109 \pm 1.8</td>
<td></td>
</tr>
<tr>
<td>2.91 \times 10^{-2}</td>
<td>negligible</td>
<td>105 \pm 1.3</td>
<td></td>
</tr>
</tbody>
</table>

\(^{17}\) Unfortunately, the determination of the equilibrium constant in the case of the direct exchange between dmfu and dmdb is not possible since an extensive decomposition takes place upon addition of the titrant dmdb to a solution of the complex \([\text{Pd}(\eta^2\text{-dmfu})(\text{BiPy})]\) (ref 14).

\(^{18}\) The value \(K_E^* = 0.236\) obviously represents a rough estimate of the equilibrium constant. However, as was already stated, the nature of the ancillary ligands hardly affects the equilibrium position since their electronic and steric characteristics equally act in stabilizing (or destabilizing) both the entering and the leaving groups. It is noteworthy that with \(K_E^* = 0.236\), \([\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]\) \((\text{mol} \text{ dm}^{-3})\) and \([\text{pna}]_0 = 1.48 \times 10^{-7} \text{ mol dm}^{-3}\), and the degree of advancement of the reaction is \(\xi = 0.97\).

Formation of the Symmetric and Unsymmetric Mellitate from Methyl (4-Nitrophenyl)propynoate. The stable palladacyclopentadiene (3b/3b') does not react with one further alkyn molecule to give the mellitate at 298 K, but the finally observed ratio of cyclotrimers (4b/4b') is the same as the observed ratio of the regioisomers (3b/3b'). We may therefore assume that, in the present case, the mellitates (4b/4b') are also arising from the reaction of 3b'/3b with \([\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]\) according to Scheme 3.

The conservation of the observed ratio of regioisomers could imply that the insertion of the third molecule of methyl (4-nitrophenyl)propynoate originates from \([\text{Pd}(\eta^2\text{-pna})(\text{BiPy})]\), which regioselectively inserts in the palladium--carbon bond of 3b'.

Conclusions

The results emerging from this kinetic study rationalize the reactivity of the monoalkyne derivatives of Pd(0) and indicate...
dissolved in freshly distilled CH$_2$Cl$_2$ (20 mL) were added 0.12 g of the monoalkyne species \( \text{[Pd}(\eta^2\text{-dmbd})(\text{BiPy})] \), \( \text{[Pd}(\eta^2\text{-pna})(\text{BiPy})] \), \( \text{[Pd}(\eta^2\text{-2-dmbd})(\text{neoc})] \), \( \text{[Pd}(\eta^2\text{-2-fn})(\text{BiPy})]\) and \( \text{[Pd}(\eta^2\text{-fn})(\text{BiPy})] \). This difference in reactivity is reflected by the difference between \( k_2 \) and \( k_3^* \), the latter being more than twice higher than the former. The formation of the symmetric and unsymmetric mellitate species can also be traced back to the reactivity of the complex \( \text{[Pd}(\eta^2\text{-pna})(\text{BiPy})] \), which reacts with the symmetric and unsymmetric palladacyclopentadienyl complexes to give both mellitate compounds and the unsaturated palladium species according to the mechanism already suggested in another paper.  

Experimental Section

NMR and UV–Vis Spectra and Elemental Analysis. The $^1$H NMR spectra were recorded on a Bruker 300 Avance spectrometer. UV–vis spectra were taken on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Perkin-Elmer PTP6 (Peltier temperature programmer) apparatus. Elemental analyses for new palladacycles are not provided in this paper, but will appear in a forthcoming paper for a number of very similar compounds that are part of this series.

Data Analysis. Mathematical and statistical analysis of equilibrium and kinetic data was carried out by a nonlinear regression of locally adapted algorithms written under Scientist environment.

Synthesis of Complexes. The synthesis of the complexes \( \text{[Pd}(\eta^2\text{-dmfu})(\text{BiPy})] \), \( \text{[Pd}(\eta^2\text{-fn})(\text{BiPy})] \), \( \text{[Pd}(\eta^2\text{-dmbd})(\text{neoc})]\) and \( \text{[Pd}(\eta^2\text{-pna})(\text{BiPy})] \) were carried out according to published procedures. Dmbd, CD$_2$Cl$_2$, CDCl$_3$, and CHCl$_3$ were commercial grade reagents and were used as purchased.

\begin{align*}
\text{[Pd}(\eta^2\text{-pna})(\text{neoc})] & \\
\text{[Pd}(\eta^2\text{-fn})(\text{BiPy})] & \\
\text{[Pd}(\eta^2\text{-dmbd})(\text{BiPy})] & \\
\text{[Pd}(\eta^2\text{-pna})(\text{BiPy})] &
\end{align*}

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\begin{align*}
\text{[Pd}(\eta^2\text{-pna})(\text{neoc})] & \\
\text{[Pd}(\eta^2\text{-fn})(\text{BiPy})] & \\
\text{[Pd}(\eta^2\text{-dmbd})(\text{BiPy})] & \\
\text{[Pd}(\eta^2\text{-pna})(\text{BiPy})] &
\end{align*}

The symmetric (4b) and unsymmetric (4b') mellitate species were obtained from (4b) and (4b') and recorded at 9.05 ppm of the H$_6$ pyr proton of the complex \( \text{[Pd}(\eta^2\text{-dmbd})(\text{BiPy})] \).
under second-order conditions ([I]₀: [dmbd]₀ = 1:1, 1:2) was investigated by dissolving the alkene complex 1 in 0.8 mL of CD₂Cl₂ ([I]₀ ≈ 1 × 10⁻² mol dm⁻³) and adding the appropriate aliquot of a mother solution of dmbd ([dmbd]₀ = 0.4 mol dm⁻³) at 213 K. In both cases the complete conversion of 1 into 2a was observed. Gradually increasing the temperature led to the reaction products, which were unreacted 1 and 3a in the case of molar 1:1 ratio and 3a and free dmfu in the case of 1:2 molar ratio. The reactions were followed up to half or total completion by monitoring the signals of the disappearance of 2a and of the contemporary appearance of those of the palladacyclopentadiene species 3a. When the alkyne under study was pna, the cyclometalation reaction was investigated by dissolving the alkene complex 1 in 0.6 mL of CDCl₃ ([I]₀ ≈ 3 × 10⁻² mol dm⁻³). The alkyne was added at 298 K as a solid in order to obtain the concentration of ∼9 × 10⁻² mol dm⁻³ in solution. The progress of the reaction toward the products 3b, 3b′ and 4b, 4b′ (in traces) was followed by monitoring the signals of the disappearance of 1 and 2b and the concomitant appearance of those belonging to 3b, 3b′, 4b and 4b′.

UV–Vis Kinetic Studies. Determination of the Equilibrium Constant K*. The equilibrium constant K* at 298 K for the reaction

\[ \text{[Pd}(\eta^2\text{-dmfu})\text{(neoc) + pna} \rightleftharpoons \text{[Pd}(\eta^2\text{-pna})\text{(neoc) + dmfu}] \]

was determined by adding to a 50 mL solution of the complex \([\text{Pd}(\eta^2\text{-dmfu})\text{(neoc)}] = 1 \times 10^{-4} \text{ mol dm}^{-3}\) in CHCl₃ increasing amounts of pna as a weighed solid in order to establish a pna concentration in the range 1 × 10⁻⁴ to 5 × 10⁻³ mol dm⁻³. The resulting absorbance spectra were recorded in the 300–500 nm wavelength interval. The equilibrium constant was calculated from the absorbance value vs pna concentration taken at λ = 435 nm.

Determination of k₁ and k₂. The rate constant k₁ was calculated from three independent determinations at three different concentrations of 1 and dmbd under equimolar second-order conditions ([I]₀: [dmbd]₀ = 1:1 = 4 × 10⁻⁴, 2 × 10⁻⁴, 1 × 10⁻⁴ mol dm⁻³) at λ = 420 nm in CHCl₃ (stored on silver foil) at 298 K.

In the case of the reaction between 1 and pna, the alkyne was added as a solid to 3 mL of a CHCl₃ solution of complex 1 ([I]₀ ≈ 1 × 10⁻⁴ mol dm⁻³) in order to realize a concentration in the range (1–3) × 10⁻² mol dm⁻³, and the absorbance change was monitored in the 400–600 nm wavelength interval at different times.

Determination of k₂. To 3 mL of a CHCl₃ solution of 1 ([I]₀ ≈ 1 × 10⁻⁴ mol dm⁻³) placed in the thermostated (298 K) cell compartment of the UV–vis spectrophotometer were added microaliquots of a concentrated solution of dmbd. The absorbance change was monitored in the 300–530 nm wavelength interval at different times. The rate constant k₂ was eventually calculated from the linear regression analysis of the ensuing kobs values (kobs = k₂ [dmbd]₀) obtained from each kinetic experiment performed under pseudo-first-order conditions ([dmbd]₀=30–60([Pd(\eta^2\text{-dmfu})(BiPy)])₀).