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(η^2-dmfu)(BiPy)] (dmfu = dimethylfumarate; BiPy = 2,2′-bipyridine) and the deactivated alkynes dmbd (dimethyl-2-butynedioate) 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(η^2-alk)(BiPy)] (alk = dmbd, pna), followed by the customary attack of the free alkyne on the intermediate [Pd(η^2-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(η^2-dmfu)(BiPy)] allows the direct determination of the bimolecular self-reaction rate constant k_c 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 palladium[3b,4] 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 diyne 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,[7] 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.[9g] Nevertheless, dentification 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(η^2-dmfu)(BiPy)] (dmfu = dimethylfumarate; BiPy = 2,2′-bipyridine) and the alkynes dmbd (dimethyl-2-butynedioate) and pna (methyl (4-nitrophenyl)propynoate) seem to be tailored for a detailed stoichiometric investigation

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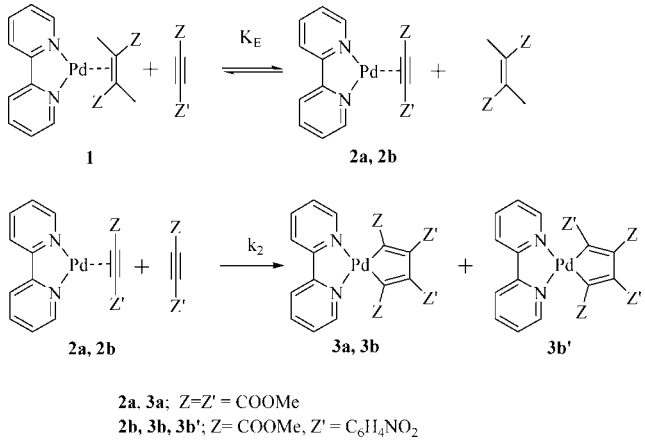
Scheme 1



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 alkyne, 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 alkyne to give palladacyclopentadiene derivatives or react with the palladacyclopentadiene itself to yield mellitate derivatives.[10] 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.[9c,d]

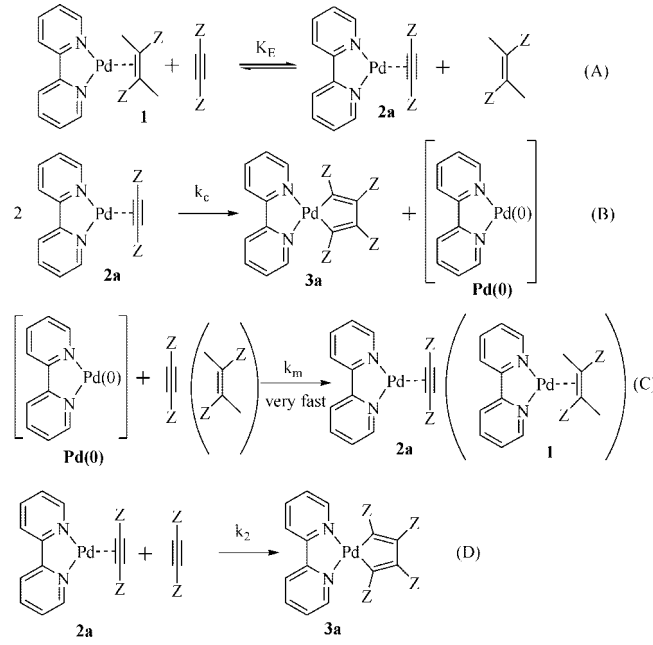
Results and Discussion

Reaction between [Pd(η^2-dmfu)(BiPy)] and Dimethyl-2-butynedioate (dmdb). When an equimolar amount of dmbd is added to a solution of [Pd(η^2-dmfu)(BiPy)] ([[Pd(η^2-dmfu)(BiPy)]] $\approx 1 \times 10^{-2}$ mol dm^{-3}), the formation of the cyclopalladate [Pd(BiPy)(C_4(COOMe)$_4$)] together with unreacted [Pd(η^2-dmfu)(BiPy)] is observed by ^{1}H NMR. The same reaction carried out in the presence of dmbd in 2-fold (or higher) excess ([[Pd(η^2-dmfu)(BiPy)]] $\approx 1 \times 10^{-2}$ mol dm^{-3}; [dmbd] $= (2-3) \times 10^{-2}$ mol dm^{-3}) yields the complex [Pd(BiPy)(C_4(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 to determine the value of K_E by titration of an [Pd(0)(η^2-alkene)] derivative with the alkyne dmbd.

Determination of K_E. It was already stated that addition of an equimolar amount of dmbd to a solution of [Pd(η^2-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 alkene is recommended in order to contrast efficiently the electrophilicity of dmbd and determine

Scheme 2



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 alkenes bonded to Pd(0) complexes,[11] which was often confirmed later.[12] Therefore, the low coordinating capability of dmfu is not surprising since this alkene 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(η^2-fn)(BiPy)] by titration with dmbd at 213 K, monitored by ^{1}H NMR. Under these conditions K became easily accessible ($K = 0.16 \pm 0.01$) 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):

$$[\underset{\mathbf{1}}{\text{Pd}(\eta^2\text{-fn})(\text{BiPy})}] + \text{dmbd} \leftrightarrow [\underset{\mathbf{2a}}{\text{Pd}(\eta^2\text{-dmbd})(\text{BiPy})}] + \text{fn};\ K$$

$$1 \quad K = [\mathbf{2a}_{eq}]^2/(([\mathbf{1}_0] - [\mathbf{2a}_{eq}])([\text{dmbd}]_0 - [\mathbf{2a}_{eq}]))$$

$$2 \quad [\mathbf{1}]_0 = 1 \times 10^{-2} \text{ mol dm}^{-3}$$

$$3 \quad [\text{dmbd}]_0 = \text{in the range } (1-6.2) \times 10^{-2} \text{ mol dm}^{-3}$$

The K_E 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 ($K_E \approx 700$) was taken as a reasonable equilibrium constant for the displacement of dmfu by dmbd at 213 K. The value of $K_E \approx 70$ estimated at 298 K justifies the almost quantitative displacement of dmfu

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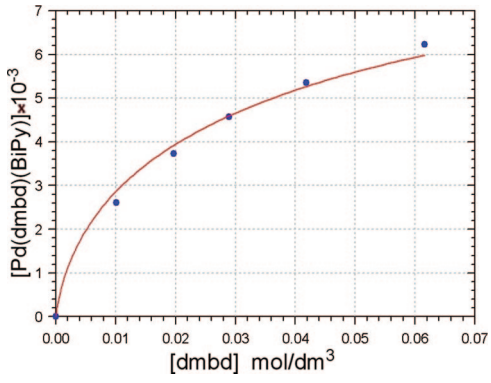

Figure 1. Nonlinear regression fit of the equilibrium concentrations determined by ^{1}H NMR technique at 213 K for the reaction [Pd(η^2-fn)(BiPy)] + dmbd ↔ [Pd(η^2-dmbd)(BiPy)] + fn.

when an equimolar amount of dmbd was added to a solution of [Pd(η^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 dmbd to a solution of [Pd(η^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 dmbd (ratio 1:1; $[\mathbf{1}]_0 = [\mathrm{dmbd}]_0 = 4 \times 10^{-4}$, 2×10^{-4}, 1×10^{-4} mol dm^{-3}) by nonlinear regression of the integrated form of the second-order differential equation model given below, with k_c and $\varepsilon_{\mathbf{2a}}$ as the parameters to be optimized:

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

$$-\mathrm{d}[\mathbf{2a}]/\mathrm{d}t = \mathrm{d}[\mathbf{Pd}]_{\mathrm{fin}}/\mathrm{d}t = 2k_c[\mathbf{2a}]^2$$

$$\mathbf{D}_t = \varepsilon_{\mathbf{2a}}[\mathbf{2a}] + \varepsilon_{\mathrm{fin}}[\mathbf{Pd}]_{\mathrm{fin}}$$

$$([\mathbf{1}] + [\mathbf{3a}] = [\mathbf{Pd}]_{\mathrm{fin}}; \varepsilon_{\mathrm{fin}} = \varepsilon_{\mathbf{1}} + \epsilon_{\mathbf{3a}})$$

$\mathbf{D}_t$ represents the optical density at time t, and $\varepsilon_{\mathbf{1}}$, $\varepsilon_{\mathbf{2a}}$, and $\varepsilon_{\mathbf{3a}}$ are the molar extinction coefficients of **1**, **2a**, and **3a** respectively. The ensuing value for the rate constant was $k_c = 44 \pm 5$ mol^{-1} dm^3 s^{-1} and was independent of the concentration of the substrates.

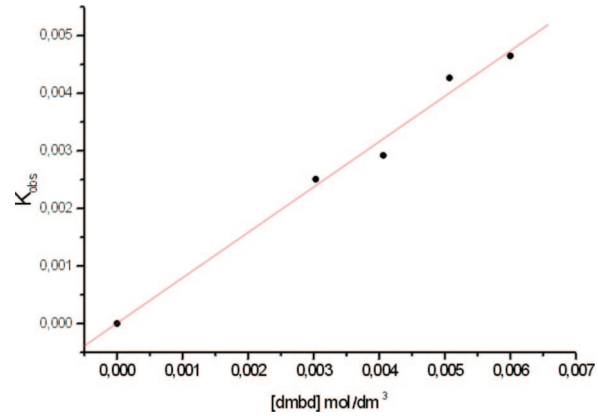

Figure 2. Linear regression plot of k_{obs} vs $[\mathrm{dmbd}]_0$ for the reaction of complex **2a** with dmbd.

Determination of k_2. The value of k_2 was also measured by UV−vis technique under pseudo-first-order conditions ($[\mathrm{dmbd}]_0 \geq 10[\mathbf{1}]_0$). The excess of dmbd 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 dmbd, 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:

$$[\mathbf{2a}]_0 = [\mathbf{1}]_0 \text{ (from the equilibrium mixture completely shifted to the right)}$$

$$[\mathbf{Pd(0)}] = [\mathbf{2a}]_0 - [\mathbf{2a}] - [\mathbf{3a}] \text{ (mass balance)}$$

$$-\mathrm{d}[\mathbf{2a}]/\mathrm{d}t = k_{obs}[\mathbf{2a}] + 2k_c[\mathbf{2a}]^2 - k_m[\mathbf{Pd(0)}][\mathrm{dmbd}]_0$$

$$\mathrm{d}[\mathbf{3a}]/\mathrm{d}t = k_{obs}[\mathbf{2a}] + k_c[\mathbf{2a}]^2$$

$$\mathbf{D}_t = \varepsilon_{\mathbf{2a}}[\mathbf{2a}] + \varepsilon_{\mathbf{3a}}[\mathbf{3a}]$$

($k_{obs} = k_2[\mathrm{dmbd}]_0$; initial conditions $[\mathbf{2a}] = [\mathbf{2a}]_0, [\mathbf{3a}] = 0$)

The regression analysis yields the values for k_{obs} at four different dmbd concentrations, with $k_c = 44$ and $k_m = 10\,000$ mol^{-1} dm^3 s^{-1} [16] held constant during the refinement process. The linear regression of the k_{obs} vs [dmbd] yielding $k_2 = 0.79 \pm 0.05$ mol^{-1} dm^3 s^{-1} is reported in Figure 2.

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

$$[\mathrm{Pd}(\eta^2\text{-}\underset{\mathbf{1}}{\mathrm{dmfu}})(\mathrm{BiPy})] + \mathrm{pna} \leftrightarrow [\mathrm{Pd}(\eta^2\text{-}\underset{\mathbf{2b}}{\mathrm{pna}})(\mathrm{BiPy})] + \mathrm{dmfu} \quad (\mathrm{K_E}^*)$$

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(η^2-dmfu)(BiPy)], is a very reactive species, and the addition (necessarily at RT) of the titrant pna into the NMR tube induces

(13) In the case of exchange between alkenes in α-diimine derivatives of Pd(0) a value of $\Delta H^0 = -3.5 \pm 0.5$ 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 alkenes to the exchange of an alkene with an alkyne, the value of K_{E298K} was calculated from the expression $\ln K_{E298K} = \ln K_{E213K} - (\Delta H^0/R)(213-298)/(213 \times 298)$; $K_E \approx 66$. We consider that approach reliable since we have also studied the RT exchange between maleic anhydride and dmdb in pyridylthioether derivatives of Pd(0)[9g] and the exchange constant between [Pd(η^2-fn)(neoc)] and dmbd.[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_E value is almost independent of the nature of the ancillary ligand.

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(15) With $K_E = 70$ the formation of complex **2** from an equimolecular addition of dmbd to **1** is about 90% of the initial concentration of $[\mathbf{1}]_0$ ($\xi = [\mathbf{1}]_0(K-(K_E)^{1/2})/(K_E-1)$).

(16) The k_m 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_{obs} value.

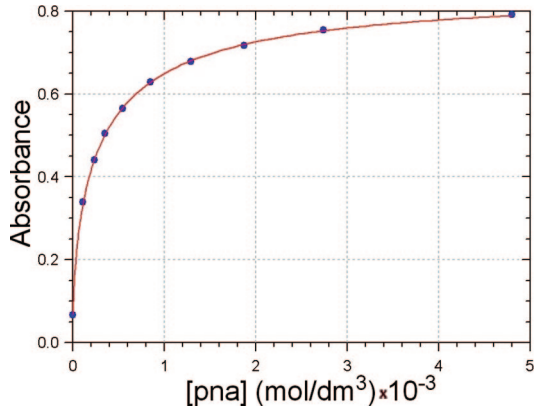
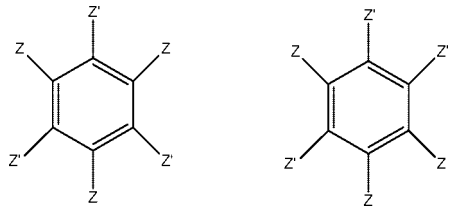


Figure 3. Nonlinear regression fit of the equilibrium determined by UV−vis technique at 298 K for the reaction [Pd(η^2-dmfu)(neoc)] + pna ↔ [Pd(η^2-pna)(neoc)] + dmfu.

the onset of the reaction with the formation of the following species:

(1) the complex [Pd(η^2-pna)(BiPy)] (**2b**);
(2) the unreacted [Pd(η^2-dmfu)(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′**).



4b **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 [Pd(η^2-dmfu)(neoc)] (neoc = 2,2′-dimethyl-*o*-phenanthroline) ([[Pd(η^2-dmfu)(neoc)]]$_0$ = 1 × 10^{-4} mol dm^{-3}) with successive weighed amounts of solid pna. As we have already stated, the peculiar steric hindrance induced by the methyl groups of the ligand neoc stabilizes the monoalkyne derivative [Pd(η^2-dmbd)(neoc)] and allows the equilibrium constant determination.[13,14,17] Figure 3 shows the regression analysis of the titration curve based on the same relationships of the equilibrium determination previously reported.

We took this equilibrium constant (K* = 0.236 ± 0.004) as a reasonable indication of the K_E*, thus, in the presence of a strong excess of pna over Pd(0) complex ([pna]$_0$ = 148−291 × [[Pd(η^2-dmfu)(BiPy)]]$_0$) it is possible to rule out the species [Pd(η^2-dmfu)(BiPy)] from the mechanistic network and consider the complex [Pd(η^2-pna)(BiPy)] as the sole starting material.[18] Under these conditions the reaction scheme becomes considerably simplified even though the independent determination of k_c* and k_2* is not possible since the equimolar reaction between [[Pd(η^2-dmfu)(BiPy)] and pna is complicated by the presence of several species and side reactions. The new conditions can be summarized as follows:

Table 1

[pna]$_0$ (mol dm^{-3})	k_2* (random and negligible)	k_c* (mol^{-1} dm^3 s^{-1})	k_c* (mol^{-1} dm^3 s^{-1}) (average)
1.48 × 10^{-2}	negligible	97 ± 1.5	103 ± 6
1.98 × 10^{-2}	negligible	109 ± 1.8	
2.91 × 10^{-2}	negligible	105 ± 1.3	

(1) **2b** + pna → **3bt** (k_2*)[19] ([**3bt**] = [**3b**] + [**3b′**])
(2) 2 **2b** → **3bt** + **Pd(0)** (k_c*)
(3) **Pd(0)** + pna → **2b** (k_m)

Therefore nonlinear regression analysis of the kinetics performed by UV−vis technique based on the model:

$$[\mathbf{2a}]_0 = [\mathbf{1}]_0 \text{ (from the equilibrium mixture completely shifted to the right)}$$

$$[\mathbf{Pd(0)}] = [\mathbf{2b}]_0 - [\mathbf{2b}] - [\mathbf{3bt}] \text{ (mass balance)}$$

$$([\mathbf{3bt}] = [\mathbf{3b}] + [\mathbf{3b'}])$$

$$-\mathrm{d}[\mathbf{2b}]/\mathrm{d}t = k_2^*[\mathrm{pna}]_0[\mathbf{2b}] + 2k_c^*[\mathbf{2b}]^2 - k_m[\mathbf{Pd(0)}][\mathrm{pna}]_0$$

$$\mathrm{d}[\mathbf{3bt}]/\mathrm{d}t = k_2^*[\mathrm{pna}]_0[\mathbf{2b}] + k_c^*[\mathbf{2b}]^2$$

$$\mathbf{D}_t = \varepsilon_{2b}[\mathbf{2b}] + \varepsilon_{\mathbf{3bt}}[\mathbf{3bt}]$$

($k_{obs} = k_2[\mathrm{dmbd}]_0$; initial conditions: [**2b**] = [**2b**]$_0$,[**3bt**] = 0)

yields the results summarized in Table 1.

Formation of the Symmetric and Unsymmetric Mellitate from Methyl (4-Nitrophenyl)propynoate. The stable palladacyclopentadiene (**3b/3b′**) does not react with one further alkyne 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 [Pd(η^2-pna)(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 [Pd(η^2-pna)(BiPy)], which regioselectively inserts in the palladium−carbon bond of **3b′**.

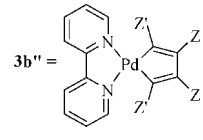
Conclusions

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

(17) Unfortunately, the determination of the equilibrium constant in the case of the direct exchange between dmfu and dmbd is not possible since an extensive decomposition takes place upon addition of the titrant dmbd to a solution of the complex [Pd(η^2-dmfu)(neoc)] (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, [**1**]$_0$ = 1 × 10^{-4} mol dm^{-3} and [pna]$_0$ = 1.48 × 10^{-2} mol dm^{-3}, and the degree of advancement of the reaction is ξ = 0.97.

(19) Formation of the symmetric **3b″** species was never detected.



a novel mechanism for the formation of palladacyclopentadienyl complexes. The peculiar reactivity of the complex [Pd(η^2-dmbd)(BiPy)], which not only reacts with one further molecule of dmbd but also yields the palladacyclopentadiene species by the more efficient bimolecular self-reaction, to the best of our knowledge implies a completely new mechanism that has never been proposed before. The presence of the elusive "palladium naked" Pd(0) species, which was already hypothesized elsewhere,[10] was also confirmed as a key intermediate in the mechanistic network depicted in Scheme 2. Moreover a first hint of the alkyne reactivity order was also provided by the marked difference between the equilibrium constants related to the displacement reactions between the alkene dmfu and the alkynes dmbd and pna. It is quite clear that the coordinating capability of pna is less strong than that of dmbd, and therefore the monoalkyne species [Pd(η^2-pna)(BiPy)] is less stable and consequently more reactive than its counterpart [Pd(η^2-dmbd)(BiPy)]. This difference in reactivity is reflected by the difference between k_c and k_c*, the latter being more than twice higher than the former. The formation of the symmetric and unsymmetric mellitate can also be traced back to the reactivity of the complex [Pd(η^2-pna)(BiPy)], which reacts with the symmetric and unsymmetric palladacyclopentadiene species to give both mellitate compounds and the unsaturated palladium species according to the mechanism already suggested in another paper.[10]

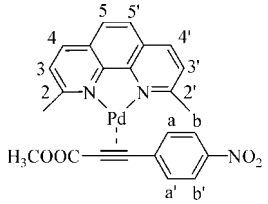
Experimental Section

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 [Pd(η^2-dmfu)(BiPy)], [Pd(η^2-fn)(BiPy)],[20] [Pd(η^2-dmfu)(neoc)],[14] [Pd(BiPy)(C_4(COOMe)$_4$)],[9d] pallada-2,5-bis(carbomethoxy)-3,4-bis(4-nitrophenyl)cyclopentadienebipyridine (**3b**),[21] pallada-2,4-bis(carbomethoxy)-3,5-bis(4-nitrophenyl)cyclopentadienebipyridine (**3b′**),[21] and pna[22] was carried out according to published procedures. Dmbd, CD_2Cl_2, $CDCl_3$, and $CHCl_3$ were commercial grade reagents and were used as purchased.

[Pd(η^2-pna)(neoc)]. To 0.05 g (0.25 mmol) of neocuproine dissolved in freshly distilled CH_2Cl_2 (20 mL) were added 0.12 g (0.116 mmol) of $Pd_2dba_3 \cdot CHCl_3$ and 0.490 g (0.24 mmol) of pna under inert atmosphere (N_2). The obtained orange solution was stirred for 20 min. Activated charcoal was then added, and the resulting mixture was eventually filtered off on a Celite filter. The resulting clear orange solution was concentrated under reduced pressure, and the title complex was obtained as orange microcrystals upon addition of diethyl ether (0.0839 g, 0.081 mmol, yield 70%).

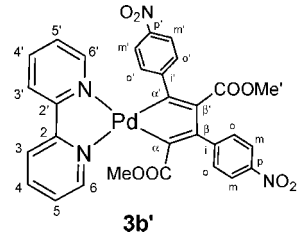


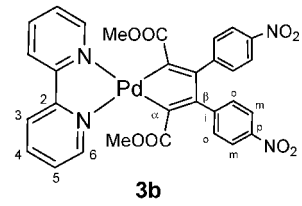
IR (KBr pellets), cm^{-1}: $\nu_{C\text{-}NO2}$ 856; ν_{NO2} 1334, 1509; $\nu_{C=N}$ 1586; $\nu_{C=O}$ 1682. ^{1}H NMR ($CDCl_3$, 298 K, δ ppm): 2.84 (s, 3H, neoc-CH_3), 3.26 (s, 3H, neoc-CH_3), 3.84 (s, 3H, COOCH_3), 7.59 (d, 2H, H_a, J = 8.9 Hz), 7.67 (d, 1H, H3, J = 8.3 Hz), 7.77 (d, 1H, H3′, J = 8.3 Hz), 7.83 (s, 2H, H5, H5′), 8.18 (d, 2H, H_b, J = 8.9 Hz), 8.29 (d, 1H, H4, J = 8.3 Hz), 9.31 (d, 1H, H4, J = 8.3 Hz).

Pallada-2,5-bis(carbomethoxy)-3,4-bis(4-nitrophenyl)cyclopentadienebipyridine (3b) and Pallada-2,4-bis(carbomethoxy)-3,5-bis(4-nitrophenyl)cyclopentadienebipyridine (3b′). MS (FAB+) *m/z*: found 673.0568 (M + H): calcd ($C_{30}H_{23}N_4O_8Pd$) 673.0563.

3b: ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 8.79 (d, 2H, H6, ^3J = 5.4), 8.09 (m, 4H, H3 and H4), 7.97 (d, 4H, H_m, ^3J = 8.1), 7.60 (pst, 2H, H5), 7.17 (d, 4H, H_o, ^3J = 8.1), 3.46 (s, 6H, 2 × OCH_3). ^{13}C NMR ($CDCl_3$, 125.70 MHz): δ 174.1 (*C*O), 156.4 (C_β), 155.5 (C2), 155.2 (C_p), 151.6 (C6), 146.3 (C_α), 146.2 (C_i), 139.6 (C4), 129.7 (C_o), 126.8 (C5), 123.2 (C_m), 122.4 (C3), 51.2 (O*C*H$_3$).

3b′: ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 8.79 (d, 1H, H6), 8.15 (d, 2H, H_m or $H_{m'}$, ^3J = 9.0), 8.13 (d, 2H, $H_{m'}$ or H_m, ^3J = 8.7), 8.15−8.12 (m, 2H, H4 and H6′), 8.08−7.95 (m, 2H, H3 and H5′), 7.60 (br, 1H, H5), 7.58 (d, 2H, H_o or $H_{o'}$, ^3J = 9.0), 8.13 (d, 2H, $H_{o'}$ or H_o, ^3J = 8.7), 7.16 (m, 2H, H3′ and H4′), 3.44 (s, 3H, COOCH_3), 3.18 (s, 3H, COOCH_3).





The symmetric (**4b**) and unsymmetric (**4b′**) mellitate from methyl (4-nitrophenyl)propynoate were isolated as a mixture of products. They were however identified from ^{1}H and ^{13}C NMR.

1,3,5-Tris(carbomethoxy)-2,4,6-tris(4-nitrophenyl)benzene (4b) and 1,2,4-Tris(carbomethoxy)-3,5,6-tris(4-nitrophenyl)benzene (4b′). MS (FAB+) *m/z*: found 616.1237 (M + H): calcd ($C_{30}H_{22}N_3O_{12}$) 616.1203.

4b: ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 8.32−8.05 (m, 6H, H_{ar}), 7.57−7.19 (m, 6H, H_{ar}), 3.26 (s, 9H, OCH_3). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 166.57 (CO), 148.24 (C_p), 142.97 (C_i), 137.1 (C), 137.0 (C), 130.8 (CH), 123.7 (CH), 52.82 (OCH_3).

4b′: ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 8.32−8.05 (m, 6H, H_{ar}), 7.57−7.19 (m, 6H, H_{ar}), 3.58 (s, 3H, OCH_3), 3.55 (s, 3H, OCH_3), 3.21 (s, 3H, OCH_3). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 166.74 (CO), 166.64 (CO), 166.46 (CO), 148.15 (C_p), 147.70 (C_p), 147.62 (C_p), 143.33 (2 × C_i), 142.97 (C_i), 139.2 (C), 138.3 (C), 137.1 (C), 135.1 (C), 134.6 (C), 133.0 (C), 130.1 (4 × CH), 129.9 (2 × CH), 124.0 (2 × CH), 123.5 (4 × CH), 53.26 (2 × OCH_3), 52.42 (OCH_3).

NMR Studies. All reactions were preliminarily carried out by ^{1}H NMR technique.

Determination of the Equilibrium Constant *K*. The equilibrium constant K for the reaction:

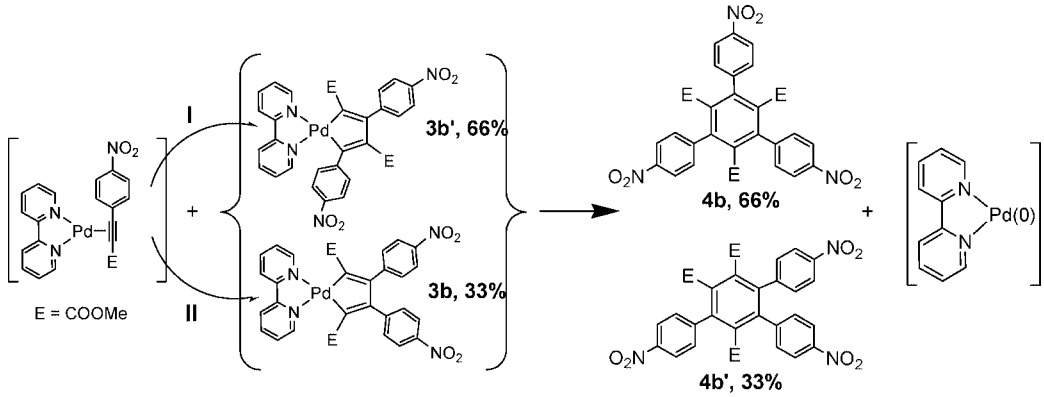
$$[Pd(\eta^2\text{-fn})(BiPy)] + dmbd \leftrightarrow [Pd(\eta^2\text{-dmbd})(BiPy)] + fn$$

was determined by adding known aliquots of dmbd ([dmbd] = 0−0.06 mol dm^{-3}) to a CD_2Cl_2 solution of the complex [Pd(η^2-fn)(BiPy)] ([[Pd(η^2-fn)(BiPy)]] = 1 × 10^{-2} mol dm^{-3}) at 213 K and recording the signal at 9.05 ppm of the $H6_{pyr}$ proton of the complex [Pd(η^2-dmbd)(BiPy)].

Formation of Palladacyclopentadiene Derivatives. The cyclometalation reaction between complex **1** and dmbd carried out

(20) Crociani, B.; Di Bianca, F.; Uguagliati, P.; Canovese, L.; Berton, A. *J. Chem. Soc., Dalton Trans.* **1991**, 71.
(21) Holuigue, A.; Sirlin, C.; Pfeffer, M.; Goubitz, K.; Fraanje, J.; Elsevier, C. J. *Inorg. Chim. Acta* **2006**, *359*, 1773.
(22) Eckert, T. Ipaktschi, J. *Synth. Commun.* **1998**, *28*, 327.

Scheme 3. Proposed Reaction Path for the Formation of 4b/4b′



under second-order conditions ([**1**]$_0$: [dmbd]$_0$ = 1:1, 1:2) was investigated by dissolving the alkene complex **1** in 0.8 mL of CD_2Cl_2 ([**1**]$_0 \approx 1 \times 10^{-2}$ 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 $CDCl_3$ ([**1**]$_0 \approx 3 \times 10^{-2}$ mol dm^{-3}). The alkyne was added at 298 K as a solid in order to obtain the concentration of $\sim 9 \times 10^{-2}$ 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

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

was determined by adding to a 50 mL solution of the complex [Pd(η^2-dmfu)(neoc)] ([[Pd(η^2-dmfu)(neoc)]]$_0 = 1 \times 10^{-4}$ mol dm^{-3}) in $CHCl_3$ increasing amounts of pna as a weighed solid in order to establish a pna concentration in the range 1×10^{-4} to 5 $\times 10^{-3}$ 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 k_c and k_c*. The rate constant k_c was calculated from three independent determinations at three different concentrations of **1** and dmbd under equimolar second-order conditions ([**1**]$_0$: [dmbd]$_0$ = 1:1 = 4×10^{-4}, 2×10^{-4}, 1×10^{-4} mol dm^{-3}) at λ = 420 nm in $CHCl_3$ (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 $CHCl_3$ solution of complex **1** ([**1**]$_0 \approx 1 \times 10^{-4}$ mol dm^{-3}) in order to realize a concentration in the range (1−3) $\times 10^{-2}$ mol dm^{-3}, and the absorbance change was monitored in the 400−600 nm wavelength interval at different times.

Determination of k_2. To 3 mL of a $CHCl_3$ solution of **1** ([**1**]$_0 \approx 1 \times 10^{-4}$ 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 k_2 was eventually calculated from the linear regression analysis of the ensuing k_{obs} values ($k_{obs} = k_2$[dmbd]$_0$) obtained from each kinetic experiment performed under pseudo-first-order conditions ([dmbd]$_0$=30−60[[Pd(η^2-dmfu)(BiPy)]]$_0$).

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