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Insertion of Alkynes into the Pd–C Bond of Palladacycles. Mechanistic Information from High-Pressure Kinetic and X-ray Structural Data

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The reaction between halo-bridged ring-substituted orthopalladated *N,N*-dimethylbenzylamines, $[Pd(C_6H_3RCH_2NMe_2)X]_2$ **1** (R = 4-MeO, 5-Me, H, 5-F, X = Cl, I) and alkynes $R'C{\equiv}CR''$ (R'/R'' = Ph/Ph, Ph/$C_6H_4CF_3$-3, Ph/$C_6H_4NO_2$-4, and Et/Et) to afford double insertion products **3** is first-order in both the reagent concentrations in chloroform at 25.0–44.1 °C. The insertion of the first alkyne molecule is the rate-determining step. Electron-donating groups R on the phenyl ring of **1** increase the rate constants and the slope of the Hammett plot equals −2.2. Variation of the nature of the alkyne results in smaller and less systematic changes in the rate constants. The volume of activation ranges from −18.6 to −14.4 $cm^3\,mol^{-1}$ in the case of $PhC{\equiv}CPh$ but is practically zero in the case of $EtC{\equiv}CEt$. The monomerization of dimers **1** by either pyridine or $[NEt_4]Cl{\cdot}H_2O$ to afford the species $[Pd(C_6H_3RCH_2NMe_2)Cl(L)]$ (L = py or Cl, charges are omitted) retards the insertion markedly, suggesting that only the dimers are the reactive species and that a halo bridge is essential for the entrance of alkyne into the coordination plane of Pd(II). The insertion of the second alkyne was kinetically studied by reacting the seven-membered complex **4** with $PhC{\equiv}CPh$. Although this step is associated with a cis → trans rearrangement about the C═C bond of **4**, as shown by X-ray crystallography, its formal kinetic characteristics are very similar to those of the first insertion step. Both the steps are driven by the nucleophilic attack of the phenyl or alkenyl carbon on the coordinated alkyne. A more complicated mechanism of the second insertion, which is essential to account for the cis → trans isomerization, is discussed in some detail.

Introduction

Insertion of alkynes into Pd–C bonds of palladacycles is one of the representative processes that makes cyclopalladated compounds attractive starting materials in organic synthesis.[2,3] In fact, much has been done in terms of synthesis of various, often unique organic and organometallic compounds starting with palladacycles and alkynes since the first report in 1979.[4] All these transformations have the same key steps, viz. the insertion of one or two alkynes into the Pd–C bond to yield complexes of type **2** or **3**, respectively, depending on the nature of the alkyne.[3] Until now, however, these transformations have not been studied kinetically, although the mechanisms have been discussed on the basis of general chemical evidence.[5] Therefore, we report in this paper a detailed high-pressure kinetic study of the insertion of alkynes into the Pd–C bonds of ring-substituted *N,N*-dimethylbenzylamine complexes **1** to afford doubly inserted species **3**, and of the insertion of diphenylethyne into the Pd–C bond of the "singly inserted" complex **4** to yield the "doubly inserted" compound **5a**. The mechanistic conclusions concerning the latter interconversion are supported by an X-ray crystallographic study of the similarly prepared model compound **5b**. The results obtained are compared with the corresponding kinetic data on reactions of alkenes with palladacycles of type **1** which have previously been reported.[6,7]

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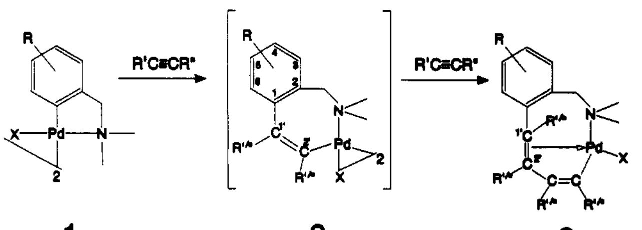
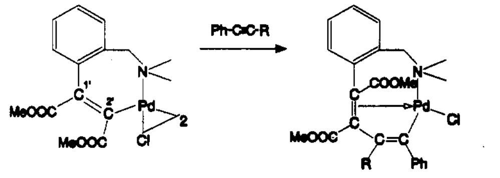
Chart I



1 2 3

R/X = 4-MeO/Cl (a), 5-Me/Cl (b), H/Cl (c), 5-F/Cl (d), H/I (e)

R'/R" = Ph/Ph, Ph/$C_6H_4NO_2$-4, Ph/$C_6H_4CF_3$-3, Et/Et



4 5 R = Ph (a), Me (b)

Experimental Section

Organic Molecules. Diphenylethyne and hex-3-yne were obtained from Aldrich. Phenyl(4-nitrophenyl)ethyne and phenyl(3-trifluorophenyl)ethyne were synthesized as described previously.[8] (Dimethylamino)methylbenzene and 1-[(dimethylamino)methyl]-3-methoxybenzene were purchased from Aldrich. Chloroform stabilized with 60 ppm 2-methyl-2-butene (Merck) was used as solvent throughout this study unless otherwise indicated. Pyridine (Merck) was distilled and tetraethylammonium chloride monohydrate (Merck) was kept at 120 °C overnight before use.

1-[(Dimethylamino)methyl]-4-fluorobenzene. 4-Fluorobenzoic acid (24 g, 0.17 mmol) was refluxed in 25 mL of $SOCl_2$ until all product had dissolved, yielding a pale yellow solution (ca. 15 min). An excess of $SOCl_2$ was distilled off under reduced pressure followed by distillation of the resulting acid chloride. After drying in vacuo, the latter was transferred into a dropping funnel and added slowly to aqueous $HNMe_2$ (40%, 100 mL). The pH of the resulting solution was adjusted to ca. 1 by concentrated HCl, and the solution was evaporated to dryness. The chlorohydrate salt of the amide was dissolved in a minimum amount of H_2O, and solid KOH was added to make the pH ca. 14. The product was extracted with 3 × 200 mL of Et_2O. After drying by $MgSO_4$ and purification with activated carbon, the solvent was evaporated to yield, after drying in vacuo, 25 g (88%) of the pure amide. This product was dissolved in 150 mL of dry Et_2O, and the solution was added slowly to a cooled, clear solution of 14 g of $LiAlH_4$ in 150 mL of freshly distilled dry Et_2O. After addition (1.5 h, the temperature should not rise above 10 °C) the mixture was refluxed for 4 h. The excess of $LiAlH_4$ was *carefully* destroyed with EtOAc followed by H_2O and finally with 15% aqueous HCl. The milky reaction mixture was left overnight and extracted with Et_2O (3 × 200 mL). After drying with $MgSO_4$ the solvent was evaporated and the resulting yellow oil distilled at reduced pressure to give 11 g (50%) of the product. ^1H NMR (δ, $CDCl_3$): 2.22 (s, 6H, CH_3), 3.38 (s, 2H, CH_2), 7.00 and 7.23 (2m, 4H, Ar).

Palladium Complexes. Dimers **1a** and **1c** were prepared according to ref 9 except they were additionally purified by column chromatography (SiO_2–$CHCl_3$); complexes **1b** and **1d** were synthesized according to a general procedure[10] in 87 and 91% yields, respectively. **1b**: ^1H NMR ($CDCl_3$ + py-d_5) 2.07 (s, CH_3), 2.91 (s, NCH_3), 3.93 (s, NCH_2), 5.79 (s, H6), 6.83 (m, H3 + H4). Anal. Calcd for $C_{20}H_{28}Cl_2N_2Pd_2$: C, 41.40; H, 4.86; N, 4.83. Found: C, 41.10; H, 4.81; N, 4.84. **1d**: ^1H NMR ($CDCl_3$ + py-d_5) 2.90 and 2.91 (2s, NCH_3), 3.95 (s, NCH_2), 5.65 (m, H6), 6.71 and 6.93 (2m, H3 + H4). Anal. Calcd for $C_{18}H_{22}Cl_2F_2N_2Pd_2$: C, 36.76; H, 3.77; N, 4.76. Found: C, 36.61; H, 3.66; N, 4.87. Iodo-bridged dimer **1e** was prepared as described in ref 11. Complexes **3c** and **3b** (R'/" = Ph) were prepared as described in refs 4 and 12, respectively. The other compounds **3** were obtained analytically pure by identical procedures starting from the corresponding cyclopalladated compounds **1**. The syntheses of **4** and **5a,b** are described elsewhere.[11] Compound **6** was obtained from **1a** and py.[9] ^1H NMR ($CDCl_3$): 2.93 (s, NCH_3), 3.71 (s, OCH_3), 3.94 (s, NCH_2), 5.89 (d, *J* 8 Hz, H6), 6.38 (dd, *J* 8, 3 Hz, H5), 6.61 (d, *J* 3 Hz, H3), 7.36 (m, H3',5'), 7.81 (m, H4'), 8.86 (m, H2',6'). Anal. Calcd for $C_{15}H_{19}ClN_2OPd$: C, 47.14; H, 5.01. Found: C, 46.77; H, 4.97.

Table I. Summary of Crystal Data and Intensity Collection of 5b

chemical formula	$C_{24}H_{26}ClNO_4Pd{\cdot}0.5C_7H_8$
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.91(1)
b, Å	14.21 (1)
c, Å	8.95 (1)
α, deg	106.01 (5)
β, deg	92.34 (5)
γ, deg	99.78 (5)
V, Å^3	1307.7
M_r, g/mol	580
Z	2
cryst dimens, mm	0.55 × 0.45 × 0.14
α(MoKα), Å	0.710 73
μ, cm^{-1}	8.3
F(000)	594
scan range, deg	1.00 + 0.35 tan θ
θ limits, deg	1–25
no. of reflctns, total	4921
no. of reflctns, used	4117 ($I > 3\sigma(I)$)
R factor, %	0.026
R_w factor, %	0.037
std error in an observn of unit weight, e	1.33

Kinetic and Other Measurements. The reactions at ambient conditions were studied spectrophotometrically on a Shimadzu UV-250 spectrophotometer equipped with a temperature-controlled (±0.1 °C) cell compartment providing three independent measurements. The reactions at pressures up to 150 MPa were studied on a Zeiss PMQII spectrophotometer equipped with a thermostated (±0.1 °C) high-pressure cell[13] by employing the pill-box technique.[14] The kinetic traces were analyzed by using a homemade computer program designed by A. Neubrand. ^1H NMR spectra were run on an AM 400 WB Bruker instrument.

X-ray Diffraction. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer. The crystal parameters and a summary of data collection and structure refinement are given in Table I. No intensity decay was observed during the data collection period. Corrections for the Lorentz and polarization

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effect were applied, but not for absorption owing to the low value of the linear absorption coefficient.

The structures were solved by the Enraf-Nonius SDP package on a PDP 11-60 computer.[15] The atomic positions of the independent non-hydrogen atoms were found with the program MULTAN and the subsequent Fourier difference synthesis. After refinement of coordinates and isotropic thermal parameters of the 31 independent atoms of the molecule, peaks corresponding to a molecule of toluene were found on a Fourier difference, near an inversion center. Three carbon atoms (C25, C26, and C27) with an occupancy factor of 0.5 constitute the independent atoms of one-half molecule of toluene per asymmetric unit. Refinement of coordinates and thermal parameters, first isotropic and then anisotropic, of the 35 independent non-hydrogen atoms with fixed coordinates and thermal parameters led to the final *R* values reported in Table I.

Results

General Observations and Rate Law. The reactions of two alkyne molecules of the type R′C≡CR″ with the Pd—C bonds of the orthopalladated *N*,*N*-dimethylbenzylamines 1 to form 3 occur under synthetic conditions in high yields.[4] The same is true when these are run under the kinetic conditions, i.e. when a large excess of alkyne, [alkyne] ≫ [1], is employed. Under these conditions, the yields of 3 exceed 90% and the reaction progress can easily be followed spectrophotometrically especially in the case of ArC≡CAr′ alkynes. In fact, complex **1c** has an absorption maximum at 340 nm ($\epsilon = 1300\ M^{-1}\ cm^{-1}$, with respect to one Pd unit), whereas **3c** ($R'/'' =$ Ph) that possesses a system of conjugated C=C bonds and phenyl rings has a shoulder at 400 nm ($\epsilon = 4000\ M^{-1}\ cm^{1}$). Since incoming alkynes do not usually absorb at 400 nm, the reactions were followed at this wavelength in the majority of cases. The exceptions are the reactions between 1c and EtC≡CEt (310 nm), 1c and PhC≡C$_6$H$_4$NO$_2$-4 (435 nm), and 4 and PhC≡CPh (410 nm).

Good pseudo-first-order behavior is a typical feature of all reactions studied, and this was the case for at least 4–5 half-lives. Observed pseudo-first-order rate constants, *k*(obsd), derived from these traces were independent of the concentration of complexes 1 and depended linearly on the concentration of the alkyne, as shown in Figure 1. The appropriate rate law is given in (1). The values of the

$$k(\text{obsd}) = k_1[\text{R}'\text{C}{\equiv}\text{CR}''] \qquad (1)$$

rate constants k_1 along with the corresponding activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from the values of k_1 measured at 25.0, 35.0, and 44.1 °C are summarized in Tables II and III.

The data in Figure 1 indicate a significant dependence of k_1 on the substituent R in the aryl ring of 1. The corresponding Hammett plot is shown in Figure 2, and the analytical form of this line is given in (2). The relatively

$$\log k_1 = (-1.24 \pm 0.05) - (2.2 \pm 0.2)\sigma \qquad (2)$$

large value of the slope for Pd(II) chemistry suggests the importance of the electronic factors and, in particular, of the nucleophilicity of the aryl carbon C1. In contrast, electronic effects in alkyne molecules are much less pronounced and rather unsystematic, as demonstrated by the data in Table III.

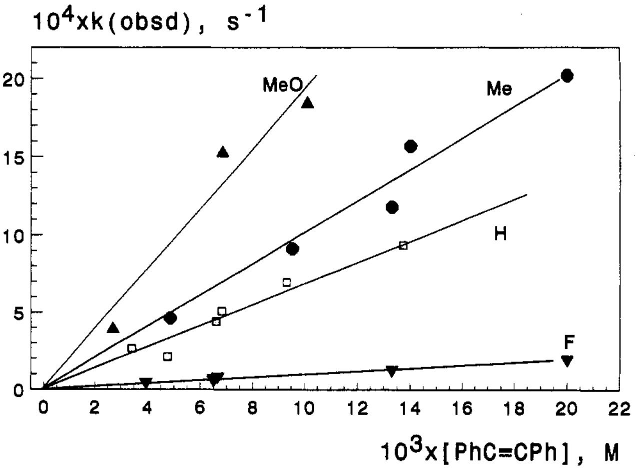

Figure 1. Pseudo-first-order rate constants for the reactions of the ring-substituted chloro-bridged complexes 1 with diphenylethyne as a function of the concentration of PhC≡CPh. Conditions: chloroform solvent; 25 °C.

Pressure Effects. The insertion of PhC≡CPh was accelerated significantly by pressure in the range 10–150 MPa in all the cases studied, Figure 3. Correspondingly, the negative activation volumes, $\Delta V^{\ddagger}$, were calculated and these are in the range −18.6 to −14.4 cm^3 mol^{-1}, Table II. The rate of the reaction of the less bulky alkyne, EtC≡CEt, with 1c was, on the contrary, unaffected by pressure, and the value of $\Delta V^{\ddagger}$ is practically zero, see Table III.

Reaction of Diphenylethyne with 4. The synthesis of **5a** by the treatment of 4 with 1 equiv of PhC≡CPh was shown to occur in a more than 60% yield.[11] We have now checked that under kinetic conditions, i.e. in excess of 20 equiv of diphenylethyne with respect to 4, the same reaction is observed, affording compound **5a** in a quantitative yield, as far as the sensitivity of ^{1}H NMR is concerned. In contrast to this result, we have recently found that the reaction of compounds analogous to 4, but with substituents in the aryl ring (5-F or 4,5-OCH$_2$O), did not lead to the expected compounds of type 5 but rather of type 3; i.e. the hex-3-yne residue is substituted by a diphenylethyne molecule. This behavior is however beyond the scope of this work and will be analyzed in detail elsewhere. To this end, we have followed the kinetics of the clean conversion of 4 into **5a** and the structure of the product has been proven by an X-ray crystallographic study of the very similar compound **5b** (see below).

From the kinetic point of view, the reaction between 4 and diphenylethyne is very similar to the corresponding reactions of complexes 1 in terms of the rate law, the values of k_1, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$, Table II. It should also be pointed out that during the synthesis of **5a**, which was followed by ^{1}H NMR, we found no evidence for the formation of any kind of intermediate, the only signals that were identifiable being those of either 4 or **5a**.

X-ray Crystal Structure of 5b. Several crystal structure determinations have been performed on compounds deriving from insertion of two alkynes into the Pd—C bond of cyclopalladated complexes.[4,16] All these structures have a common feature in that they all display

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Table II. Second-Order Rate Constants k_1 and Activation Parameters for the Insertion of PhC≡CPh into the Pd—C Bond of Cyclopalladated Complexes in Chloroform

Complex (R, X)	T/°C	k_1/M^{-1} s^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/JK^{-1} mol^{-1}	$\Delta V^{\neq}$/cm^3 mol^{-1}
1d	25	$(0.75 \pm 0.04) \times 10^{-2}$			
(F, Cl)	35	$(2.49 \pm 0.08) \times 10^{-2}$	71 ± 1	−47 ± 5	−18.6 ± 0.9
	44.1	$(5.46 \pm 0.14) \times 10^{-2}$			
	35	$(1.63 \pm 0.03) \times 10^{-2}$ [a])			
1c	25	$(7.1 \pm 0.6) \times 10^{-2}$			
(H, Cl)	35	0.146 ± 0.003	50 ± 2	−99 ± 6	−15.0 ± 0.5
	44.1	0.253 ± 0.017			
	25	$(6.4 \pm 0.9) \times 10^{-2}$ [a]			
1e	25	$(4.9 \pm 0.4) \times 10^{-2}$			
H, I)	35	$(9.4 \pm 0.5) \times 10^{-2}$	56 ± 5	−82 ± 17	
	44.1	0.20 ± 0.02			
1b	25	0.102 ± 0.007			
(Me, Cl)	35	0.218 ± 0.013	50 ± 4	−97 ± 12	
	44.1	0.363 ± 0.013			
1a	25	0.196 ± 0.027			
(MeO, Cl)	35	0.30 ± 0.04	50.1 ± 0.7	−93 ± 2	−16.2 ± 1.4
	44.1	0.53 ± 0.05			
4	25	$(1.48 \pm 0.12) \times 10^{-2}$			
(H, Cl)	35	$(3.66 \pm 0.23) \times 10^{-2}$	70.1 ± 2.1	−42.9 ± 6.9	−14.4 ± 1.2
	44.1	$(7.96 \pm 0.23) \times 10^{-2}$			

[a] HOAc as solvent.

Table III. Second-Order Rate Constants k_1 and Activation Parameters for the Insertion of R'C≡CR" into the Pd—C Bond of Complex 1c in Chloroform

alkyne R'/R"	T/°C	k_1/M^{-1} s^{-1}	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}
Ph/Ph	25	$(7.1 \pm 0.6) \times 10^{-2}$	50 ± 2	−99 ± 6
Ph/$C_6H_4CF_3$-3	25	$(3.2 \pm 0.2) \times 10^{-2}$		
	35	$(6.8 \pm 0.3) \times 10^{-2}$	59 ± 2	−76 ± 8
	44.1	0.144 ± 0.005		
Ph/$C_6H_4NO_2$-4	25	$(4.9 \pm 0.4) \times 10^{-2}$		
Et/Et[a]	25	$(7.46 \pm 0.06) \times 10^{-2}$		
	35	0.14 ± 0.01	57 ± 5	−76 ± 18
	44.1	0.32 ± 0.04		

[a] $\Delta V^{\neq}$ = 0.9 ± 0.7 cm^3 mol^{-1}.

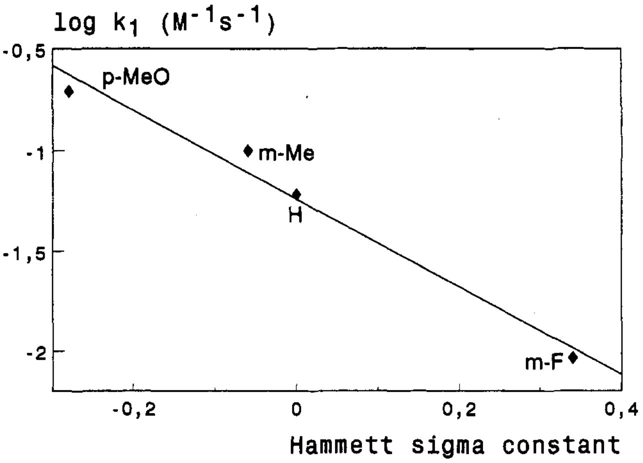

Figure 2. Hammett plot for the second-order rate constants k_1 (25 °C) versus the σ constants of substituents in the phenyl ring of chloro-bridged complexes **1**.

the same trans arrangement about the alkene C1'═C2' bond. All these compounds, however, were directly obtained from either diphenylethyne or hex-3-yne; i.e. in none of their syntheses was the singly inserted intermediate isolated, and therefore there was no evidence that the latter had indeed a cis arrangement of the palladated C1'═C2' alkenyl unit. We have therefore performed an X-ray diffraction study on a single crystal of **5b** which has indeed been synthesized in a stepwise fashion from complex **4** and 1-phenylpropyne. The result of this study is given in Figure 4 and in Tables IV–VI. The molecule **5b** consists of a butadienyl chain $\eta^1;\eta^2$-bonded to the Pd atom, the third and the fourth coordination sites of the latter being occupied by the nitrogen and a chloro ion, respectively. The distances and the angles are within the expected range;[4,16] however, the most important information is that the two methoxycarbonyl groups are mutually trans in the alkenyl unit η^2-bonded to the palladium center. This result is thus a definite proof that the insertion of the second alkyne into the Pd—C bond and the isomerization of the alkenyl unit in **4** are taking place simultaneously.

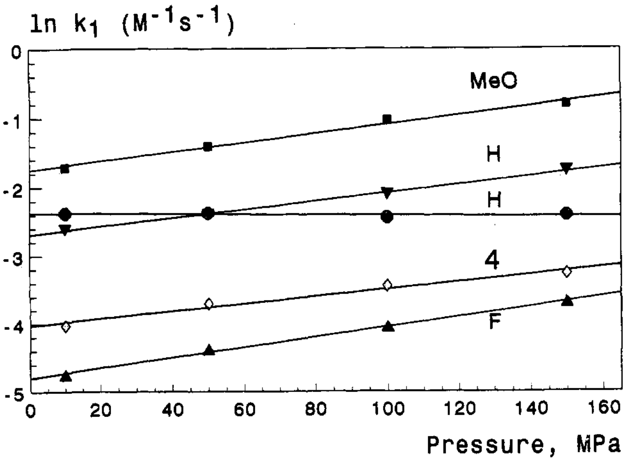

Figure 3. Effect of pressure on the second-order rate constants k_1 for reactions of the ring-substituted chloro-bridged complexes **1a** (■), **1c** (▼), **4** (dvo), and **1d** (▲) with diphenylethyne and complex **1c** (●) with hex-3-yne. Conditions: chloroform solvent; 25 °C.

Reactivity of Monomeric Palladacycles. From a mechanistic point of view it is of importance to compare the reactivity of the dimeric complexes **1** and their monomeric counterparts derived from **1** in the presence of either pyridine[17] or chloro[18] ligands according to eq 3. When isolated complex **6** was introduced into the reaction

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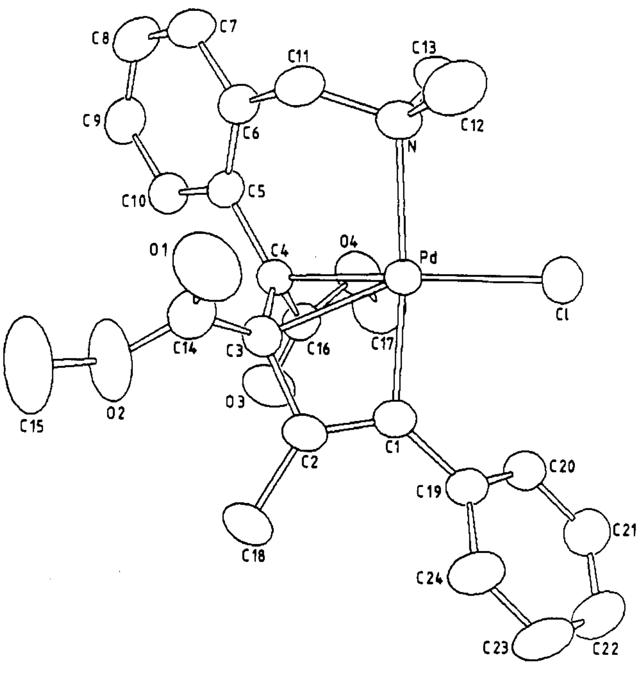


Figure 4. ORTEP view of complex **5b**.

Table IV. Final Positional and Equivalent Isotropic Thermal Parameters (Å^2) with Esd's in Parentheses for the Non-Hydrogen Atoms of Compound 5b

atom	*x*	*y*	*z*	B^a
Pd	0.08773(1)	0.28883(1)	0.15994(2)	2.416(3)
Cl	–0.07224(5)	0.37435(5)	0.14388(7)	4.08(1)
N	0.1667(2)	0.3267(2)	–0.0441(2)	3.62(4)
C1	0.0161(2)	0.2367(2)	0.3311(2)	2.80(4)
C2	0.0728(2)	0.1596(2)	0.3171(3)	3.00(4)
C3	0.1667(2)	0.1667(2)	0.2024(2)	2.74(4)
C4	0.2604(2)	0.2513(1)	0.2349(2)	2.42(4)
01	0.1212(3)	0.0572(2)	–0.0607(2)	5.96(6)
02	0.2176(2)	0.0116(1)	0.1246(3)	5.76(5)
03	0.2969(2)	0.2832(1)	0.5126(2)	4.26(4)
04	0.3079(2)	0.4119(1)	0.4140(2)	3.80(4)
C5	0.3731(2)	0.2623(1)	0.1452(2)	2.51(4)
C6	0.3713(2)	0.2715(2)	–0.0062(3)	3.04(4)
C7	0.4860(2)	0.2865(2)	–0.0696(3)	4.00(5)
C8	0.5977(2)	0.2918(2)	0.0123(3)	4.26(6)
C9	0.5991(2)	0.2801(2)	0.1589(3)	3.77(6)
C10	0.4880(2)	0.2665(2)	0.2254(3)	3.13(4)
C11	0.2556(2)	0.2617(2)	–0.1101(3)	3.62(5)
C12	0.0665(3)	0.3108(3)	–0.1693(3)	6.38(8)
C13	0.2287(3)	0.4324(2)	0.0006(3)	5.26(6)
C14	0.1666(2)	0.0745(2)	0.0691(3)	3.44(5)
C15	0.2088(4)	–0.0893(2)	0.0235(5)	7.6(1)
C16	0.2872(2)	0.3153(2)	0.4038(2)	2.72(4)
C17	0.3408(4)	0.4794(2)	0.5689(4)	5.47(7)
C18	0.0578(3)	0.0806(2)	0.4005(3)	4.37(6)
C19	–0.0803(2)	0.2690(2)	0.4308(2)	2.85(4)
C20	–0.0691(2)	0.3686(2)	0.5159(3)	3.42(5)
C21	–0.1554(3)	0.3995(2)	0.6159(3)	4.35(6)
C22	–0.2562(3)	0.3323(2)	0.6325(3)	5.08(7)
C23	–0.2695(3)	0.2331(2)	0.5498(3)	5.06(7)
C24	–0.1826(2)	0.2018(2)	0.4484(3)	4.08(6)
C25	0.4287(4)	0.0462(3)	0.4286(6)	7.1(1)
C26	0.5147(4)	–0.0041(3)	0.3463(6)	8.0(1)
C27	0.5904(4)	–0.0525(3)	0.4220(6)	0.2(1)
C28	0.5390(9)	–0.0069(7)	0.199(1)	8.8(3)

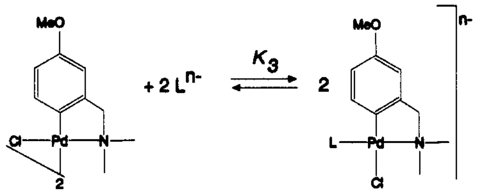
[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameters defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)$.

Table V. Selected Bond Lengths (Å) with Esd's in Parentheses for Compound 5b

Pd–Cl	2.310(1)	C4–C5	1.505(3)
Pd–N	2.209(2)	C5–C6	1.397(3)
Pd–C1	2.007(2)	C6–C11	1.499(3)
Pd–C3	2.177(2)	C11–N	1.481(3)
Pd–C4	2.171(2)	C3–C4	1.392(3)
C1–C2	1.326(3)	C4–C16	1.521(3)
C2–C3	1.490(3)	N–C12	1.475(3)
C3–C4	1.392(3)	N–C13	1.474(3)

Table VI. Selected Bond Angles (deg) with Esd's in Parentheses for Compound 5b

Cl–Pd–N	91.08(5)	N–C11–C6	116.0(2)
C1–Pd–Cl	93.14(6)	C11–C6–C5	125.1(2)
N–Pd–C1	172.90(7)	C6–C5–C4	125.2(2)
N–Pd–C3	109.32(7)	C5–C4–C3	125.1(2)
N–Pd–C4	92.81(7)	C4–C3–C2	119.0(2)
C1–Pd–C3	65.08(8)	C3–C2–C1	106.3(2)
C1–Pd–C4	84.95(8)	C3–C4–C16	117.4(2)



(3)

L = py (n=0) **6**; Cl (n=1) **7**

mixture and reacted with PhC≡CPh instead of the parent dimer **1a**, the value of k_1 was (6.4 ± 0.1) × 10^{-3} M^{-1} s^{-1} at 25 °C in $CHCl_3$; i.e. the reaction rate decreased by a factor of 31. In the presence of 0.004 M py the rate decreased further and the second-order rate constant k_1 appeared to be equal to (3.9 ± 0.1) × 10^{-4} M^{-1} s^{-1}, as was estimated from the initial rate of formation of **3a**, since the rate was too slow to use the integral method. The overall rate retardation on going from dimer **1a** to monomer **6**, stabilized against the reverse dimerization by 0.004 M py, appeared to be a factor of 500. This effect demonstrates the negligible reactivity of the "py" monomer as compared to the parent dimer **1a**.

The effect of monomerization of **1a** by $[NEt_4]Cl{\cdot}H_2O$ was investigated in more detail by generating the monomeric species **7** in situ. A plot of k_1 as a function of concentration of the salt is shown in Figure 5. As in the py case, there is a strong rate retardation. In order to prove that the effect is due to conversion of **1a** into **7**, the interaction between the dimer and $[NEt_4]Cl{\cdot}H_2O$ was studied spectrophotometrically in $CHCl_3$ at 25.0, 35.0, and 44.1 °C. Dimer **1a** has a maximum at 341 nm (ϵ = 1435 M^{-1} cm^{-1}). On addition of the salt the absorbance decreases slightly, the maximum moves to 339 nm, and the isosbestic point at 307 nm is observed. The equilibrium is reached much faster as compared to the insertion reaction. The dependence of absorbance on the concentration of $[NEt_4]Cl{\cdot}H_2O$ is demonstrated in Figure 6. The two profiles in Figures 5 and 6 are very similar, indicating that the one and the same phenomenon, namely the dimer ⇄ monomer equilibrium (3) must account for both. From the equilibrium measurements, using the approach described in detail elsewhere,[19] the equilibrium constant K_3 of 95.1 ± 1.9 M^{-1} (25 °C) was calculated for the chloro case and the values of K_3 showed a minor temperature dependence. Using this value of K_3, the equilibrium concentrations of dimer **1a** in the presence of $[NEt_4]Cl{\cdot}H_2O$ were calculated and the values of k_1 are plotted against

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(18) Braunstein, P.; Dehand, J.; Pfeffer, M. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 581.

(19) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252.

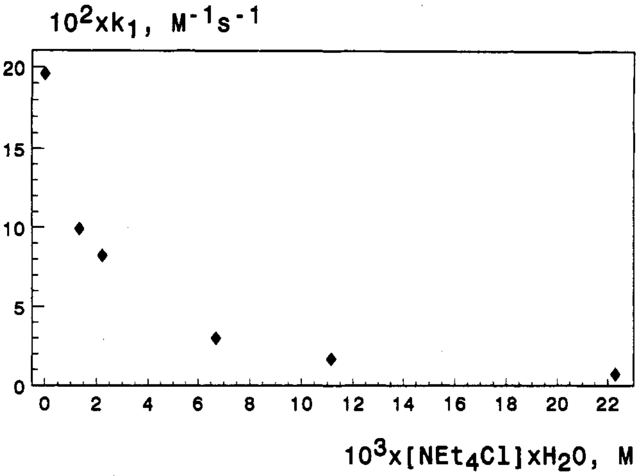


Figure 5. Effect of $[NEt_4]Cl{\cdot}H_2O$ on the rate constants k_1 for insertion of PhC≡CPh into the Pd—C bond of complex **1a** in chloroform at 25 °C. [PhC≡CPh] = 8.77×10^{-3} M and $[Pd(II)]_t = 2.0 \times 10^{-4}$ M.

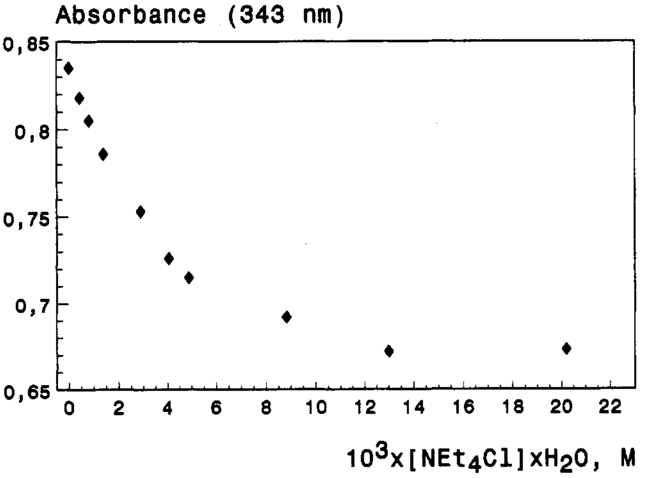


Figure 6. Change in absorbance of solutions of complex **1a** in $CHCl_3$ on consecutive addition of $[NEt_4]Cl{\cdot}H_2O$ at 25 °C and $[Pd(II)]_t = 5.56 \times 10^{-4}$ M.

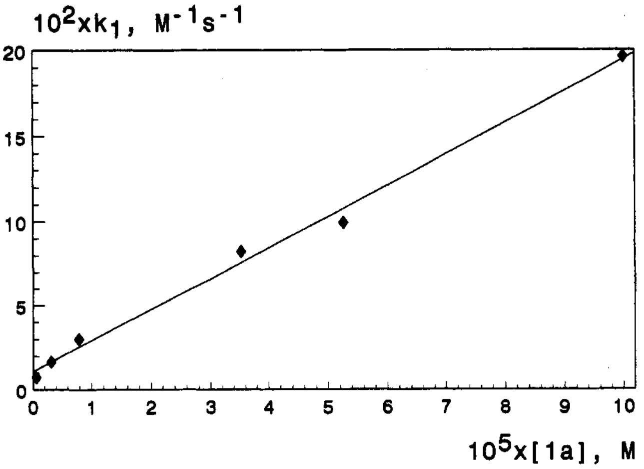


Figure 7. Rate constants k_1 for the reaction of PhC≡CPh with **1a** in the presence of $[NEt_4]Cl{\cdot}H_2O$ from Figure 5 plotted as a function of the calculated concentration of the dimeric species from the equilibrium constant K_3 estimated from the data in Figure 6.

these in Figure 7. A satisfactory correlation is evident and supports a decisive role of the dimeric species in the reaction.

Reactions in Acetic Acid as Solvent. Styrenes react with the Pd–C bonds of orthometalated *N,N*-dimethylbenzylamines showing a strong acid catalysis.[6,7] The reactions do not occur in $CHCl_3$, and acids, HOAc or $HClO_4$, are required to trigger the process. It was thus interesting to compare the reactivity of alkenes and alkynes with respect to **1** from the point of view of the acid catalysis. The reactions of diphenylethyne with **1c** and **1d** were run in acetic acid as solvent. In both cases the reactions proceed with measurable rates and the rate constants k_1 are included in Table II. As seen, the values of k_1 for HOAc are only slightly lower as compared to $CHCl_3$ as solvent. Thus, there is no acid catalysis in reactions of alkynes with orthopalladated *N,N*-dimethylbenzylamines.

Discussion

Formal Kinetics. The simple rate law (1) and the first-order dependence in the concentration of alkyne, in particular, support the "synthetic" evidence[11] for the fact that the insertion of the first alkyne molecule is the rate-determining step. In fact, when a 1:1 mixture of **1c** and PhC≡CPh was reacted, the products were still complex **3c** (R'/'' = Ph) and nonreacted **1c**; the formation of **2** was never observed.[11] From the kinetic standpoint, one may write the following formal sequence:

$$1 + R'C{\equiv}CR'' \rightleftarrows 2 \qquad k_4, k_{-4} \tag{4}$$

$$2 + R'C{\equiv}CR'' \rightarrow 3 \qquad k_5 \tag{5}$$

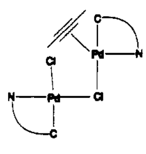
Application of the steady-state approximation with respect to the concentration of **2** results in the expression for k(obsd) given in eq 6. The first-order dependence in [R'C≡CR''] only holds on the condition that k_5[R'C≡CR''] ≫ k_{-4}. If so, eq 6 transforms into eq 7, which is in agreement with the experimental rate law, for which $k_1 = k_4$. Another source of evidence for the slower first

$$k(\text{obsd}) = \frac{k_4 k_5 [R'C{\equiv}CR'']^2}{k_{-4} + k_5[R'C{\equiv}CR'']} \tag{6}$$

$$k(\text{obsd}) = k_4[R'C{\equiv}CR''] \tag{7}$$

insertion reaction may be obtained from the comparison of the rate constants k_1 for the ring-substituted complexes **1** and complex **4**. From the Hammett equation (2) it is possible to estimate the rate constant k_1 for the insertion of PhC≡CPh into the complex of type **1** with two MeOOC substituents and to compare it with the measured rate constant for the second insertion of PhC≡CPh into **4**, since this complex contains also two electron-withdrawing MeOOC groups. Naturally, this comparison assumes a close sensitivity of the first and the second insertion toward electronic effects. Using the Hammett value for the MeOOC group of 0.4, the calculated value equals 0.1×10^{-2} M^{-1} s^{-1} and must be compared with the measured one of 1.48×10^{-2} M^{-1} s^{-1} at 25 °C. The former is in fact by a factor of 15 lower.

What Is k_4? One of the key questions related to the mechanisms of insertion of unsaturated molecules into Pd–C bonds of dimeric halo- or acetato-bridged palladacycles is how the incoming molecule enters the coordination sphere of Pd(II) for the subsequent insertion into the Pd–C bond.[6,7] There are two possibilities in the present case, i.e. the "bridge-opening" entrance via intermediate **8** and



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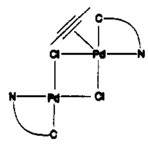

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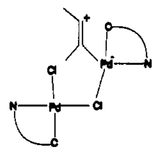

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the axial route via **9**, where the latter is actually indistinguishable from the direct insertion of alkyne from the bulk solvent. Since alkynes react readily in aprotic chloroform and the reactions are not subjected to acid catalysis, the entrance via Pd–N bond breaking[7] can be excluded from the present considerations.

Negligible reactivity of the monomeric species **6** and **7** as compared to the parent dimer, is strong evidence in favor of the bridge-opening entrance via **8**. Conversion of the dimers into **7**, in particular, must increase the nucleophilicity of the complex and hence, as suggested by the Hammett plot in Figure 2, enhance the reactivity. However, the opposite effect is observed, indicative of the primary importance of the bridging structure. Bridging ligands, in principle, are always a potential site of coordinative unsaturation, since a cleavage of one bridge immediately creates a coordinative vacancy at the metal center. Another way to enforce coordination unsaturation and, thus, to initiate the reactions of alkynes with low reactive palladacycles is to abstract the chloro ligands by $AgBF_4$ to produce solvento species.[11,20] From the point of view of the bridging entrance, the reactions of alkenes[7] and alkynes are similar: this seems to be a dominant path. "Synthetic" evidence for the importance of this route comes from the C—C bond formation that is occurring in the reaction between metallacarbynes and cyclopalladated compounds. We have indeed shown that metallacarbynes do behave like organic alkynes and the M$\equiv$C bond undergoes formal insertion into Pd—C bonds. An interesting feature of this reaction is that we could demonstrate that prior to the insertion, an intermediate compound having the metallacarbyne unit coordinated to Pd(II) is formed.[21] The stoichiometric mechanism of the first insertion may be written as shown in Scheme I.

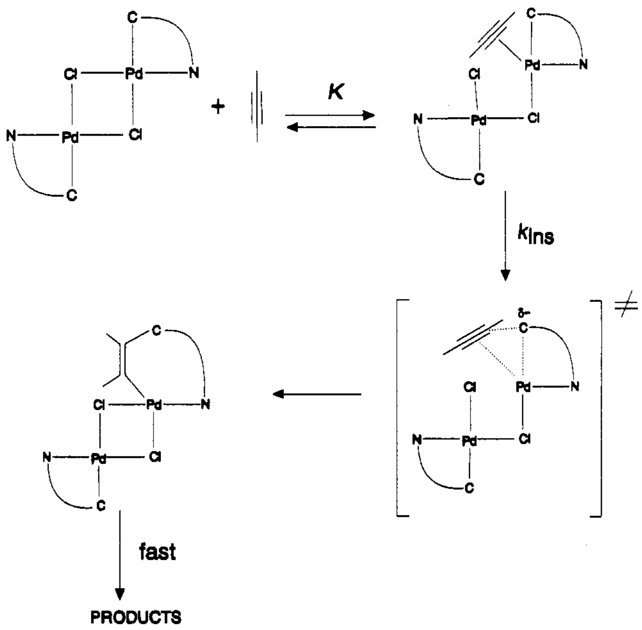
The equilibrium driven by K must be shifted strongly to the left, since no intermediates were detected spectrophotometrically. Therefore, the rate constant k_4 (or k_1) is given by $k_4 = Kk_{\text{ins}}$, and hence, the substituent effect and all activation parameters are the sum of terms arising from K and k_{ins}. Thus, these parameters must be considered separately.

Substituent Effect. The slope of the Hammett plot of −2.2 is rather negative[22] and must be compared to the ρ values of −1.13 and −1.57 for reactions of styrene with the Pd–C bonds of **1** and orthopalladated acetanilide, respectively.[7] This implies that the negative charge at the C1 carbon plays an important role in the reaction. Unfortunately, it is impossible to study the substituent effects on K and k_{ins} separately, but some literature comparisons, namely an equation of type (3) for 2-phenylpyridine,[19] suggest that a slightly positive value of $\rho(K)$ is to be expected. Since

$$\rho(\text{obsd}) = \rho(K) + \rho(k_{\text{ins}}) \tag{8}$$

the value of $\rho(k_{\text{ins}})$ may be more negative than −2.2. This means that the transition state for the first insertion is to a large extent nonconcerted and C1–C1′ bond making plays a major role in the transition state.

Scheme I



Pressure Effects. In terms of the suggested mechanism in Scheme I the observed volume of activation will be given by the sum of the reaction volume for the formation of the adduct and the activation volume for the rate-determining insertion step, eq 9. It seems reasonable

$$\Delta V^{\ddagger}(\text{obsd}) = \Delta V^{0}(K) + \Delta V^{\ddagger}(k_{\text{ins}}) \tag{9}$$

to expect that the insertion step itself will not be associated with a large change in volume[23,24] such that $\Delta V^{\ddagger}$(obsd) will mainly represent $\Delta V^{0}(K)$ for the addition process. This value should correlate with the bulkiness of the alkynes, since the larger these are the more effective will the overlap of the molecular spheres be, i.e. a more negative reaction volume. This is indeed the case when the data for the insertion of $\mathrm{PhC{\equiv}CPh}$ and $\mathrm{EtC{\equiv}CEt}$ are compared. The precoordination of the incoming alkynes via the bridge-opening process can be visualized as an associative process that is accompanied by a significant volume collapse. By way of comparison, $\Delta V^{\ddagger}$ values between −17 and −25 $cm^3\ mol^{-1}$ have been reported for the insertion of electron-rich triple-bonded systems into metal–carbene bonds of pentacarbonyl(methoxyphenylcarbene)chromium and -tungsten complexes.[25] Similarly, the [2 + 2] cycloaddition reactions on the coordinated ligand of chromium and tungsten pentacarbonyl carbene complexes are characterized by significantly negative volumes of activation, viz. between −15 and −18 $cm^3\ mol^{-1}$.[26] It follows that the insertion of alkynes is in line with an associative

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(20) Wu, G.; Rheingold, A. L.; Heck, R. F. *Organometallics* **1987**, *6*, 2386.

(21) Engel, P. F.; Pfeffer, M.; Fischer, J.; Dedieu, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1275.

(22) For other "Hammett" extremes in Pd(II) chemistry see: Yatsimirsky, A. K.; Deiko, S. A.; Ryabov, A. D. *Tetrahedron* **1983**, *39*, 2381 (ρ = −3.0). Reference 19 (ρ = −2.93).

(23) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

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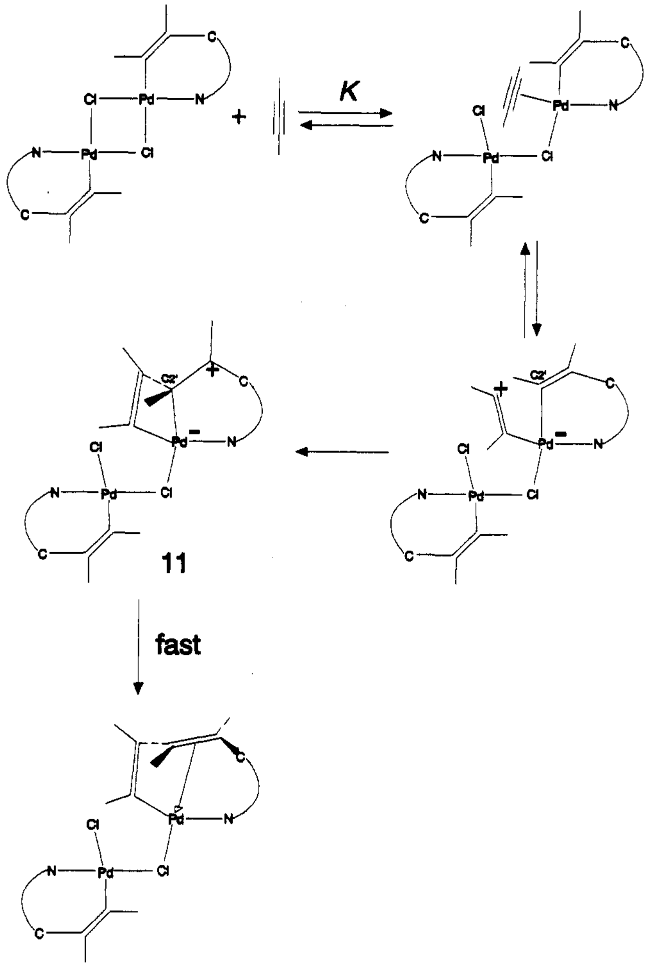
process during which the volume collapse is mostly due to the precoordination of the incoming alkynes via the bridge-opening reaction. The associative nature is most probably the reason why chloro and iodo complexes **1c** and **1f**, respectively, react with similar rates, since it is well decumented that associative reactions have a reduced sensitivity toward the nature of the leaving groups.[27]

The mechanism in Scheme I is very similar to that proposed for insertion of alkenes[6,7] into the Pd–C bonds of complexes **1**, but the reaction rates are markedly different. Alkynes react much faster, and the difference is really enormous in nonprotic solvents. The possible reason is that an η^2-coordinated alkyne in **8** type intermediates has to a considerable extent a contribution from the resonance structure of type **10**. This hypothesis is in line with that proposed recently by Sylvestre and Hoffmann who analyzed the η^2-alkyne–vinylidene rearrangement occurring in T-shaped d^8 ML$_3$(alkyne) complexes.[28] Therefore, alkynes should attain enhanced reactivity toward nucleophiles on coordination to Pd(II).

Speculations about the Insertion of the Second Alkyne. The conversion of **2** into **3** cannot be probed kinetically. However, this is possible for the formation of **5a** from **4**. Since **2** and **4** are both halo-bridged dimers, it is reasonable to assume that the second insertion matches the first one, i.e. the bridge-opening entrance is followed by the nucleophilic attack of the C2′ atom at the alkyne. However, the cis to trans isomerization at the C═C bond is still poorly understood. One might speculate that a reasonable reaction sequence might be as shown in Scheme II. The key intermediate here might be complex **11** formed after nucleophilic attack of the alkenyl C2′ carbon σ-bonded to Pd at the positively charged carbon of coordinated alkyne. It may appear that the Pd—C2′ bond is not broken after the new C—C bond formation, and this would lead to the palladacyclobutenyl intermediate **11**. The latter may undergo the Pd—C2′ bond cleavage accompanied by the reformation of the C1′═C2′ double bond. Manipulations with the molecular models support the idea that this reformation can easily bring about the trans arrangement of R groups at the C1′═C2′ double bond. The isomerization is likely of a "thermodynamic" origin, since, as suggested again by the molecular models, only the trans-configurated η^2-coordinated alkenyl fragment C1′═C2′ will be perpendicular to the palladium plane, if the Pd—N bond is still present. For the cis-configurated fragment, one must expect the C1′═C2′ bond to be in the Pd plane, and this is, of course, thermodynamically less favorable.

The mechanism in Scheme II is different as compared to that proposed previously[3] for the cis → trans isomerization which was based upon a metallacyclic flip that might occur *after* the insertion of the second alkyne has taken place. This possibility cannot totally be ruled out in light of results described in this paper, though it seems to be less likely than the mechanism shown in Scheme II.

Scheme II



Conclusions. This study has shown that prior to the rate-limiting insertion into Pd—C bonds of halo-bridged palladacycles, alkynes can precoordinate Pd(II) via the bridge-opening route. The insertion reaction itself seems to be to a significant extent nonconcerted, and the nucleophilic attack of the C1 carbon at the coordinated alkyne, which might be to a significant extent η^1-bound, plays an important role. Similar consideration of the elementary steps of the second insertion gives understanding to how the cis to trans isomerization of the alkene C═C bond may take place.

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Supplementary Material Available: Tables of positional parameters of the hydrogen atoms, bond lengths and angles, and anisotropic thermal parameters for **5b** (5 pages). Ordering information is given on any current masthead page.

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[28] Sylvestre, J.; Hoffmann, R. *Helv. Chim. Acta* 1985, *68*, 1461.