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Comparative study of the mechanism of alkenylation of *ortho*-palladated benzylamines and acetanilides

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Abstract

The *ortho*-palladated derivative of *N,N*-dimethylbenzylamine, the complex $[Pd(OAc)(C_6H_4CH_2NMe_2)]_2$, reacts with styrene in acetic acid solution with a final product of $o\text{-}Me_2NCH_2C_6H_4CH{=}CHC_6H_5$. Two parallel second-order pathways, are involved catalysed, respectively by acetic acid (k_3) and perchloric acid (k_H). The rate constants k_3 and k_H at 30 °C are 0.021 ± 0.005 and 6.8 ± 0.5 dm^3 mol^{-1} s^{-1}, while the pK_a is 4.6. In the case of the corresponding acetanilide derivative, the complex $[Pd(OAc)(C_6H_4NHCOMe)]_2$, the catalysis by perchloric acid is much weaker than for the amine complex, the k_3 and k_H being 0.0206 ± 0.0005 and 0.049 ± 0.003 dm^3 mol^{-1} s^{-1}, respectively. The pK_a in this case is 4.5. Despite the great difference in basicity of *N,N*-dimethylbenzylamine and acetanilide, the values for pK_a are very similar, providing evidence that the perchloric acid-catalysed pathway involves the protonation of groups of comparable basicity in both complexes, that is to say the bridging acetates, while the great variation in the values of k_H suggests the existence of other route of acid catalysis for amine complexes. The chloro-bridged acetanilidide complex $[PdCl(C_6H_4NHCOMe)]_2$ reacts with styrene in various organic solvents without the perchloric acid-catalysed pathway (k_H). The Hammett equations $\log k_3 = -(1.58 \pm 0.02) - (1.57 \pm 0.06)\sigma_m$ and $\log k_3 = -(1.49 \pm 0.02) - (0.79 \pm 0.15)\sigma_P$ were obtained in acetic acid solution at 30 °C varying ring-substituents in the acetanilide complex and styrene, respectively. On the basis of these and previously reported results the mechanism of the k_3 pathway for acetanilide complexes is discussed.

Introduction

Insertion of alkenes into M–H or M–C bonds occurs via two main pathways, either the migratory path (when precoordination of alkene is followed by the nucleophilic attack of hydride or organic fragment at a double bond carbon) or the nonmigratory pathway (when insertion of alkane proceeds from the bulk solvent without formation of stable π complexed intermediates) [1,2]. The two routes may be governed by the same rate law and cannot be discriminated from the kinetic data. We could not choose between pathways in our previous kinetic study of the reaction between chloro-bridged dimeric *ortho*-palladated derivatives of *N,N*-di-

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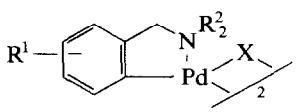
methylbenzylamines, complexes **1a** and **1c**, and *para*-substituted styrenes affording stilbene derivatives **2** [3]. The reaction was found to follow second-order kinetics, the corresponding rate constant k_2 depending strongly on low concentrations of perchloric acid according to eq. 1.

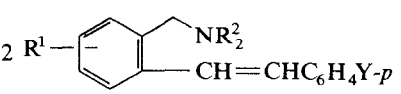
$$k_2 = k_3 + k_4[HClO_4] \quad (1)$$

We have interpreted the perchloric acid-catalysed path (k_4) in terms of the migratory mechanism of insertion of alkenes into the M–C bonds, and assumed that the acidic catalyst promotes styrene precoordination through a process either of "bridging" or "chelating". The former implies that protons attack the bridging ligands of dimeric molecule **1** effecting partial bridge cleavage and, hence, alkene precoordination. The latter implies cleavage of the palladium–nitrogen bond, made irreversible by protonation of the tertiary nitrogen donor. This work is an attempt to clarify some aspects of the reactivity with alkenes of *ortho*-palladated molecules, benzylamines and acetanilides, such as (i) the site of proton attack in the acid catalysed route (note that for complexes **1** the k_3 path is also acid catalysed, by acetic acid, since no reaction occurs without acid), (ii) the mechanistic features typical of acetanilide complexes **3** which are known to react with alkenes [4] as well as with terminal [5] and internal alkynes [6], (iii) the comparison of the reaction of dimeric and monomeric complexes in different solvents. Hence, we have studied the influence of the nature of bridging ligands (complexes **1a** and **1b**, **3a** and **3b**) and chelate arms (complexes **1** and **3**), according to eqns. 2 and 3, as well as the effect of monomerization of palladacycles (complexes **5** and **6**) in the reaction with alkenes.



(**1**)

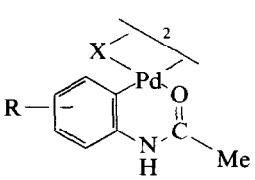
$$+ 2\ H_2C{=}CHC_6H_4Y\text{-}p \longrightarrow$$



(**2**)

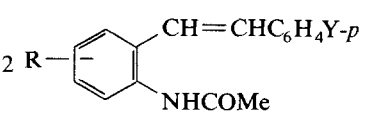
$$+ 2\ Pd^0 + 2\ HX \quad (2)$$

(Y = MeO, Me, H, Cl, Br; **a**: R^1 = H, R^2 = Me, X = Cl; **b**: R^1 = H, R^2 = Me, X = $MeCO_2$; **c**: R^1 = 5-Me, 5-MeO, 4,5-$(MeO)_2$, H, 5-Cl, 5-Br, R^2 = Et, X = Cl; **d**: R^1 = 5-NO_2, R^2 = Et, X = Cl)



(**3**)

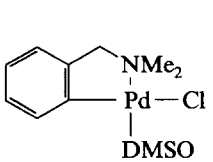
$$+ 2\ H_2C{=}CHC_6H_4Y\text{-}p \longrightarrow$$



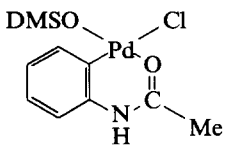
(**4**)

$$+ 2\ Pd^0 + 2\ HX \quad (3)$$

(**a**: R = H, X = Cl; **b**: R = H, X = $MeCO_2$; **c**: R = EtO; X = Cl; **d**: R = MeO; X = Cl; **e**: R = Me, X = Cl; **f**: R = 4,5-Me_2, X = Cl; **g**: R = EtOOC, X = Cl; **h**: R = Br, X = Cl; **i**: R = O_2N, X = Cl)



(5)



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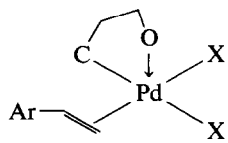


(10)

Experimental

Materials

All *para*-substituted styrenes were commercially available (Koch-Light). Metallation of *N*,*N*-dimethylbenzylamine (Koch-Light) by Pd^{II} acetate to afford di-μ-acetatobis[(2-dimethylaminomethylphenyl-C^1,*N*)palladium(II)] (**1b**) was performed as described previously [7]. The nitro-substituted complex di-μ-chlorobis[(2-diethylaminomethyl-4-nitrophenyl-C^1,*N*)palladium(II)] (**1d**) was obtained using the ligand exchange approach [8]. The enantiomeric complex $[PdCl(S\text{-}C_6H_4CH(Me)NMe_2)]_2$ was synthesised as described [9]. *ortho*-Palladated acetanilides were prepared according to the procedure of Horino and Inoue [4] using chloroform instead of benzene or toluene as solvent. All other chemicals used were essentially the same as in the previous work [3].

Kinetic measurements

These were also done in a similar fashion [3]. The formation of stilbene derivatives **2** and **4** was followed spectrophotometrically (Hitachi 356) at ca. 310 nm. The slightly soluble acetanilide chloro-bridged complexes **3a**, **c**–**i** were added to the reaction medium from the stock solution containing up to 10% dimethylsulfoxide (10^{-3}–10^{-2} *M*). The final content of DMSO in the reaction mixture did not exceed 0.2%. Concentrations of **3** ranged from 10^{-6} to 10^{-5} *M*, but those of styrenes ranged from 10^{-4} to 10^{-2} *M* ensuring pseudo-first order conditions with respect to the palladium species. The $\ln(A_\infty - A)$ versus time plots were usually linear for at least 3 half-lives. The slow reactions were treated by the Guggenheim method.

^1H NMR measurements

^1H NMR spectra of the amine complexes were measured using a Tesla BS 467 (60 MHz) equipped with a temperature control device and a Bruker 200 CXP. Fully deuterated solvents $CDCl_3$ and D_3CCOOD were employed with hexamethyldisiloxane as an internal standard. Similar measurements for acetanilide complexes **3** were precluded due to rapid reaction of **3** and deposition of palladium metal.

Results

N,N-*Dimethylbenzylamine acetato-bridged dimer (**1b**)*

The pseudo-first order rate constants, k_{obs}, were found to be independent of the concentration of **1b** and increased linearly with increase of the styrene concentration. The second order rate constant k_2 has been calculated from these data. The

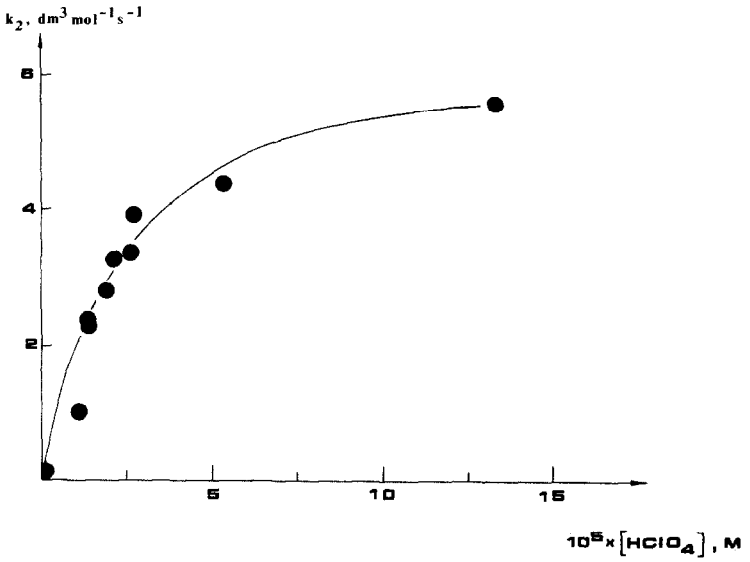


Fig. 1. The dependence of k_2 on the concentration of added $HClO_4$ for **1b**.

profile of strong dependence of k_2 on the $HClO_4$ concentration in Fig. 1 suggests the following rate equation:

$$k_2 = \frac{k_3 K_a + k_H[HClO_4]}{K_a + [HClO_4]} \tag{4}$$

with the values k_3, k_H and K_a summarised in Table 1. Equation 4 is a generalised version of eq. 1. It transforms into eq. 1, when $K_a \gg [HClO_4]$ with $k_4 = k_H/K_a$. The latter ratio in the case of **1b** is 26.2×10^4 dm^6 mol^{-2} s^{-1} and should be compared with the measurement of k_4 as 2.9×10^4 dm^6 mol^{-2} s^{-1} for **1a** [3]. Equation 4 agrees with the earlier proposal [3] that reaction 2 proceeds through two parallel pathways, k_3 and k_H, respectively. Inability to observe the limiting kinetics

Table 1

Kinetic and equilibrium parameters of the acid catalysed reaction of acetato-bridged complexes **1b** and **3b** and monomeric complexes **5** and **6** with styrene at 30 °C

Complex	Solvent	$10^2 \times k_3$ (dm^3 mol^{-1} s^{-1})	k_H (dm^3 mol^{-1} s^{-1})	$10^5 \times K_a$ (mol dm^{-3})	pK_a	k_H/K_a (dm^6 mol^{-2} s^{-1})
1b	HOAc	2.1 ± 0.5	6.8 ± 0.5	2.6 ± 1.3	4.6	2.6×10^5
3b	HOAc	2.06 ± 0.05	0.049 ± 0.003	3.5 ± 1.1	4.5	1.4×10^3
5	HOAc	0.29 ± 0.09				70 ± 7
	DMSO [a]	–				0.002 ± 0.0001
6	HOAc	1.55 ± 0.05				
	DMSO [a]	0.0045 ± 0.0006	0.039 ± 0.005	160 ± 20	2.8	0.24

[a] The rate constants are calculated from the initial rates of the reaction.

Table 2

The second-order rate constants (k_3) of the reaction of acetylanilide complexes **3** with styrene

Complex **3** (ring substituent)	σ_m	Y–$C_6H_4CH{=}CH_2$ Y	σ_p	k_3 ($dm^3\ mol^{-1}\ s^{-1}$)
3a (*H*)	0	H	0	0.027 ±0.001
3a (H)	0	Br	0.232	0.022 ±0.0003
3a (H)	0	Cl	0.227	0.023 ±0.0009
3a (H)	0	Me	−0.170	0.045 ±0.002
3a (H)	0	MeO	−0.268	0.057 ±0.003
3f $(Me)_2$	−0.239	H	0	0.058 ±0.001
3e (Me)	−0.069	H	0	0.033 ±0.02
3c (EtO)	0.1	H	0	0.024 ±0.002
3d (MeO)	0.115	H	0	0.017 ±0.001
3g (EtOOC)	0.37	H	0	0.0074±0.0004
3h (Br)	0.391	H	0	0.0052±0.0003
3i (NO_2)	0.710	H	0	0.0018±0.0003

for chloro-bridged complex **1a** is probably due to the much lower value of pK_a compared to that of **1b**. In the scheme shown below:

$$\text{DIMER} + HClO_4 \rightleftharpoons [\text{DIMER}, HClO_4] \qquad (K_a^{-1})$$

$$\text{DIMER} + \text{alkene} \rightarrow \text{products} \qquad (k_3)$$

$$[\text{DIMER}, HClO_4] + \text{alkene} \rightarrow \text{products} \qquad (k_H)$$

we specify neither a site of acid attack, nor a particular form of perchloric acid that interacts with a dimeric molecule. It should be only noted that the perchloric acid "complex" is 57 times as reactive as the acetic acid one.

*Acetanilide acetato-bridged dimer (**3b**)*

The kinetic behaviour of this compound in the reaction with styrene was essentially the same as that of **1b** with the only important difference being that the catalytic effect of $HClO_4$ was much less. The k_3, k_H and K_a values are summarised in Table 1.

*Reactivity of acetanilide chloro-bridged dimers (**3a, c – i**)*

The reaction between **3a** and styrene in acetic acid as well as in other organic solvents has been the subject of a preliminary communication [10]; it follows second order kinetics. We now report k_2 to have a negligibly small dependence on $[HClO_4]$, and therefore $k_4 \approx 0$ and $k_2 = k_3$. The latter values are given in Table 2. *para*-Substituted styrenes, eq. 3, react according to the same rate law (1) with $k_4 \approx 0$. Rate constants k_3 are independent of acidity and are summarised in Table 2 with the values of k_3 for reactions of ring substituted acetanilide complexes **3c–i** with styrene.

Hammett plots depicting substituent effects in complex **3** and styrene are given in Figs. 2 and 3. Note that in the former case σ_m constants are correlated with log k_3 with slope of -1.57 ± 0.06. Changing the substituents on the styrene molecule similarly reveals a correlation of log k_3 with σ_p, with slope of -0.79 ± 0.15. The negative slopes of these plots indicate that both reagents are formally nucleophiles with respect to each other.

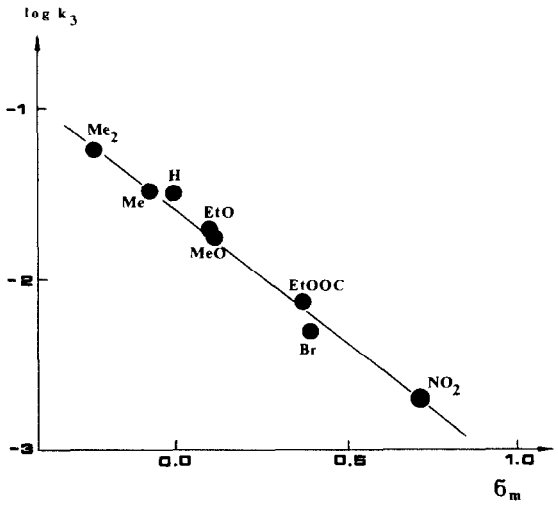


Fig. 2. The Hammett plot of log k_3 versus σ_m for the reaction of substituted complexes **3** with styrene in acetic acid at 30 °C. Data from Table 2.

Kinetic measurements for complexes **1** and **3** were made under slightly different conditions since the latter is only slightly soluble. The reaction mixtures in the case of **3** always contained small amounts of DMSO. The latter might cause rate retardation and loss of sensitivity to acid catalysis due to partial monomerization. UV-Vis spectral changes of **3a** in dioxane, with higher DMSO concentrations (10^{-4}–10^{-3} *M*) showed complexation by DMSO with 1 : 1 stoichiometry. The stability constant of 25 dm^3 mol^{-1} demonstrates a rather weak interaction which probably involves the axial coordination site. Using this value of the equilibrium constant it was calculated that in the kinetic experiments only 2–5% of **3a** contained coordinated DMSO.

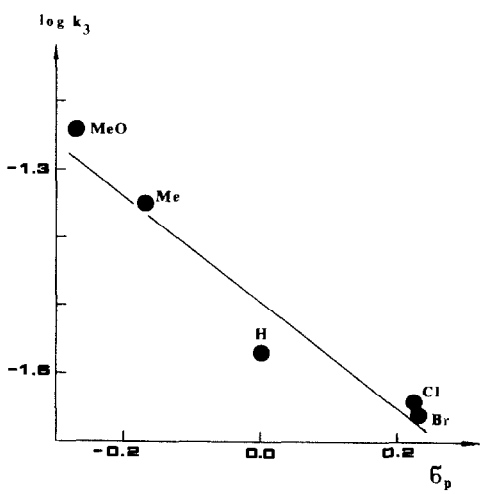


Fig. 3. The Hammett plot of log k_3 versus σ_p for the reaction of **3a** with *para*-substituted styrenes in acetic acid at 30 °C. Data from Table 2.

Substituent effect in N,N*-diethylbenzylamine chloro-bridged complexes (1)*

The Hammett dependence was investigated further when the rate of the reaction between **1d** and styrene was measured at 30 °C with 0.1 *M* $NaClO_4$, to yield the second order rate constant of 0.018 ± 0.001 dm^3 mol^{-1} s^{-1}. This value together with those previously measured [3] for **1c** gave the Hammett equation in the form $\log k_2 = -(0.80 \pm 0.03) - (1.13 \pm 0.09)\sigma_p$.

Behaviour in solution of 1 and related complexes

This spectral work was performed in the hope of observing reversible Pd–N bond breaking in complexes of type **1** in acetic acid solution. An *ortho*-palladated derivative of S–$Me_2NCH(Me)C_6H_5$, the complex $[PdCl(C_6H_4CH(Me)NMe_2)]_2$, has been used as its diastereotopic *N*-methyls would be expected to be a good label for the study of such a reversible process, as they should result in broadening and, perhaps, coalescence of the methyl resonances. We recorded ^1H NMR spectra of the complex in the temperature range 30–85 °C in a $CDCl_3/DOC(O)CD_3$ mixture (1 : 1 by volume) but there were no spectral changes even on addition of $LiClO_4$. Therefore, as in the previous study [11] we conclude that the palladium–nitrogen bond is resistant to reversible cleavage by acetic acid solvent.

We also failed to detect any π complex formation between $[PdCl(C_6H_4CH(Me)NMe_2)]_2$ and styrene via the Pd–N bond or bridge cleavage, though Kurosawa [12] reported such an effect for the dimeric chloro-bridged π-allyl platinum(II) complex. The spectrum of the 1 : 2 mixture of reagents represented a trivial superposition of spectra of the starting materials.

The acetato-bridged dimer **1b** does show dynamic behaviour in acetic acid solvent. A quartet of methylene $ArCH_2N$ protons and two singlets of NCH_3 groups collapses into singlets at higher temperatures, the temperature of the coalescence being identical (60 °C) for both groups. A detailed consideration of this system has, however, revealed [13] these changes to be in better agreement with an acetate-bridge inversion, first studied by Powell [14], rather than with a cleavage of the palladium–nitrogen bond. It should be noted that the rate of the inversion increases in the presence of acidic catalysts, lithium perchlorate in particular.

The ^1H NMR spectrum of **1a** in $CDCl_3$ at 200 MHz showed two *N*-methyls to give signals at δ 2.85 and 2.87 collapsing into a singlet at δ 2.88 on addition of $DOC(O)CD_3$. The two signals from *N*-methyls may be caused by a minute non-planarity of either the five-membered palladacycle of **1a** or the $Pd(\mu\text{-}Cl)_2Pd$ fragment. The former case was in fact observed by X-ray crystallography in the related benzylamine complex [15]. The coalescence may thus arise from either Pd–N bond rupture, or from partial bridge cleavage. The latter hypothesis is supported by the fact that the same spectral changes are caused by addition of pyridine-d_5 to a solution of **1a** in $CDCl_3$, i.e. due to the monomerisation of the dimer. It is clear that the experiments described do not also reveal the true reason for the coalescence, since even monomerisation by py-d_5 may also induce a conformational change of the five-membered palladacycle.

Reactions of monomeric ortho*-palladated complexes (5 and 6)*

We have studied the reaction of *ortho*-palladated complexes **1a** and **3a** with styrene in pure dimethylsulfoxide, where the complexes exist as monomers with coordinated DMSO (**5**, **6**) [16]. This permits comparison of the sensitivity to acid

catalysis of the corresponding monomeric and dimeric species. Complex **5** showed no reaction with styrene in the absence of perchloric acid, while **6** reacted at a significant rate [10]. The reaction of both complexes was catalysed by perchloric acid and the rate constants are given in Table 1. The susceptibility of **6** to acid catalysis was much greater than that of **5**.

The reaction of monomeric species **5** and **6** was also studied in acetic acid. The DMSO content in this case was about 10–15% and UV-Vis spectra showed no maximum in the 340–320 nm region that is characteristic for dimeric complexes [10]. For both complexes, the reaction is much faster in HOAc than in DMSO but slower as compared with the corresponding dimers. At the same time the sensitivity to perchloric acid catalysis is much greater for **5** than for **6** (Table 1).

Discussion

General remarks

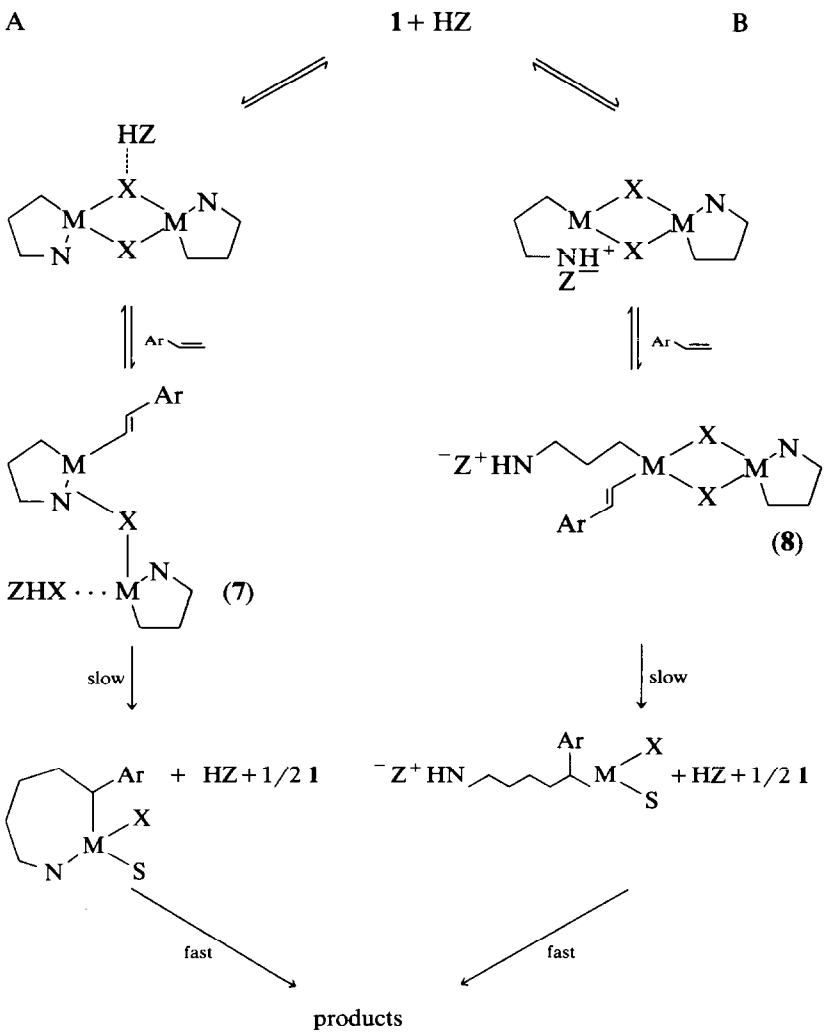
The present investigation confirms that *ortho*-palladated complexes react with styrene via acid catalysed and uncatalysed pathways. The former is the only way to react for complexes **1** since the reaction needs the presence of acetic or perchloric acid. Measurements of the kinetic isotope effects have revealed that in both paths the styrene C–H bond is cleaved rapidly after the rate-limiting insertion of alkene into the palladium–carbon bond [3].

Acid catalysed pathway

Reactivity patterns of the acetato-bridged compound **1b** gave more information than the chloro-bridged counterpart **1a**, since in the latter case no saturation in the acid was found and the value of K_a could not be determined. The fact that an electrophilic species, $HClO_4$ in particular, increases the rate of the reaction, which at the same time is facilitated by electron-rich ring substituents (the Hammett ρ value is -0.80 for **1c,d**), may imply a complicated mechanism where the action of the acid and the electronic effects govern different steps. We have already indicated [3] that $HClO_4$ favours π-complex formation between palladium(II) species and styrenes, though the driving force is unknown [17]. Therefore, we conclude that acid catalysis should be associated with an intermediate formation of π-complex. Interaction of the dimeric palladium species with electrophilic $HClO_4$ molecule would increase acceptor properties of the metal centre increasing its ability to coordinate styrene, since this process is controlled by the ligand-to-metal charge transfer [18]. The question thus arises what particular site of the metallacycle is subject to acid attack. We failed to obtain direct evidence from the ^1H NMR data as the results may be interpreted in terms of the protonation of either bridging ligands or the Pd–N bond. That is why the information may be extracted only from the comparison of the kinetic data obtained.

We have found that monomeric complexes **5** and **6** retain their susceptibility to acid catalysis in DMSO solvent while in acetic acid only the reaction of **5** is catalysed by $HClO_4$. At the same time no interaction of **5** with styrene was detected in the absence of acid ($HClO_4$ or HOAc), while such a 'solvolytic' reaction takes place for **6** as well as for **3a**. The reaction of the monomeric complexes is much slower than that of their dimeric analogues. The retardation may arise from DMSO coordination causing loss of electrophilicity of palladium(II) and elimination of the

bridging structure. These two effects cannot be studied independently. The only site of protonation of *ortho*-palladated acetanilide complexes **3** is the chloro- or acetato-bridging ligands, since the chelate arm is of too weak basicity [19]. Therefore, acid catalysis, when observed for acetanilide complexes **3**, is concerned only with the protonation of the bridging ligands. Note that the catalysis of **3** is much less pronounced than that of complexes **1**. In the case of **6**, the acid catalysis with $HClO_4$ is seen only in DMSO, not in HOAc, while the reaction of **6** in pure acetic acid is much faster than in DMSO. This means that acetic acid also catalyses the reaction and the acidic saturation is already achieved in this solvent. The same is probably true for **3a**. On the other hand, the reaction of **3b**, which has more basic bridging ligands, did show some perchloric acid catalysis in HOAc and the calculated pK_a value was close to that found for **1b**. The catalytic effect was, however, weaker by a factor of 140. The fact that the pK_a values for **1b** and **3b** coincide means that the



Scheme 1

groups protonated are of similar basicity. Hence, the measured pK_a values may be attributed to the bridging acetates. The "bridging" mechanism of the acid catalysed path of reaction 2 (Scheme 1, path A) finds additional support in other related systems where the reactivity of alkenes [3,20] or alkynes [21] towards cyclopalladated compounds with and without bridging ligands have been studied. A higher reactivity of the former compounds appears to be the rule. Additional less direct evidence for the bridging mechanism can be as follows: if there are both amino and acetato ligands present in the coordination sphere of platinum(II), the latter rather than the former accept proton [22]. Heck et al. have demonstrated that the reactivity of *ortho*-palladated azobenzene toward alkynes increases dramatically on treatment of the chloro-bridged dimer with $AgBF_4$ [23]. This may be considered as an alternative to acid catalysis aimed at the bridging ligands (Scheme 1, path A).

At the same time comparison of the catalytic sensitivity and the values of k_4 for the chloro-bridged as well as for the monomeric complexes shows that there is another pathway for **1** which involves cleavage of the chelate arm (Scheme 1, path B). The existence of this is confirmed also by the Hammett correlation of log k_4 with σ_p for **1** while the log k_3 values for **3** correlate with σ_m. For both pathways protonation is followed by styrene coordination to palladium, in *cis*-position to the Pd–C bond. The next step involves the rate-limiting insertion of styrene into the Pd–C bond since "in plane" alkene coordination is already achieved both in **7** and **8**. The subsequent migration of the phenyl group to alkene β-carbon proceeds as a concerted process [3].

In summary, the "bridging" mechanism of acid catalysis (Scheme 1, path A) seems to operate for both acetanilide and benzylamine complexes, while the "chelate" mechanism (Scheme 1, path B) is realised only for benzylamine complexes where it affects a great acceleration of alkene insertion.

"Solvolytic" pathway

Complexes **1** do not react with styrenes in aprotic solvents without acetic or perchloric acid. Therefore, the k_3 pathway for **1** is also acid catalysed. It should be pointed out that, in contrast to reaction 2 occurring only in the presence of acidic reagents, reaction 3 proceeds in various organic solvents permitting separate analysis of the solvation of both initial and transition states [10]. Figure 4 shows the effects of solvation of initial ($\delta\mu^0$) and transition ($\delta\mu^{\ddagger}$) states for the reaction of **3a** and styrene. Applying the approach previously discussed in detail [24], we plotted the Gibbs transfer functions $\delta\mu^0$ and $\delta\mu^{\ddagger}$ against empirical solvent parameters. The best fit equations are:

$$\delta\mu^0(\text{kJ mol}^{-1}) = -(0.3 \pm 0.5) - (0.15 \pm 0.03)\text{DN}(\text{kJ mol}^{-1}) - (16.3 \pm 4.6)\pi^{\star} \quad (5)$$

$$\delta\mu^{\ddagger}(\text{kJ mol}^{-1}) = -(4.6 \pm 2.5) - (6.1 \pm 0.9)\pi^{\star} \quad (6)$$

where DN and $\pi^{\star}$ are the Gutman donor numbers [25] and the Kamlet–Taft parameters of solvent polarity [26], respectively. Equations 5 and 6 show that the initial state and the transition state are stabilised by polar solvents. Donor properties of the solvent do not play a significant role in solvating the transition state, but their contribution to stabilising the initial state reaches 58% (calculated according to ref. 27). The latter effect is not unexpected since donor molecules can stabilize

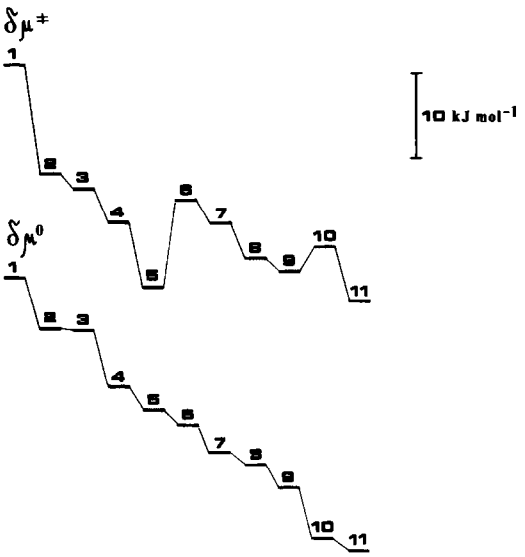
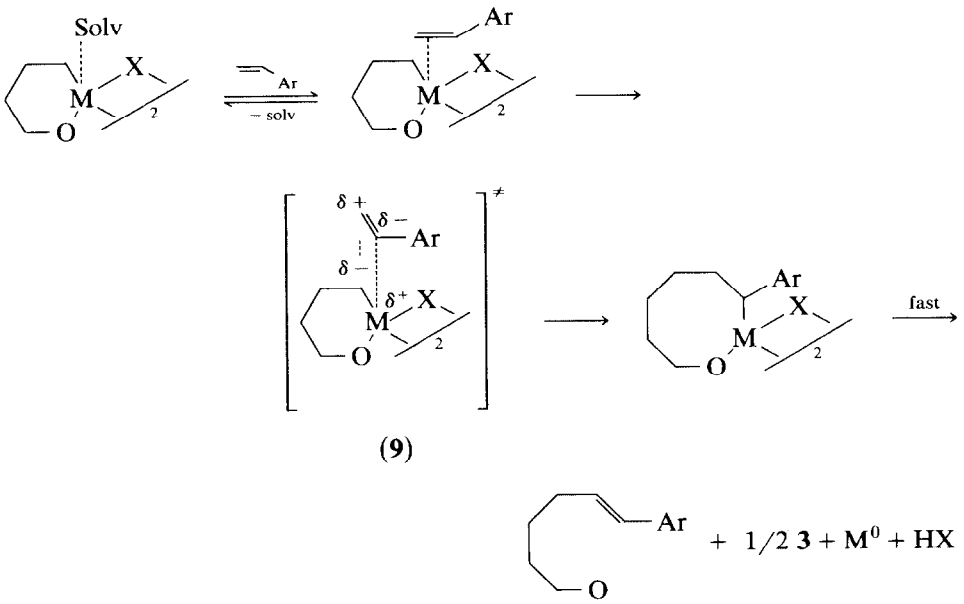


Fig. 4. The transfer functions of initial ($\delta\mu^0$) and transition ($\delta\mu^{\ddagger}$) states of the reaction of **3a** with styrene in different solvents (n-heptane as a reference solvent): 1 = n-heptane, 2 = benzene, 3 = carbon tetrachloride, 4 = acetic acid, 5 = chloroform, 6 = ethyl acetate, 7 = methanol, 8 = dioxane, 9 = acetonitrile, 10 = DMF, 11 = DMSO.

square planar d^8 complexes through the fifth axial site [28]. The absence of the corresponding term from eq. 6 suggests that this site may already be occupied by an alkene molecule in the transition state; in other words, styrene is apically coordinated in the activated complex. It means that insertion can occur without preliminary 'in-plane' coordination, i.e. one can speak of a nonmigratory [1,2] mechanism of alkene insertion in the case of amide complexes **3**. The absence of the DN contribution to $\delta\mu^{\ddagger}$ may also be explained by a solvent or styrene induced reversible cleavage of a rather weak palladium–oxygen bond in **3**. If solvents in fact cleave the Pd–O bond and the solvent molecule is then substituted by styrene in the transition state, 'in-plane' coordination of the aryl group and styrene would be achieved. The axial site could be occupied by the amide oxygen permitting the restoration of the Pd–O bond and exclusion of a solvent molecule from the transition state. Migration of the aryl to styrene β carbon in **10** can then occur. A very similar mechanism was recently proposed for insertion of hexafluorobut-2-yne into the Ni–C bond of cyclonickelated 2-dimethylaminotoluene [29]. Some of our results support this idea too. In particular, the substituent effects can readily be explained by assuming that alkene will insert into the Pd–C bond from the apical position in a concerted way via the four-centred cyclic transition state as shown in Scheme 2. If the charge distribution is as shown in **9**, development of a partial negative charge on the α alkene carbon arising from electron donating *para*-substituents in styrene will favour interaction with the metal centre, while a negative charge on the phenyl carbon will make a nucleophilic attack on the β alkene carbon accounting for the correlation of log k_3 with σ_m shown in Fig. 2. Such a highly ordered transition state would be in agreement with the rather low activation enthalpy, $\Delta H^{\ddagger}$, of 35 kJ mol^{-1} and highly negative activation entropy, $\Delta S^{\ddagger}$, of -159 J K^{-1} mol^{-1} in the



Scheme 2

reaction of **3a** and styrene calculated from the temperature dependence of k_3 in the range 20–40 °C.

In conclusion, both acetato-bridged *ortho*-palladated derivative of *N*,*N*-dimethylbenzylamine **1b** and acetanilide **3b** react via the acid catalysed pathway, which is particularly significant for the former complex. The latter reacts with styrene in the absence of any acid. Its uncatalysed path may involve no Pd–O or Pd–Cl bond cleavage and styrene is inserted into the palladium–carbon bond either from axial position or after the substitution of chelated oxygen by styrene followed by phenyl migration.

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