Kinetics and Mechanism of Vinylation of ortho-Palladated **NN-Dialkylbenzylamines by para-Substituted Styrenes †**

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> The kinetics of vinylation of ortho-palladated NN-dialkylbenzylamines (1a-g) by CH₂=CHC₆H₄R³-p (R³ = H, Cl, Br, Me, and MeO) to form the respective 2-dialkylaminomethylstilbenes (2) has been studied mainly at 30 °C in acetic acid solvent. The reaction follows second-order kinetics: d[(2)]/dt = $k_2[(1)]$ [styrene]. The rate constants k_2 increase markedly in the presence of both alkali-metal per-chlorates (MCIO₄) and small concentrations of perchloric acid, k_2 being directly proportional to [HCIO₄]. It is shown that the salt effect originates from the solvolytic reaction MCIO₄ + HOAc - MOAc + $HClO_4$. Conversion of dimer (1a) into the respective monomer (3) stops the reaction, but the latter species readily forms π -complexes with styrenes. The stability constants of 1:1 π -complexes have been determined and their Hammett correlation with a slope of -1.87 is established. For a series of substituted styrenes $\lg k_2$ is the linear function of Hammett σ_p values with a slope of ca. -1. For a series of ring-substituted complexes (1) $\lg k_2$ correlates with the pK_a of the parent benzylamines with a slope of 0.98. The results are interpreted in terms of a mechanism involving intermediate protonation of (1), π -co-ordination of alkene, and subsequent rate-determining intramolecular insertion of styrene into a Pd-C bond through a four-centred transition state.

Cyclometallation and reactions of cyclometallated compounds have recently received considerable attention.1 Complexes with palladocycles are of unique importance, since they appear to be valuable intermediates for regioselective carbonylation,² vinylation,³ alkylation,^{4,5} halogenation,⁶ and phosphination 7 of organic moieties. In all these reports attention has been focused on the synthetic aspects of the reactions. Little if any effort has been expended on the systematic investigation of the reaction mechanisms on the basis of kinetic data. In this paper we report the first results of a kinetic study of the vinylation of ortho-palladated NN-dialkylbenzylamines by para-substituted styrenes in acetic acid solvent [reaction (1)]. Reaction (1) is of interest not only as an example of the conversion of cyclopalladated complex. It may also serve as a good model for arylation of olefins both by arenes and organometallic compounds in the presence of palladium salts.⁸ since it is known⁹ that the rate-determining step in these reactions is the formation of unstable arylpalladium intermediates. The subsequent interaction of arylpalladium species with alkenes is fast and it is impossible to study this step by direct kinetic methods. The presence of the stable Pd-C bond in (1) provides a good opportunity to investigate not only olefin insertion processes, but also other fast steps of various palladium-catalysed reactions.10

Results

The Rate Law.---It has been demonstrated in the preceding paper¹¹ that under the synthetic conditions used the interaction between (1a) and styrene under argon in the presence of 0.1M-NaClO₄ gives 2-dimethylaminomethylstilbene in a 57% yield. Under kinetic conditions, e.g. at low concentrations of (1a) $(10^{-6}-10^{-4}M)$ and at least a 20-fold excess of styrene $(10^{-4}-10^{-1}M)$ in pure acetic acid under argon, the yield of (2) usually exceeds 80%, providing a convenient system for kinetic study.

The dimeric compounds (1) do not dissociate to form monomeric complexes in the chosen concentration range, as is evident from the constancy of the extinction coefficients of the former.¹² The reaction was found to be first order in (1), and the observed pseudo-first-order rate constants were linear functions of alkene concentration [equation (2)]. Thus

$$k_{\rm obs.} = k_2[\text{styrene}] \tag{2}$$

$$d[(2)]/dt = k_2[(1)]$$
 [styrene] (3)

the complete rate expression can be written as (3). The k_2 values obtained under various conditions together with the

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Figure 1. A plot of k_2 versus salt concentration for the reaction of (1a) with styrene at 30 °C: \bigcirc , LiClO₄; \bigcirc , NaClO₄; \triangle , Mg(ClO₄)₂; and \diamond [Buⁿ₄N]ClO₄



Figure 2. A plot of k_2 versus [LiOAc] at a fixed concentration of LiClO₄ (0.01m) for the reaction of (1a) with styrene at 30 °C

respective activation parameters $(\Delta H^{\ddagger}, \Delta S^{\ddagger})$ are collected in Table 1.

The Effects of Salts and Acid.—It has been found previously ¹¹ that addition of alkali-metal perchlorates strongly reduces the reaction time. Figure 1 shows the dependence of k_2 on salt concentration. The considerable rate enhancement reaching two orders of magnitude is evident. The effect of salt depends on the nature of the cation, Mg²⁺ being the most effective and Buⁿ₄N⁺ the least. The strong salt effect exists, however, only in acetic acid solvent. The reaction is not accelerated by LiClO₄ (up to 0.175M) or [Buⁿ₄N]ClO₄ in aprotic dioxane or protic, but less acidic than acetic acid, methanol. In both solvents the reaction rate is extremely low even in the presence of salts or at elevated temperatures and cannot be measured reliably.

Lithium acetate exhibits very little effect on the reaction



Figure 3. The dependence of k_2 on the concentration of added HClO₄ (\triangle) and the data of Figure 1 recalculated to plot k_2 against [HClO₄], the latter liberated in solvolytic reaction (4), for the reaction of (1a) with styrene: O, LiClO₄; \bullet , NaClO₄

rate in the absence of LiClO₄. However, addition of LiOAc to a 0.1M solution of LiClO₄ decreases the rate (Figure 2), k_2 being inversely proportional to the LiOAc concentration.

Taking into account these observations we assume that the salt effect results from the solvolysis of metal perchlorates $(MClO_4)$ in acetic acid to form strong perchloric acid, the latter being responsible for the catalytic effect [equation (4)].

$$MClO_4 + HOAc \Longrightarrow HClO_4 + MOAc (K_M) \quad (4)$$
$$M = Li, Na; K_M = [HClO_4][MOAc]/[MClO_4]$$

In order to verify this assumption we have studied the effect of small concentrations of HClO₄ on the rate of reaction (1). The second-order rate constant k_2 was found to be directly proportional to the concentration of HClO₄ according to equation (5) (Figure 3) where $k_3 = k_2$ in the absence of salt

$$k_2 = k_3 + k_4[\text{HClO}_4]$$
 (5)

or HClO₄ and $k_4 = 2.9 \times 10^4 l^2 \text{ mol}^{-2} \text{ s}^{-1}$ at 30 °C. Perchloric acid catalyses the reaction not only in HOAc, but in those solvents where the reaction is unmeasurably slow in the absence of acid, *e.g.* in dioxane and methanol. In these two solvents the reaction rate follows equation (5) with k_4 equal to 39.7 and 1.79 l² mol⁻² s⁻¹ at 30 °C, respectively, but k_3 is close to zero in both solvents.

Some other salts have also been tested, but none of them catalyses the reaction as metal perchlorates do. For instance, lithium chloride inhibits the reaction completely due to the cleavage of chloro-bridges of (1a) to form the unreactive anionic complex (3).¹³ It is interesting to note that (1a) does not react with LiCl in methanol. However, addition of catalytic quantities of HClO₄ leads to the cleavage of chloro-bridges to give (3). In the presence of LiNO₃ a process similar to that in the case of LiCl proceeds, but since it does not result in the enhancement of the rate of reaction (1) we have not studied this interaction in detail.

Substituent Effects.—Figure 4 shows the plot $\lg k_2$ versus Hammett constants σ_p for the reaction of (1a) with parasubstituted styrenes at [NaClO₄] 0.1M. A satisfactory linear plot is observed with slope ρ^{R^3} -1.06. In the absence of salt,

Table 1. The second-order rate constants k_2 and the activation parameters of reaction (1) in the absence and in the presence of salt (0.1M) in acetic acid solvent ^a

A 1	CH₂CHC6H4R3-p					
(1a)	R3 H	T/K 298 303	Salt	$k_2/1 \text{ mol}^{-1} \text{ s}^{-1}$ 1.1 × 10 ⁻² 1.3 × 10 ⁻²	$\Delta H^{\ddagger}/kJ mol^{-1}$	$\Delta S^{\ddagger}/J \text{ K}^{-1} \text{ mol}^{-1}$
		308 318		1.8×10^{-2} 2.3×10^{-2}	26.8	- 192
		293 298 303 308	NaClO4 NaClO4 NaClO4 NaClO4 NaClO4	0.32 0.62 0.84 1.3	16.1	- 190
		303 303 303	LiClO4 Mg(ClO4)2 Bu4NClO4 ^b	0.91 1.7 0.35		
	Br	303		9.3×10^{-3}		
		293 303 308 318	NaClO4 NaClO4 NaClO4 NaClO4 NaClO4	0.51 0.62 1.1 1.7	37.0	- 124
	Cl	303		7.7×10^{-3}		
		293 303 313	NaClO₄ NaClO₄ NaClO₄	0.53 0.75 1.3	31.8	- 141
	Me	303		2.9×10^{-2}		
		293 298 303 318	NaClO₄ NaClO₄ NaClO₄ NaClO₄	1.2 1.3 1.9 2.2	27.8	- 148
	OMe	298 303 313		$\begin{array}{c} 5.0 \times 10^{-2} \\ 6.9 \times 10^{-2} \\ 1.1 \times 10^{-1} \end{array}$	37.8	- 143
		293 298 303	NaClO₄ NaClO₄ NaClO₄	1.9 2.1 2.2	9.8	- 206
(15)	Н	303	NaClO₄	0.18		
	Br	303	NaClO ₄	0.09		
	Cl	303	NaClO₄	0.09		
	OMe	303	NaClO₄ NaClO₄	0.19		
(1c)	Н	303	NaClO ₄	0.27		
(1d)	Н	303	NaClO₄	0.28		
(1e)	н	303	NaClO ₄	0.19		
(1f)	н	303	NaClO ₄	0.11		
(1g)	H	303	NaClO ₄	0.16		
Errors in κ_2 and	Δn + are 5—10%,	ш д 5 + 10—20%	. ⁻ U.U8M.			

when the reaction rate is much lower, the slope is more negative $(\rho^{R^3} - 1.26)$. The analogous plot is observed for the reaction of (1b); at [NaClO₄] 0.1 M the slope is equal to -0.86. The lengthening of the alkyl chain at the nitrogen donor atom of (1) retards the reaction rate slightly (Table 1). However, the unambiguous discrimination between electronic and steric effects might be misleading in the light of recent work.¹⁴

The variation of ring substituents in complexes (1b-f) results in little change in k_2 . No straightforward correlation

has been found when lgk_2 values are plotted against σ_m Hammett constants, but in general, electron-donating ring substituents favour the reaction. A clear correlation exists between lgk_2 and the basicity of substituted benzylamines (Figure 5) with a slope of +0.98.

Kinetic Isotope Effects.—The ratios $k_2^{\text{PhCHCH}_2}/k_2^{\text{PhCHCD}_2}$ have been measured at three different NaClO₄ concentrations, 0.00, 0.015, and 0.0744M. The respective values are 1.15, 1.01,



Figure 4. A Hammett plot of $\lg_2 versus \sigma_p$ for the reaction of (1a) with *para*-substituted styrenes at [NaClO₄] 0.1M and 30 °C. The data are from Table 1



Figure 5. The effect of substituents in (1). The correlation of \lg_{k_2} with pK_a of ring-substituted benzylamines, taken from ref. 39

and 1.06. These quantities show that the cleavage of the C-H bond of alkene is not involved in the rate-determining step.

π-Complex Formation of Styrenes with Mononuclear Species (3).—As mentioned above the monomeric complex (3) could not be converted into (2). However, addition of styrene $(10^{-3}-10^{-1}M)$ to a solution of (3) in HOAc $(10^{-4}-10^{-5}M)$ results in a change of spectrum (Figure 6) due to π-complex formation. The change of absorbance, ΔA , as a function of alkene concentration has been fitted to equation (6) for 1 : 1 complex formation. In equation (6) $\Delta \varepsilon = \varepsilon_{\pi} - \varepsilon$; ε_{π} and ε are the extinction coefficients of the π-complex and of the starting



Figure 6. The spectral changes on addition of *p*-methoxystyrene to the solution of (3) in HOAc: (a) the spectrum of (3) in HOAc; (b) the spectrum of (3) in the presence of 6.3×10^{-3} M of *p*-methoxy-styrene: 30 °C, [(3)] 2.85 × 10⁻⁴M



Figure 7. The Hammett correlation of stability constants K_{π} of monomeric π -complexes. The data from Table 2

$$\frac{\Delta A}{[(3)]_0} = \frac{\Delta \varepsilon \ K_{\pi}[\text{styrene}]}{1 + K_{\pi}[\text{styrene}]}$$
(6)

complex, respectively. At high LiCl concentration $(8 \times 10^{-2} - 0.15 \text{ M}) \Delta A$ is inversely proportional to [LiCl], but addition of LiCl over the concentration range close to [(3)] has no effect on ΔA . These observations indicate that in dilute solutions (3) dissociates according to equation (7) where L is the cyclo-

$$(3) \rightleftharpoons LPdCl + LiCl$$
(7)

palladated ligand, and styrene interacts further with LPdCl [equation (8)]. Intermediate complex LPdCl probably con-

LPdCl + styrene
$$\swarrow^{K_{\pi}}$$
 LPdCl(styrene) (K_{π}) (8)

tains co-ordinated solvent molecule. The stability constants K_{π} are given in Table 2. They show a good Hammett correlation with a slope -1.87 (Figure 7).

Addition of small concentrations of HClO₄ to the mixture of

Table 2. The stability constants of monomeric π -complexes derived from (3) [equation (8)] in acetic acid solvent

$CH_2CHC_6H_4R^3-p$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		$K_{\pi}/$	•
R	T/K	[HClO₄]/M	I mol	λ_{max}/nm
н	303		50	340
Br	303		21	350
Cl	303		23	360
	303	2.7×10^{-4}	40	
	303	8.0×10^{-4}	47	
	303	1.3×10^{-3}	106	
Me	303		98	380
OMe ^b	298		260	440
	303		234	
	308		220	
	318		204	
The error in K_{π} is ol^{-1} .	5—10%.	$^{b}\Delta H^{\circ} - 9.2 \text{ kJ}$	mol ^{−1} , ΔS	° 15 J K⁻¹

(3) and styrene does not induce the type (1) reaction and has no effect on π -complex stability. However, an increase [HClO₄] enhances K_{π} values (Table 2).

Discussion

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The most remarkable feature of reaction (1) is the unprecedently high positive salt effect, induced by addition of metal perchlorates. Qualitatively it seems reasonable to ascribe this effect to acid catalysis by perchloric acid liberated in solvolytic reaction (4), as was suggested previously ¹⁵ to account for the effect of salts in mercuriation of arenes by Hg(OAc)₂ in acetic acid. To verify the proposal quantitatively one should recalculate the data of Figure 1 on the basis of equation (4) to plot k_2 against [HClO₄], the latter formed in the presence of alkali-metal perchlorates. The appropriate equilibrium constants $K_{\rm M}$ were calculated according to equation (9), where $pK_{\rm a}^{\rm HOAc} = 14.45$, $pK_{\rm a}^{\rm HClO_4} = 4.87$; dis-

$$K_{\rm M} = K_{\rm a}^{\rm HOAc} K_{\rm d}^{\rm MCIO_4} / K_{\rm a}^{\rm HCIO_4} K_{\rm d}^{\rm MOAc}$$
(9)

sociation constants for MClO₄ $pK_d^{\text{LiClO_4}} = 5.11$ and $pK_d^{\text{NaClO_4}} = 5.73$, and those for MOAc $pK_d^{\text{LiClO_4}} = 6.87$ and $pK_d^{\text{NaOAc}} = 6.58$. The equilibrium constants (in acetic acid solvent) of acids and salts were taken from refs. 16 and 17, respectively. The resulting values are $K_{\text{Li}} = 1.51 \times 10^{-8}$ and $K_{\text{Na}} = 4.27 \times 10^{-9}$ mol l⁻¹. The plot of k_2 , taken from Figure 4, against [HClO₄], calculated using these K_{M} constants, is presented in Figure 3. A satisfactory agreement is evident between calculated and directly obtained dependences.

The catalytic effect of salts depends on the nature of the cation, and according to our treatment, this dependence should be governed by $pK_d^{MCIO_4}$ and pK_d^{MOAc} of the respective salts. Unfortunately, there are no appropriate data for Mg^{2+} and $Bu^{n}_4N^+$ cations.

The inhibition of the reaction by LiOAc (Figure 2) appears to be another quantitative argument to support our interpretation. Combination of equations (4) and (5) gives equation (10). It is seen from equation (10) that at low concentrations of

$$k_2 = k_3 + k_4 K_{\rm M} [\text{LiClO}_4] / [\text{LiOAc}]$$
(10)

LiClO₄, when k_2 is approximately a linear function of [LiClO₄], the reaction rate should be inversely proportional to [LiOAc]. The data presented on Figure 2 are in full accord with these considerations.

Equation (5) shows that reaction (1) proceeds through two parallel pathways, one of which is 'solvolytic' (k_3) and the

other an acid-catalysed process (k_4) . Both paths have general features in common, *e.g.* rate law, substituent effects, kinetic isotope effects, and similar values for activation parameters. These findings suggest similar mechanistic patterns for 'solvolytic' and acid-catalysed pathways. The similarity arises probably from the ability of acetic acid solvent to act as a general acid catalyst in the reaction. Thus it becomes clear why acetic acid is the best solvent for reaction (1).

Consider now the mechanistic features of the reaction. The acid catalysis may arise from protonation of (1) or the styrene molecule. In the latter case the carbenium ion $\operatorname{ArCHCH_3}^+$ should be formed according to the Markovnikoff rule. It might attack the negatively charged carbon of the Pd-C bond of (1). However, one would expect the formation of 1,1-diphenylethylenes rather than stilbenes in this case. Since stilbene derivatives are the main products ^{11,18} and a 1,1-diphenylethylene-type compound is formed only as a by-product in very low yield in the case of *o*-chlorostyrene,¹⁸ a route with alkene protonation is hardly acceptable.

Protonation of (1) should enhance the reaction rate, since it leads to an increase of the positive charge on Pd¹¹, and in general, the attack of the metal centre on alkene is an electrophilic process. Complex (1) has three possible sites of protonation: chloro-bridges, the nitrogen donor atom, and the metal centre. The protonation of the latter has been involved to account for the acid-catalysed substitutions at Pt¹¹.¹⁹ Though it is guite reasonable in the case of Pt¹¹ this mechanism, however, seems to be rather improbable for Pd¹¹. We prefer the chloro-bridges as the site of proton attack on the basis of the reasons stated below. (i) The rupture of the Pd-N bond as a result of protonation of the nitrogen donor appears unnecessary for the insertion of unsaturated molecules into the Pd-C bond of type (1) complexes. This is strongly supported by reactions of (1a) with some alkynes, which proceed under mild conditions in the absence of any reagent able to cleave a Pd-N bond.²⁰ (ii) Dechelation leads in some cases to the protonolysis of the Pd-C bond with concomitant dissociation of the NN-dimethylamine ligand.¹³ (iii) The monomeric complexes (3) and (4) without chloro-bridges are completely inert with respect to styrenes even in the presence of MClO₄, although they both have Pd-N fragment. (iv) HClO₄ promotes the cleavage of chloro-bridges of (1a) by LiCl to form (3) in methanol solvent. It is reasonable to assume that H⁺ attacks a bridging chloride since in the case of protonation of the nitrogen donor the transformation of the palladocycle seems to be more probable. Moreover, chloride appears to be as basic as tertiary amines in acetic acid solvent. In particular, the pK_a value of HCl is 8.55 and that of tribenzylammonium ion is 9.07.16 Protonation of (1) is also consistent with the observed correlation between k_2 and amine basicity (Figure 5). The additional negative charge on nitrogen could be transferred to chloride, as was exemplified recently in the mercuryassisted aquation of cis-CoCl(en)₂(X-py)²⁺ through a Hg-ClCo(en)₂(X-py)⁴⁺ intermediate.²¹ A linear plot of lgk versus pK_a^{X-py} with a slope of 0.5 has been found. We believe that in our case a similar correlation is manifest in facilitating protonation of bridging chloride provided by the increase in benzylamine basicity.

The detection of styrene π -complexes in the case of monomeric species (3) suggests that an intermediate π -complex formation may be involved in reaction (1). On the other hand, we have not registered any π -complexes in the case of dimers (1). These findings have a close analogy with complex formation in the palladium(II) acetate system. The trimer Pd₃(OAc)₆, which contains bridging acetates only, does not form detectable olefin π -complexes, while the dimer Na₂Pd₂-(OAc)₆ with four terminal acetates co-ordinates olefins



 $El = HOAc (k_3 \text{ path}), HClO_4 (k_4 \text{ path})$

readily.^{22,23} At the same time both trimer and dimer react with unsaturated compounds to form oxidation products through intermediate π -co-ordination.^{23,24} In our case, (1), with bridging chlorides only, could be much less effective with respect to π -complex formation compared to monomer (3), which has terminal chlorides, but nevertheless form an unstable intermediate π -complex in reaction (1).

The enhancement of the stability of π -complexes in the presence of HClO₄ (Table 2) could account for the acid catalysis in reaction (1). The absence of any effect on the stability constants K_{π} at [HClO₄] comparable with [(3)], results from neutralization of HClO₄ by Cl⁻ ions, released upon dissociation of (3). At higher HClO₄ concentrations K_{π} is approximately a linear function of [HClO₄], but the catalytic effect of the latter is much weaker compared with that in reaction (1) (*cf.* Figure 3).

On the basis of all the results obtained a mechanism of the reaction could be proposed [steps (11)-(14)].

The first step is the reversible protonation of chlorobridges of (1) by acetic $[k_3$ path, equation (5)] or perchloric acid (k_4 path), leading to the increase of the positive charge on palladium(II). The resulting complex (5) in fact might be mono-bridged with a vacant co-ordination site on one of the Pd¹¹ centres. Mono-bridged cyclopalladated compounds are known.²⁵ Evidently, intermediate (5) could form a π -complex more readily compared with starting complex (1). So the next step (12) is alkene co-ordination to afford the π -complex (6) with styrene *cis* to the palladium-carbon bond. This type of equilibrium is generally accepted for olefin insertion reactions.²⁶ A similar situation has been observed, for example, in the reaction of (1a) with isonitriles.²⁷ We consider step (12) to be a fast equilibrium, because in the related system coordination of styrenes with (3) proceeds almost immediately after mixing of the reagents.

The rate-limiting insertion (13) through the transition state (7) follows π -co-ordination. The final β -hydrogen abstraction (14), with subsequent reduction of Pd¹¹, should be fast, since no deuterium kinetic isotope effect has been found in the reaction with $\beta\beta$ -dideuteriostyrene.

Although the proposed mechanism seems to be probable,

we cannot exclude completely the alternative path with protonation of nitrogen donor atom of (1).

Apparently, in terms of the proposed mechanism, the rate constants k_3 and k_4 are composite, $k_3 = K_{11}K_{12}k_{13}$ and $k_4 = K_{11}'K_{12}'k_{13}'$, where the prime denotes the HClO₄-catalysed pathway. Thus, for the k_3 path we obtain equation

$$\Delta H_{3}^{\ddagger} = \Delta H_{11}^{\circ} + \Delta H_{12}^{\circ} + \Delta H_{13}^{\ddagger}$$
(15)

(15) for the activation enthalpy. Taking into account the fact that the enthalpies of protolytic equilibria are usually close to zero ²⁸ one can estimate ΔH_{13}^{\ddagger} 47 kJ mol⁻¹ in the case of *p*-methoxystyrene with the assumption $\Delta H_{12}^{\circ} = \Delta H_{\pi}^{\circ}$, the latter value being taken from Table 2. This rather low value of ΔH_{13}^{\ddagger} is in good agreement with the concerted mechanism of insertion through a transition state of type (7).

Now we turn to Hammett-type correlations. The effect of substituents in styrene is the sum of two components for both k_3 and k_4 paths [equation (16)]. The ρ_{12} value cannot be

$$\rho = \rho_{12} + \rho_{13} \tag{16}$$

measured directly, and we assume that $\rho_{12} = \rho_{\pi}$ [equation (8)]. We have obtained $\rho_{\pi} - 1.87$ and this negative value is in agreement with those previously reported by Powell²⁹ (-0.54 for σ^+) and Kurosawa³⁰ (-1.14 to -0.94 for σ_p) for other Pd¹¹ complexes. Using $\rho_{12} - 1.87$ we obtain $\rho_{13} + 0.61$ in pure acetic acid. The positive ρ for the insertion of styrene into a Pd^{-C} bond is in accord with Murahashi's data³¹ for the reaction of 'methylpalladium' with substituted styrenes ($\rho + 2.68$) and Powell's data³² for the insertion of aromatic isocyanides into the palladium–carbon bond ($\rho + 1.13$). The positive slope +0.61 indicates that the rate-limiting step (13) is governed by nucleophilic attack of the phenyl group on the β carbon of styrene rather than electrophilic attack of Pd¹¹ on the α -carbon.

Experimental

Materials.—All para-substituted styrenes were commercially available (Koch-Light). ββ-Dideuteriostyrene was prepared according to ref. 33. NN-Dimethyl- and NN-diethyl-benzylamine were Koch-Light and Reakhim reagents, respectively. NN-Di-n-propylbenzylamine, NN-diethyl-4-chloro-, and NNdiethyl-4-methylbenzylamine were prepared by amination of the respective benzyl chlorides by either HNPrⁿ₂ or HNEt₂.³⁴ NN-Diethyl-4-methoxyand NN-diethyl-3,4-dimethoxybenzylamine were obtained by treating 4-methoxy- or 3,4dimethoxy-benzaldehyde with NN-diethylformamide in the presence of HCO₂H.³⁵ NaClO₄ and LiClO₄ were obtained by neutralization of HClO₄ by Na₂CO₃ and Li₂CO₃, respectively.³⁶ Mg(ClO₄)₂ (Reakhim) and [Buⁿ₄N]ClO₄ (Fluka) were commercially available. Acetic acid (Reakhim) was purified by a standard procedure,³⁷ and since it was found that water only very slightly increased the reaction rate, no attempt was made to remove traces of water.

The metallation of all *NN*-dialkylbenzylamines to form cyclopalladated complexes (1a-g) was carried out as described in ref. 11. The synthesis of 2-dialkylaminomethyl-stilbenes (2) is described in ref. 11. The properties of these compounds are given elsewhere.^{11,38}

Kinetic Measurements.—Reaction rates were obtained from absorbance versus time measurements with a Hitachi 356 spectrophotometer. Rates of appearance of (2) were measured at a wavelength of *ca*. 310 nm in acetic acid. At these wavelengths stilbenes (2) were the only absorbing species in the concentration range used. The general procedure was as follows. A stream of argon was bubbled through the solution of (1) in acetic acid to remove oxygen. Then at least a 20-fold excess of styrene with respect to (1) was added to this solution and the increase of absorption accompanying the formation of (2) was monitored. Good pseudo-first-order kinetic curves were obtained. Observed pseudo-first-order rate constants were calculated from a least-squares treatment of the linear $\ln(A_{\infty} - A)$ versus time plots. The slow reactions were also treated by the Guggenheim method. It was verified that both methods gave identical k_{obs} values. Freshly prepared solutions of (1) were used throughout.

 π -Complex Formation of Styrenes with Monomer (3).—To the solution of complex (3), the latter prepared according to ref. 13, in acetic acid (10^{-5} — 10^{-4} M) styrene (10^{-3} — 10^{-2} M) was added, and the electronic spectrum of the solution was recorded. A new intense band appeared immediately after the mixing of the reagents and remained unchanged for *ca*. 1 h. These π -complexes decomposed on standing overnight. The wavelengths of maximum absorption of π -complexes together with stability constants, K_{π} , calculated as described in the text, are given in Table 2. In the case of unsubstituted styrene the co-ordination of the second styrene molecule was observed at higher olefin concentration up to 1.0M.

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