Reaction Paths in the Cyclopalladated *NN*-Dialkylbenzylamine–Substituted Styrene System in Acetic Acid as Solvent. The Structure of Palladated 2-Dialkylaminomethylstilbenes †

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The reaction between di-μ-chlorobis(*NN*-dialkylbenzylamine-2*C*,*N*)dipalladium(II) (1) and a *para*-substituted styrene at 50 °C in 1 : 1 benzene–acetic acid affords 2-dialkylaminomethylstilbene (2) and its ring-palladated derivative di-μ-chlorobis(2-dialkylaminomethylstilbene-6*C*′,*N*)dipalladium(II) (3). The structure of (3) was established on the basis of ^{1}H n.m.r. measurements. The relative amounts of (2) and (3) formed are strongly dependent both on the atmosphere and the presence of alkali-metal perchlorates. Free (2) dominates under argon, but (3) under oxygen. The salts $MClO_4$ (M = Na, Li) accelerate the reaction markedly. Formation of (2) is a Fujiwara–Moritani or Heck-type reaction, but at least two paths contribute to the appearance of (3): (i) direct metallation of (2) by reoxidized palladium(II) and (ii) an exchange reaction between (1) and (2) affording (3).

The reaction of cyclopalladated compounds with alkenes to give substituted olefins is a subject of current interest.[1] The first example of such a process was the reaction of *ortho*-palladated *NN*-dimethylbenzylamine (1a) with styrene reported by Tsuji [1a] without experimental details. The reaction was described to proceed easily in acetic acid as solvent at room temperature. However, later, Heck and his co-workers [1l] were unable to perform the reaction in acetonitrile at 150 °C using the analogous acetato-bridged complex (1c). More recently Brisdon *et al.*[1l] reported the successful synthesis of substituted stilbenes by reaction of styrenes activated by the methoxy-substituted complex (1d). The non-activated compound (1a) was found to react smoothly only with olefins containing polar fragments such as carbonyl [1c] or carboxy [1l] adjacent to the double bond.

These observations demonstrate the complexity of the system. Generally speaking the factors which control the reactivity of cyclopalladated compounds with respect to olefins are poorly understood. To throw some light on the subject we have studied the interaction of complex (1a) with *para*-substituted styrenes. The results reported here show that this process is not as simple as can be concluded on the basis of Tsuji's paper.[1a] In particular we have found that the *ortho*-palladated complexes (1a and b) react with styrenes affording both the expected 2-dialkylaminomethylstilbenes (2) and their palladated derivatives (3). Furthermore, an exchange of cyclometallated ligands and an unexpectedly strong salt effect have been observed. A preliminary account has been published.[2]

Results and Discussion

General Procedure.—Experiments with (1a) and styrene in benzene or toluene in the presence of triethylamine in the temperature range 80—110 °C were unsuccessful although (1a) reacts with enones smoothly under the same conditions.[1c] This is in line with recently reported observations that (1c) does not react with styrene in MeCN even at 150 °C [1l] nor does (1d) in benzene at elevated temperatures.[1l] Evidently non-polar solvents are unfavourable media for the reaction. The more polar acetic acid was found to be a more useful solvent for this type of reaction [1c,l] and for some related processes.[3] Indeed experiments in acetic acid–benzene (1 : 1 v/v), the latter added to increase the solubility of (1), gave more promising results. The reaction between (1a) and styrene in the air at 50 °C is complete within 8 h. Separation of the reaction products by column chromatography gives two major products, 2-dimethylaminomethylstilbene (2a) in 3% yield and its palladated derivative (3a) in 33% yield (Scheme). Small amounts of *NN*-dimethylbenzylamine were also detected, but we did not determine these quantitatively. Unexpectedly we found that addition of alkali-metal perchlorates ($NaClO_4$, $LiCLO_4$) strongly accelerates the process, substantially lowering the reaction time and shifting the product distribution towards (2a) (Table 1). Another factor affecting the course of the reaction has been found to be the atmosphere under which the reaction is performed. It is seen from Table 1 that an atmosphere of argon favours the formation of (2a), but under oxygen the palladated complex (3a) is the main product.

Structures of the Reaction Products.—The substituted stilbenes (2) which are the expected reaction products were isolated as the hydrochlorides and characterized by elemental analysis, u.v., i.r., and mass spectral data (Table 2). The yields of (2) as white solids were usually close to those in Table 1 under identical conditions. Electronic spectra of (2a—h) show the typical pattern for *trans*-stilbenes with absorption maxima near 300 nm indicative of conjugation between the C=C bond and two phenyl groups.[4] I.r. spectra of (2a—h) were consistent with the proposed stilbene structure. Some characteristic absorptions are included in Table 2. Mass spectra gave the expected molecular ions (M) but of very low intensity (Table 2). Probably this is due to the presence of dialkylaminomethyl fragments which are rather unstable towards electron impact. More reliable data were obtained using the chemical ionization technique in ethanol vapour developed recently.[5] In this case quasi-molecular ions $M +$ H]$^+$ of high intensity were observed (Table 2). The details of the mass spectral behaviour of these stilbenes are reported elsewhere.[6]

Analytical and spectral data of palladated stilbenes (3) isolated as yellow crystalline solids are presented in Table 3. Since cyclometallated complexes with metal-bound σ-vinylic fragments are known,[7,8] two additional structures (5) and (6) which are isomeric with (3) may be proposed for these complexes. The data from Table 3 indicate reliably that (i) a given stilbene is bound to one PdCl fragment, (ii) this binding causes only a slight modification of the stilbene molecule since the u.v. spectral characteristics are essentially the same for a free and a complexed stilbene; and (iii) the compounds have a dimeric

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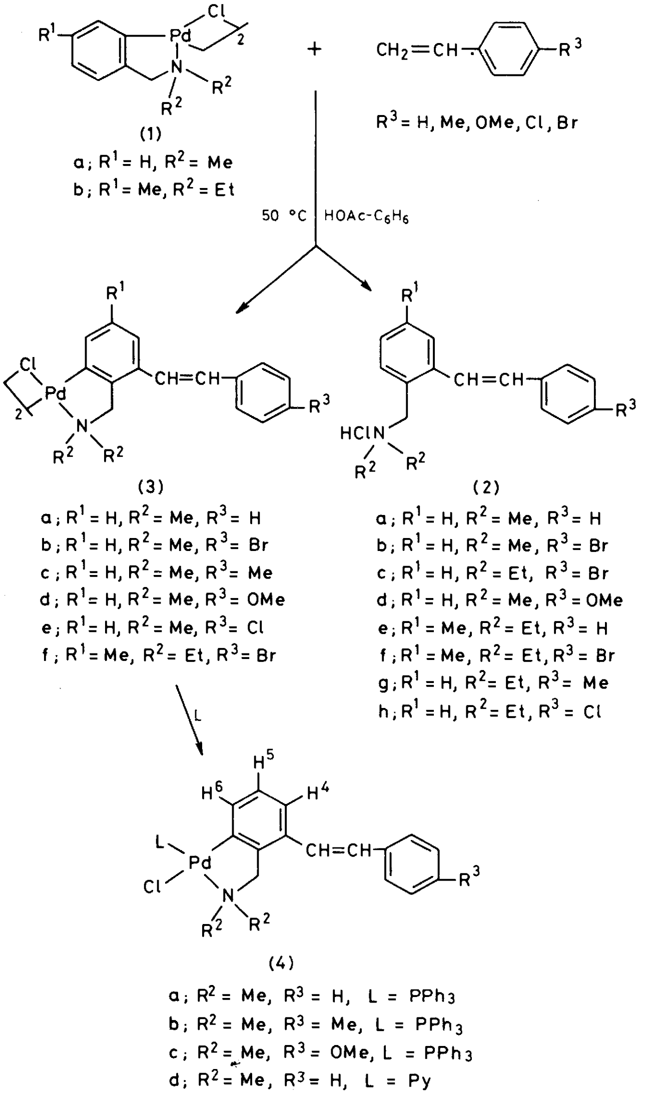
Table 1. The influence of the reaction conditions on the interaction between (1a) and styrene: (1a) 0.505 mmol; styrene 1.14 mmol; HOAc 10 ml; C_6H_6 10 ml

Run	Temperature (°C)	$[NaClO_4]$/M	Atmosphere	Reaction time (h)	Yield [a] (%)	
					(2a)	(3a)
1	50		Air	1.5		7
2	50		Air	8.0	3	33
3	50	0.1	Air	1.5	32	21
4	50	0.1	Argon	1.5	57	12
5	55	0.1	Oxygen (60 atm)	1.5	3	51

[a] Based on (1a).



Scheme.

structure as it is evident from molecular weight measurements for (3a). I.r. spectral data, also included in Table 3, have no characteristic features in favour of any of the three possible structures. The ^{1}H n.m.r. measurements of these dimeric compounds (Table 4) were not useful also since all aromatic and vinylic protons overlap in the range δ 7—8. Some information comes, however, from the signals of aliphatic protons. Singlet resonances of the $N-CH_2$ and $N-CH_3$ protons suggest the co-ordination plane of palladium is a plane of symmetry.[9] The signals from the $N-CH_2$ and $N-CH_3$ protons of (3) are observed at a lower field compared with those of free bases (2). For example, the $N-CH_2$ and $N-CH_3$ protons of (3a) resonate at δ 4.12 and 2.87, respectively, but those of (2a) (free base) at δ 3.50 and 2.26, respectively. This shift indicates that nitrogen is co-ordinated to palladium.[7c] Note that the $N-CH_2$ and $N-CH_3$ protons in the hydrochloride of (2a) appear at δ 4.45 and 2.80, respectively.

In our preliminary communication [2] we assigned structure (5) to the palladated 2-dimethylaminomethylstilbene (2a) in the light of Heck's results [11] on the reaction of (7) with two molecules of methyl acrylate to form (8) through the proposed intermediate (9). However, the results presented below show (3) to be the true structure.

Attempts to prepare crystals of these complexes suitable for *X*-ray diffraction analysis were unsuccessful. Fortunately the ^{1}H n.m.r. study of monomeric derivatives (4) gave sufficient information to discriminate among the possible structures. It is known [1k,m,9] that the conversion of dimeric cyclopalladated complexes into monomers in the presence of aromatic ligands, such as pyridine, leads to an essential simplification of the ^{1}H n.m.r. spectra of the latter. In particular, the signal of the proton *ortho* to palladium migrates strongly to high field due to anisotropic shielding from the pyridine ring.[9] These monomeric compounds (4) were prepared according to general procedures.[10] Their characteristics and ^{1}H n.m.r. data are given in Tables 3 and 4, respectively. In fact such complexes may be prepared *in situ* by addition of an excess of a ligand to a solution of (3). A few complexes (10a—c) with [$^2H_5$]pyridine as a ligand were prepared in $CDCl_3$ by addition of a 50% excess of [$^2H_5$]pyridine to the respective dimers and their ^{1}H n.m.r. spectra were recorded (Table 4). The conversion of dimers into monomers was almost quantitative, as shown by the n.m.r. spectra, and this is in accord with recent equilibrium measurements.[9] The identity of proton signals in complexes prepared in this way and in those synthesized independently according to ref. 10 was confirmed by comparison of the spectra of (4d) and (10a).

The ^{1}H n.m.r. spectrum of (4d) [or (10a)] in $CDCl_3$ solution contains a double doublet at δ 5.88 [1 H, ^3J(HH) 7, ^4J(HH) 1 Hz] which could be attributed to the 6-H. However, if structures (5) or (6) are valid, this doublet, in principle, may be assigned to 2-H in the respective monomeric complexes. To rule out the latter possibility the spectrum of (10c) obtained from (3f) was recorded. The same double doublet should be observed in the case of (5) or (6), but the double singlet expected for (10c) was found at δ 5.70 [1 H, ^4J(HH) 1 Hz] ascribed to 6-H.

It is interesting to note that $N-CH^{\alpha}H^{\beta}-Me$ protons in (3f) and (10c) appear as two well separated multiplets, but not quartets. The same was observed earlier for some related cyclopalladated compounds [11] and recently for [CpClTiμ-

Table 2. Analytical and spectral data of 2-dialkylaminomethylstilbene hydrochlorides, $[2\text{-}(R^2)_2NCH_2\text{-}5\text{-}R^1C_6H_3CH{=}CHC_6H_4R^3\text{-}4]\cdot HCl$ (2)

Compound	Molecular formula (M)[a]	M.p. (°C)	Analytical data Found (Calc.) C	H	N
(2a)	$C_{17}H_{19}N\cdot HCl\cdot H_2O$ (237.7)	222	69.9 (69.9)	7.35 (7.6) Cl 12.2 (12.15)	5.75 (4.8)
(2b)	$C_{17}H_{18}BrN\cdot HCl$ (316.2)	223	57.6 (57.9)	5.4 (5.45)	3.95 (3.95)
(2c)	$C_{19}H_{22}BrN\cdot HCl\cdot 0.5H_2O$ (344.3)	114—115	58.4 (58.55)	5.9 (6.2)	3.5 (3.6)
(2d)	$C_{18}H_{21}NO\cdot HCl\cdot H_2O$ (267.35)	205—207	67.35 (67.2)	6.9 (7.5)	4.25 (4.35)
(2e)	$C_{20}H_{25}N\cdot HCl$ (279.4)	185—186	75.4 (76.05)	8.3 (8.3)	4.35 (4.45)
(2f)	$C_{20}H_{24}BrN\cdot HCl$ (358.3)	188—190	59.45 (60.85)	6.4 (6.4)	3.5 (3.55)
(2g)	$C_{20}H_{25}N\cdot HCl$ (279.4)	180—182	76.05 (76.05)	8.25 (8.3)	4.45 (4.45)
(2h)	$C_{19}H_{22}ClN\cdot HCl$ (299.8)	159	67.05 (67.85)	6.6 (6.9)	3.95 (4.15)

Compound	U.v. spectra $\lambda_{max.}$ (HOAc)/nm ($\varepsilon_{max.}$/l mol^{-1} cm^{-1})		I.r. spectra $\nu_{max.}$ (KBr)/cm^{-1} $R_3\overset{+}{N}{-}H$	C=C	*trans*-HC=CH	Mass spectra (rel. int., %) M^+	$M + H^+$ [b]
(2a)	295 (22 100)	295 [c] (23 700)	2 650 2 720	1 600 1 570	980	238 (4.1)	239 (80)
(2b)	295 (26 000)		2 650	1 590	965	316 (4.2)	317 (60)
(2c)	300 (20 800)		2 460 2 600	1 600 1 590	990	344 (2.5)	345 (50)
(2d)	310 (23 300)		2 600	1 610 1 570	960	267 (4.4)	268 (80)
(2e)	295 (26 500)		2 475	1 610	970	279 (2.1)	280 (80)
(2f)	303 [c] (23 400)		2 610	1 620 1 605	985		
(2g)	300 (19 700)		2 480 2 600	1 600 1 570	965	279 (2.7)	280 (80)
(2h)	295 (17 800)		2 600	1 595 1 570	970	300 (2.5)	301 (80)

[a] $M = [2\text{-}(R^2)_2NCH_2\text{-}5\text{-}R^1C_6H_3CH{=}CHC_6H_4R^3\text{-}4]$. [b] Chemical ionization (in EtOH vapour). [c] Ethanol solvent.

$(NEt)_2TiClCp]$.[12] In the CH_3-decoupled spectra these multiplets transform to a couple of doublets, indicating that the two methylene protons H^α and H^β are not equivalent. The reason is not well understood since the $N{-}CH_2{-}Ar$ protons appear as one singlet. This non-equivalence is not due to the presence of vinylic group in the molecule. Although in the starting compound (1b) these multiplets overlap, in the respective monomer, obtained from the dimer in the presence of $[^2H_5]$pyridine, these complex signals are well resolved.

Further simplification of the spectra that allowed us to assign all aromatic and vinylic signals was achieved using the starting deuteriated compound (11) converted into dimers (12a,b) and the respective monomers (13a,b). The low-field region of the ^1H n.m.r. spectrum of (12a) is shown in Figure A. The AB pattern of vinylic protons is clearly seen here, the H^α and H^β protons being centred at δ 7.03 and 6.80 [2 H, ^3J(HH) 15 Hz]. The value of the coupling constant suggests a *trans*-configuration for the olefinic protons and this is in accord with i.r. spectral data (Table 3). The spectrum of respective monomer (13a) is very close to that of dimer (12a) (Table 4). No signal migrating to high field was observed in this case and this is additional evidence in favour of structure (3).

Figures B and C show the high-field regions of the ^1H n.m.r. spectra of (13b) and (10b), respectively. The spectrum of (13b) exhibits a clear AB pattern for the vinylic protons centred at δ 7.07 and 6.79 [2 H, ^3J(HH) 16 Hz] together with the AA′BB′ pattern assigned to the non-palladated *para*-substituted aromatic ring centred at δ 7.40. Based on this spectrum all the proton low-field resonances of (10b) can be assigned (Figure C, Table 4). This procedure was also applied to another pair of complexes, (10a) and (13a), and roughly the same results were obtained.

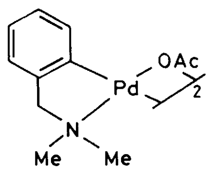
Finally, the ^1H n.m.r. spectrum of a phosphine-containing monomer (4a) was recorded. The signals from the $N{-}CH_2$ and $N{-}CH_3$ protons appear as doublets due to coupling with phosphorus nuclei. They are transformed into singlets in the phosphorus-decoupled spectrum.

Some Chemical Properties of the Palladated Stilbenes.— The dimeric complexes (3) undergo some reactions typical of such compounds.[7] The bridge-splitting reaction with donor ligands gives monomeric complexes (4) (see preceding section). The palladium–carbon bond of (3) may be easily ruptured with hydrochloric acid. Addition of HCl to a dioxane solution of (3) turns the yellow colour of the solution to dark red, indi-

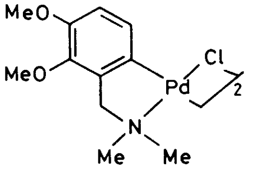
Table 3. Analytical and spectral data of palladium(II) dimeric complexes (3) and monomeric complexes (4)

			Analytical data Found (Calc.)					U.v. spectra $\lambda_{max.}$ (EtOH)/ nm ($\varepsilon_{max.}$/ l mol^{-1} cm^{-1})	I.r. spectra $\nu_{max.}$ (KBr)/ cm^{-1}	
Compd.	Molecular formula (*M*)	M.p. (°C)	C	H	N	Cl	Pd		C=C	*trans*- HC=CH
(3a)	$[C_{17}H_{18}ClNPd]_2$	174—177	52.9	4.85	3.5	9.4	28.05	297	1 610, 1 580	975
	(756.3) [a]	(decomp.)	(54.0)	(4.8)	(3.7)	(9.35)	(28.15)	(37 700)	1 560	
(3b)	$[C_{17}H_{17}BrClNPd]_2$	174—178	44.55	3.9	3.05	25.3 [b]	23.4	304	1 580, 1 550	960
	(914.1)	(decomp.)	(44.65)	(3.75)	(3.05)	(25.25)	(23.3)	(52 000)		
(3c)	$[C_{18}H_{20}ClNPd]_2$	176—178	54.25	5.1	3.2	9.1	27.1	300	1 580, 1 555	970
	(784.4)	(decomp.)	(55.1)	(5.15)	(3.55)	(9.05)	(27.15)	(45 300)		
(3d)	$[C_{18}H_{20}ClNOPd]_2$	167—170	51.7	5.05	3.45	8.7	26.3	305	1 610, 1 580	970
	(816.4)	(decomp.)	(52.95)	(4.95)	(3.45)	(8.7)	(26.05)	(42 500)	1 555	
(3e)	$[C_{17}H_{17}Cl_2NPd]_2$	151—153	48.7	4.7	3.0	17.5		302	1 585, 1 555	965
	(825.2)	(decomp.)	(49.5)	(4.15)	(3.4)	(17.2)		(34 500)		
(3f)	$[C_{20}H_{23}BrClNPd]_2$	195	48.5	5.05	2.7			313	1 620, 1 580	955
	(996.3)	(decomp.)	(48.2)	(4.65)	(2.8)			(54 100)		
(4a)	$C_{35}H_{33}ClNPPd$	136—138	65.9	5.65		5.65			1 600, 1 570	970
	(640.4)		(65.65)	(5.2)		(5.55)			1 550	
(4b)	$C_{36}H_{35}ClNPPd$	212—214	66.05	5.7		5.35		306	1 580, 1 570	970
	(654.5)		(66.05)	(5.4)		(5.4)		(32 200)		
(4c)	$C_{36}H_{35}ClNOPPd$	121—125	64.0	5.7		5.3			1 605, 1 570	970
	(670.5)		(64.5)	(5.25)		(5.3)			1 550	
(4d)	$C_{22}H_{23}ClN_2Pd$	191—193	57.2	5.25		7.75	23.35	302	1 600, 1 570	965
	(457.3)	(decomp.)	(57.8)	(5.05)		(7.75)	(23.25)	(27 900)	1 550	

[a] Found 748 (ebullioscopic in $CHCl_3$). [b] (Cl + Br).



(1c)



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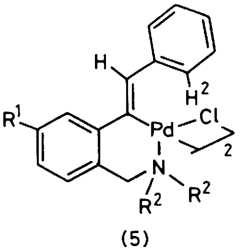

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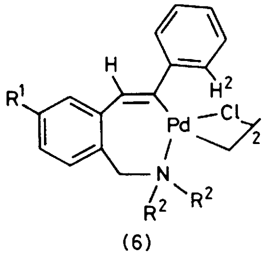

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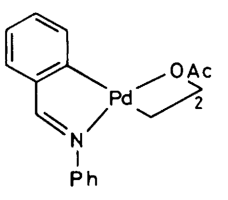

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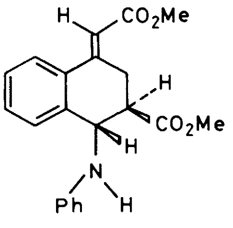

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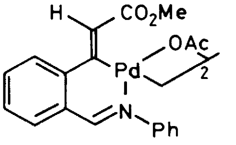

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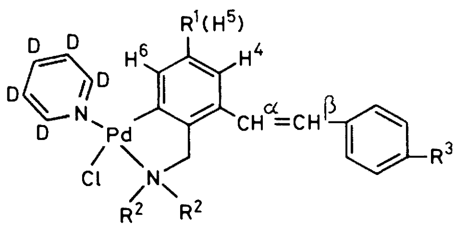
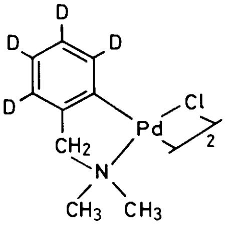


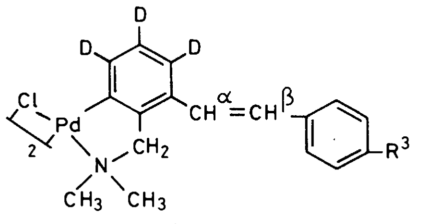
(10)a; R¹ = H, R² = Me, R³ = H

b; R¹ = H, R² = Me, R³ = Br

c; R¹ = Me, R² = Et, R³ = Br

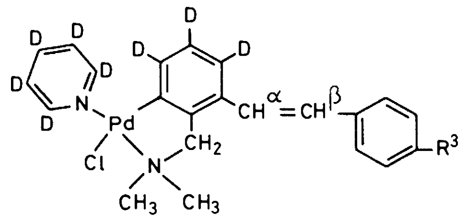


(11)



(12)a; R³ = H

b; R³ = Br



(13) a; R³ = H

b; R³ = Br

Table 4. ^1H N.m.r. data [a] for palladium complexes

Complex	Solvent	N–CH_3	Ar–CH_2–N	Unresolved aromatic or aromatic–vinylic protons	Vinylic protons	Assigned aromatic protons	Other protons
(3a)	$CDCl_3$	2.87 (s)	4.12 (s)	6.80—7.45	*b*		
(3b)	$(CD_3)_2SO$	2.74 (s)	4.30 (s)	6.70—7.60	*b*		
(3c)	$CDCl_3$	2.90 (s)	4.13 (s)	6.76—7.30	*b*		2.38 (s) (Ar–CH_3)
(3d)	$CDCl_3$	2.80 (s)	4.00 (s)	6.60—7.30	*b*		3.73 (s) (Ar–OCH_3)
(3e)	$(CD_3)_2SO$	2.85 (s)	4.30 (s)	6.84—7.65	*b*		
(3f)	$CDCl_3$	2.72 (m) [c] 3.49 (m)	4.07 (s)	6.60—7.60	6.85 (d) ^3J(HH) 15 Hz 7.10 (d)		1.68 (t) (CH_2–CH_3) 2.27 (s) (Ar–CH_3)
(4a)	$CDCl_3$	2.87 (d) ^4J(P–CH_3) 3.3 Hz	4.29 (d) ^4J(P–CH_2) 2.2 Hz	6.60—7.90	*b*	6.33 (m) (6-H)	
(4d)	$CDCl_3$	2.89 (s)	4.10 (s)	6.20—7.60	6.81 (d) ^3J(HH) 15 Hz 7.02 (d)	5.88 (dd) ^3J(HH) 7, ^4J(HH) 1 Hz (6-H)	
(10a)	$CDCl_3$	2.89 (s)	4.10 (s)	6.20—7.60	6.81 (d) ^3J(HH) 15 Hz 7.02 (d)	5.88 (dd) ^3J(HH) 7, ^4J(HH) 1 Hz (6-H)	
(10b)	$CDCl_3$	2.94 (s)	4.15 (s)		6.79 (d) ^3J(HH) 15 Hz 7.08 (d)	5.93 (dd) ^3J(HH) 8, ^4J(HH) 1 Hz (6-H) 6.81 (t) ^3J(HH) 8 Hz (5-H) 7.21 (dd) ^3J(HH) 8, ^4J(HH) 1 Hz (4-H) 7.40 (m) (AA′BB′ of *p*-C_6H_4)	
(10c)	$CDCl_3$	2.72 (m) [c] 3.49 (m)	4.14 (s)		6.77 (d) ^3J(HH) 16 Hz 7.07 (d)	5.70 (d) ^4J(HH) 1 Hz (6-H) 7.08 (d) ^4J(HH) 1 Hz (4-H) 7.40 (m) (AA′BB′ of *p*-C_6H_4)	1.67 (t) (CH_2–CH_3) 2.08 (s) (Ar–CH_3)
(12a)	$CDCl_3$	2.85 (s)	4.10 (s)	7.25—7.45 [d]	6.80 (d) ^3J(HH) 15 Hz 7.03 (d)		
(13a)	$CDCl_3$	2.94 (s)	4.16 (s)	7.20—7.60 [d]	6.41 (d) ^3J(HH) 16 Hz 7.09 (d)		
(13b)	$CDCl_3$	2.96 (s)	4.15 (s)		6.79 (d) ^3J(HH) 16 Hz 7.08 (d)	7.40 (m) (AA′BB′ of *p*-C_6H_4)	

[a] Recorded at 28 °C; δ scale (p.p.m.), s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet. [b] Vinylic protons overlap with aromatic protons. [c] H^α and H^β protons of the N–$CH^\alpha H^\beta$–Me moiety. [d] Phenyl protons of the C_6H_5-group.

cating the decomposition of the complex and the formation of $PdCl_4^{2-}$ ion. Treatment of the resulting solution with an anion-exchange resin gives a palladium-free colourless solution from which hydrochloride (2) could be isolated. However, the product obtained was sometimes tinted brown, because of palladium impurities.

Reaction Scheme.—The intimate mechanism of vinylation of cyclopalladated species by styrenes will be discussed in the subsequent paper on the basis of the kinetic data.[13] So here only the general reaction paths leading to 2-dialkylaminomethylstilbenes (2) and their palladated derivatives (3) will be considered (Scheme).

The formation of (2) seems to be a typical Fujiwara–Moritani [14,15] or Heck [15,16] olefin arylation reaction. The important result from Table 1 is the strong salt effect induced by alkali-metal perchlorates. The reaction time is lowered in the presence of 0.1M-$NaClO_4$ from 8 to 1.5 h. The kinetic study has shown,[13] however, that the real rate acceleration in the presence of salts is much higher, reaching two orders of magnitude. This observation together with above mentioned unfavourable effect of non-polar solvents shows that polar intermediates should be involved in the reaction mechanism. The origin of the 'salt effect' was found to be solvolysis of alkali-metal perchlorates in acetic acid according to equation (1), the strong perchloric acid liberated being the true catalyst.[13]

$$MClO_4 + HOAc \rightleftharpoons HClO_4 + MOAc \qquad (1)$$

An obvious route to (3) is a direct palladation of (2). In fact, palladium(II) acetate reacts with (2a) to afford (3a) in good yield under the same reaction conditions both in the presence and in the absence of salt [equation (2)]. Since the

$$(2a) + Pd(OAc)_2 \longrightarrow (3a) + 2HOAc \qquad (2)$$

formation of (2) is accompanied by Pd^{II} reduction, only the reoxidation of Pd^0 by oxygen would lead to palladium(II) acetate. It is seen from Table 1 that under the oxygen-containing atmosphere the yields of (3a) are, in fact, higher compared with those of (2a). The ability of oxygen to reoxidize Pd^0 under enhanced pressure is well known.[17] Even in air Pd^0 may be partly reoxidized in benzene solvent.[18] The effect of salt on relative amounts of (2a) and (3a) formed in air (Table

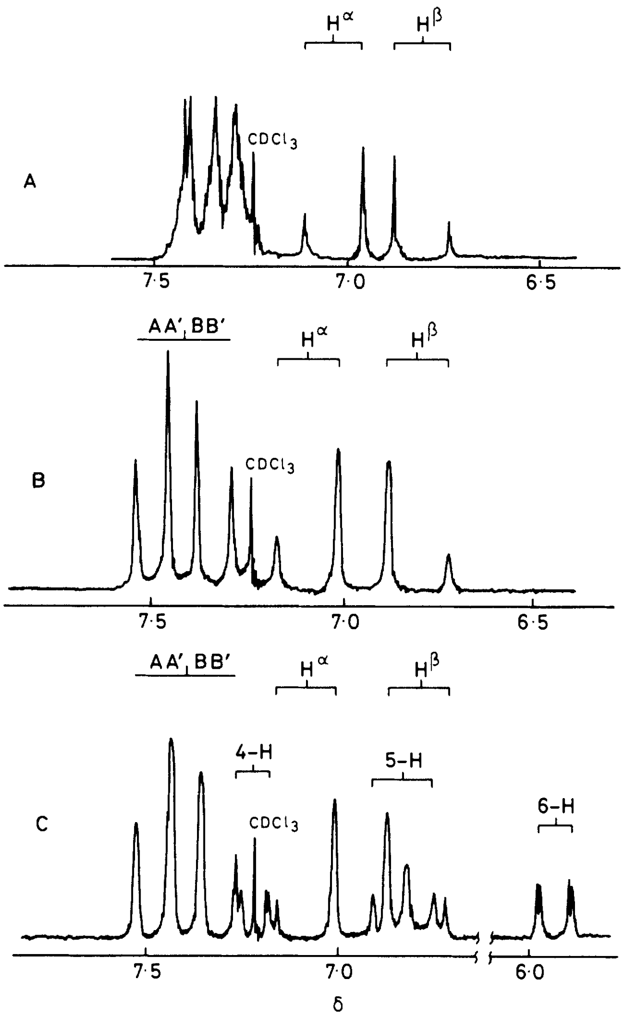


Figure. Low-field regions of the ^{1}H n.m.r. spectra of (12a), A; (13b), B; and (10b), C

1, Run 3) is also in accord with this proposal since salts usually reduce the solubility of gases, oxygen in particular, in solvents.[19] However, this explanation is not correct for the oxygen-free system: palladated stilbene is formed in 12% yield even under argon (Table 1, Run 4). To account for this observation we suggest a novel type of ligand-exchange reaction, that is the substitution of the cyclopalladated ligand by a non-metallated free ligand to give a new palladocycle. We have examined the interaction of the starting complex (1a) with (2a) and found that palladated product (3a) is actually formed. Reaction (3) proceeds under rather mild conditions

$$(1a) + (2a) \longrightarrow (3a) + Me_2NCH_2Ph{\cdot}HCl \qquad (3)$$

in HOAc–C_6H_6 at 50 °C affording (3a) in 42 and 39% yields in the absence and in the presence of 0.05M-$NaClO_4$, respectively. We can barely estimate the relative contributions of paths (2) and (3) to the formation of (3). Probably they play a different role depending on reaction conditions and the nature of starting reagents. For example, (1a) reacts with (2f) to give (3f) in 21% yield. Reaction (3) could also be invoked to account for the fact that total reaction yield never exceeds 70% (Table 1), since this process consumes the starting complex (1) converting it into (3).

Experimental

U.v. spectra were recorded on a Hitachi 356 spectrophotometer. I.r. spectra were recorded on JASCO-200 and UR-20 spectrophotometers for KBr pellets. ^{1}H N.m.r. spectra were obtained on JEOL C60 and Tesla BS-497 (100 MHz) spectrometers with tetramethylsilane as internal standard. M.p.s were determined with a VEB Analytic Dresden PHMK apparatus and are uncorrected. Mass spectra were obtained with a Ribermag R10-10 chromatograph–mass spectrometer.

Reagents.—*NN*-Dimethylbenzylamine and all styrenes were commercially available (Koch–Light); *NN*-diethyl-4-methylbenzylamine was obtained by alkylation of Et_2NH with 4-methylbenzyl chloride according to the standard procedure.[20] [$^2H_5$]-*NN*-Dimethylbenzylamine [$(CH_3)_2NCH_2C_6D_5$] was prepared as follows. [$^2H_5$]Toluene was brominated with *N*-bromosuccinimide according to ref. 21 and the resulting $C_6D_5CH_2Br$ was aminated with $(CH_3)_2NH$.[20]

Di-μ-chlorobis(NN-*dimethylbenzylamine*-2C,N)*dipalladium*-(II) (1a). This compound was prepared according to a slightly modified procedure of Cope.[22] *NN*-Dimethylbenzylamine (0.87 g, 6.45 mmol) was added to a solution of Li_2PdCl_4 (1.69 g, 6.45 mmol) and NaOAc (0.54 g, 6.45 mmol) in aqueous 80% dioxane. The solution was allowed to stand at room temperature for 24 h. The yellow *precipitate* was filtered, washed with water–dioxane, and dried *in vacuo* over P_2O_5, yield 70% (Found: C, 39.2; H, 4.3; Cl, 12.9; Pd, 38.8. $C_9H_{12}ClNPd$ requires C, 39.1; H, 4.4; Cl, 12.8; Pd, 38.5%). Di-μ-chlorobis(*NN*-diethyl-4-methylbenzylamine-2*C*,*N*)dipalladium(II) (1b) and di-μ-chlorobis([$^2H_4$]-*NN*-dimethylbenzylamine-2*C*,*N*)dipalladium(II) (11) were prepared analogously and characterized by standard procedures.

General Procedure.—To a solution of styrene (0.13 ml, 1.14 mmol) in glacial acetic acid (10 ml; pure or containing 0.2M-$NaClO_4$–$LiClO_4$), a solution of (1a) (0.301 g, 0.545 mmol) in benzene (10 ml) was added. The mixture was thermostatted at 50 °C under argon or in the air for an appropriate period (Table 1). After the reaction had been completed the precipitated palladium was filtered off, and the filtrate was evaporated *in vacuo*. The residue was extracted twice with chloroform. These fractions were combined and the solution was concentrated. Then the latter was chromatographed on a silica gel column. First, (3a) was eluted with $CHCl_3$–EtOAc (95 : 5). Next (2a) was eluted with acetic acid. The yields of (2a) and (3a) were determined spectrophotometrically. Products (2) and (3) were isolated as follows. The solution of (3) in $CHCl_3$ was concentrated and the addition of n-hexane precipitated the compounds, which could be obtained as yellow crystals on recrystallization from benzene–hexane. For (2), the acetic acid was removed *in vacuo* and the residue could be worked up either according to method A or B as follows. A To the residual product, dioxane (5 ml) and 3M-HCl (5 ml) were added. The solution was strongly diluted with water and passed through an anion-exchange column (IRA-400, Cl^- form) to remove traces of $PdCl_4^{2-}$. The solution was then concentrated on a water-bath and allowed to stand overnight at room temperature. Crystals of (2) were filtered and dried *in vacuo*. B 3M-NH_4OH (10 ml) was added and the product was extracted with $CHCl_3$ (15 ml). The aqueous layer was washed twice with $CHCl_3$, the organic fractions were combined, and the solvent was evaporated *in vacuo*. Then dioxane (5 ml) and 3M-HCl (5 ml) were added, the solution was diluted with water, concentrated on a water-bath, and allowed to stand overnight to form crystals of (2). The yields of isolated materials were usually 5—10% less than those determined spectrophotometrically.

Di-μ-*chlorobis*(2-*dimethylaminomethylstilbene*-6C′,N)*dipal*-

ladium(II) (3a). To obtain complex (3a) or other complexes (3b—h) in maximum yields, the reaction between (1) and styrene should be performed under the conditions of Runs 2 or 5 of Table 1, *e.g.* either in air within 8 h without any salt or in 1.5 h in the presence of $NaClO_4$ under oxygen.

2-Dimethylaminomethylstilbene hydrochloride (2). The maximum yield of this compound was attained in Run 3 of Table 1, *e.g.* in the presence of $NaClO_4$ under argon. The same is true for other starting complexes and other substituted styrenes.

Protonolysis of Compound (3a).—To a solution of (3a) (0.10 g, 0.132 mmol) in dioxane (5 ml) concentrated HCl (5 ml) was added. The initial yellow-green solution turned to dark red. The latter was much diluted with water and passed twice through a column with an anion-exchange resin. This solution free from Pd^{II} was concentrated on a water-bath and allowed to stand overnight to form crystals of (2a), which were filtered, washed with a small quantity of cold water, and dried *in vacuo* (yield 48%).

Chloro(2-*dimethylaminomethylstilbene*-6C′,N)*triphenylphosphinepalladium*(II) (4a).—This compound and other monomeric complexes (4b—d) were prepared according to ref. 10 from the respective chloro-dimers. Yields of the products were not less than 75%.

Metallation of 2-*Dimethylaminomethylstilbene Hydrochloride by Palladium*(II) *Acetate*.—To the solution of $(2a)\cdot H_2O$ (0.050 g, 0.17 mmol) in HOAc (5 ml) a solution of palladium(II) acetate (0.041 g, 0.18 mmol) in benzene (5 ml) was added. The reaction mixture was thermostatted at 50 °C under argon for 1.5 h. To the reaction mixture $CHCl_3$ (20 ml) was added and the solution was strongly diluted with water. The aqueous layer was washed with $CHCl_3$ (15 ml), organic fractions were combined, washed twice with water, and dried ($MgSO_4$). Product (3a) was isolated by column chromatography (SiO_2; $CHCl_3$–EtOAc 95 : 5). The identity of the product with that obtained from the reaction of (1a) with styrene was confirmed by analytical, u.v., and i.r. spectral data. Palladation also occurs in the presence of 0.1M-$NaClO_4$. In this case, however, reduction of Pd^{II} is observed, and the yield of (3a) is lower, 47% after 3 h.

Ligand Exchange Reaction.—To a solution of $(2a)\cdot H_2O$ (0.015 g, 0.052 mmol) in HOAc (3 ml) a solution of (1a) (0.021 g, 0.077 mmol) in benzene (3 ml) was added and the mixture was thermostatted at 50 °C under argon for 1 h. Work-up was the same as in the metallation reaction. The concentration of (3a) was measured spectrophotometrically. The yield was 42% in the absence and 39% in the presence of 0.05M-$NaClO_4$.

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