Journal of Organometallic Chemistry, 273 (1984) 401–413
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF PALLADIUM(II) CYCLOMETALLATED BENZYLIDENEANILINE SCHIFF'S BASES. SOME RELATIVE RATES FOR THE SYNTHESIS OF *ortho*-SUBSTITUTED CARBOMETHOXY DERIVATIVES VIA CO INSERTION

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(Received April 27th, 1984)

Summary

The synthesis and characterisation of the complexes $[(p\text{-}CH_3C_6H_4\text{-}N{=}CH(C_6H_3Y))Pd(OAc)]_2$ (II) are reported. These complexes react at very different rates with carbon monoxide in methanol to give the *ortho*-substituted esters, $p\text{-}CH_3\text{-}C_6H_4N{=}CHC_6H_3Y - 2R$, $R = CO_2CH_3$, with electron withdrawing Y substituents slowing the reaction. The $^{13}C\{^1H\}$ data for II show a linear correlation of $\delta(C(2))$ in the 5′-complexes (Y *trans* to Pd–C) with $\delta(C(4))$ of monosubstituted benzene compounds. For Y = 5′-NO_2, 4′-NO_2 and 4′-Cl, the bis complex $[\{p\text{-}CH_3C_6H_4N{=}CH(C_6H_3Y\}_2Pd]$ is formed in a secondary reaction.

Introduction

The applications of organometallic palladium(II) chemistry in organic synthesis are rapidly expanding [1], with both stoichiometric and catalytic reactions in common use. Nevertheless, there have been relatively few studies on the mechanistic aspects of this chemistry, and specifically the reactivity of the Pd–C bond towards insertion reactions. Heck and coworkers have shown [2] that the *para* substituent of the aryl ligand in *trans*-$[PdI(p\text{-}YC_6H_4)(PPh_3)_2]$ strongly influences the rate of insertion of CO into the Pd–C bond, such that electron-withdrawing Y groups slow the reaction; however, for the palladium-catalysed benzamidation of aryl iodide the substituent Y plays only a secondary role [2].

Our interest in selectively synthesizing *ortho*-substituted aromatic aldehydes (see eq. 1) led us to consider the route shown in Scheme 1 for introduction of an $o\text{-}CO_2CH_3$ group. This strategy involves preparation of a Schiff's base I followed

$$C_6H_5CHO \rightarrow \rightarrow \rightarrow o\text{-(substituent)}C_6H_4CHO \qquad (1)$$

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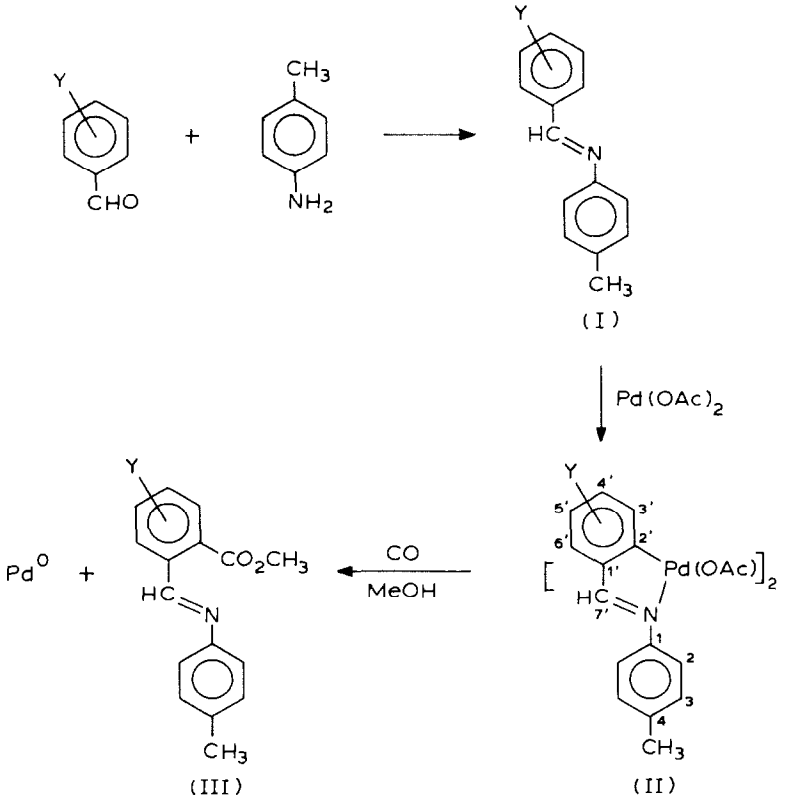
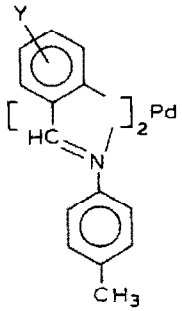
SCHEME 1



by a cyclopalladation with the metallation occurring at the position *ortho* to the imine carbon. This type of reaction frequently gives the dimer II as the product, due to the labilizing effect of the Pd–C bond. Further reaction with carbon monoxide results in insertion of CO into the Pd–C bond to give an acyl complex (not shown), which is then decomposed by attack of solvent to give product plus metallic palladium.

The imines III can then be hydrolysed to give the desired *ortho*-substituted aldehydes. Since this route involves selective formation of a palladium–carbon bond via cyclometallation, the carbomethoxy substituent in the aromatic ring is restricted to the *ortho* position. There are several comprehensive reviews describing cyclometallation with palladium(II) and other metals [2–5] as well as a number of articles dealing specifically with Schiff's bases [6–9] and closely related functional groups [10–13].

The generality of Scheme 1 as a synthetic route depends upon the effects of Y on both the cyclometallation and subsequent insertion reaction. We report here (a) the syntheses of II and III, (b) ^{1}H and ^{13}C NMR parameters for II and III, and (c) qualitative rate data for the conversion II → III, including partial suppression of this reaction for Y = 5′-NO_2 (*meta* with respect to the imine) with the formation of IV.



(IV)

Results and discussion

1. Synthesis and characterization of II

The cyclometallation of the compounds I was found to proceed smoothly with $Pd(OAc)_2$ in glacial acetic acid at 100°C, although satisfactory results for the 4′-CH_3 complex were also obtained using recrystallized $Pd(OAc)_2$ in methanol at room temperature. Schiff's bases containing electron-withdrawing substituents react slowly relative to those having electron donors, in keeping with literature suggestions involving electrophilic attack of palladium(II) on the ring [3–6,14].

The products were obtained in 80–98% yields and were characterised by microanalysis (see Table 1) and NMR spectroscopy (see below and Tables 2 and 3). The imine stretch, ν(C=N) at ~ 1590 cm^{-1} in the infrared is not clearly defined in the spectra, since it overlaps with the bands for ν(C=C) and ν(C=O)(μ_2-acetate). The free ligand ν(C=N) appears at ~ 1630 cm^{-1}.

The imine proton of II, H(7′), appears at δ 7.54–7.84 ppm with the 5′-NO_2 complex showing the lowest, and the 4′-OCH_3 species the highest field signal. This represents an upfield shift of ≃ 0.8 ppm for this proton upon coordination. Proton H(3′), immediately adjacent to the palladium–carbon bond, appears at δ 6.00–7.22, shifted 0.83–1.46 ppm to high field from its position in the free ligand. The ^1H resonances at ≃ δ 2.35 and 1.83–2.02 ppm are assigned to the methyl protons of the aniline and μ_2-acetate groups, respectively.

The $^{13}C\{^1H\}$ spectra for II show nine aromatic carbon resonances, plus the imine and μ_2-acetate-carboxylate signals at lower field. The aromatic methyl resonances appear at ~ δ 21.3 ppm and the acetate at ~ δ 24.3 ppm. The signal for the palladium-bound carbon, C(2′), ranges from δ 145.68–164.96 ppm, and appears to vary with the ring substituent, Y, in the normal fashion. Thus, a plot of δ(C(2′)) for the 5′-substituted complexes vs. δ(C(4)) in monosubstituted benzenes (see Fig. 1) does not deviate significantly from linearity, suggesting that the palladium atom is not interfering with the normal resonance and inductive effects of the Y groups. Consequently, either the palladium has only a very small π-interaction with the benzene ring to which the ^{13}C shift is insensitive, or this interaction does not vary with Y. Interestingly, there is considerable deviation from linearity if δ(C(2′)) values for the 4′-substituted analogues are used (see Fig. 1). The aniline ^{13}C signals are relatively unaffected by the changes in the aldehyde ring, and both the μ_2-carboxylate signals at δ 180.26–181.48 ppm and the imine carbon resonances at δ 170.46–172.33 ppm, are not significantly altered by the Y substituent.

2. Reaction of II with carbon monoxide

Bubbling CO through methanol solutions of II at room temperature gives the compounds III plus metallic palladium. The complexes III were isolated and characterized by microanalysis (Table 1) and ^{1}H and ^{13}C NMR spectroscopy (Tables 4 and 5). Yields are typically in the range 70–96%. In contrast to Thompson and Heck [7], we did not observe heterocyclic products arising from either AcO^- or MeOH attack at the imine carbon.

TABLE 1

ANALYTICAL DATA FOR THE COMPLEXES[a] AND PRODUCT ESTERS

	Microanalyses Calcd. (found)(%)				Reaction time (h)	Yield (%)	
Y in II	C	H	N	O			
H	53.43	4.20	3.89		0.5	80	
	(53.66)	(4 33)	(3.85)				
4′-CH_3	54.64	4.59	3.75		1.0	96	
	(54.13)	(4.64)	(3.63)				
5′-CH_3	54.64	4.59	3.75		0.5	80	
	(54.82)	(4.72)	(3.48)				
4′-OCH_3	52.39	4.40	3.59		1.5	89	
	(52.40)	(4.46)	(3.61)				
5′-OCH_3	52.39	4.40	3.59		0.5	86	
	(52.16)	(4.61)	(3.90)				
4′-Cl[b]	48.76	3.58	3.55		1.0	98	
	(48.93)	(3.63)	(3.63)				
5′-Cl[c]	48.76	3.58	3.55		1.5	95	
	(48.77)	(3.55)	(3.53)				
4′-NO_2	47.49	3.49	6.92		6 0	95	
	(47.76)	(3.60)	(7.11)				
5′-NO_2	47.49	3.49	6.92		3 0	96	
	(47.54)	(3.40)	(6 76)				
Y in III							
H	75.87	5.97	5.53	12.63	0.5	91	100
	(76.29)	(5.95)	(5.49)	(12.77)			
4′-CH_3	76.38	6.41	5 24		1	91	66
	(76.43)	(6.40)	(5.22)				
5′-CH_3	76.38	6.41	5.24	11.97	0.5	96	
	(76.54)	(6.62)	(5.20)	(12.14)			
4′-OCH_3	72.07	6.05	4.94		3.0	94	93
	(71.22)	(6.09)	(5.34)				
5′-OCH_3	72.07	6.05	4.94	16.94	0.25	88	71
	(72.01)	(6.15)	(4.96)	(17.43)			
4′-Cl	66.79	4.90	4.87		2.0	83	94
	(66.69)	(4.96)	(4.79)				
5′-Cl[d]	66.79	4.90	4.87	11.12	1.0	94	98
	(66.32)	(5.03)	(4.53)	(11.10)			
4′-NO_2	64.42	4.73	9.39	21.45	15	~ 80	147
	(63.99)	(4.87)	(8.99)	(20.85)			
5′-NO_2	64.42	4.73	9.39	21.45	15	~ 70	143
	(63.88)	(4.83)	(8.98)	(21.39)			

[a] The 4′-NO_2 and the 5′-NO_2 complexes are red and orange, respectively. All other complexes are yellow in color. [b] Cl: 8.99 (9.38). [c] Cl: 8.99 (9.09). [d] Cl: 12.32 (12.30).

^{1}H NMR spectroscopy reveals the imine proton at δ 9.13–9.34 ppm, and all the derivatives show ester OCH_3 protons at δ 3.93–4.02 ppm. The imine ^{13}C signal appears in the range δ 155.78–159.68 ppm, whereas the carbonyl and methoxy absorptions fall at δ 165.68–167.80 and 52.34–53.28 ppm, respectively.

Table 6 shows some relative reaction rates as well as an estimate of the time for reaction of 50% of the starting complex II. These rate data are based on NMR integrals, and although an attempt has been made to compensate for differences in spin-lattice relaxation times (T_1's) and other problems, e.g. signal overlap, we feel our results must be interpreted only qualitatively, not quantitatively. As may be seen from the Table the substituent Y exerts a significant influence on the rate and, to some extent, on the product. For electron-withdrawing groups in position 4′, *meta* to the palladium–carbon bond, the time for reaction of half of II is usually more than 20 minutes; thus, the 4′-NO_2, 4′-OCH_3, and 4′-Cl compounds all react relatively slowly. Contrasting with these are the rate data for the 5′ derivatives in which Y is a π-donor.

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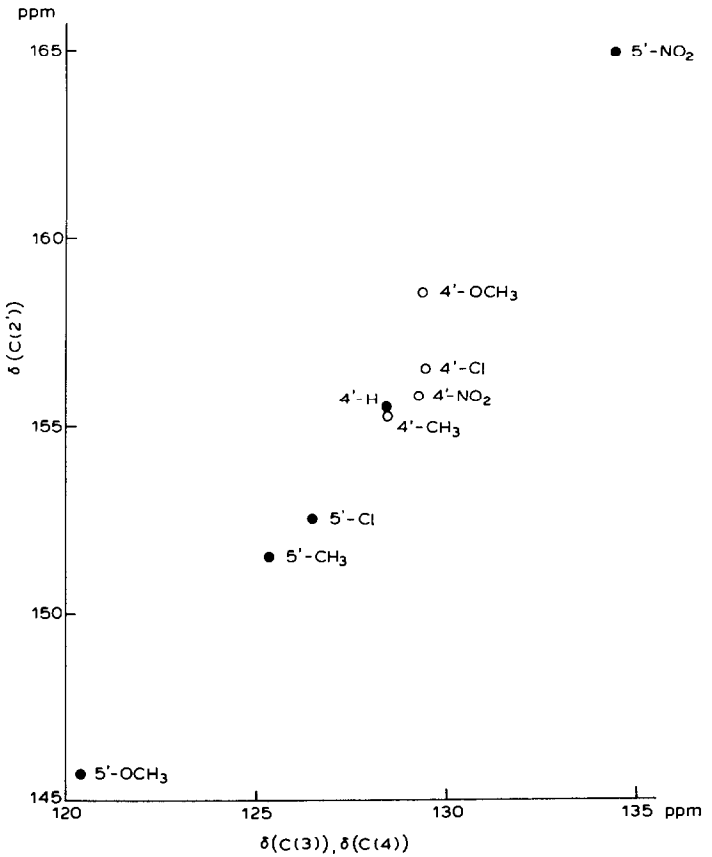

Fig. 1. Plot showing δ(C(2′)) (carbon bound to palladium) for the 5′-Y complexes vs. δ(C(4)) in monosubstituted benzenes (closed circles), and δ(C(2′)) for the 4′-Y complexes vs. δ(C(3)) in monosubstituted benzenes (open circles).

TABLE 2

^{1}H NMR DATA FOR THE COMPLEXES II [a,b]

Y	H(2)	H(3)	H(7′)	H(3′)	H(4′)	H(5′)	H(6′)	p-CH_3	H_3C-COO^-	OCH_3
4′-H	6.77	7.01	7.60	6.67 [c]	6.95	7.06	7.19 [c]	2.36	1.83	
	(8.7)	(8.7)		(0.9/7.6)	(1.5/7.6) [d]	(0.9/7.3)	(1.5/7.3)			
4′-CH_3	6.73	6.99	7.56	6.42	–	6.85	7.09	2.35/2.25	1.86	
	(8.4)	(8.4)		(1.2)		(1.2/7.5)	(7.5)			
5′-CH_3	6.75	6.98	7.59	6.53	6.75		7.03	2.35/2.32	1.84	
	(8.1)	(8.1)		(8.0)	(8.0/1.5)		(1.5)			
4′-OCH_3	6.63	6.94	7.54	6.00		6.57	7.16	2.33	1.90	3.54
	(8.2)	(8.2)		(2.5)		(8.3/2.5)	(8.3)			
5′-OCH_3	6.80	7.01	7.62	6.54	6.60		6.81	2.36	1.83	3.82
	(8.0)	(8.0)		(8.5)	(8.5/2.6)		(2.6)			
4′-Cl	6.75	7.10	7.62	6.54		7.06	7.13	2.38	1.83	
	(8.4)	(8.4)		(1.8)		(8.0/1.8)	(8.0)			
5′-Cl	6.75	7.02	7.67	6.52	6.86		7.23	2.37	1.89	
	(8.2)	(8.2)		(8.3)	(8.3/2.2)		(2.2)			
4′-NO_2	6.66	6.92	7.81	7.22		7.94	7.39	2.30	2.02	
	(8.1)	(8.1)		(2.2)		(8.2/2.2)	(8.2)			
5′-NO_2	6.73	7.00	7.84	6.77	7.74		8.09	2.39	1.96	
	(8.3)	(8.3)		(8.1)	(8.1/2.3)		(2.3)			

[a] $CDCl_3$, room temperature. [b] See Scheme for numbering sequence. J(H,H) in parenthesis. [c] Tentative assignment. [d] There is another ^3J(H,H) of ~ 7–8 Hz.

TABLE 3

^{13}C NMR PARAMETERS FOR COMPLEXES II [a,b]

Y	C(1)	C(2)	C(3)	C(4)	C(7′)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	H_3C-COO^-	$CH_3(OCH_3)$
4′-H	145.34 [c]	123.29	128.76	137.50	172.23	145.99 [c]	155.47	132.81	130.24	124.07	127.46	180.70	24.27/21.32
4′-CH_3	145.56	123.09	128.64	136.91	171.76	143.38 [c]	155.34	133 49	140.71	124.95	127.36	180.46	24.30/22.51/21.19
5′-CH_3	145.67 [c]	123.28	128.67	137.32	172.33	145.80 [c]	151.50	132.63	131.18	133.29	127.93	180.58	24.34/21.34/21.11
4′-OCH_3	145.68	122.97	128.64	136.57 [c]	171.00	138.63	158.61	116.01	160.27	111.60	128.89	180.26	(54.77)/24.41/21.20
5′-OCH_3	145.41 [c]	123.25	128.75	137.53	172.04	145.48 [c]	145.68	133.14	116.52	157.22	112.57	180.65	(55.78)/24.30/21.35
4′-Cl	144.97 [c]	122.93	129.18	138.07 [c]	171.34	144.16 [c]	156.47	132.40	136.21 [c]	124.25	128.24	181.12	24.28/21.39
5′-Cl	145.25 [c]	123.04	128.91	138.18	171.18	146.56 [c]	152.54	133.76	129.92 [c]	129.98 [c]	126.80	180.92	24.37/21.37
4′-NO_2	144.84	122.52	129.04	139.67	170.46	150.62	155.82	127.29	147.13	119.65	126.41	181.48	24.44/21.08
5′-NO_2	144.86 [c]	122.85	129.13	139.15	170.99	145.51 [c]	164.96	133.06	124.23	145.44 [c]	121.60	181.39	24.33/21.34
4′-H(I)	149.53			135.41	158.81				130.91				

[a] $CDCl_3$, room temperature. [b] See numbering, Scheme 1. [c] Tentative assignment.

TABLE 4

^{1}H NMR DATA FOR THE PRODUCT METHYLESTERS [a]

Y	H(3′)	H(4′)	H(5′)	H(6′)	H(7′)	Aniline	CH_3	CO_2CH_3
4′-H	7.99	7.52	7.64	8.25	9.23	7.21	2.39	3.96
	(1.3/7.8)	(7.8/1.2/?)	(7.7/1.3/?)	(7.7/1.2)				
4′-CH_3	7.78	–	7.43	8.17	9 18	7 21	2.45 2.38	3.95
	(1.1)		(8.0/1.1)	(8.0)				
5′-CH_3	7.91	7.33		8.06	9.26	7.21	2.47 2.39	3.93
	(8.0)	(1.2/8.0)		(1.2)				
4′-OCH_3	7.45		7.15	8.24	9.13	7 19	2.38	3.95 3.91
	(2.6)		(8.7/2.6)	(8.7)				
5′-OCH_3	7.99	7.02		7.76	9.33	7 22	2.38	3.95 3.92
	(8.7)	(2.7/8.7)		(2.7)				
4′-Cl	7.97		7.59	8.25	9.20	7.21	2 39	3.96
	(2.2)		(8.5/2.2)	(8.5)				
5′-Cl	7.95	7.48		8.28	9.24	7.22	2.39	3.95
	(8.5)	(2.2/8.5)		(2.2)				
4′-NO_2	8.86		8.44	8.52	9.34	7.25	2.41	4.02
	(2.0)		(2.0/8.6)	(8.6)				
5′-NO_2	8.13	8.31		9.13	9.23	7.25	2.40	4.01
	(8.6)	(2.4/8.6)		(2.4)				

[a] $CDCl_3$ at room temperature, see Scheme 1 for numbering sequence.

TABLE 5

^{13}C NMR DATA FOR THE PRODUCT METHYLESTERS [a]

Y	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)	C(7′)	C(1)	C(2)	C(3)	C(4)	CO_2CH_3	OCH_3	CH_3
4′-H	137.60	130.58 [b]	130.40 [b]	130.82 [b]	132.55	128.68	159.10	149.69	121.38	130.00	136.24	167.65	52.57	21.20
4′-CH_3	134.81 [b]	130.77	131.05	140.87	133.26	128.65	158.99	149.79	121.37	129.96	136.05 [b]	167.80	52.54	21.21
														21.54
5′-CH_3	137.71 [b]	127.93	130.88	131.23	143.40	129.02	159.68	149.72	121.41	129.99	136.24 [b]	167.55	52.48	21.26
														21.76
4′-OCH_3	130.19 [b]	132.49	115.11	161.28	118.62	130.39 [b]	158.40	149.87	121.33	129.97	135.94	167.49	52.69	21.21
													55.87	
5′-OCH_3	140.26	122.97	132.96	117.08 [b]	162.97	112.11 [b]	159.45	149.61	121.49	130.01	136.36	167.17	52.34	21.24
													55.91	
4′-Cl	136.04 [b]	132.01	130.59	136.63 [b]	132.63	130.11	157.64	149.31	121.39	130.03	136.63	166.40	52.87	21.27
5′-Cl	139.40 [b]	128.76	132.17	130.36	139.24 [b]	128.57	157.54	149.07	121.43	130.04	136.80	166.73	52.75	21.28
4′-NO_2	143.00	131.53	126.07	148.63 [c]	126.81	130.19 [d]	156.35	148.63 [c]	121.64	130.19 [d]	137.68	165.68	53.28	21.35
5′-NO_2	139.29 [b]	137.42 [b]	131.88	124.35	150.23	123.74	155.78	148.50	121.53	130.12	135.51	166.07	53.26	21.32

[a] $CDCl_3$ at room temperature. [b] Tentative assignment. [c] Integral shows two carbons. [d] Integral shows three carbons.

The 5′-CH_3 and 5′-OCH_3 species (Y *para* to the Pd–C bond) react relatively quickly, so that half of the starting complex is consumed in less than five minutes at room temperature. This change in relative rates is clearly visible from Fig. 2, which shows plots of ln [II], vs. time, *t*, for the 5′- and 4′-OCH_3 complexes. This difference in reactivity as a function of the aromatic substituent is not sufficient to negate the general synthetic approach shown in Scheme 1, but it can represent a restriction if the trend as a function of Y is not recognized. Moreover, with the slower reactions we find that a secondary process, i.e. the formation of IV, can become signficant. We have observed NMR spectra for complexes of type IV with the 4′-Cl and 4′-NO_2 derivatives but have so far only succeeded in isolating and characterizing the 5′-NO_2 complex (see Experimental). An interesting ^1H feature of complexes IV concerns H(3′). Relative to II, this proton is shifted downfield by 1.36, 1.61 and 1.38 ppm for the 5′-NO_2, 4′-NO_2 and 4′-Cl derivatives, respectively, thereby providing an NMR fingerprint for the identification of this type of complex. After 45 minutes reaction time we observe 15–20% of this bis-cyclometallated material for all three of these Y substituents. Figure 3 shows a representative plot of product distributions vs. time for the 4′-Cl analogue. We are as yet uncertain as to the geometry at palladium.

A satisfactory explanation for the appearance of IV, which involves two ligands per metal, is not yet available.

Experimental

NMR spectra were measured as $CDCl_3$ solutions using a WM-250 NMR spectrometer. Infra-red spectra were measured as KBr pellets on a Beckmann 4250. Microanalyses were performed in the analytical laboratory of the E.T.H., Zürich.

All syntheses were performed in air. Solvents were dried, but not degassed. The $CDCl_3$ was passed through Al_2O_3 to eliminate traces of HCl, which facilitates hydrolysis of the Schiff's base products.

Samples for the kinetic measurements were prepared as follows: The complex (0.20 mmol) was suspended/dissolved in 150 ml MeOH and then treated with carbon monoxide (1 atm. 20 °C) for the appropriate time period (depending on the aromatic ring substituent). During the reaction at least ten 10 ml samples were

TABLE 6

SOME RELATIVE REACTION RATES

$$II + CO \xrightarrow[CH_3OH]{} III + Pd^0 + HOAc$$

Y	Relative rate	$t_{50\%}$ (min)
H	1.0	6
4′-CH_3	1.3	4.5
5′-CH_3	1.7	3.5
4′-OCH_3	0.3	22
5′-OCH_3	2.4	2.5
4′-Cl	0.2	25
5′-Cl	0.6	10
4′-NO_2	< 0.1	60–90
5′-NO_2	0.1	45

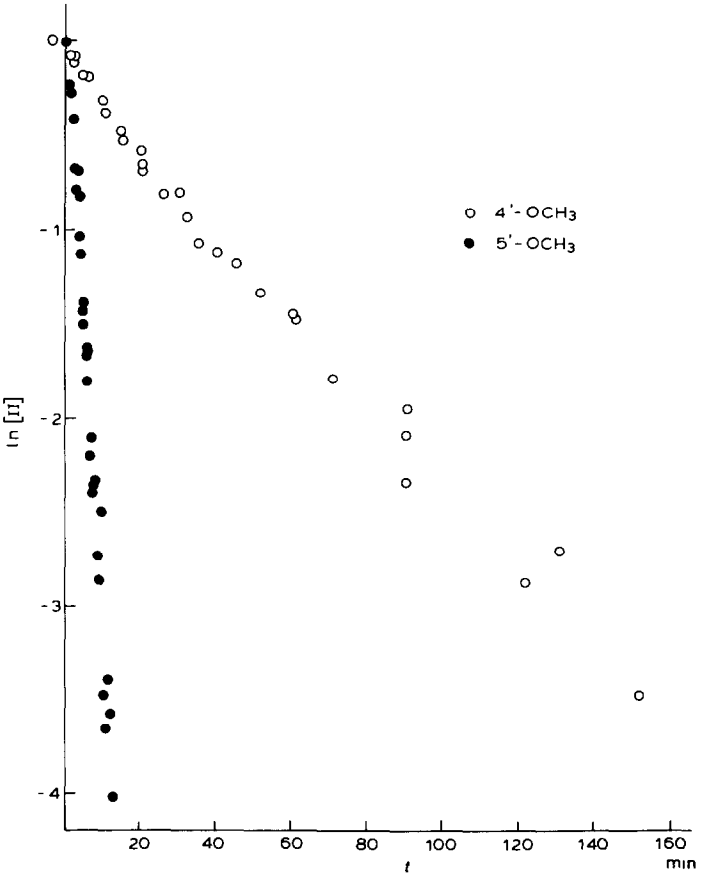

Fig. 2. Relative reaction rates for the 4'-OCH_3 and 5'-OCH_3 complexes II. The Y axis represents ln [II], 100% II is set equal to 1. Closed circles are for the 5'-OCH_3 complex.

withdrawn. These were cooled to −78°C and then individually concentrated *, redissolved in CH_2Cl_2, filtered through Celite, concentrated once again, dried for 3 h, and then finally taken-up in 0.5 ml $CDCl_3$. The imine, *H*–C=N, signals were integrated and the sum was assumed to correspond to 100%. An identical process using the OCH_3 of the product ester and/or the CH_3 of the aniline ring gave qualitatively identical results. The proton measurements for the kinetic runs were performed using ~ 25° pulses with a 3 sec delay between pulses.

Synthesis of the Schiff's base

All of the Schiff's bases were prepared by dissolving equimolar quantities of aldehyde and aniline in methanol and refluxing for 0.5 h. Removal of the methanol using a rotary evaporator gave the products, which were used directly without further purification.

Palladium acetate was obtained from Johnson–Matthey and recrystallized from benzene/acetic acid before use.

* A rotary evaporator was used and the temperature never exceeded 0 °C.

Synthesis of the cyclopalladated Schiff's bases

The complexes were all prepared in a similar fashion. Typically, the 4′-CH_3 Schiff's base I, (419 mg, 2.0 mmol) and $Pd(OAc)_2$ (499 mg, 2.0 mmol) were dissolved in 15 ml HOAc and then heated at 100 °C for 1 h. Water (25 ml) was then added and the mixture allowed to cool to room temperature. Extraction with CH_2Cl_2 (4 × 25 ml portions) was followed by drying ($MgSO_4$), filtration, and concentration. Recrystallization from CH_2Cl_2/n-hexane gave the product (718 mg, 96%). Found: C, 54.13; H, 4.64; N, 3.63. C_xH_yNOPd calcd.: C, 54.64; H, 4.51; N, 3.75%.

Preparation of the methyl esters III and complex IV, Y = 5′-NO_2

The reactions of the complexes II with CO were carried out in an identical fashion. Typically; a solution of the 4′-CH_3 complex II (74.7 mg, 0.10 mmol) in 75 ml MeOH was treated with gaseous carbon monoxide for 1 h. The palladium metal which precipitated during the reaction was removed by filtration through Celite and the MeOH filtrate concentrated. The residue can be recrystallized from low boiling petroleum ether (30–60 °C) by cooling to −20 °C. The product (49 mg, 91%) is a pale yellow solid.

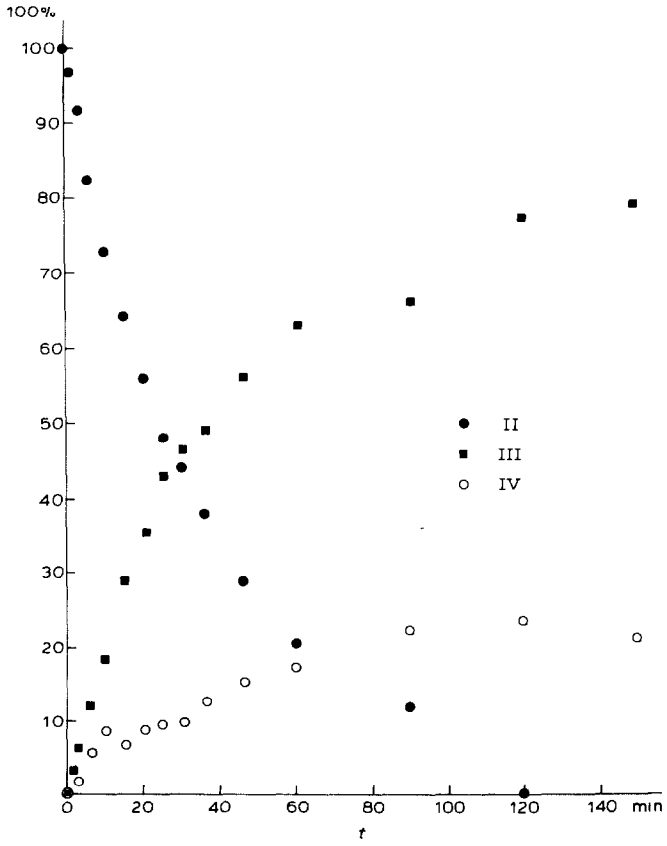

Fig. 3. Product distribution for the reaction of the 4′-Cl complex II with CO in MeOH.

For the reaction of the 5′-NO_2 complex (81 mg, 0.10 mmol) 15 h of contact with CO were allowed. Removal of the methanol was then followed by extraction with CH_2Cl_2 and filtration through Celite to remove palladium metal. The Celite was washed several times with CH_2Cl_2 until the filtrate was colourless. Concentration of the solvent and subsequent extraction with ether gave the methyl ester III. The complex IV (41 mg, 70% *) remained. Found: C, 57.61; H, 3.77; N, 9.53. C_xH_yNOPd calcd.: C, 57.50; H, 3.79; N, 9.58%. $\delta(^1H)$: H(3′), 8.13 d; H(4′), 8.24 d of d ; H(6′), 8.30 d; H(7′), 8.34 s, aniline protons, 6.75; CH_3, 2.25 $\delta(^{13}CH{=}N)$, 172.73.

Acknowledgements

We thank the firm of Ciba-Geigy, Basel, for support for this research and Johnson-Matthey Research Center, England, for the loan of palladium salts.

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* On several occasions yields were of the order of 20–30%.