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STERIC ROLE OF AROMATIC RING *ortho*-SUBSTITUENTS IN THE MECHANISM OF CARBENE FORMATION FROM PALLADIUM(II) ARYLISOCYANIDE COMPLEXES AND ANILINES

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Summary

The kinetics of carbene formation from *cis*-[$PdCl_2(CNR)(PPh_3)$] (R = *p*-C_6H_4-NO_2, *p*-C_6H_4Cl, *o*-C_6H_4Me, *o,o'*-$C_6H_3Me_2$) and *para*- or *ortho*-substituted anilines have been studied in 1,2-dichloroethane at 30°C. The reaction proceeds stepwise through an intermediate adduct produced by nucleophilic attack by the amine on the isocyanide carbon. Steric strain in the intermediate caused by *ortho*-substituents produces an overall decrease in rate and makes the reversal of the formation of the intermediate comparable in rate with the subsequent steps leading to the final carbene complex. The results allow a unified picture to be presented for the general mechanism operating for both primary and secondary aromatic amines.

Introduction

We previously studied the mechanism of carbene formation from palladium(II) isocyanide complexes and *para*-substituted primary anilines [1]:

$$cis\text{-}[PdCl_2(CN\text{-}p\text{-}C_6H_4X)(PPh_3)] + p\text{-}YC_6H_4NH_2 \xrightarrow[30°C]{1,2\text{-dichloroethane}} cis\text{-}[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4X)NH\text{-}p\text{-}C_6H_4Y\}(PPh_3)] \quad (1)$$

(X = MeO, Me, H, NO_2; Y = Cl, H, Me, MeO)

The dependence of the pseudo-first order rate constant, k_{obs}, on amine concentration was of the form shown in eq. 2 where the second-order rate constant, k_2,

$$k_{obs} = k_2[\text{Amine}] \quad (2)$$

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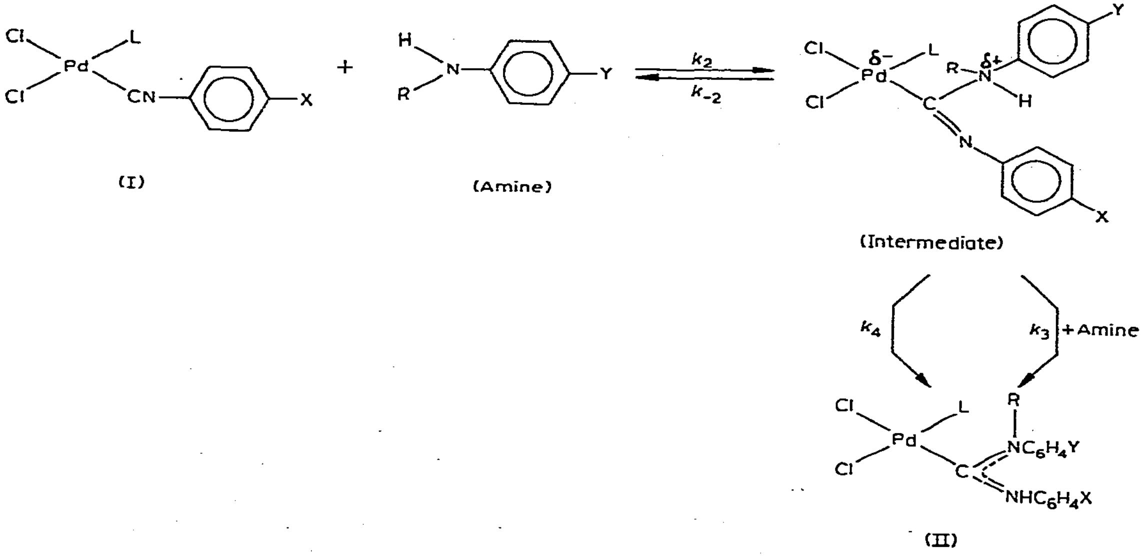
appeared to be markedly affected by the electronic properties of substituents X and Y.

Subsequently, an extension of these kinetic studies to secondary amines [2,3] revealed the stepwise nature of the general mechanism of these reactions (Scheme 1) according to the following rate law:

$$k_{\mathrm{obs}}/[\mathrm{A}] = k_{\mathrm{A}} = k_2 \frac{k_4 + k_3[\mathrm{A}]}{k_{-2} + k_4 + k_3[\mathrm{A}]} \tag{3}$$

SCHEME 1



Nucleophilic attack by the entering amine on the isocyanide carbon is suggested to lead to a labile intermediate which undergoes proton transfer to the final carbene complex II, both intramolecularly in a four-membered cyclic transition state (k_4) and intermolecularly by intervention of a further amine molecule serving as a bifunctional catalyst in a six-membered transition state (k_3).

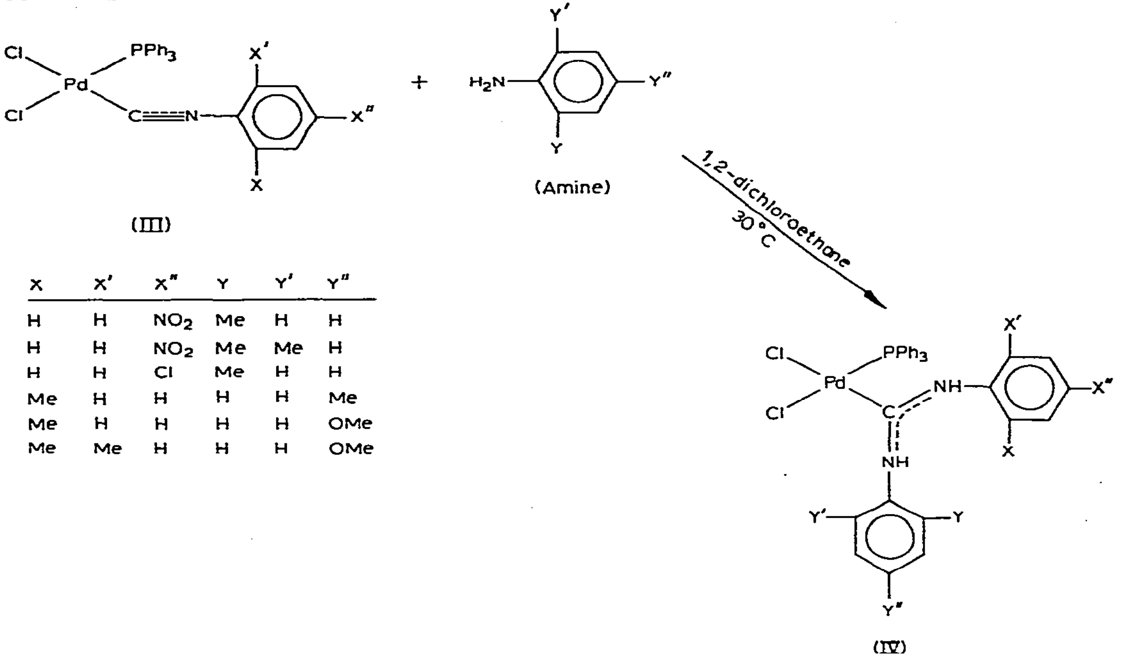
The observed rate law (eq. 2) for *para*-substituted primary anilines may be considered as a particular case of the general equation 3 with the assumption that $k_{-2} << k_4 + k_3[\mathrm{A}]$, implying that formation of the intermediate is the rate-determining step for these amines.

On the other hand, increasing steric requirements of either the *N*-substituent R or the *cis*-ligand L were found to cause a significant decrease of the k_3/k_{-2} ratio, corresponding to an increased tendency of the intermediate to revert to the starting isocyanide substrate I, relative to further reaction to the final carbene [3]. We therefore reasoned that increased steric crowding around the isocyanide carbon in the intermediate would make the k_{-2} term comparable with the $k_4 + k_3[\mathrm{A}]$ term, so that the general form of rate law 3 would also be observed for primary amines in the appropriate concentration range. We sought to achieve this by use of *ortho*-substituted arylisocyanide complexes and/or anilines. The results are described below.

Results and discussion

The reactions studied are shown in Scheme 2. Two sets of kinetic investigations were carried out; (a) reactions of *ortho*-methylanilines with *para*-substituted isocyanides; (b) reactions of *para*-substituted anilines with *ortho*-methylisocyanides.

SCHEME 2



(III)

(Amine)

(IV)

X	X'	X"	Y	Y'	Y"
H	H	NO$_2$	Me	H	H
H	H	NO$_2$	Me	Me	H
H	H	Cl	Me	H	H
Me	H	H	H	H	Me
Me	H	H	H	H	OMe
Me	Me	H	H	H	OMe

In order to ascertain whether the presence of *ortho*-substituents has any effect on the nature of the products, the complexes IV have been prepared and characterised (see Table 4 in the Experimental section). The IR spectra show the typical bands of coordinated bis(arylamino)carbene groups in the ranges 3320—3110 (ν(N—H)), 1543—1540 and 1340—1310 cm^{-1} (ν(C⋯N)) [4—8]. The *cis* configuration of the starting isocyanide substrate is retained in the reaction, as shown by the occurrence of two ν(Pd—Cl) bands in the range 310—282 cm^{-1}.

The rate data are reported in Table 1 and Table 2 for the reactions of set (a) and (b) respectively. In general, the steric hindrance by *ortho*-substituents caused a marked decrease in the overall reaction rates relative to those of the analogous *para*-substituted reactants [1]. Therefore we used isocyanides activated by good electron-withdrawing groups (*p*-Cl and *p*-NO$_2$) in the substrates reacting with *o*-toluidine and *o,o'*-dimethylaniline. The complexes III with the less activated *p*-tolyl- and *p*-methoxyphenyl-isocyanide reacted extremely slowly with these *o*-hindered amines under the conditions used. For the same reason, the more basic *p*-substituted anilines (*p*-Me and *p*-MeOC$_6$H$_4$NH$_2$) had to be used for the reactions with *o*-tolyl- and *o,o'*-dimethylphenyl-isocyanide complexes. When steric hindrance was introduced into both reactants, the rates were too low to allow reliable measurements under the same experimental conditions.

TABLE 1

RATE DATA FOR THE REACTIONS OF *cis*-[$PdCl_2(CN$-*p*-$C_6H_4X)(PPh_3)$] WITH *ortho*-SUBSTITUTED ANILINES (A) AT 30°C IN 1,2-DICHLOROETHANE (UNCERTAINTIES ARE ESTIMATED STANDARD ERRORS)

X	A	10^2[A] (M)	10^2k_{obs} (min^{-1})	k_A (M^{-1} min^{-1}) [a]	k_2 (M^{-1} min^{-1})	k_3/k_{-2} (M^{-1})	k_4/k_{-2}
NO_2	*o*-$MeC_6H_4NH_2$	0.28	2.37	8.46	8.4 ± 0.1 [b]		
		0.54	4.84	8.96			
		1.37	11.95	8.79			
		1.95	16.63	8.53			
		3.01	25.13	8.35			
		3.75	31.39	8.37			
		4.72	40.07	8.49			
NO_2	*o,o'*-$Me_2C_6H_3NH_2$	0.27	0.58	2.13	6.02 ± 0.06 [c]	152 ± 3 [d]	~0 [e]
		0.70	2.16	3.09			
		0.95	3.40	3.58			
		1.37	5.73	4.18			
		3.11	15.13	4.88			
		4.10	21.30	5.20			
		5.88	31.75	5.40			
		9.70	54.81	5.65			
		12.12	69.08	5.70			
Cl	*o*-$MeC_6H_4NH_2$	3.00	3.03	1.01	1.60 ± 0.006 [c]	48 ± 1 [d]	0.18 ± 0.08 [e]
		4.31	4.78	1.11			
		5.96	7.09	1.19			
		8.31	10.72	1.29			
		10.41	13.95	1.34			
		13.13	18.12	1.38			
		16.96	24.25	1.43			
		19.92	28.88	1.45			

[a] $k_A = k_{obs}/[A]$. [b] Slope of plot of k_{obs} vs. [A]. [c] Calculated from intercepts of linear portions of plots of $1/k_A$ vs. $1/[A]$. [d] Slopes of plots of $k_A/(k_2 - k_A)$ vs. [A]. [e] Intercepts of plots of $k_A/(k_2 - k_A)$ vs. [A].

TABLE 2

RATE DATA FOR THE REACTIONS OF *cis*-[$PdCl_2$(CNR)(PPh_3)] WITH *p*-$YC_6H_4NH_2$ (A) AT 30°C IN 1,2-DICHLOROETHANE (UNCERTAINTIES ARE ESTIMATED STANDARD ERRORS)

CNR	Y	10^2[A] (M)	10^2k_{obs} (min^{-1})	$10k_A$ (M^{-1} min^{-1}) [a]	k_2 (M^{-1} min^{-1}) [b]	k_3/k_{-2} (M^{-1}) [c]	k_4/k_{-2} [d]
o-MeC_6H_4NC	Me	0.98	0.14	1.43	0.43 ± 0.001	42.6 ± 0.5	~0
		1.84	0.37	2.04			
		3.38	0.86	2.56			
		5.06	1.49	2.94			
		7.60	2.51	3.30			
		10.21	3.60	3.53			
		14.05	5.19	3.70			
		22.45	8.80	3.92			
		31.45	12.64	4.02			
		41.67	17.00	4.08			
		50.25	20.75	4.13			
o-MeC_6H_4NC	OMe	1.02	0.47	4.61	1.02 ± 0.003	45.3 ± 0.4	0.25 ± 0.07
		2.19	1.30	5.92			
		4.02	2.70	6.71			
		5.03	3.64	7.24			
		7.98	6.49	8.13			
		10.01	8.47	8.47			
		18.01	16.51	9.17			
		25.09	23.67	9.43			
o,o-$Me_2C_6H_3NC$	OMe	5.01	0.13	0.26	0.40 ± 0.05	1.43 ± 0.03	~0
		7.61	0.30	0.40			
		10.30	0.52	0.50			
		15.05	1.05	0.70			
		21.85	1.97	0.90			
		29.94	3.56	1.19			
		41.77	6.31	1.51			

[a] $k_A = k_{obs}/[A]$. [b] Calculated from intercepts of linear portions of plots of $1/k_A$ vs. $1/[A]$. [c] Slopes of plots of $k_A/(k_2 - k_A)$ vs. [A]. [d] Intercepts of plots of $k_A/(k_2 - k_A)$ vs. [A].

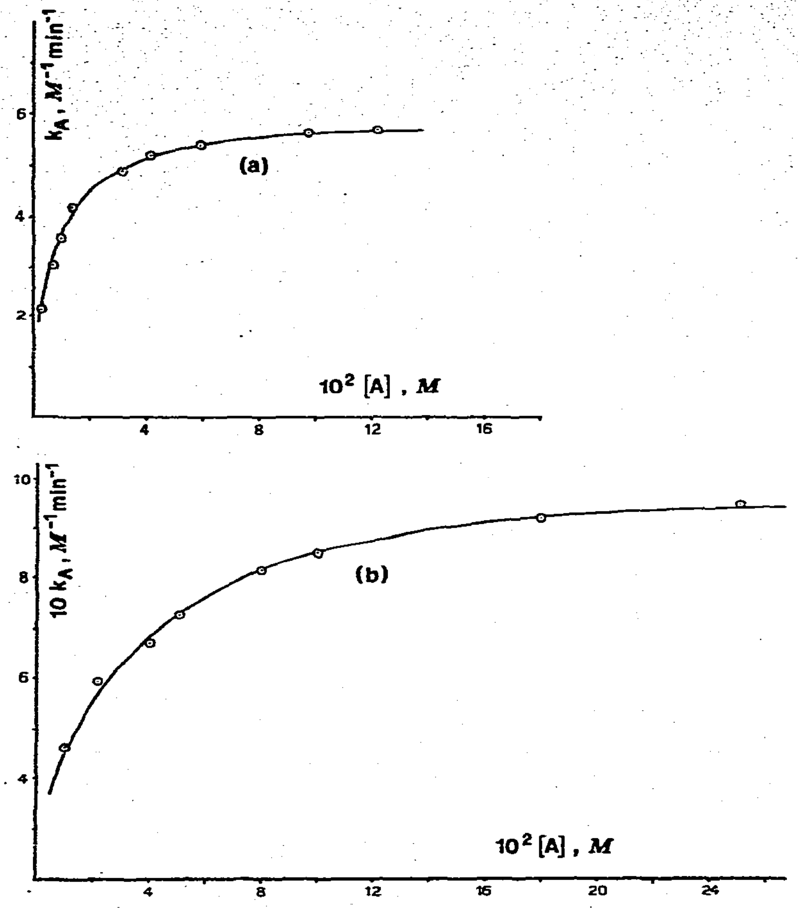


Fig. 1. Dependence of the second-order rate coefficient k_A, on the amine concentration [A], for the reaction of *cis*-[$PdCl_2(CN$-*p*-$C_6H_4NO_2)(PPh_3)$] with *o,o'*-dimethylaniline (a) and of *cis*-[$PdCl_2(CN$-*o*-$C_6H_4Me)(PPh_3)$] with *p*-anisidine (b).

The dependence of the second-order rate parameter, k_A, on the amine concentration for some reactions of Table 1 and 2 is shown in Fig. 1.

As can be seen in Table 1 for the reaction of the *p*-$NO_2C_6H_4NC$ complex with *o*-toluidine, k_A is a constant, according to the rate law 2 already observed for unhindered reactants [1]. By contrast, the dependence of k_A on [A] is curvilinear for all other reactions, indicating the stepwise nature of the mechanism (cf. Scheme 1). The rate data for the latter reactions fit the general rate law 3 already observed with secondary amines [2,3]. This can be converted into eq. 4, which

$$1/k_A = \frac{k_{-2}}{\{k_4 + k_3[A]\}k_2} + 1/k_2 \tag{4}$$

gives a linear dependence of $1/k_A$ vs. $1/[A]$ in the range of amine concentrations for which $k_4 << k_3[A]$. Examples of this doubly reciprocal plot are given in Fig. 2.

A least-squares fit of the linear portion of such plots gave the k_2 and k_3/k_{-2} terms as the inverse intercept and intercept/slope ratio, respectively. Straight

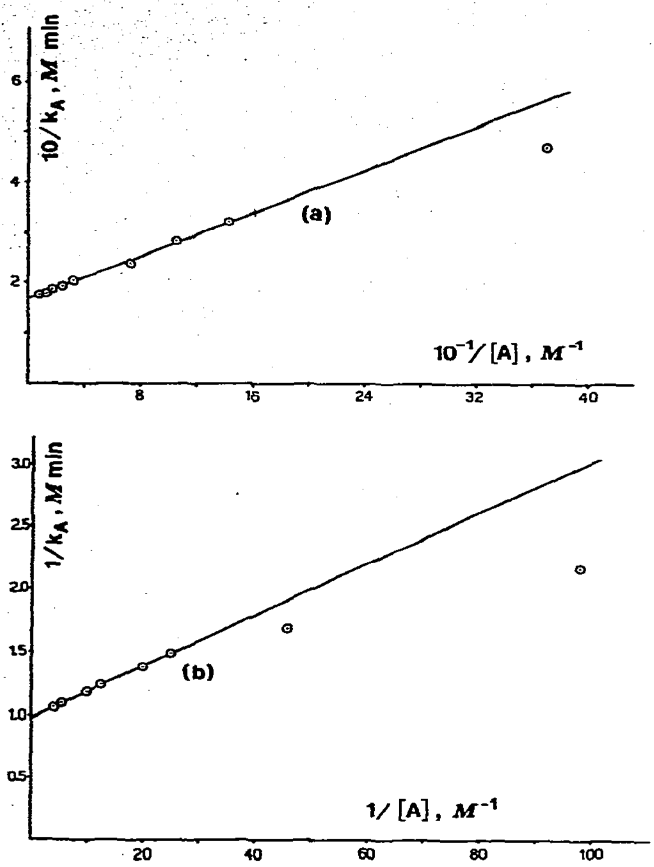


Fig. 2. Dependence of the inverse second-order rate coefficient $1/k_A$, on inverse amine concentration for the reaction of *cis*-[$PdCl_2(CN$-*p*-$C_6H_4NO_2)(PPh_3)$] with *o,o'*-dimethylaniline (a) and of *cis*-[$PdCl_2(CN$-*o*-$C_6H_4Me)(PPh_3)$] with *p*-anisidine (b).

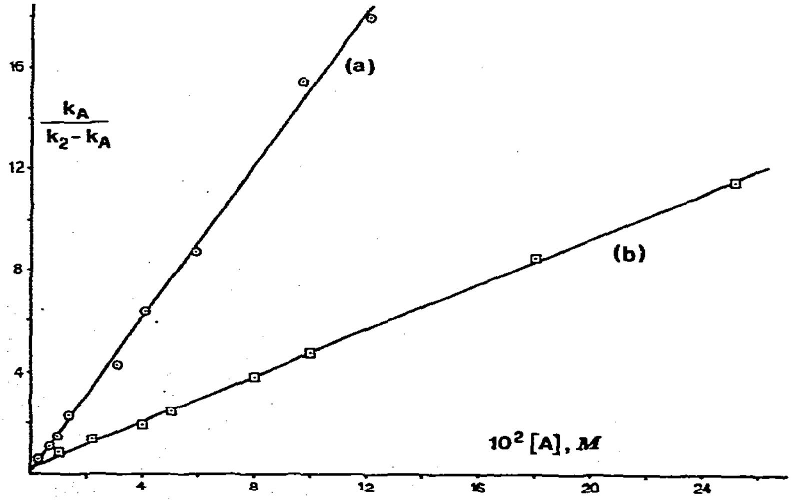


Fig. 3. Plots of $k_A/(k_2 - k_A)$ vs. amine concentration for the reaction of *cis*-[$PdCl_2(CN$-*p*-$C_6H_4NO_2)(PPh_3)$] with *o,o'*-dimethylaniline (a) and of *cis*-[$PdCl_2(CN$-*o*-$C_6H_4Me)(PPh_3)$] with *p*-anisidine (b).

lines throughout the amine concentration ranges investigated were obtained on plotting $k_A/(k_2 - k_A)$ vs. [A], by the use of an alternative form of eq. 3 and the appropriate k_2 values obtained as above:

$$k_A/(k_2 - k_A) = k_4/k_{-2} + (k_3/k_{-2})[A] \tag{5}$$

An example of such plot is reported in Fig. 3.

Plots according to eq. 5 gave k_3/k_{-2} ratios in good agreement with those obtained from the linear portions of reciprocal plots of $1/k_A$ vs. $1/[A]$. The intercepts (k_4/k_{-2}) were either statistically insignificant at the 95% confidence level of the least-squares treatment or comparatively small and affected by large relative errors (Tables 1 and 2). This indicates that conversion of the intermediate (Scheme 1) to the final carbene complex IV takes place preferentially through the catalytic action of the amine (k_3 step). These results show that the same mechanism of carbene formation from palladium(II) isocyanide complexes applies to primary and secondary amines.

It is also confirmed that the peculiar rate law 2 observed for *p*-substituted primary anilines is associated with the fact that for these amines the k_{-2} term is negligible as compared to the $k_4 + k_3[A]$ one in the general eq. 3. When sufficient steric strain is introduced into the intermediate by the presence of *ortho*-substituents, the k_{-2} term (which relates to collapse to the starting reactants) increases while at the same time k_4 and k_3 decrease [2,3], thereby yielding the rate law, eq. 3. The form of this law is such that the amine concentrations at which k_A approaches the limiting value k_2 are lower the higher the k_3/k_{-2} ratio. Therefore, since with unhindered primary amines and isocyanides the limiting value k_2 was reached even at the lowest feasible amine concentrations *, we can confidently conclude that the k_3/k_{-2} ratios for these systems are very large.

The data in Table 1 and plots in Fig. 1 are very revealing in this context. In the reactions of *o*-toluidine with *cis*-[$PdCl_2$(CN-*p*-C_6H_4X)(PPh_3)], rate law 2 is still observed for X = NO_2 whereas with X = Cl the general law 3 applies. The latter law was restored for X = NO_2 by the use of the more hindered *o,o'*-dimethylaniline. Apparently, one single substituent on the amine reacting with the *p*-nitrophenylisocyanide complex is not sufficient to enhance the k_{-2} term, owing to the overwhelming stabilization of the intermediate which arises from the strongly electron-withdrawing *p*-nitro group. This is borne out by the changes in the k_3/k_{-2} ratio which result from a net balance of combined steric and electronic factors [2,3]. Thus, the larger value (152 M^{-1}) for the *p*-$NO_2C_6H_4NC$ complex reacting with *o,o'*-dimethylaniline compared to that for the *p*-ClC_6H_4NC complex reacting with *o*-toluidine (48 M^{-1}) is mainly due to a decrease in k_{-2} related to a more electronically stabilized intermediate, in spite of the higher steric hindrance of the reacting amine.

Rate data in Table 2 show that *o*-substitution on the coordinated isocyanide increases the k_{-2} term to such an extent that rate law 3 in generally observed. In these cases the k_3/k_{-2} ratio appears to be mainly influenced by steric factors, as can be seen from the comparatively low value found for the reaction of *p*-anisidine with the more hindered *o,o'*-dimethylphenylisocyanide complex (a result of concom-

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* To check this we have repeated some of the kinetic studies reported earlier [1], extending the amine concentrations to the lowest possible ranges (Table 3).

TABLE 3

k_2 VALUES FOR THE REACTIONS OF *cis*-[$PdCl_2(CN$-*p*-$C_6H_4X)(PPh_3)$] WITH *para*- AND *ortho*-SUBSTITUTED ANILINES AT 30°C IN 1,2-DICHLOROETHANE

X	Amine	k_2 ($M^{-1}min^{-1}$)
NO_2	*p*-toluidine	54.02 [a]
NO_2	*o*-toluidine	8.40
NO_2	*o,o'*-dimethylaniline	6.02
Cl	*p*-toluidine	4.03 [a]
Cl	*o*-toluidine	1.60
Me	*p*-toluidine	0.75 [a]

[a] Values reassessed from ref. 1.

itant decrease in k_3 and increase in k_{-2}). On the other hand, changes in the *para*-substituent on the entering amine have little influence on the k_3/k_{-2} ratio for the reactions of *p*-$MeC_6H_4NH_2$ and *p*-$MeOC_6H_4NH_2$ with the *o*-tolylisocyanide substrate.

The interplay of electronic vs. steric effects is also borne out by the k_2 values listed in Table 3.

As can be seen, the k_2 term increases with increasing electron-withdrawing properties of the *p*-substituent on the isocyanide and decreases with increasing steric hindrance on the entering amine, other things being equal, in agreement with the k_2 step being a direct nucleophilic attack by the amine on the isocyanide carbon [1—3].

The same arguments apply to the k_2 values in Table 2 relating to reactions of *o*-substituted isocyanide complexes. In this case, the accelerating effect of electron-releasing groups on the amine is also evident.

Experimental

Materials

The complexes *cis*-[$PdCl_2(CNR)(PPh_3)$] (R = *p*-$C_6H_4NO_2$, *p*-C_6H_4Cl, *o*-C_6H_4Me, *o,o'*-$C_6H_3Me_2$) and the corresponding carbene derivatives *cis*-[$PdCl_2\{C(NHR)NHR'\}(PPh_3)$] (R' = *o*-$C_6H_4Me$, *o,o'*-$C_6H_3Me_2$, *p*-$C_6H_4Me$, *p*-$C_6H_4OMe$) were prepared according to the general methods reported earlier [4,6,9]. In the case of the more hindered reactants (*o,o'*-$Me_2C_6H_3NH_2$ or *o,o'*-$Me_2C_6H_3NC$) a molar ratio amine/isocyanide complex ≃30 was used and the reaction mixture was kept at room temperature for 4 days. All products were purified by successive reprecipitations from chloroform or acetone by addition of ethyl ether and identified by elemental analysis and IR spectra (Table 4). The amines were purified by sublimation or by distillation at reduced pressure over KOH. The solvent, 1,2-dichloroethane, was purified by standard methods [10].

Kinetics

The reactions were followed spectrophotometrically by measuring changes in

TABLE 4

ANALYTICAL AND PHYSICAL DATA

Complex	Colour	M.P. [a] (°C)
cis-$[PdCl_2(CN\text{-}o,o'\text{-}C_6H_3Me_2)(PPh_3)]$	Pale-yellow	235—237
cis-$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4NO_2)NH\text{-}o\text{-}C_6H_4Me\}(PPh_3)]$	Pale-yellow	247—250
cis-$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4NO_2)NH\text{-}o,o'\text{-}C_6H_3Me_2\}(PPh_3)]$	Off-white	201—204
cis-$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4Cl)NH\text{-}o\text{-}C_6H_4Me\}(PPh_3)]$	White	250—252
cis-$[PdCl_2\{C(NH\text{-}o\text{-}C_6H_4Me)NH\text{-}p\text{-}C_6H_4Me\}(PPh_3)]$	White	248—250
cis-$[PdCl_2\{C(NH\text{-}o\text{-}C_6H_4Me)NH\text{-}p\text{-}C_6H_4OMe\}(PPh_3)]$	White	215—218
cis-$[PdCl_2\{C(NH\text{-}o,o'\text{-}C_6H_3Me_2)NH\text{-}p\text{-}C_6H_4OMe\}(PPh_3)]$	Off-white	240—245

[a] Uncorrected values; all complexes decompose on melting.

optical density in the range 330—360 nm with time by means of an Optica CF-4R double-beam instrument.

Freshly prepared solutions of the complex, stored under nitrogen in an aluminum-foil wrapped flask, were used for each kinetic run. The reactions were started by mixing known volumes of pre-thermostatted standard solutions of the reagents in the thermostatted (±0.1°C) cell compartment of the spectrophotometer. A solution containing the same concentration of the entering amine was used as a reference. The reacting amine was present in sufficient excess to provide pseudo-first-order conditions and to force the reactions to completion. The final spectra were generally in good agreement with those of the products prepared and characterized independently. The values of pseudo-first-order rate constants k_{obs}, were obtained from the slopes of plots of $\log(D_t - D_\infty)$ vs. time, where D_t and D_∞ are the optical densities of the reaction mixture at time t and after 7—8 half-lives, respectively. The values of k_{obs} were reproducible to better than ±10%.

Infrared spectra

Infrared spectra were recorded on a Perkin—Elmer 457 spectrophotometer using hexachlorobutadiene mulls and NaCl windows in the region 4000—1200 cm^{-1}, nujol mulls and CsI windows in the region 1700—250 cm^{-1}. Calibration was performed with a polystyrene film.

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Analysis found (calcd.) (%)				Characteristic IR bands (cm^{-1})		
C	H	N	Cl	ν(NH)	ν(CN)	ν(PdCl)
56.5 (56.81)	4.3 (4.24)	2.4 (2.45)	12.5 (12.42)		2209 vs	344ms, 295 s
55.6 (55.31)	4.1 (4.06)	6.0 (6.05)	10.2 (10.20)	3250(sh), 3230(sh) 3208 ms(br), 3170 w, 3120 w	1543 s, 1330 s	310 ms, 282 m
55.6 (55.91)	4.3 (4.26)	5.9 (5.93)	9.9 (10.00)	3320(sh), 3310 ms, 3165 ms(br)	1542 s, 1340 s	315 ms, 283 ms
55.8 (56.16)	4.1 (4.12)	4.1 (4.09)	15.6 (15.54)	3240(sh), 3180 ms(br), 3110(sh)	1540 s, 1327 s	315 ms, 282 ms
59.8 (59.70)	4.8 (4.71)	4.2 (4.22)	10.7 (10.68)	3225(sh), 3210 ms(br) 3120(sh)	1540 s, 1329 s	306 ms, 283 ms
58.2 (58.29)	4.6 (4.59)	4.1 (4.12)	10.5 (10.43)	3190 s(br), 3120(sh)	1540 s, 1331 s	305(sh), 294 ms, 285 ms
58.9 (58.85)	4.8 (4.79)	4.0 (4.04)	10.1 (10.22)	3320 m, 3185 ms(br) 3120(sh)	1540 s, 1310 ms	307 m, 282 ms

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