MECHANISM OF FORMATION OF CARBENE DERIVATIVES FROM THE REACTION OF BINUCLEAR HALO-BRIDGED PALLADIUM(II) ISOCYANIDE COMPLEXES WITH AROMATIC AMINES

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Summary

A mechanistic study is reported of the reaction of dimeric complexes $[PdCl_2-(CNAr)]_2$ (Ar = p-C_6H_4OMe, p-C_6H_4Me) with *ortho*- and *para*-substituted primary and secondary anilines, $NHRAr'$ (R = H, Me, Et; Ar' = Ph, p-C_6H_4Me, p-C_6H_4Cl, o-C_6H_4Me). The reaction involves an initial fast halide-bridge splitting to give *trans*-$[PdCl_2(CNAr)(NHRAr')]$, followed by a reaction of a second molecule of amine with the coordinated isocyanide to give the carbene derivatives *trans*-$[PdCl_2\{C(NHAr)NRAr'\}(NHRAr')]$. This latter stage takes place stepwise via direct nucleophilic attack on the isocyanide carbon followed by proton transfer to the final carbene complex. The rates of carbene formation depend on the steric and electronic characteristics of both the metal complex and the amine.

Introduction

We have previously described the preparation of binuclear halo-bridged complexes $[PdX_2(CNR)]_2$ (R = Ph, p-C_6H_4Me; X = Cl, Br) and their halide-bridge splitting reaction with a variety of neutral and anionic ligands [1]. The reaction of $[PdCl_2(CNPh)]_2$ with an excess of p-toluidine yields the carbene derivative $[PdCl_2\{C(NHPh)NH$-p-$C_6H_4Me\}(NH_2$-p-$C_6H_4Me)]$.

As part of our programme of mechanistic studies of nucleophilic attack by aromatic amines on coordinated isocyanide in complexes of type *cis*-$[PdCl_2-(CNR)(L)]$ [2—6] (L = tertiary phosphine, phosphite, isocyanide) we have
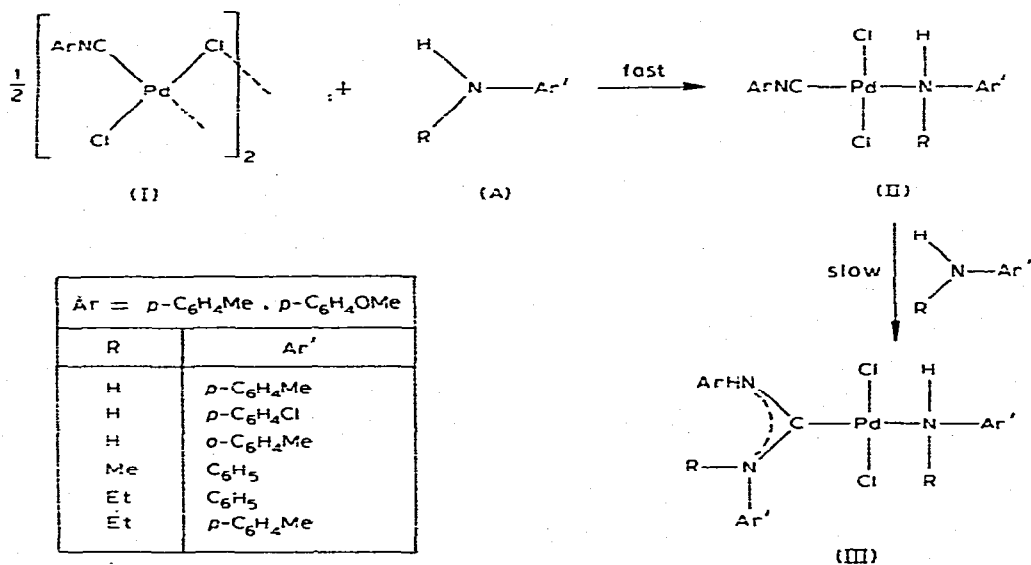
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carried out a kinetic investigation of the reaction of the halo-bridged dimers with a series of primary and secondary anilines. These dimers are of interest since we find that the first step of reaction is the formation of mononuclear *trans*-amine complexes [PdCl$_2$(CNR)(Amine)]. Therefore, the final carbene product comes from an isocyanide complex which, unlike previous ones, has a *trans* configuration and a N-donor ancillary ligand, thereby providing a means of comparison on both electronic and steric points of view.

Results and discussion

The reaction of binuclear chloro-bridged complexes, [PdCl$_2$(CNAr)]$_2$ (I) with primary and secondary anilines (A) takes place according to Scheme 1, as indicated by spectroscopic measurements in 1,2-dichloroethane or CDCl$_3$ solution.

SCHEME 1

Ar = p-C$_6$H$_4$Me , p-C$_6$H$_4$OMe	
R	Ar'
H	p-C$_6$H$_4$Me
H	p-C$_6$H$_4$Cl
H	o-C$_6$H$_4$Me
Me	C$_6$H$_5$
Et	C$_6$H$_5$
Et	p-C$_6$H$_4$Me

The first step is a very fast, virtually quantitative splitting of the chloro bridges of I to yield the *trans* monomeric species II (*trans*-derivatives similar to II have been obtained from the reaction of binuclear complexes I with other nitrogen donor ligands, such as pyridine [1]). These complexes have been isolated and characterized (see Experimental). Their *trans* configuration was proved by the presence of only one Pd—Cl stretching absorption in the 350—340 cm^{-1} range of the far I.R. spectrum of the nujol mulls. This step can be monitored in 1,2-dichloroethane solution by the immediate change of the C≡N stretching frequencies of coordinated isocyanides on going from I [ν(C≡N) at 2235 and 2230 cm^{-1} for Ar = p-C$_6$H$_4$Me and p-C$_6$H$_4$OMe, respectively] to II [ν(C≡N) in the narrow range 2225—2220 cm^{-1}] and by the simultaneous appearance of the ν(N—H) of coordinated amine in the range 3350—3250 cm^{-1}.

The second step is the much slower formation of the carbene species III by

nucleophilic attack of the amine on the isocyanide carbon of II; the major spectral changes are the decay of the $\nu(C\equiv N)$ band of II and the concomitant growth of the N—H stretching frequency of the carbene ligand as a broad and strong band around 3200 cm^{-1}. The final carbene species III have *trans* configurations, as shown by far IR spectra [one single $\nu(Pd—Cl)$ band in the range 340—330 cm^{-1}, see Experimental]. This is consistent with what appears to be a general feature of carbene formation by amine attack on coordinated isocyanides, viz. retention of configuration around the metal center [1—8].

The stepwise nature of these reactions was confirmed by spectral observations in the UV-visible region. As an example in Fig. 1 are illustrated the optical density changes in the range 430—330 nm during the reaction of $[PdCl_2(CN-p-C_6H_4OMe)]_2$ (I) with p-toluidine (A) (substrate/amine molar ratio ca. 800).

The first stage appears to be over within the time of mixing of the reactants, as indicated by the immediate and complete disappearance of the absorption due to $[PdCl_2(CN-p-C_6H_4OMe)]_2$. Within the same time a new absorption ap-
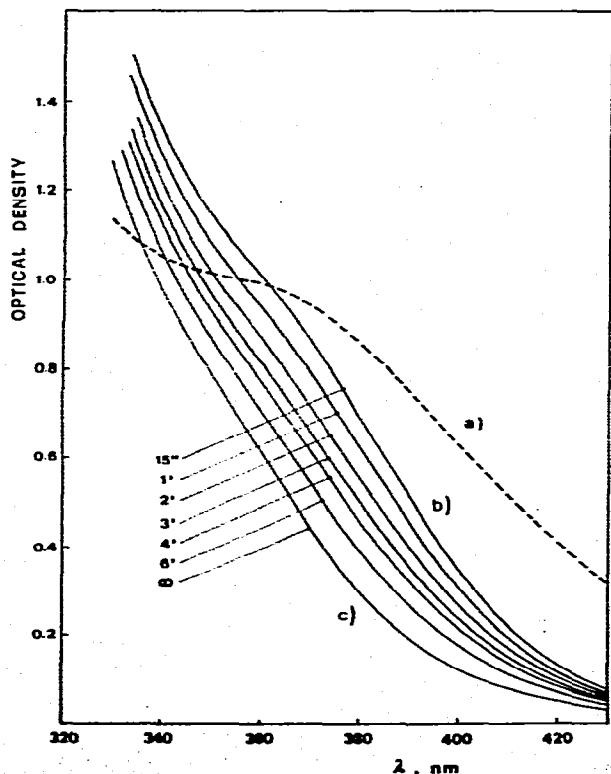

Fig. 1. Spectral changes occurring during the reaction of $[PdCl_2(CN-p-C_6H_4OMe)]_2$ (I) with p-toluidine in 1,2-dichloroethane at 25°C. The reference cell contains a 8×10^{-2} M solution of p-toluidine. (a) Spectrum of a 10^{-4} M solution of I in 1,2-dichloroethane. (b) Spectrum of reaction mixture after mixing a 2×10^{-4} M solution of I with a 16×10^{-2} M solution of p-toluidine. (c) Spectrum of reaction mixture after completion of reaction. This spectrum is the same as that of a 10^{-4} M solution of *trans*-[PdCl_2-{C(NH-p-C_6H_4OMe)NH-p-C_6H_4Me}(H_2N-p-C_6H_4Me)] with a 8×10^{-2} M solution of p-toluidine in the reference cell.

pears which corresponds to the intermediate II formed in the first stage. The intensity of the new band is independent of the concentration of the amine present in excess provided that the initial concentration of metal substrate is the same in every run. These spectral observations suggest that, in solutions of I and A an equilibrium exists between the reactants and the intermediate such that the intermediate is rapidly formed in the time of mixing, and that the equilibrium lies essentially completely over towards the intermediate. In the second, slower stage of the reaction, the disappearance of the latter rather than the disappearance of the starting substrate I, is being followed spectrally. The absorption band of the intermediate slowly decreases in intensity to give a final spectrum which is identical with that of the carbene product III under comparable experimental conditions. Similar spectral changes were observed for all other I-A systems under study.

We have also carried out kinetic measurements of the rate of reaction of the second, slow step of Scheme 1 under pseudo-first order conditions. Rate parameters are listed in Tables 1 and 2 for CNAr= CN-p-C$_6$H$_4$OMe and CN-p-C$_6$H$_4$Me,

TABLE 1

RATE DATA FOR THE REACTIONS OF [PdCl$_2$(CN-p-C$_6$H$_4$OMe)]$_2$ WITH ANILINES (A) IN 1,2-DI-CHLOROETHANE AT 25°C (uncertainties are estimated standard errors)

A	10^2 [A] (M)	k_A (M^{-1} min^{-1}) [a]	k_2 (M^{-1} min^{-1}) [b]	k_3/k_{-2} (M^{-1}) [c]
p-MeC$_6$H$_4$NH$_2$	1.51	1.91	3.18 ± 0.01	99 ± 1
	2.32	2.20		
	4.43	2.59		
	8.85	2.85		
	14.88	2.99		
p-ClC$_6$H$_4$NH$_2$	4.34	0.39	0.59 ± 0.001	44.6 ± 0.4
	9.78	0.48		
	14.50	0.51		
	19.34	0.53		
	26.44	0.54		
o-MeC$_6$H$_4$NH$_2$	5.31	1.08	1.57 ± 0.01	42 ± 1
	8.72	1.24		
	11.46	1.31		
	18.14	1.38		
C$_6$H$_5$NHEt	2.40	0.90	8.1 ± 0.5	5.2 ± 0.3
	6.88	2.07		
	9.65	2.75		
	13.70	3.43		
	14.62	3.55		
p-MeC$_6$H$_4$NHEt	1.92	2.74	25 ± 1	6.4 ± 0.3
	4.14	5.24		
	7.31	7.85		
	10.87	10.44		
C$_6$H$_5$NHMe	1.64	2.49	22.5 ± 2	7.6 ± 0.6
	3.20	4.54		
	4.38	5.65		
	11.46	10.73		
	17.34	12.05		

[a] k_A = k_{obs}/[A]. [b] Calculated from intercepts of plots of $1/k_A$ vs. $1/[A]$. [c] Calculated from slopes of plots of $1/k_A$ vs. $1/[A]$.

TABLE 2

RATE DATA FOR THE REACTIONS OF $[PdCl_2(CN\text{-}p\text{-}C_6H_4Me)]_2$ WITH ANILINES (A) IN 1,2-DI-CHLOROETHANE AT 25°C (uncertainties are estimated standard errors)

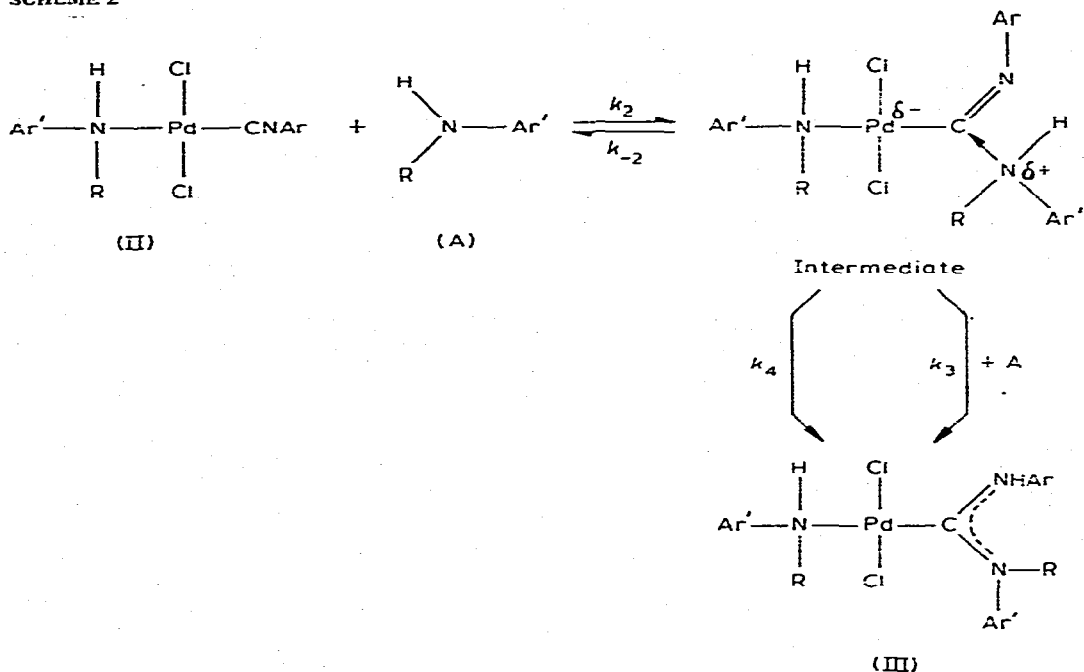| A	10^2 [A] (M)	$k_A (M^{-1}\ min^{-1})^a$	$k_2 (M^{-1}\ min^{-1})^b$	$k_3/k_{-2} (M^{-1})^c$
$p\text{-}MeC_6H_4NH_2$	4.30	3.25	4.00 ± 0.01	100 ± 2
	7.42	3.51		
	9.56	3.62		
	12.98	3.72		
	17.74	3.79		
$p\text{-}ClC_6H_4NH_2$	2.12	0.36	0.88 ± 0.03	32 ± 2
	2.97	0.42		
	7.41	0.60		
	10.37	0.69		
	15.59	0.75		
$o\text{-}MeC_6H_4NH_2$	5.14	1.36	1.89 ± 0.01	50 ± 1
	6.51	1.44		
	8.82	1.55		
	12.82	1.63		
	17.26	1.69		
C_6H_5NHEt	2.84	1.69	12.5 ± 0.8	5.5 ± 0.3
	6.98	3.33		
	9.34	4.20		
	12.22	5.25		
	15.71	5.75		
	16.46	6.00		
$p\text{-}MeC_6H_3NHEt$	1.70	4.59	30 ± 2	10.6 ± 0.6
	2.19	5.75		
	2.35	6.00		
	3.31	8.00		
	4.54	9.75		
	5.59	11.10		
C_6H_5NHMe	2.44	5.61	23.9 ± 0.3	12.6 ± 0.2
	4.30	8.44		
	5.40	9.62		
	7.42	11.57		
	11.99	14.30		

$^a k_A = k_{obs}/[A]$. ^{b} Calculated from intercepts of plots of $1/k_A$ vs. $1/[A]$. ^{c} Calculated from slopes of plots of $1/k_A$ vs. $1/[A]$.

respectively. In all cases examined the second order rate parameter $k_A = k_{obs}/[A]$ obeys the general rate law 1.

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

corresponding to the stepwise mechanism shown in Scheme 2. The first step (k_2) in this mechanism is the nucleophilic attack of the entering amine on the coordinated isocyanide carbon, producing a labile intermediate which may either revert to reactants (k_{-2}) or yield the final carbene complex III through parallel proton transfer reactions. These take place either intramolecularly, in a four-membered cyclic transition state (k_4), or intermolecularly by the agency of one further amine molecule (A, k_3) serving as a proton acceptor—donor in a six-membered transition state.

SCHEME 2

H   Cl
| |
Ar'——N——Pd——CNAr +   N——Ar' $\overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}}$
| |
R   Cl

(II)   (A)

Intermediate

k_4 k_3 + A

(III)

The same rate law 1 and mechanism were observed for the reaction of the same entering amines with a variety of complexes, cis-[PdCl$_2$(CNR)(L)] (L = tertiary phosphines, phosphites, isocyanides) [3—6]. The values of rate parameters, k_2 and k_3/k_{-2}, in Tables 1 and 2 were obtained by a non-linear least-squares fit of eq. 1 (uncertainties are estimated standard errors).

Non-linear regression analysis gave statistically insignificant values for the k_4 term, indicating that conversion of the intermediate (Scheme 2) to the final carbene III takes place preferentially through the catalytic action of the amine (k_3 step). Hence, rate law 1 can be treated graphically as

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

or

$$k_A/(k_2 - k_A) = (k_3/k_{-2})[A] \tag{3}$$

Typical examples of plots according to eq. 2 and 3 are shown in Fig. 2 and 3, respectively, for the reaction of [PdCl$_2$(CN-p-C$_6$H$_4$Me)]$_2$ with N-methylaniline.

The course of the reaction in Scheme 1 was also confirmed by the fact that rate parameters for the overall reaction of [PdCl$_2$(CN-p-C$_6$H$_4$OMe)]$_2$ with p-ClC$_6$H$_4$NH$_2$ are identical with those obtained separately for the reaction of the same amine with the isolated trans-[PdCl$_2$(CN-p-C$_6$H$_4$OMe)(H$_2$N-p-C$_6$H$_4$Cl)]. The rate data in Tables 1 and 2 for the various amines under study can be compared with a fair degree of confidence even though the use of different entering amines necessarily implies different substrates II: in fact, the ν(C≡N) bands of
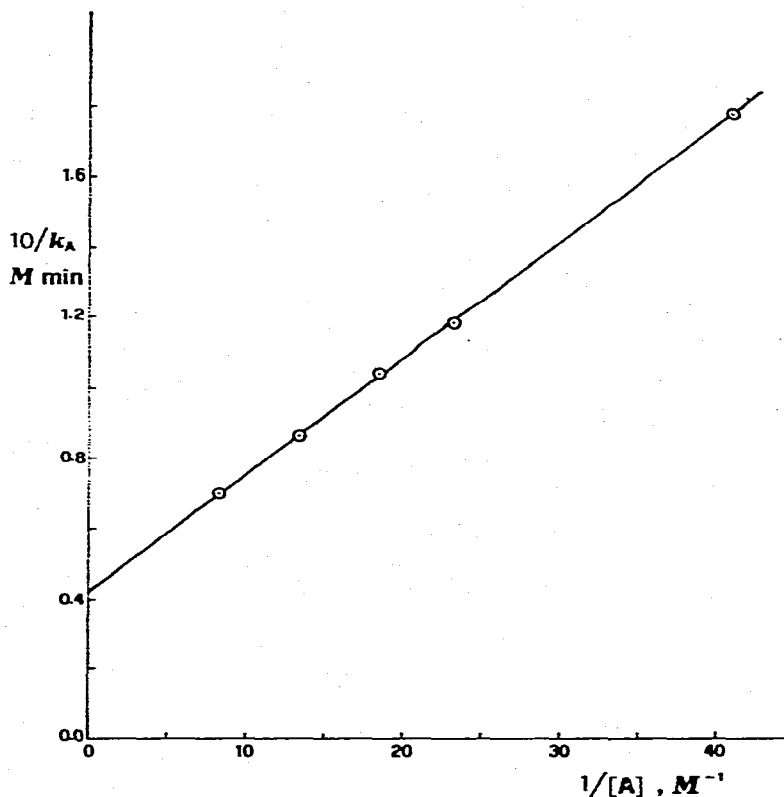
Fig. 2. Plot of $1/k_A$ vs. $1/[A]$ for the reaction of trans-[PdCl$_2$(CN-p-C$_6$H$_4$Me)(NHMeC$_6$H$_5$)] with NHMeC$_6$H$_5$.

coordinated isocyanide in II fall virtually at the same frequency within experimental error, and are thus independent of the trans-amine ligand. This fact, taken along with the trans-configuration of II, implies that in all substrates II the electrophilic character of the isocyanide carbon and the steric requirements around such reacting center are little affected by the nature of the coordinated amine. This is a rather fortunate situation, since attempted kinetic studies of attack by different amines on a fixed trans-amine substrate II were always hampered by scrambling of the coordinated amine with the entering one.

trans-[PdCl$_2$(CNAr)(A)] + A′ ⇌ trans-[PdCl$_2$(CNAr)(A′)] + A
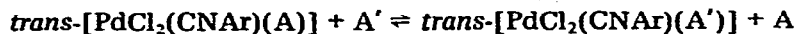
The k_2 values, which are related to direct nucleophilic attack on the isocyanide carbon, increase with (i) increasing donor ability, (ii) decreasing steric hindrance of the entering amine, and (iii) decreasing electron-releasing abilities of the p-substituent on the isocyanide. Secondary anilines have k_2 values much higher than primary anilines, clearly as a consequence of their higher basicity. Electronic effects are evident on comparing the k_2 values for the pair p-MeC$_6$H$_4$-NH$_2$/p-ClC$_6$H$_4$NH$_2$ (or C$_6$H$_5$NHEt/p-MeC$_6$H$_4$NHEt) in which the amines have the same steric hindrance at the reaction site. Steric effects are easily recognized on
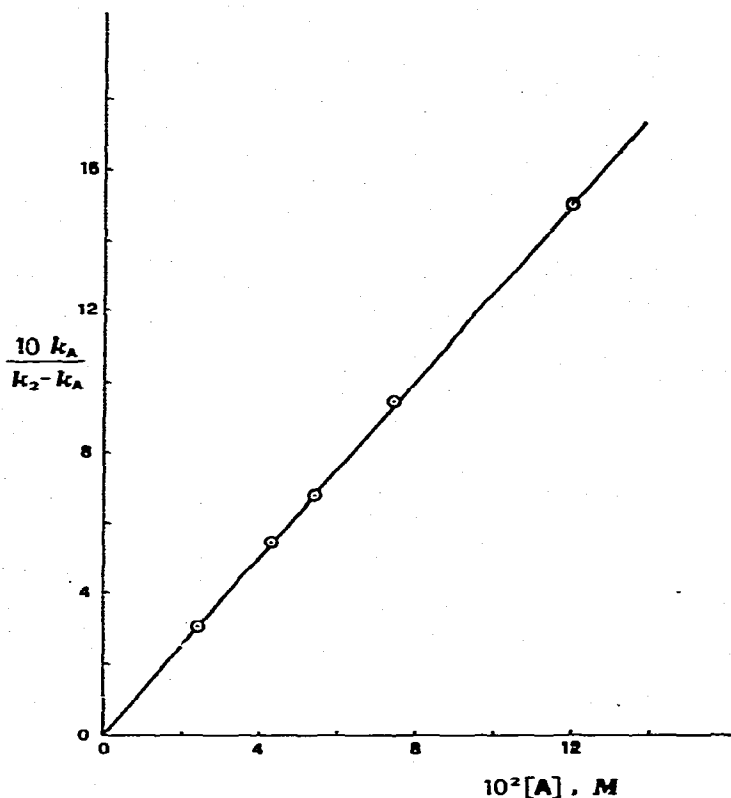
Fig. 3. Plot of $k_A/(k_2 - k_A)$ vs. [A] for the reaction of trans-[PdCl$_2$(CN-p-C$_6$H$_4$Me)(NHMeC$_6$H$_5$)] with NHMeC$_6$H$_5$.

comparing the pair p-MeC$_6$H$_4$NH$_2$/o-MeC$_6$H$_4$NH$_2$ (or C$_6$H$_5$NHEt/C$_6$H$_5$NHMe).

The k_2 value for the reaction of [PdCl$_2$(CN-p-C$_6$H$_4$Me)]$_2$ with C$_6$H$_5$NHMe is higher than that for the reaction of cis-[PdCl$_2$(CN-p-C$_6$H$_4$Me){P(OMe)$_3$}] [4] with the same amine. We have shown previously [4] that the stretching frequency, ν(C≡N), of coordinated isocyanide can be reasonably taken as a measure of the electrophilic character of the isocyanide carbon. Since this frequency falls at 2223 cm^{-1} for both $trans$-[PdCl$_2$(CN-p-C$_6$H$_4$Me)(C$_6$H$_5$NHMe)] and cis-[PdCl$_2$-(CN-p-C$_6$H$_4$Me){P(OMe)$_3$}] the higher reactivity of the former towards C$_6$H$_5$-NHMe can be related to the lower steric hindrance at the reacting site which arises from the $trans$ configuration of the substrate.

As observed in our previous studies [3—5], the k_3/k_{-2} values (Tables 1 and 2) are affected by both steric and electronic factors. The k_3/k_{-2} ratios for primary anilines are much higher than those for secondary anilines, because of the greater steric crowding by the substituent R at the nitrogen atom, which increases the tendency of the intermediate in Scheme 2 to revert to the starting isocyanide substrate II (increased k_{-2} term, despite the higher basicity of secondary amines). Steric effects are also evident on comparing the pairs p-MeC$_6$H$_4$NH$_2$/o-MeC$_6$H$_4$-NH$_2$ or C$_6$H$_5$NHMe/C$_6$H$_5$NHEt. On the other hand, other things being equal, increased donor ability in the amine nitrogen causes an increased k_3/k_{-2} value,

as illustrated by the pairs p-MeC$_6$H$_4$NH$_2$/p-ClC$_6$H$_4$NH$_2$ and C$_6$H$_5$NHEt/p-MeC$_6$-H$_4$NHEt.

We wish to emphasize that the use of *trans*-substrates II has allowed the measurement of k_3/k_{-2} values for unhindered primary anilines (p-toluidine and p-chloroaniline) reacting with unhindered coordinated isocyanides. In the reactions of the same amines with the substrates *cis*-[PdCl$_2$(CNAr)(L)] (Ar = p-C$_6$H$_4$Me, p-C$_6$H$_4$OMe; L = π-bonding ligand) which we have examined, the k_3/k_{-2} ratios were so high as to reduce the general rate law 1 to the simple limiting form $k_A = k_2$ [2,5,6]. This is probably due to the fact that the *trans* amine ligand, lacking π-bonding ability, is less effective in stabilizing the intermediate of Scheme 2 towards collapse to the starting reactants, thereby making the k_{-2} term in rate law 1 comparable with the k_3[A] value.

Experimental

Materials

The amines were purified by sublimation or by distillation at reduced pressure over KOH. The 1,2-dichloroethane was purified by a standard procedure [9]. The chloro-bridged complexes [PdCl$_2$(CNAr)]$_2$ (Ar = p-C$_6$H$_4$OMe, p-C$_6$H$_4$Me) were prepared by published methods [1]. The bridge-splitting products, *trans*-[PdCl$_2$(CNAr)(NHRAr')], and the final carbene derivatives, *trans*-[PdCl$_2${C(NH-Ar)NRAr'}(NHRAr')] (R = H, Me, Et; Ar' = Ph, p-C$_6$H$_4$Me, p-C$_6$H$_4$Cl, o-C$_6$H$_4$Me) were prepared and characterized as described below for two typical examples.

Preparation and characterization of trans-[PdCl$_2$(CN-p-C$_6$H$_4$OMe)(NH$_2$-p-C$_6$H$_4$Cl)]

A stirred suspension of the binuclear complex [PdCl$_2$(CN-p-C$_6$H$_4$OMe)]$_2$ (0.310 g, 0.5 mmol) in 10 ml of 1,2-dichloroethane was treated dropwise with p-chloroaniline (0.128 g, 1 mmol) in 10 ml of the same solvent. After the addition a red-orange solution was obtained, the IR spectrum of which showed two ν(N—H) bands of the coordinated amine at 3320 and 3260 cm^{-1}, and one ν(C≡N) band of the coordinated isocyanide at 2223 cm^{-1}. This solution was treated with charcoal, filtered, and concentrated to small volume under reduced pressure. The yellow product was precipitated by adding an ethyl ether/n-hexane mixture (1/2 in volume). It was purified by reprecipitation from the same solvents (yield ≈70%). Anal. Found (%): C, 38.4; H, 3.0; N, 6.4; Cl, 24.4. C$_{14}$H$_{13}$N$_2$OCl$_3$Pd calcd.: C, 38.39; H, 2.99; N, 6.40; Cl, 24.28%.

The ^{1}H NMR spectrum (δ (ppm) from TMS) in CDCl$_3$ solution showed the phenyl protons as overlapping multiplets in the range 7.6—6.7, the NH$_2$ protons as a broad singlet at 5.26 (which disappears upon treatment with D$_2$O) and the OMe protons as a sharp singlet at 3.83. The IR spectrum (cm^{-1}) of the solid showed ν(N—H) bands at 3225 ms, 3200 (sh), 3185 (sh); one ν(C≡N) band at 2225 vs and one ν(Pd—Cl) band at 343 s; all other complexes of this type have only one strong ν(Pd—Cl) absorption in the range 350—340 cm^{-1}, a typical feature for the *trans* configuration.

Preparation and characterization of trans-[PdCl$_2${C(NH-p-C$_6$H$_4$OMe)NH-p-C$_6$H$_4$Me}(NH$_2$-p-C$_6$H$_4$Me)]

A stirred suspension of the binuclear complex [PdCl$_2$(CN-p-C$_6$H$_4$OMe)]$_2$

(0.310 g, 0.5 mmol) in 20 ml of 1,2-dichloroethane was treated dropwise with
p-toluidine (0.107 g, 1 mmol) in 20 ml of the same solvent. A red-orange solu-
tion was obtained, the IR spectrum of which was identical with that of $trans$-
$[PdCl_2(CN-p-C_6H_4OMe)(NH_2-p-C_6H_4Me)]$ prepared as previously described
[ν(N—H) 3325 and 3260 cm^{-1}; ν(C≡N) 2225 cm^{-1}]. This solution was then
treated with further 1.5 mmol of p-toluidine and set aside overnight, whereupon
the IR spectrum showed the disappearance of the ν(C≡N) band and the presence
of the ν(N—H) band of the final carbene complex at 3315, 3280 and 3210 cm^{-1}.
After concentration to small volume under reduced pressure, addition of ethyl
ether gave the carbene product as a pale-yellow solid, which was reprecipitated
from CHCl$_3$/Et$_2$O. Anal. Found: C, 50.1; H, 4.80; N, 8.0; Cl, 13.3. C$_{22}$H$_{25}$N$_3$OCl$_2$-
Pd calcd.: C, 50.35; H, 4.80; N, 8.01; Cl, 13.51%.

The ^{1}H NMR spectrum (δ (ppm) from TMS) in CDCl$_3$ showed the phenyl
protons as overlapping multiplets in the range 7.8—6.5, the NH$_2$ protons of
coordinated p-toluidine as a broad singlet at 4.65, the NH protons of the car-
bene moiety as broad singlets at 10.0 and 7.4. The OMe protons appear as two
singlets at 3.82 and 3.77 (ratio ca. 3/1) indicating the presence of two conforma-
tional isomers of the carbene grouping [10]. The methyl protons of the p-tolyl
groups produce a single unresolved signal at 2.33. The IR spectrum (cm^{-1}) in the
solid showed ν(N—H) bands at 3285 ms, 3240 ms and 3153 m; ν(C≡N) carbene
at 1535 s (br); ν(Pd—Cl) at 333 ms; all other carbene derivatives have a single
medium-strong to strong ν(Pd—Cl) band in the range 340—330 cm^{-1}.

Kinetics

The reactions were followed spectrophotometrically by measuring changes in
optical density in the range 330—380 nm with time by means of a Shimadzu—
Bausch and Lomb instrument equipped with a Houston Instruments Omnigraphic
Recorder.

Freshly prepared solutions of the complex, stored under nitrogen in an alumi-
num-foil wrapped flask, were used for each kinetic run. The reactions were start-
ed by mixing known volumes of pre-thermostatted standard solutions of the
reagents in the thermostatted (±0.1°C) cell compartment of the spectrophoto-
meter. A solution containing the same concentration of the entering amine was
used as a reference. The reacting amine was present in sufficient excess to pro-
vide pseudo-first order conditions and to force the reactions to completion.
The final spectra were 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 and ^{1}H NMR 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}. Solution
spectra were obtained by the use of NaCl liquid cells of 0.5 or 1.0 mm path
length. Calibration was performed with a polystyrene film.

The ^{1}H NMR spectra were recorded with a Varian NV-14 60 MHz instrument using TMS as internal standard.

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