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SOLVENT, LIGAND AND TEMPERATURE EFFECTS ON THE RATES OF REACTIONS OF *cis*-[$PdCl_2$(CNR)(L)] WITH SECONDARY AMINES

P. UGUAGLIATI, B. CROCIANI, U. BELLUCO

Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Istituto di Chimica Industriale, Venezia (Italy)

and L. CALLIGARO *

Cattedra di Chimica, Istituto di Chimica Industriale, Università di Padova, Via Marzolo 9, Padova (Italy)

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Summary

The kinetics of the reaction of *cis*-[$PdCl_2(CN\text{-}p\text{-}C_6H_4Cl)(PPh_3)$] with *N*-methylaniline yielding the carbene derivative *cis*-[$PdCl_2\{C(NH\text{-}p\text{-}C_6H_4Cl)NMePh\}(PPh_3)$] have been studied in various solvents such as acetone, 1,4-dioxane, 1,2-dichloroethane, and benzene. Overall rates for the stepwise process increase with decreasing ability of the solvent to form hydrogen bonds with the attacking amine. A kinetic study is also reported for the reactions of *N*-methylaniline with *cis*-[$PdCl_2(CN\text{-}p\text{-}C_6H_4Me)(L)$] in 1,2-dichloroethane (L = $P(OMe)_3$, $P(OMe)_2Ph$, PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PCy_3). The *cis* ligand L affects reaction rates through both steric and electronic factors. The nucleophilic attack of the amine on the C≡N carbon atom of coordinated isocyanide is favoured by low steric requirements and high π-acceptor ability of L. The activation parameters for the bimolecular nucleophilic attack when L = PPh_3 are $\Delta H_2^{\ddagger} = 9.8 \pm 0.7$ kcal/mol and $\Delta S_2^{\ddagger} = -30 \pm 2$ e.u.

Introduction

In a previous study [1,2] we found that the formation of carbene derivatives from isocyanide palladium(II) complexes and primary and secondary amines (A) in 1,2-dichloroethane takes place by the following stepwise mechanism:

$$\begin{tikzcd} \underset{\sim}{I} + A \arrow[r, shift left, "k_2"] & \text{Intermediate} \arrow[l, shift left, "k_{-2}"] \arrow[r, bend left=60, "{+A \atop k_3}"] \arrow[r, bend right=60, "k_4"'] & \underset{\sim}{II} \end{tikzcd}$$

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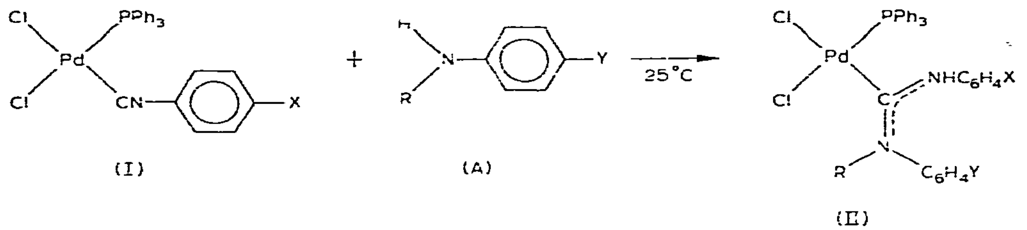
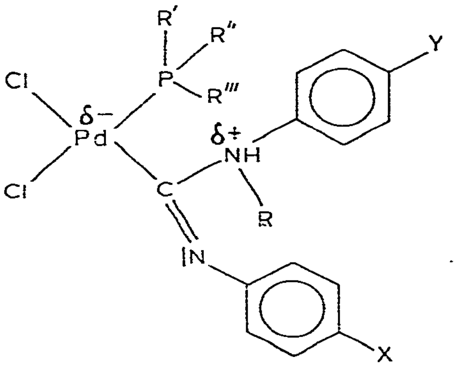
* To whom correspondence should be addressed.



(1)

(X = MeO, Me, H, Cl, NO$_2$; Y = MeO, Me, H, Cl; R = H, Me, Et)

The intermediate is formed by nucleophilic attack of the entering amine on the carbon atom of coordinated isocyanide, probably having structure B.



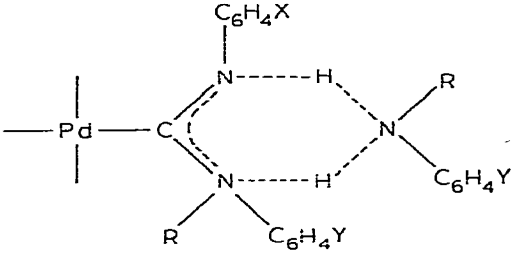
(B)

Rate data fit the equation:

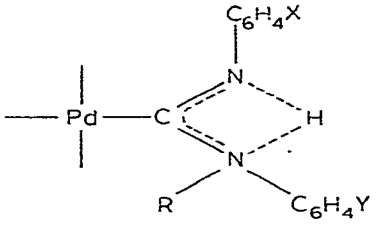
$$k_A = k_{obs}/[A] = k_2 \cdot \frac{k_4 + k_3[A]}{k_{-2} + k_4 + k_3[A]} \qquad (2)$$

where k_{obs} is the pseudo-first-order rate constant.

The proton transfers in the intermediate leading to the final carbene complexes II take place both intramolecularly, in a four-membered cyclic transition state (k_4), and intermolecularly, with an additional amine molecule serving in this case as bifunctional catalyst in a six-membered transition state (k_3):



T.S. for k_3



T.S. for k_4

We have now extended the mechanistic study of this system in order to elucidate solvent, temperature, and *cis*-ligand effects.

Results and discussion

Solvent effect

The kinetics of the reaction *cis*-$[PdCl_2(CN\text{-}p\text{-}C_6H_4Cl)(PPh_3)]$ + PhNHMe → *cis*-$[PdCl_2\{C(NH\text{-}p\text{-}C_6H_4Cl)NMePh\}(PPh_3)]$ have been investigated at 25°C in acetone, 1,4-dioxane, 1,2-dichloroethane, and benzene. The results are reported in Table 1 and Fig. 1. As can be seen, the overall second-order rate constant, k_A, decreases in the order of solvent: benzene > 1,2-dichloroethane > acetone ~ dioxane at comparable amine concentrations. Further, the dependence of k_A on [A] is curved in benzene and 1,2-dichloroethane and linear in acetone and 1,4-dioxane. Both these facts are in agreement with the general rate law (eq. 2), depending on whether $k_4 + k_3$ [A] is comparable with or much smaller than k_{-2}, respectively. In other words, the same stepwise mechanism as was proposed earlier [1] is operative in all solvents examined. Accordingly, in benzene and dichloroethane, where k_4 is negligible [1] *, the observed form of eq. 2 is

$$k_A = k_2 \cdot \frac{k_3[A]}{k_{-2} + k_3[A]} \tag{3}$$

which gives a nonlinear response of k_A to [A] (Fig. 1). Eq. 3 can be converted into

$$1/k_A = 1/k_2 + \frac{k_{-2}}{k_2k_3[A]} \tag{4}$$

Table 1 lists the values of k_2 and k_2k_3/k_{-2} obtained from least-squares fits of eq. 4.

In acetone and 1,4-dioxane the observed form of eq. 2 becomes

$$k_A = \frac{k_2k_4}{k_{-2}} + \frac{k_2k_3[A]}{k_{-2}} \tag{5}$$

which gives rise to a linear dependence of k_A on [A] (Fig. 1). Table 1 lists the values of k_2k_4/k_{-2} and k_2k_3/k_{-2} from least-squares fits of eq. 5.

The observed differences in reactivity between the two pairs of solvents are mainly related to a greater stabilization of the attacking amine by solvation and hydrogen bonding with the solvents acetone and dioxane. This can be deduced from the lower values of amine ν(N—H) in such solvents (Table 1). Deactivation of the amine will bring about a decrease in the overall reaction rates, which will be reflected in both the bimolecular nucleophilic attack term, k_2, and in the catalytic k_3 path. A decrease in the k_3 term will account for the linear dependence of k_A on [A] in these solvents, as expected from eq. 2 when $k_{-2} >> k_4 + k_3[A]$.

The ν(C≡N) of the coordinated isocyanide is very little affected by changes in the solvent.

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* k_4 has been found to be negligible for all cases in which curved plots of k_A vs. [A] are obtained, as shown by the fact that linear plots of $k_A/(k_2 - k_A)$ vs. [A] have statistically insignificant intercepts: eq. 2 can be rearranged into $k_A/(k_2 - k_A) = k_4/k_2 + (k_3/k_{-2})$[A] (vide infra).

TABLE 1

SOLVENT EFFECT ON THE RATES OF REACTION OF *cis*-[$PdCl_2(CN$-*p*-$C_6H_4Cl)(PPh_3)$] WITH *N*-METHYLANILINE (A) AT 25°C (UNCERTAINTIES ARE 95% CONFIDENCE LIMITS).

Solvent	10^2 [A] (M)	k_A (M^{-1} min^{-1}) [a]	k_2k_4/k_{-2} (M^{-1} min^{-1})	k_2k_3/k_{-2} (M^{-2} min^{-1})	k_2 (M^{-1} min^{-1}) [e]	ν(C≡N) (cm^{-1}) [f]	ν(N—H) (cm^{-1}) [g]
Acetone	1.48	4.97	3.3 ± 1 [b]	128 ± 17 [c]		2210	3400
	3.53	8.36					
	6.42	11.25					
	8.55	14.10					
	8.88	14.90					
1,4-Dioxane	2.55	6.57	3.4 ± 2 [b]	120 ± 40 [c]		2207	3388
	5.38	9.41					
	6.87	12.14					
	9.72	14.98					
1,2-Dichloroethane [h]	0.74	5.23	~0	800 ± 45 [d]	50 ± 11	2210	3427
	1.27	8.45					
	2.55	15.00					
	6.95	25.60					
	9.78	29.96					
Benzene	0.93	12.69	~0	1642 ± 100 [d]	76 ± 11	2207	3423
	1.68	20.18					
	2.84	28.80					
	4.37	38.84					
	6.66	42.45					

[a] $k_A = k_{obs}/[A]$. [b] Intercepts of linear plots of k_A vs. [A]. [c] Slopes of linear plots of k_A vs. [A]. [d] Calculated from slopes of plots of $1/k_A$ vs. $1/[A]$. [e] Calculated from intercepts of plots of $1/k_A$ vs. $1/[A]$. [f] Coordinated isocyanide. [g] *N*-Methylaniline. [h] Data from ref. 1.

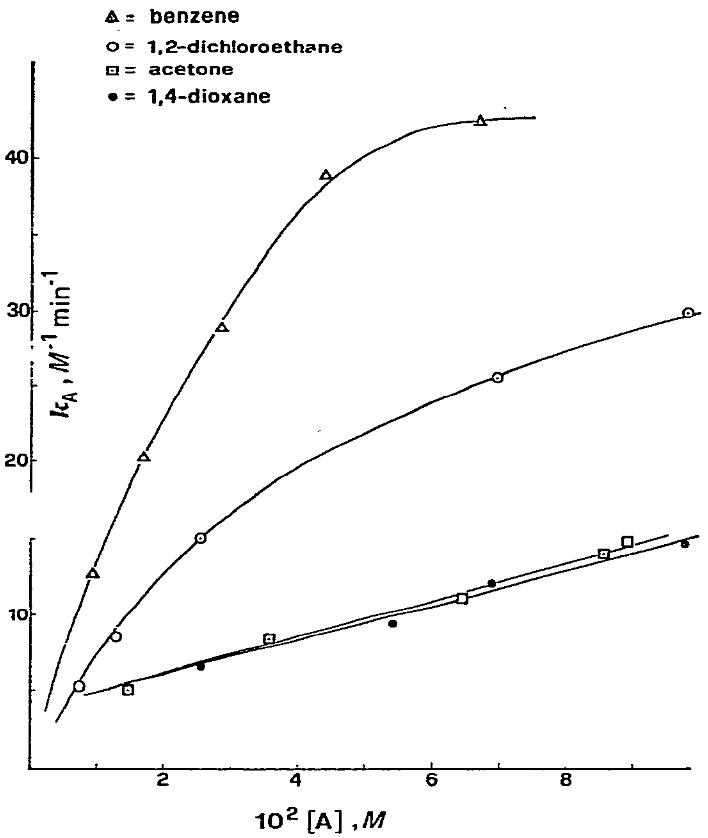

Fig. 1. Dependence of second-order rate coefficient, k_A, on [A] in the various solvents for the reaction of *cis*-[$PdCl_2(CN\text{-}p\text{-}C_6H_4Cl)(PPh_3)$] with *N*-methylaniline at 25°C.

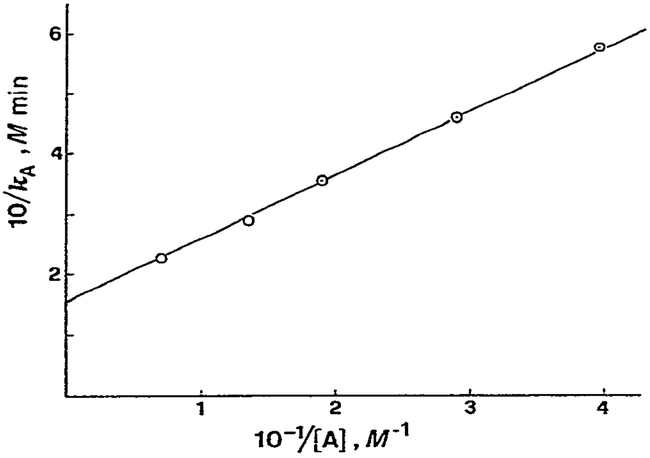

Fig. 2. Dependence of inverse second-order rate coefficient, $1/k_A$, on inverse amine concentration for the reaction of *cis*-[$PdCl_2(CN\text{-}p\text{-}C_6H_4Me)(PMe_2Ph)$] with *N*-methylaniline in 1,2-dichloroethane at 25°C.

However, differential interaction of the solvent with the complex substrate also must play some role, since both the overall rate, k_A, and the k_2 term in benzene are higher than in 1,2-dichloroethane, even though ν(N—H) is virtually the same in these solvents. This may be due to a greater stabilization of the polar *cis*-substrate $\underset{\sim}{\mathrm{I}}$ by interaction with the C—Cl bond dipoles of 1,2-dichloroethane. This interaction will also stabilize the activated complex for the k_2 stage through the incipient separation of charge which accompanies the activation process, but this stabilization appears to be more than offset by concomitant stabilization of the ground state, resulting in a net decrease in rate. To put it in another way, charge creation in dichloroethane during the k_2 step must be outweighed by an increased need to desolvate the reacting substrate prior to bonding. Owing to the form of rate law in eq. 3, only the ratio k_3/k_{-2} can be determined from experimental data (16 M^{-1} in 1,2-dichloroethane and 21.6 M^{-1} in benzene), so that it is hard to assess solvent effects on the separate rate constants. The same situation obtains for ratios k_2k_4/k_{-2} and k_2k_3/k_{-2} in acetone and 1,4-dioxane.

The above-mentioned differential interaction of the solvent with the polar *cis*-substrate will probably explain the fact that the rates in acetone and 1,4-dioxane are the same within experimental error, even though the entering amine should be more reactive in acetone insofar this is indicated by ν(N—H) values.

Cis-ligand effect

In order to elucidate this effect we have studied the reactions of *cis*-[$PdCl_2(CN\text{-}p\text{-}C_6H_4Me)(L)$] with *N*-methylaniline in 1,2-dichloroethane at 25° C (L = $P(OMe)_3$, $P(OMe)_2Ph$, PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PCy_3).

The rate data are reported in Table 2. In all cases the observed rate law is given by eq. 4 which can be obtained from eq. 2 when k_4 is negligible. A typical plot of $1/k_A$ vs. $1/[A]$ is reported in Fig. 2 for L = PMe_2Ph. On the other hand, eq. 2 can also be written in the form

$$\frac{k_A}{k_2 - k_A} = \frac{k_4}{k_{-2}} + \frac{k_3}{k_{-2}}[A] \tag{6}$$

Accordingly, plots of $k_A/(k_2 - k_A)$ vs. [A], using k_2 values obtained from the doubly reciprocal plots of eq. 4, gave straight lines with statistically insignificant intercepts (k_4/k_{-2}) at the 95% confidence level of the least-squares treatment (Fig. 3).

The values of ratios k_3/k_{-2} calculated from plots of eq. 4 agree very satisfactorily with slopes of plots of eq. 6, indicating the internal consistency of the data.

The effects of the *cis*-ligand are both electronic and steric in nature. The second-order rate constant, k_2, increases in the order $PEt_3 < PMePh_2 < PPh_3 < PMe_2Ph < P(OMe)_2Ph < P(OMe)_3$, depending on the net balance between the steric requirements of L and its π-acceptor vs. σ-donor abilities. In this closely related series of complexes one can reasonably assume the stretching frequency of coordinated isocyanide, ν(C≡N), as a measure of the electrophilic character of the isocyanide carbon which is dictated by the electronic properties of L, as far as these affect the charge density on the central metal. Thus, ligands with better π-acceptor and poorer σ-donor abilities will enhance the reactivity of the

TABLE 2

LIGAND EFFECT ON THE RATES OF REACTION OF *cis*-[$PdCl_2(CN\text{-}p\text{-}C_6H_4Me)(L)$] WITH *N*-METHYLANILINE (A) IN 1,2-DICHLOROETHANE AT 25°C (UNCERTAINTIES AS IN TABLE 1).

L	10^2[A] (*M*)	k_A (M^{-1} min^{-1}) [a]	k_3/k_{-2} (M^{-1}) [b]	k_2 (M^{-1} min^{-1}) [c]	ν(C≡N) (cm^{-1}) [d]	Cone angle of L [e] (°)
$P(OMe)_3$	0.94	6.13	149 ± 10	10.5 ± 0.3	2223	107
	1.48	7.14				
	2.71	8.33				
	5.30	9.34				
	8.98	9.80				
$P(OMe)_2Ph$	1.30	3.86	82.4 ± 3	7.4 ± 0.1	2218	120
	2.13	4.75				
	2.99	5.31				
	5.43	6.16				
	8.28	6.55				
	11.32	6.65				
PPh_3 [f]	5.34	1.05	4.1 ± 1	5.8 ± 1	2212	145
	7.98	1.42				
	15.14	2.32				
	21.94	2.74				
	30.01	3.15				
$PMePh_2$	3.65	0.80	10.1 ± 1	3.0 ± 0.2	2210	136
	8.02	1.31				
	15.87	1.81				
	23.78	2.12				
PMe_2Ph	2.54	1.73	13.9 ± 1	6.7 ± 0.4	2208	125 [g]
	3.43	2.18				
	5.28	2.81				
	7.41	3.41				
	14.34	4.38				
PEt_3	12.07	0.56	6.8 ± 1	1.2 ± 0.1	2204	132
	15.26	0.61				
	30.63	0.84				
	50.69	0.95				
	70.33	1.01				

[a] $k_A = k_{obs}/[A]$. [b] Calculated from slopes of plots of $1/k_A$ vs. $1/[A]$. [c] Calculated from intercepts of plots of $1/k_A$ vs. $1/[A]$. [d] Coordinated isocyanide in 1,2-dichloroethane solution. [e] Values from refs. 3 and 4. [f] Data from ref. 1. [g] Value from ref. 5.

isocyanide carbon towards direct attack by the amine because of the reduced charge density on the metal which depresses the palladium-isocyanide $d \rightarrow \pi^*$ back-donation and shifts the C≡N stretching band to higher frequencies.

The left-hand side of Fig. 4 shows a correlation of k_2 with ν(C≡N) of the appropriate complex for the various *cis*-ligands L examined. As can be seen (Fig. 4) k_2 increases regularly with increasing ν(C≡N), the only exception being the complex with L = PMe_2Ph, which appears to display a higher reactivity than expected on purely electronic grounds. Such ranking of PMe_2Ph in the reactivity series stems from the favourably low steric hindrance of this phosphine which acts as the overriding factor. If we assume the cone angle of the phosphorus ligand, as reported by Tolman [3,4], as a measure of the steric requirements of L in these complexes, we can correlate k_2 with steric properties as shown on the right-hand

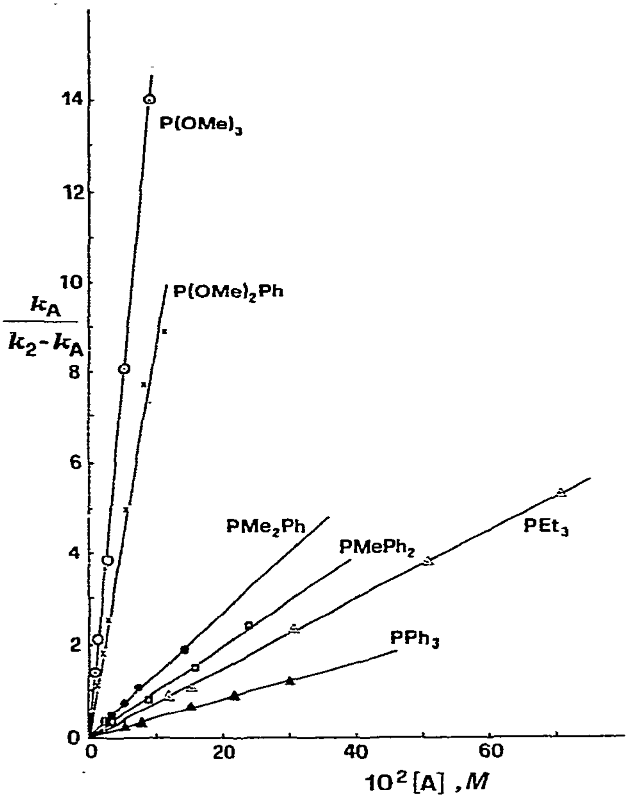

Fig. 5. Plots of $k_A/(k_2 - k_A)$ vs. amine concentration for the reactions of *cis*-[PdCl$_2$(CN-*p*-C$_6$H$_4$Me)(L)] with *N*-methylaniline in 1,2-dichloroethane at 25°C; k_2 calculated from least-squares intercepts of plots analogous to that of Fig. 2.

side of Fig. 4. As expected, the position of PMe$_2$Ph appears now well correlated with its cone angle, whereas the predominant importance of electronic factors is borne out by the fact that the PPh$_3$ is much more reactive than the PEt$_3$ complex in spite of the reverse order of bulkiness of the ligands. When both electron-withdrawing properties and low steric requirements obtain, as with P-(OMe)$_2$Ph and P(OMe)$_3$ derivatives, the highest rates are observed. In the case of L = tricyclohexylphosphine the steric bulkiness and poorer π-acceptor ability of the ligand concur to reduce the rate below the limits of experimental observation at 25°C.

A similar interplay of electronic and steric factors related to phosphorous ligands has been observed to affect the rates of attack of amines or carbanions on substituted metal carbonyl complexes leading to carbamoyl or acylate derivatives [6—8].

The k_3/k_{-2} ratio is also markedly affected by changes in the properties of the *cis*-ligand L (see Table 2 and slopes of plots in Fig. 3). The following order is observed: PPh$_3$ < PEt$_3$ < PMePh$_2$ < PMe$_2$Ph < P(OMe)$_2$Ph < P(OMe)$_3$. Good π-acceptor ligands with lower bulkiness will increase the k_3/k_{-2} ratio by stabilizing the intermediate toward breakdown to starting substrate while favouring its further reaction with the amine in the catalytic step k_3. By contrast, increasing bul-

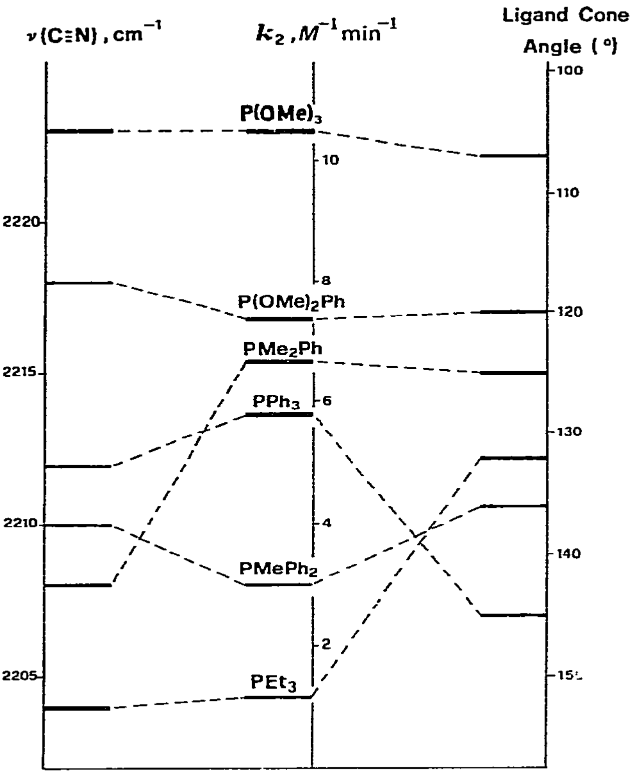

Fig. 4. Correlation of k_2 with $\nu(C{\equiv}N)$ of coordinated isocyanide and with ligand cone angle of L for the reactions of *cis*-[$PdCl_2(CN$-*p*-$C_6H_4Me)(L)$] with *N*-methylaniline (all parameters to scale).

kiness of L will simultaneously reduce k_3 and increase k_{-2} by steric crowding and repulsion around the metal atom in the activation processes of these competing steps. That steric factors are now overwhelming is clearly shown by the observed trend, $PPh_3 < PMePh_2 < PMe_2Ph$, which is the reverse order of electron-withdrawing ability. We are carrying out further kinetic studies in order to assess the effect of steric crowding around the metal atom brought about by *ortho*-substituents on both the isocyanide and amine aromatic rings.

Activation parameters

Kinetic runs were carried out at various temperatures for the reaction of *cis*-[$PdCl_2(CN$-*p*-$C_6H_4Me)(PPh_3)$] with *N*-methylaniline in 1,2-dichloroethane. Rate data, listed in Table 3 fit the doubly reciprocal rate law (eq. 4) at all temperatures studied, thereby enabling us to obtain the corresponding k_2 values. The activation parameters for the nucleophilic attack by amine (k_2 step) were calculated from a weighted linear least-squares fit of $\ln(k_2/T)$ to $1/T$, with the weighting scheme $W_i = (k_i/\sigma_i)^2$, where σ_i is the estimated standard error of k_i. The resulting values are $\Delta H^{\ddagger} = 9.8 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -30 \pm 2$ e.u. (correlation coefficient $|r| = 0.9953$; uncertainties are estimated standard errors from linear regression analysis). The comparatively low enthalphy of activation fits well into the picture of the k_2 step as a direct attack of the reacting amine on the coordi-

TABLE 3

TEMPERATURE EFFECT ON THE RATES OF REACTION OF *cis*-[$PdCl_2(CN$-*p*-$C_6H_4Me)(PPh_3)$] WITH *N*-METHYLANILINE (A) IN 1,2-DICHLOROETHANE.

Temperature (°C)	10^2 [A] (*M*)	k_A (M^{-1} min^{-1}) [a]	k_3/k_{-2} (M^{-1}) [c]	k_2 (M^{-1} min^{-1}) [c]
20	6.12	0.91	4.5 ± 2	4.3 ± 1
	7.71	1.14		
	10.83	1.38		
	18.19	1.92		
	24.10	2.22		
25 [b]	5.34	1.05	4.1 ± 1	5.8 ± 1
	7.98	1.42		
	15.14	2.32		
	21.94	2.74		
	30.01	3.15		
35	3.55	0.65	1.8 ± 0.6	11 ± 3
	6.12	1.05		
	8.32	1.42		
	12.04	1.92		
	24.10	3.33		
45	4.01	0.82	1.3 ± 0.7	16 ± 8
	5.02	1.02		
	9.40	1.81		
	14.91	2.66		
	18.19	3.12		

[a] $k_A = k_{obs}/[A]$. [b] Data from ref. 1. [c] Uncertainties are 95% confidence limits.

nated isocyanide carbon leading to the intermediate adduct without the breaking of any bonds in the reactants. The activation entropy is largely negative, as expected for an associative process where neutral reactants develop some charge separation in the transition state which involves the "freezing" of solvent molecules in the highly ordered region around the constrained, strongly oriented activated complex. Low activation enthalpies and largely negative entropies have been previously observed for nucleophilic attacks on metal-coordinated carbonyl and isocyanide ligands [2,7] or on carbon—carbon double bonds of activated olefins [9].

The decrease of k_3/k_{-2} with temperature is a consequence of the composite nature of this ratio and indicates a higher $\Delta H^{\ddagger}$ for the k_{-2} process relative to the k_3 one.

Experimental

Materials

The complexes *cis*-[$PdCl_2(CN$-*p*-$C_6H_4X)(L)$] (X = Cl, Me; L = $P(OMe)_3$, $P(OMe)_2Ph$, PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PCy_3) and the corresponding carbene complexes *cis*-[$PdCl_2\{C(NH$-*p*-$C_6H_4X)NMePh\}(L)$] were prepared by general methods reported previously [10].

N-Methylaniline was purified by fractional distillation over potassium hydroxide under nitrogen. All solvents were purified by standard procedures [11].

Kinetics

The reactions were followed spectrophotometrically by measuring changes in optical density in the range 330—360 nm with time by means of an Optica CF-4R double-beam recording instrument.

Freshly prepared solutions of the complex, stored under nitrogen in a flask wrapped in aluminum foil, 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 entering ligand 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 $\log(A_t - A_\infty)$ vs. time, where A_t and A_∞ 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%.

Uncertainties in rate constants quoted are 95% confidence limits, except wher otherwise stated.

Infrared spectra

Infrared spectra were recorded in solution on a Perkin—Elmer 621 spectrophotometer in the region 3500—3300 cm^{-1} for *N*-methylaniline and in the region 2300—2100 cm^{-1} for isocyanide complexes by the use of NaCl liquid cells of 0.1 and 0.5 mm path length respectively. Calibration was performed with polystyrene film and carbon monoxide vibro-rotational spectrum. Accuracy is believed to be better than ±1 cm^{-1}.

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