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MECHANISM OF FORMATION OF CARBENE COMPLEXES BY REACTION OF *cis*-[$PdCl_2(PPh_3)(CNR)$] WITH SECONDARY AMINES

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Summary

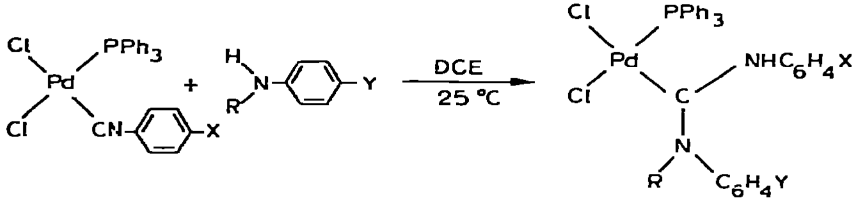
A kinetic study is reported for the reactions of secondary aromatic amines *p*-YC_6H_4NHR (Y = MeO, Me, H; R = Me, Et) with the isocyanide complexes *cis*-[$PdCl_2$(*p*-XC_6H_4NC)(PPh_3)] (X = Me, H, Cl) leading to the carbene derivatives *cis*-[$PdCl_2${C(NH-*p*-C_6H_4X)NR-*p*-C_6H_4Y}(PPh_3)] in 1,2-dichloroethane at 25°C. A stepwise mechanism is proposed which involves a direct nucleophilic attack of the entering amine on the isocyanide carbon followed by proton transfers to the final carbene complexes. These take place both intramolecularly in a four membered cyclic transition state and by the agency of one further amine molecule serving as a proton acceptor-donor in a six membered transition state. Competition experiments with primary amines and trends in rate parameters are discussed to support the mechanism.

Introduction

Nucleophilic attack on the unsaturated carbon atom of coordinated ligands such as olefins or acetylenes [1], carbon monoxide [2], isocyanides [3,4], and carbenes [5] is well documented. Scant information on the mechanisms of these reactions is available at present. Kinetic studies have been carried out on the attack by amines on methoxyphenylcarbene [6], substituted carbonyl [7], and isocyanide complexes [8]. The latter study showed that the formation of carbene complexes of the type *cis*-[$PdCl_2${C(NHR)NHR'}(PPh_3)] from the reaction of *cis*-[$PdCl_2(CNR)(PPh_3)$] with primary aromatic amines $R'NH_2$ in 1,2-dichloroethane involves rate-determining nucleophilic attack by the entering amine on the carbon atom of coordinated isocyanide. The reaction rates were first-order with respect to the attacking amine. Preliminary results with secondary aromatic amines pointed to an apparent kinetic order greater than one for the amine [8] This prompted us to extend the mechanistic study to a series of *p*-substituted *N*-alkyl anilines reacting with the same substrate, in order to ascertain the general mechanistic pattern of these reactions and the factors related to the steric and electronic properties of substituents on both the entering amine and the coordinated isocyanide The results are reported here

Results and discussion

The reactions studied are represented in eqn 1 The final products were



(1)

I A II

(X = Me, H, Cl, Y = MeO, Me, H, R = Me, Et)

isolated and identified as the carbene complexes II [9] All the products have a *cis* structure, as do the starting isocyanide complexes I, shown by the occurrence of two ν(Pd—X) bands in the far IR spectra (303 309, 278 282 cm^{-1}) [9] The reactions were followed spectrophotometrically in 1,2-dichloroethane (DCE) in the presence of a large excess of the entering amine A over the palladium substrate I ([Pd] ca 2×10^{-4} *M*) in order to provide pseudo first-order conditions and to force the reactions to completion The pseudo-first-order rate constants, k_{obs} (min^{-1}), were determined from the spectra at the wavelength where the difference in optical density between the starting materials and the reaction products was largest

In all cases examined, k_{obs} values show a rather complex dependence on the concentration of A, since the second-order coefficient $k_{obs}/[A] = k_A$ (M^{-1} min^{-1}) is a function of [A] Two distinct patterns of kinetic behavior are observed In one, plots of k_A vs [A] are linear (Table 1, as an example, see Fig 1) In the other, plots of k_A vs [A] are curvilinear (Table 2, as an example, see Fig 2), but straight lines are obtained on plotting $1/k_A$ vs $1/[A]$ (Fig 3) A complex dependence of pseudo-first-order rate constants on the concentration of entering amine was also observed for the reactions with carbonyl [7a] and carbene complexes [6]

These findings can be rationalized in terms of a two-step intermediate complex mechanism (eqn 2)

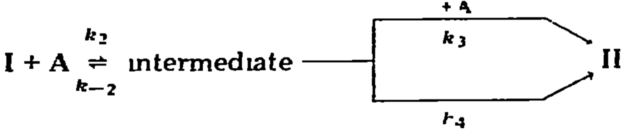


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TABLE 1

RATE DATA FOR THE REACTION OF *cis* [Pd(PPh$_3$)(XC$_6$H$_4$NC)Cl$_2$] WITH *p* YC$_6$H$_4$NHR AT 25°C COMPLEX CONCN *ca* 2 X 10^{-4} *M*

X	Y	R	10^2[YC$_6$H$_4$-NHR] (*M*)	k_A (M^{-1} min^{-1})^a	k_2k_3/k_{-2} (M^{-2} min^{-1})	k_2k_4/k_{-2} (M^{-1} min^{-1})
H	MeO	Me	0 15	4 08	2100 ± 130	0 7 ± 1
			0 23	6 05		
			0 36	8 45		
			0 82	18 08		
			1 15	24 96		
			1 50	33 87		
H	H	Et	4 52	0 13	3 2 ±0 8	≈0
			10 10	0 33		
			14 96	0 50		
			20 29	0 64		
			30 41	0 89		
			40 19	1 25		
Cl	MeO	Me	0 32	60 83	8800 ± 900	32 ± 8
			0 65	87 88		
			1 03	121 30		
			1 44	160 01		

^{a} $k_A = k_{obs}/[YC_6H_4NHR]$

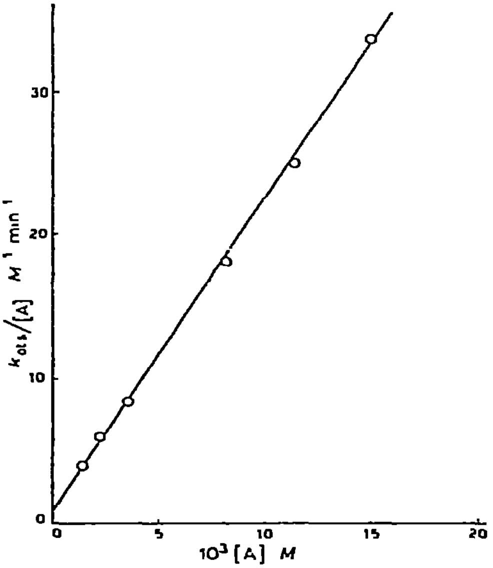


Fig 1 Dependence of second-order rate coefficient $k_{obs}/[A]$ on amine concentration for the reaction of *cis* [PdCl$_2$(C$_6$H$_5$NC)(PPh$_3$)] with *p* MeOC$_6$H$_4$NHMe (A)

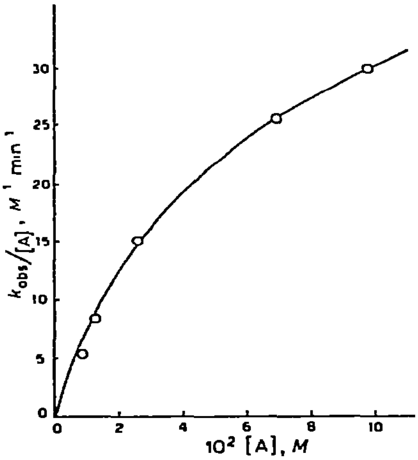


Fig 2 Dependence of second-order rate coefficient $k_{obs}/[A]$ on amine concentration for the reaction of *cis* [PdCl$_2$(*p* ClC$_6$H$_4$NC)(PPh$_3$)] with C$_6$H$_5$NHMe (A)

TABLE 2

SECOND ORDER RATE CONSTANTS k_A (M^{-1} min^{-1})^a FOR THE REACTIONS OF *cis* [Pd(PPh$_3$)(XC$_6$H$_4$NC)Cl$_2$] WITH *p* YC$_6$H$_4$NHR AT 25 C COMPLEX CONCN *ca* 2 X 10^{-4} *M*

X	Y	R	10^2[YC$_6$H$_4$NHR] (*M*)	k_A (M^{-1} min^{-1})
Me	H	Me	5 34	1 05
			7 98	1 42
			15 14	2 32
			21 94	2 74
			30 01	3 15
Me	MeO	Me	0 32	2 47
			0 40	3 59
			0 60	5 23
			1 00	7 85
			1 53	10 31
			2 13	12 39
			2 89	13 42
H	H	Me	3 24	1 59
			5 73	2 57
			10 40	4 11
			14 56	5 31
H	Me	Et	4 93	1 85
			6 45	2 34
			9 78	3 22
			15 13	4 33
			19 74	5 01
Cl	H	Et	2 96	1 11
			5 00	1 77
			7 40	2 53
			11 34	3 57
			15 40	4 44
			19 50	5 48
			24 72	6 05
			30 70	6 67
Cl	Me	Et	0 97	3 34
			1 54	5 37
			2 46	7 75
			5 03	13 84
			7 35	17 00
Cl	H	Me	0 74	5 23
			1 27	8 45
			2 55	15 00
			6 95	25 60
			9 78	29 96

^{a} $k_A = k_{obs}$/[YC$_6$H$_4$NHR]

On applying the steady-state approach, the following general rate law is obtained

$$k_{obs}/[A] = k_A = k_2 \cdot \frac{k_4 + k_3\,[A]}{k_{-2} + k_4 + k_3\,[A]} \qquad (3)$$

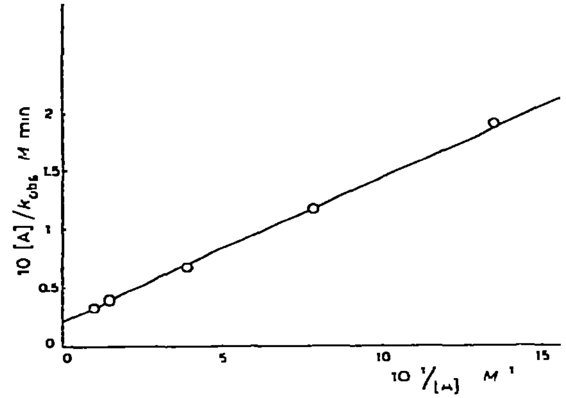


Fig 3 Dependence of inverse second-order rate coefficient [A]/k_{obs} on inverse amine concentration for the reaction of *cis* [$PdCl_2(p\ ClC_6H_4NC)(PPh_3)$] with C_6H_5NHMe (A)

Depending on the relative magnitudes of k_{-2} k_4 and k_3, three types of k_A vs [A] plots may occur When $k_{-2} \gg k_4 + k_3$ [A], eqn 3 becomes eqn 4

$$k_A = \frac{k_2k_4}{k_{-2}} + \frac{k_2k_3\,[A]}{k_{-2}} \tag{4}$$

k_A is a linear function of [A] Columns 6 and 7 in Table 1 set forth the intercepts and slopes of such linear plots calculated by a least-squares program When k_{-2} and $k_4 + k_3$ [A] are comparable, eqn 3 cannot be simplified and will give rise to a nonlinear response to [A], however, if the k_4 term is negligible, eqn 3 can be rearranged to eqn 5

$$1/k_A = \frac{1}{k_2} + \frac{k_{-2}}{k_2k_3\,[A]} \tag{5}$$

In these cases linear plots of $1/k_A$ vs 1/[A] will be observed, from the intercepts of which values of k_2 constants can be calculated directly (Table 3) The assumption that the k_4 term is negligible for all cases where plots of k_A vs [A] are non linear is supported by the observation that plots of $k_A/(k_2 - k_A)$ vs [A] for all such cases are straight lines with zero intercepts (eqn 3 can be re-

TABLE 3

RATE DATA FOR THE REACTION OF *cis* [$Pd(PPh_3)(XC_6H_4NC)Cl_2$] WITH p C_6H_4NHR AT 25°C

X	Y	R	k_2 (M^{-1} min^{-1})^a	k_3/k_{-2} (M^{-1})^b
Me	H	Me	5 8	4 1
Me	MeO	Me	28 3	36 5
H	H	Me	14 8	3 7
H	Me	Et	12 1	3 7
Cl	H	Et	17 0	2 4
Cl	Me	Et	51 3	7 3
Cl	H	Me	49 8	16 1

^{a} Calculated from intercepts of plots of $1/k_A$ vs 1/[A] (eqn 5) ^{b} Calculated from slopes of plots of $1/k_A$ vs 1/[A] (eqn 5)

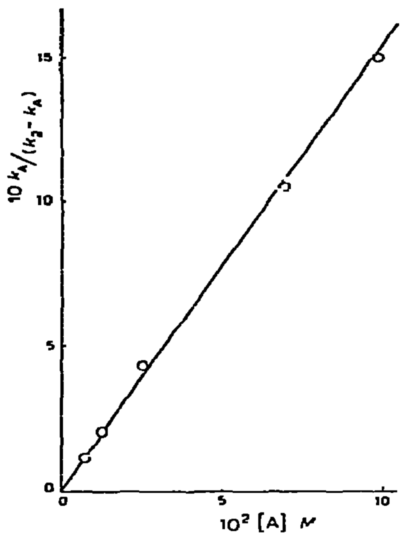


Fig 4 Plot of $k_A/(k_2-k_A)$ vs. amine concentration for the reaction of *cis* [$PdCl_2(p\text{-}ClC_6H_4NC)(PPh_3)$] with C_6H_5NHMe $k_A = k_{obs}/[A]$ k_2 calculated from least-squares intercept of plot of Fig 3

arranged with no simplifications to eqn 6)

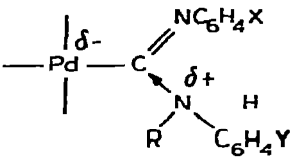
$$\frac{k_A}{k_2-k_A}=\frac{k_4}{k_{-2}}+\frac{k_3[A]}{k_{-2}} \tag{6}$$

An example of this plot is given in Fig 4*

Finally, when $k_{-2} \ll k_4 + k_3[A]$, eqn 3 simplifies to eqn 7

$$k_A = k_2 \tag{7}$$

and k_A is then independent of [A] This latter case was only observed in our previous work with primary amines [8], the behavior of which appears to represent a particular facet of the more general mechanism of eqn 2 A rate law analogous to that of eqn 3 was found to hold for the aminolysis of esters [10] and for nucleophilic aromatic substitutions [11] The first step (k_2) in the mechanism of eqn 2 can be interpreted as a nucleophilic attack of the entering amine on the carbon of coordinated isocyanide, producing the intermediate shown below



This can be looked at as an imidopalladium(II) complex and is reminiscent of

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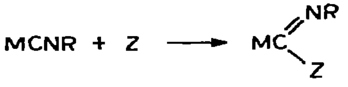
* The values of ratios k_3/k_{-2} calculated from plots of eqn 6 agree very satisfactorily with those from plots of eqn. 5 indicating the internal consistency of the treatment

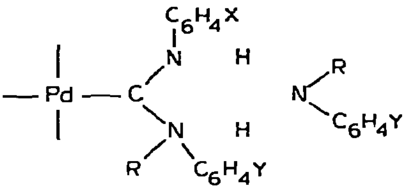
similar species MC(=NR)Z obtained by the general reaction [12]



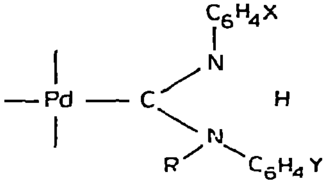
$$MCNR + Z \longrightarrow MC(=NR)Z$$

$(Z = HO^-, RO^-, HS^-, RHN^-)$

The following steps producing the final carbene complex II involve proton transfers which may occur either intramolecularly (path k_4) in a four-membered cyclic transition state, or by the agency of one further amine molecule (A) (path k_3) serving as a proton acceptor-donor in a six membered cyclic transition state

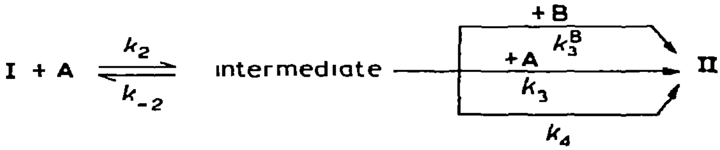


T S for k_3



T S for k_4

In other words, path k_3 is a virtual catalytic contribution to carbene formation by the entering amine itself acting as a bifunctional catalyst To confirm this interpretation we have repeated kinetic runs for the reaction of *cis* [$PdCl_2(CNPh)(PPh_3)$] with *p*-MeC_6H_4NHEt, at constant concentration, in the presence of variable amounts of *p*-$BrC_6H_4NH_2$ (B) This primary amine was chosen since it was found to be too weak a nucleophile to compete with the secondary amine in forming a palladium—carbene species itself*, while being yet a strong enough base to contribute along with the secondary one in catalyzing the proton transfer from the intermediate In this case eqn 2 becomes



(8)

and the rate law 3 becomes

$$k_A = k_2 \frac{k_4 + k_3[A] + k_3^B[B]}{k_{-2} + k_4 + k_3[A] + k_3^B[B]} \tag{9}$$

which rearranges to eqn 10

$$k_A/(k_2 - k_A) = \frac{k_4}{k_{-2}} + \frac{k_3[A]}{k_{-2}} + \frac{k_3^B[B]}{k_{-2}} \tag{10}$$

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[*] No appreciable reaction of B with the substrate was detected in the absence of *p* MeC_6H_4NHEt over a period of 20 min which is far in excess of that required by the secondary amine to react completely under the same experimental conditions

TABLE 4

RATE DATA FOR THE REACTION OF *cis* [Pd(PPh$_3$)(C$_6$H$_5$NC)Cl$_2$] WITH *p* MeC$_6$H$_4$NHEt CATALYZED BY *p*-BrC$_6$H$_4$NH$_2$ AT 25°C [*p* MeC$_6$H$_4$NHEt] = 10 24 X 10^{-2} *M*

10^2[*p*-BrC$_6$H$_4$NH$_2$] (*M*)	k_A (M^{-1} min^{-1})	$k_A/(k_2-k_A)$ [b]
0	3 31	0 38
5 28	5 24	0 77
10 10	6 22	1 08
15 00	7 18	1 49

[a] $k_A = k_{obs}/$[*p* MeC$_6$H$_4$NHEt] [b] k_2 calculated from least-squares intercept of plot of $1/k_A$ vs $1/$[*p* MeC$_6$H$_4$NHEt] in the absence of *p* BrC$_6$H$_4$NH$_2$ (see text)

Rate data for these kinetic runs are reported in Table 4 and bear out clearly the additional catalytic contribution of B since k_A values increase with increasing concentration of the primary amine On plotting $k_A/(k_2 - k_A)$ vs [B] at constant [A] according to eqn 10, a straight line is obtained (Fig 5) with slope = 7 3 ± 0 2 M^{-1} (k_3^B/k_{-1}) and intercept = (3 8 ± 1) X 10^{-1} Bearing in mind that $k_4 \simeq 0$ for this system, from the intercept value and the known concentration of A (10 24 X 10^{-2} *M*) a value of 3 7 ± 1 M^{-1} for k_3/k_{-1} is obtained which is in excellent agreement with that found in the absence of B (see Table 3)

On the other hand, we have found that the tertiary amine *N*,*N*-dimethyl aniline (DMA) has no appreciable effect on the rates of reaction 1 for X = Me, Cl, H, Y = H, R = Me, Et over a wide range of concentration

In other words, the dimethylamino group, although having good basic properties and small steric requirements, is incapable of bifunctional catalysis, lacking a transferable proton This confirms the proposed cyclic structure for

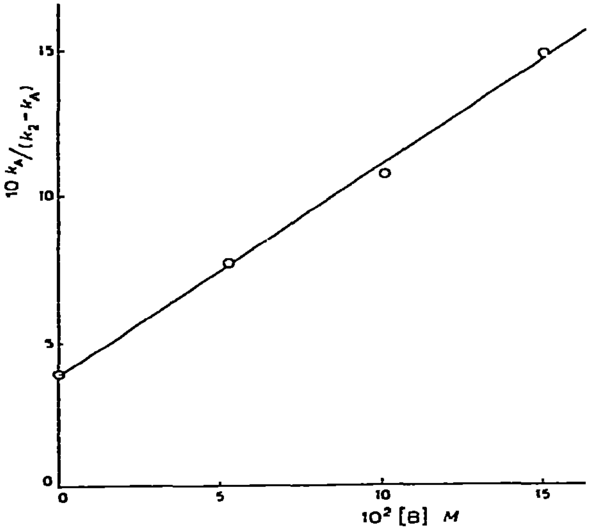

Fig 5 Plot of $k_A/(k_2-k_A)$ vs the concentration of *p* BrC$_6$H$_4$NH$_2$ (B) for the reaction of *cis* [PdCl$_2$(C$_6$H$_5$NC)(PPh$_3$)] with *p* MeC$_6$H$_4$NHEt (10 24 X 10^{-2} *M*) catalyzed by *p* BrC$_6$H$_4$NH$_2$ $k_A = k_{obs}/$[*p*-MeC$_6$H$_4$NHEt] k_2 calculated from least-squares intercept of plot of $1/k_A$ vs. $1/$[*p* MeC$_6$H$_4$NHEt] in the absence of *B*

the transition state of path k_3, which requires that the nitrogen of both participating amine molecules bear at least one hydrogen. If a non-cyclic transition state for k_3 were involved, any base, even a relatively sterically hindered one such as DMA, should be able to replace the second amine molecule since only proton acceptance would be required of it. The ineffectiveness of tertiary amines in catalyzing similar proton transfers when cyclic transition states are involved is a feature of some ester aminolyses [13] and ketene acylations [14].

The observed catalytic ability of p-BrC$_6$H$_4$NH$_2$ shows that the same mechanism as in eqn. 2 is operating for the reactions of *cis*-[PdCl$_2$(CNR)(PPh$_3$)] with primary amines previously studied [8]. In these cases however, the formation of the intermediate rather than its further reactions to the final carbene is rate-determining and the rate law 7 will prevail. Since the discriminating k_{-2} term is likely to increase with increasing steric requirements of the reacting amine, we are carrying out kinetic runs of *ortho* substituted anilines with complexes containing *ortho* substituted isocyanides with the aim of proving that the general rate law 3 is also valid for these sterically hindered systems. A solvent and ancillary ligand effect can also be foreseen in principle, and appropriate experiments are under way.

It is noteworthy that the catalytic step rate constants k_3 for p-BrC$_6$H$_4$NH$_2$ and p-MeC$_6$H$_4$NHEt have comparable values ($k_3^B/k_3 \approx 2$), indicating that these amines compete effectively for the intermediate. At this stage it is not feasible to provide an explanation for the different mechanistic behavior displayed by secondary amines as represented by rate laws 4 and 5. Probably a complex interplay of steric and electronic factors is involved which is hard to disentangle. However, certain reactivity trends can be recognized which support the mechanism proposed. As can be seen in Table 1, the ratio k_2k_3/k_{-2} for amines obeying the rate law 4 increases with increasing amine basicity, increasing electron-withdrawing ability of *para* substituent on the isocyanide, and decreasing steric requirements at the amine nitrogen donor site. For the amines pertaining to rate law 5 it is possible to discuss the separate values of k_2 and k_3/k_{-2} parameters (Table 3). Both these rate coefficients increase with increasing donor ability of the amine, decreasing steric hindrance and increasing electrophilic character of the isocyanide carbon. In particular, changes in the k_2 term are in accord with the k_2 path being a direct nucleophilic attack of the amine on the carbon atom of coordinated isocyanide, as found also for the reactions of primary amines [8].

Experimental

Materials

The complexes *cis*-[PdCl$_2$(p-XC$_6$H$_4$NC)(PPh$_3$)] and the corresponding carbene derivatives *cis*-[PdCl$_2${C(NH-p-C$_6$H$_4$X)NR-p-C$_6$H$_4$Y}(PPh$_3$)] (X = Me, H, Cl, Y = MeO, Me, H, R = Me, Et) were prepared according to the general methods reported earlier [9].

The commercial amines were purified by either sublimation or fractional distillation on potassium hydroxide under nitrogen. 1,2-Dichloroethane was purified according to standard methods.

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 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 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%

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