Journal of Organometallic Chemistry, 134 (1977) 249—257

MECHANISM OF NUCLEOPHILIC ATTACK BY AROMATIC AMINES ON PALLADIUM(II) BIS-ISOCYANIDE COMPLEXES. FACTORS AFFECTING THE FORMATION OF MONO- AND BIS-CARBENE DERIVATIVES

E. ROTONDO, M. CUSUMANO

Istituti di Chimica Generale e Chimica Fisica, Università di Messina, Messina (Italy)

B. CROCIANI, P. UGUAGLIATI and U. BELLUCO *

Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione CNR, c/o Istituto Chimica Industriale, Università di Padova, Via Marzolo, 9, 35100 Padova (Italy)

(Received January 18th, 1977)

Summary

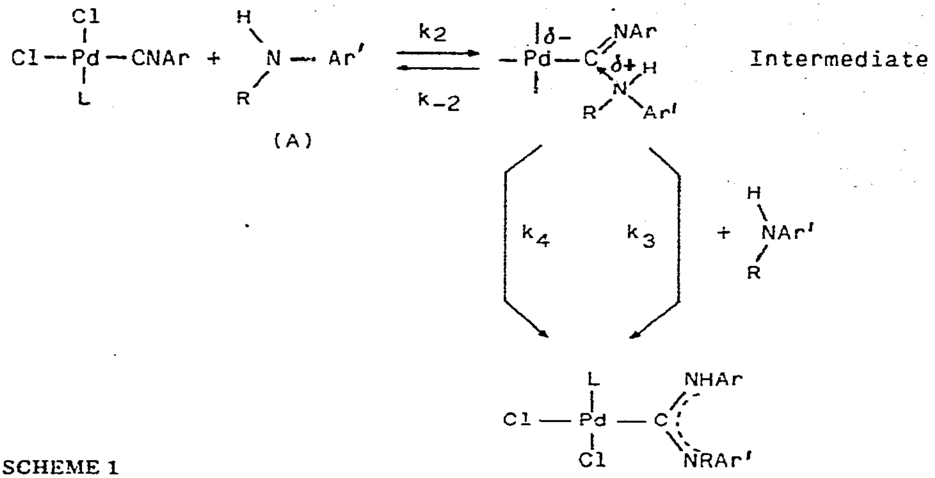
A kinetic study of the reactions of aromatic amines with the bis-isocyanide complexes *cis*-$[PdCl_2(CNAr)_2]$ (Ar = Ph, *p*-MeC_6H_4, *o,o'*-$Me_2C_6H_3$) is described. Secondary amines give the monocarbene derivatives *cis*-$[PdCl_2\{C(NHAr)NRAr'\}(CNAr)]$ (R = Me, Et; Ar' = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$), while unhindered primary anilines such as *p*-toluidine react further to give the bis-carbene species *cis*-$[PdCl_2\{C(NHAr)NH\text{-}p\text{-}C_6H_4Me\}_2]$.

A stepwise mechanism is proposed which involves a direct nucleophilic attack of the entering amine on the isocyanide carbon followed by proton transfer to the final mono- or bis-carbene complexes. Formation of the latter is sterically hindered by either N- or aromatic ring *ortho*-substituents in the amine.

The complex *trans*-$[PdI_2(CNPh)_2]$ fails to react with primary anilines but yields the monocarbene species, *trans*-$[PdI_2\{C(NHPh)NMe\text{-}p\text{-}MeOC_6H_4\}(CNPh)]$ with an excess of the more basic *N*-methyl-*p*-anisidine. The failure to obtain a bis-carbene derivative from this reaction is ascribed to a reduced electrophilic character of the remaining isocyanide carbon caused by the good σ-donor ability of the initially formed *trans*-carbene moiety.

Introduction

We previously described the preparation of bis-carbene complexes of palladium(II) by reaction of bis-isocyanide complexes *cis*-$[PdCl_2(CNAr)_2]$ with primary and secondary amines [1]. We observed that the reaction with a secondary aromatic amine, such as *N*-methylaniline, led to a mixture of mono- and bis-carbene species, even after prolonged reaction times and at elevated temperatures in the presence of a large excess of amine. It seemed of interest to carry out a mechanistic study of this reaction in the light of the general mechanism of nucleophilic attack by amines on coordinated isocyanides which we recently established [2—5] (Scheme 1). In this paper we describe the results of this study, which was aimed at elucidating the factors that affect the preferential formation of mono- compared with bis-carbene derivatives in the reaction of bis-isocyanide complexes with secondary aromatic amines.



SCHEME 1

$$k_{obs}/[A] = k_A = k_2 \frac{k_4 + k_3[A]}{k_{-2} + k_4 + k_3[A]} \quad (1)$$

Results and discussion

The reaction of bis-isocyanide complexes, *cis*-[PdCl$_2$(CNAr)$_2$], with primary and secondary anilines to give amino-carbene species involves two distinct stages (eq. 2).

$$\begin{array}{l} \underset{(I)}{cis\text{-}[PdCl_2(CNAr)_2]} + \underset{(A)}{Ar'NHR} \rightarrow \underset{(II)}{cis\text{-}[PdCl_2\{C(NHAr)NRAr'\}(CNAr)]} \\ \qquad\qquad\qquad\qquad\qquad\qquad \Big\downarrow + Ar'NHR \\ \qquad\qquad\qquad\qquad\qquad \underset{(III)}{cis\text{-}[PdCl_2\{C(NHAr)NRAr'\}_2]} \end{array} \quad (2)$$

Preliminary results of a mechanistic study of this reaction with primary anilines (R = H) showed that the first stage is much faster than the second one. However, when secondary anilines are used the second stage becomes so slow that it cannot be kinetically followed at ambient temperature and the final product is the monocarbene species of type II. The kinetic data for the first stage of reaction 2 with secondary anilines are listed in Table 1. Three typical examples of the kinetic behaviour we observed are shown in Fig. 1.

As can be seen, for the reactions of *cis*-$[PdCl_2(CN\text{-}p\text{-}C_6H_4Me)_2]$ with *N*-methyl- and *N*-ethyl-aniline, the limiting value $k_A = k_2$ is quickly reached on increasing the amine concentration, owing to the high value of k_3/k_{-2} in eq. 1. (The form of rate law 1 is such that the amine concentration at which k_A approaches the limiting value k_2 is lower the higher the k_3/k_{-2} ratio.) For the reaction with *N*-ethyl-*p*-toluidine this ratio is so high as to make $k_A \approx k_2$ throughout the feasible range of amine concentrations, so that in this case the data fit rate law 3.

$$k_{obs} = k_2[A] \tag{3}$$

Rate equation 3 appears to apply most often to these reactions (Table 1). It also holds for reactions of mono-isocyanide complexes *cis*-$[PdCl_2(CNAr)(ER_3)]$ with unhindered primary anilines [2], but it is a particular case of the more general rate equation 1 for $(k_4 + k_3[A]) \gg k_{-2}$, corresponding to the k_2 step being rate determining. In other words, the intermediate in eq. 1 is stabilized toward collapse to the initial reactants.

TABLE 1

RATE DATA FOR THE REACTION OF *cis*-$[PdCl_2(CNAr)_2]$ WITH SECONDARY ANILINES (A) IN 1,2-DICHLOROETHANE AT 25° C (uncertainties are estimated standard errors)

ArNC	A	k_2 (M^{-1} sec^{-1})	k_3/k_{-2} (M^{-1})
C_6H_5NC	*N*-Methylaniline	9.5 ± 0.2 [a]	
C_6H_5NC	*N*-Methyl-*p*-anisidine	48 ± 1 [a]	
C_6H_5NC	*N*-Ethylaniline	5.67 ± 0.1 [b]	
		(5.7 ± 0.1) [c]	306 ± 34 [d]
C_6H_5NC	*N*-Ethyl-*p*-toluidine	19.9 ± 0.7 [a]	
p-MeC_6H_4NC	*N*-Methylaniline	4.56 ± 0.08 [b]	529 ± 13 [d]
		(4.57 ± 0.04) [c]	
p-MeC_6H_4NC	*N*-Methyl-*p*-anisidine	30.9 ± 0.1 [b]	
		(31.2 ± 0.3) [c]	816 ± 34 [d]
p-MeC_6H_4NC	*N*-Ethylaniline	2.54 ± 0.02 [b]	
		(2.53 ± 0.002) [c]	561 ± 2 [d]
p-MeC_6H_4NC	*N*-Ethyl-*p*-toluidine	10.1 ± 0.2 [a]	
p-$MeOC_6H_4NC$	*N*-Methylaniline	2.9 ± 0.1 [a]	
p-$MeOC_6H_4NC$	*N*-Methyl-*p*-anisidine	21.4 ± 0.4 [a]	
p-$MeOC_6H_4NC$	*N*-Ethylaniline	1.6 ± 0.04 [a]	
p-$MeOC_6H_4NC$	*N*-Ethyl-*p*-toluidine	6.4 ± 0.2 [a]	
o,o'-$Me_2C_6H_3NC$	*N*-Methylaniline	0.19 ± 0.003 [a]	
o,o'-$Me_2C_6H_3NC$	*N*-Methyl-*p*-anisidine	1.4 ± 0.09 [a]	
o,o'-$Me_2C_6H_3NC$	*N*-Ethylaniline	0.08 ± 0.009 [e]	9 ± 1 [f]
o,o'-$Me_2C_6H_3NC$	*N*-Ethyl-*p*-toluidine	0.24 ± 0.03 [e]	44 ± 5 [f]

[a] Slope of plot of k_{obs} vs. [A]. [b] Slope of plot of k_{obs} vs. [A] for the points in the linear portions of curves (b) and (c) of Fig. 1. [c] Calculated from intercept of plot of $1/k_A$ vs. $1/[A]$ for points in the curvilinear portions of curves (b) and (c) of Fig. 1 ($k_A = k_{obs}/[A]$). [d] Calculated from slope of plot of $1/k_A$ vs. $1/[A]$ for the points in the curvilinear portions of curves (b) and (c) of Fig. 1. [e] Calculated from intercept of plot of $1/k_A$ vs. $1/[A]$ for all points. [f] Calculated from slope of plot of $1/k_A$ vs. $1/[A]$ for all points.

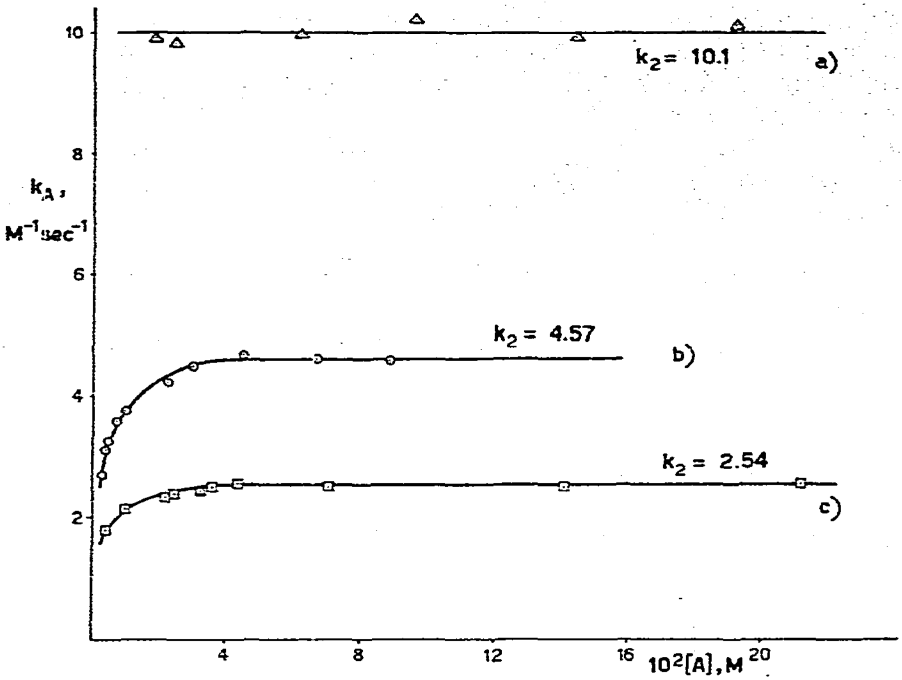


Fig. 1. Dependence of $k_A = k_{obs}/[A]$ on amine concentration for the reactions of *cis*-[$PdCl_2(CN$-*p*-$MeC_6H_4)_2$] with (a) *N*-ethyl-*p*-toluidine, (b) *N*-methylaniline and (c) *N*-ethylaniline at 25°C in 1,2-dichloroethane.

We have also shown previously that when sufficient steric strain is introduced into the intermediate, the k_{-2} term increases while k_4 and k_3 decrease, so that the general law 1 applies again [3—5]. Steric hindrance in the intermediate can be brought about by the presence of substituents on the amine nitrogen or on the *ortho*-position of both amine and isocyanide, also by the presence of bulky ancillary *cis*-ligands in the metal substrate.

For the systems showing the curve (a) behaviour in Fig. 1, the k_2 value was obtained as the slope of the least-squares fit of k_{obs} to [A]. For the systems showing curve (b) or (c) behaviour, k_2 was evaluated in the same way by the use of the linear portion of such fit, whereas for the initially curvilinear portions rate equation (1) was used in the form 4, which gives a linear dependence of

$$1/k_A = 1/k_2 + k_{-2}/(k_4 + k_3[A])k_2 \qquad (4)$$

$1/k_A$ vs. $1/[A]$ if $k_4 \ll k_3[A]$. Least-squares fits of such plots gave the k_2 and k_3/k_{-2} terms as the inverse intercept and intercept/slope ratio, respectively.

The assumption that k_4 is always negligible compared to $k_3[A]$ is justified by the fact that plots of $k_A/(k_2 - k_A)$ vs. [A] for all such cases are straight lines with statistically insignificant intercepts (k_4/k_{-2}) at the 95% confidence level of the least-squares treatment (eq. 4 can be recast into eq. 5). An example of

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

these plots is shown in Fig. 2 for the reaction of *cis*-[$PdCl_2(CN$-*p*-$MeC_6H_4)_2$] with *N*-methylaniline.

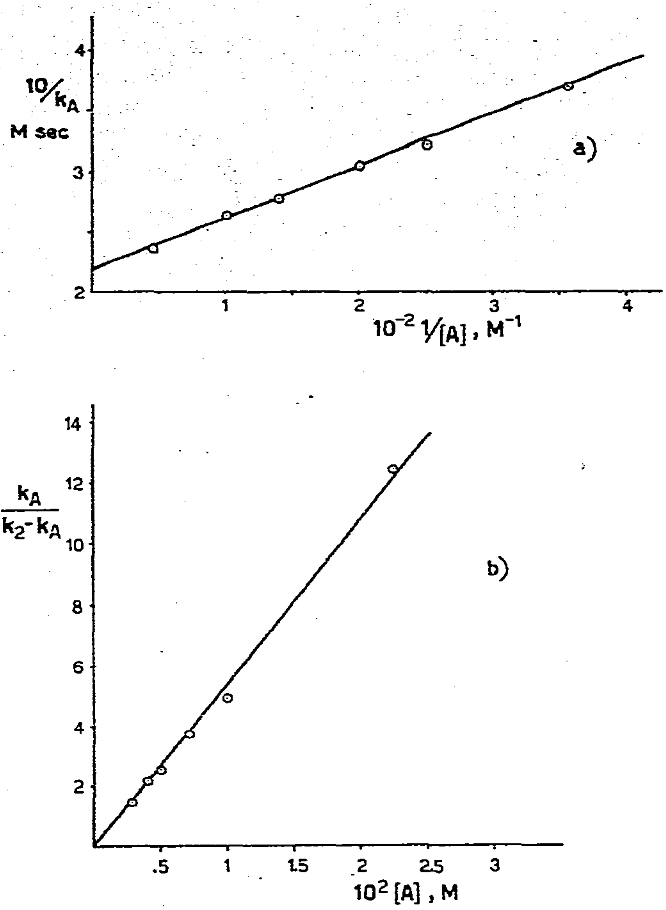


Fig. 2. (a) Dependence of inverse second-order rate coefficient, $1/k_A$, on inverse amine concentration and (b) plot of $k_A/(k_2 - k_A)$ vs. amine concentration for the reaction of *cis*-[PdCl$_2$(CN-*p*-MeC$_6$H$_4$)$_2$] with *N*-methylaniline.

It should be noted that the k_2 value from the plot of $1/k_A$ vs. $1/[A]$ is almost identical to the k_2 value from the linear portion of curve (b) in Fig. 1, as described earlier. This good agreement was found for all cases where this treatment was feasible (Table 1).

The k_3/k_{-2} ratio from the plot of $1/k_A$ vs. $1/[A]$ agrees very satisfactorily with that from eq. 5, indicating again the internal consistency of the treatment. When the k_3/k_{-2} ratio is relatively low, as in the reactions of *cis*-[PdCl$_2$(CN-*o,o'*-Me$_2$C$_6$H$_3$)$_2$] with *N*-ethylaniline and *N*-ethyl-*p*-toluidine, the limiting value $k_A = k_2$ was not reached in the amine concentration range examined, and rate equation 4, with $k_4 \sim 0$, applied throughout.

The k_2 values in Table 1 are the highest so far observed for reactions of amines with coordinated isocyanides. In most cases the first stage of reaction 2 could only be followed by stopped-flow spectrophotometric techniques. Even if we take into account a statistical factor of two (there are two coordinated isocyanide ligands available for nucleophilic attack in these substrates), the corrected k_2 term for the reaction of *cis*-[PdCl$_2$(CN-*p*-MeC$_6$H$_4$)$_2$] with *N*-methylaniline is ca. 14 times higher than the corresponding value for the reaction of the same amine with *cis*-[$PdCl_2$(CN-*p*-MeC_6H_4){$P(OMe)_3$}], in which the *cis*-trimethylphosphite ligand has good electron-withdrawing (viz. activating) properties and low steric requirements [4]. The high k_2 values are likely to be related to the fact that in these substrates the neutral ligand *cis* to the reacting isocyanide is another isocyanide, which has good π-acceptor ability while offering a much lower steric hindrance than phosphites and phosphines in the vicinity of the reaction center because of the almost linear arrangement along the M—C—N—Ar axis [6,7]. The enhanced electrophilic character of the isocyanide carbon can be gauged by the high CN stretching frequencies of these complexes in 1,2-dichloroethane solution; ν_{asym}(CN) and ν_{sym}(CN) fall in the range 2208—2236 cm^{-1}, the lowest being observed for the bis(*o*,*o*'-dimethylphenylisocyanide) complex at 2208 and 2224 cm^{-1}, respectively.

In general the k_2 values increase with increasing basicity of the amine and decreasing bulk of the N-substituent, in agreement with the fact that the k_2 step involves direct nucleophilic attack on the coordinated isocyanide. The rates also increase with increasing electron-withdrawing ability of the *para*-substituent in the benzene ring of the isocyanide. For the complex with *o*,*o*'-$Me_2C_6H_3NC$ the rates are reduced by one order of magnitude, owing to the combined effects of a reduced electrophilic character of the reacting carbon atom and increased steric repulsion by the *ortho*-substituents.

The marked sensitivity of the carbene formation to steric and electronic factors is also borne out by the observation that the second stage of reaction 2, i.e., the formation of a bis-carbene species, is much slower than the first with primary anilines and does not occur at appreciable rates with secondary anilines, despite the higher nucleophilicity of the latter. Once the first carbene moiety has formed, its good σ-donating ability [1,8,9] and bulk [10] make the remaining *cis*-isocyanide less susceptible to further attack. The ensuing lower electrophilic character of the isocyanide in the mono-carbene complexes II is reflected in the comparatively low CN stretching frequency, which now appears at ca. 2200 cm^{-1}.

The inability of secondary anilines to react to an appreciable extent with mono-carbene isocyanide complexes under these conditions is apparently linked to increased steric repulsion between the reacting centers. For instance, the complex *cis*-[$PdCl_2${C(NH-*p*-MeC_6H_4)NMePh}(CN-*p*-MeC_6H_4)] (produced in the reaction of *cis*-[$PdCl_2$(CN-*p*-$MeC_6H_4)_2$] with *N*-methylaniline) reacts easily with *p*-toluidine to give a mixed bis-carbene species [11], whereas it is virtually inert towards *N*-methylaniline under the conditions used for the kinetic studies. In keeping with this reasoning we found that it is possible to block the second stage of reaction 2 even for primary anilines by introduction of *ortho*-substituents in the amine phenyl ring. In Table 2 we list the rate data for the reactions of *cis*-[$PdCl_2$(CN-*p*-$MeC_6H_4)_2$] with *o*-toluidine and *o*,*o*'-dimethylaniline, which yield mono-carbene species of type II. The rate data for the first stage of the reaction with *p*-toluidine [11] are also shown for comparison. Once again, the k_2 term for *ortho*-substituted anilines is lower than that for the unhindered *p*-toluidine, and the k_3/k_{-2} ratio is such as to produce curves of type (a) in Fig. 1 for both *ortho*- and *para*-toluidine. This ratio for *o*,*o*'-dimethylaniline is so much reduced by steric factors that it can be evaluated by the treatment described

TABLE 2

RATE DATA FOR THE REACTION OF *cis*-[$PdCl_2(CN$-*p*-$MeC_6H_4)_2$] WITH PRIMARY ANILINES (A) AT 25°C IN 1,2-DICHLOROETHANE

A	k_2 (M^{-1} sec^{-1})	k_3/k_{-2} (M^{-1})
o-Toluidine	0.19 ± 0.01 [a]	
o,o'-Dimethylaniline	0.27 ± 0.002 [b]	321 ± 8 [c]
p-Toluidine	1.21 ± 0.02 [a]	

[a] Slope of plot of k_{obs} vs. [A]. [b] Calculated from intercept of plot of $1/k_A$ vs. $1/[A]$ ($k_A = k_{obs}/[A]$).
[c] Calculated from intercept and slope of plot of $1/k_A$ vs. $1/[A]$.

earlier for a kinetic behaviour of type (b) in Fig. 1.

We have also examined the reactions of primary and secondary anilines with *trans*-[$PdI_2(CNPh)_2$]. The single ν(CN) band at 2200 cm^{-1} (in 1,2-dichloroethane) indicates a poor electrophilic character of the isocyanide carbon in this complex. Accordingly, carbene formation does not take place at detectable rates under ambient conditions with primary anilines such as *p*-toluidine and *p*-anisidine. Therefore we chose *N*-methyl-*p*-anisidine as the most basic secondary aniline available. The rate data were found to be $k_2 = 1 \pm 0.1$ M^{-1} sec^{-1} and $k_3/k_{-2} = 3 \pm 0.$ M^{-1}. This reaction also yields a mono-carbene species even with a large excess of the entering amine:

$$\textit{trans}\text{-}[PdI_2(CNPh)_2] + p\text{-}MeOC_6H_4NHMe \rightarrow$$

$$\textit{trans}\text{-}[PdI_2\{C(NHPh)NMe\text{-}p\text{-}MeOC_6H_4\}(CNPh)]$$

(IV) (V)

Furthermore, unlike complexes of type II, product V does not react further with *p*-substituted primary anilines. Evidently, the good σ-donor carbene group *trans* to the remaining isocyanide in V * makes this ligand even less susceptible to nucleophilic attack by enhancing $d \rightarrow \pi^*$ back-donation in the Pd—CNPh bond (the CN stretching frequency in V has the low value of 2190 cm^{-1} in 1,2-dichloroethane).

Experimental

Materials

The complexes *cis*-[$PdCl_2(CNAr)_2$] (Ar = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$, *o,o'*-$Me_2C_6H_3$) and *trans*-[$PdI_2(CNPh)_2$] were prepared by published methods [8]. The mono-carbene complexes *cis*-[$PdCl_2\{C(NHAr)NRAr'\}(CNAr)$] (R = Me, Et; Ar' = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) and *trans*-[$PdI_2\{C(NHPh)NMe$-*p*-$MeOC_6H_4\}$-(CNPh)] were prepared by reaction of the bis-isocyanide derivatives with secondary anilines in a molar ratio 1/2 in 1,2-dichloroethane solution at room temperature for 1—4 h. The progress of the reaction was monitored by IR spectroscopy. The products were purified by successive reprecipitations from chloro-

---

* The *trans* structure was assigned to V in the light of the fact that all reactions of carbene formation from palladium(II) isocyanide complexes we have studied occur with retention of configuration at the metal center.

form or acetone by addition of ethyl ether, and characterised by elemental analysis and IR spectra. The analytical data (%) with the calculated values in parentheses and characteristic IR bands (cm^{-1}) of two typical mono-carbene complexes are listed below:

cis-$[PdCl_2\{C(NH\text{-}p\text{-}MeC_6H_4)NMePh\}(CN\text{-}p\text{-}MeC_6H_4)]$: C, 53.4 (53.25); H, 4.5 (4.47); N, 8.2 (8.10); Cl, 13.8 (13.67); $\nu(NH)$ 3180m(br), 3125(sh); $\nu(CN)_{isocyanide}$ 2205vs; $\nu(CN)_{carbene}$ 1540s(br), 1360ms; $\nu(PdCl)$ 318s, 285s.

trans-$[PdI_2\{C(NHPh)NMe\text{-}p\text{-}MeOC_6H_4\}(CNPh)]$: C, 37.8 (37.55); H, 3.1 (3.01); N, 6.0 (5.97); I, 36.3 (36.07); $\nu(NH)$ 3295s; $\nu(CN)_{isocyanide}$ 2190 vs; $\nu(CN)_{carbene}$ 1445s, 1360s.

The reactions of *cis*-$[PdCl_2(CN\text{-}p\text{-}MeC_6H_4)_2]$ with *o*-toluidine and *o,o'*-dimethylaniline were carried out similarly.

The mono- and bis-carbene derivatives obtained by the reaction of *cis*-$[PdCl_2(CN\text{-}p\text{-}MeC_6H_4)_2]$ with *p*-toluidine were isolated and characterised as described previously [1,8].

The amines were purified by sublimation or by distillation under reduced pressure over KOH. 1,2-Dichloroethane was purified by a standard method [12].

Kinetics

The formation of mono-carbene complexes was followed spectrophotometrically by measuring changes in optical density in the range 330—380 nm with time by means of an Optica CF-4R double beam instrument or a Durrum-Gibson D-110 stopped-flow apparatus with a 2 cm observation cell. A Tektronix Model 564 storage oscilloscope equipped with a Polaroid camera was used to record the data.

Freshly prepared solutions of the complex, stored under nitrogen in an aluminium-foil wrapped flask, were used for each run. The reactions were started by mixing known volumes of pre-thermostatted standard solutions of 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 ensure pseudo-first-order conditions and to force the reactions to completion. The final spectra were in good agreement with those of authentic samples of the products. 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 densi-

TABLE 3

RATE DATA FOR THE REACTION OF *trans*-$[PdI_2(CNPh)_2]$ WITH *N*-METHYL-*p*-ANISIDINE (A) AT 25°C IN 1,2-DICHLOROETHANE

10^2 [A] (M)	$10^3\,k_{obs}$ (sec^{-1})	k_2 [a] ($M^{-1}\,sec^{-1}$)	k_3/k_{-2} [b] (M^{-1})
1.79	0.92	1 ± 0.1	3 ± 0.3
3.57	3.52		
8.58	17.9		
11.40	31.0		
17.87	58.6		

[a] Calculated from intercept of plot of $1/k_A$ vs. $1/[A]$. [b] Calculated from slope of plot of $1/k_A$ vs. $1/[A]$.

ties of the 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. Liquid cells with NaCl windows and 0.1 or 0.5 path length were used for 1,2-dichloroethane solution spectra. Solid state spectra were recorded using hexachlorobutadiene mulls and NaCl plates in the region 4000—1200 cm^{-1}, Nujol mulls and CsI plates in the region 1700—250 cm^{-1}. Calibration was performed with a polystyrene film.

References

1 B. Crociani, T. Boschi, G.G. Troilo and U. Croatto, Inorg. Chim. Acta, 6 (1972) 655.
2 B. Crociani, T. Boschi, M. Nicolini and U. Belluco, Inorg. Chem., 11 (1972) 1292.
3 L. Calligaro, P. Uguagliati, B. Crociani and U. Belluco, J. Organometal. Chem., 92 (1975) 399.
4 P. Uguagliati, B. Crociani, U. Belluco and L. Calligaro, J. Organometal. Chem., 112 (1976) 111.
5 B. Crociani, P. Uguagliati and U. Belluco, J. Organometal. Chem., 117 (1976) 189.
6 B. Jovanovic and L.M. Muir, J. Chem. Soc. Dalton, (1972) 1176.
7 B. Jovanovic, L.M. Muir and K.W. Muir, J. Chem. Soc. Dalton, (1972) 1178.
8 B. Crociani, T. Boschi and U. Belluco, Inorg. Chem., 9 (1970) 2021.
9 E.M. Badley, J. Chatt and R.L. Richards, J. Chem. Soc. A, (1971) 21.
10 B. Crociani and R.L. Richards, J. Chem. Soc. A, (1974) 693.
11 E. Rotondo et al., to be published.
12 A. Weissberger and E.S. Proskaner, Organic Solvents, Interscience, New York, 1955.