

### Mechanism of Nucleophilic Attack by Secondary Anilines on the Nitrile Group in Platinum(II) *ortho*-Cyanobenzyl Complexes

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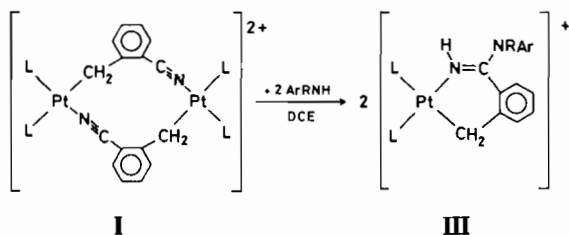
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The growing interest in transition metal nitrile complexes stems from the possibility of exploiting both the lability of the metal-bound CN group in substitution reactions, and its activation upon coordination towards addition of nucleophiles such as alcohols, thiols, water, or amines yielding iminoether, iminothioether, amido, or amidino complexes [1]. Whereas few kinetic studies on the hydrolysis of coordinated nitriles have appeared [2], the addition of amines has not yet been studied from a mechanistic point of view.

The cationic dimeric complex **I** has been shown to form chelate amidino complexes of type **III** upon reaction with both primary and secondary amines [3]. A mechanistic study of the reaction with primary anilines is now being completed [4]. We report here the kinetics of the reactions of **I** with secondary anilines:



(L = PPh<sub>3</sub>; R = Me, Ar = *p*-C<sub>6</sub>H<sub>4</sub>OMe; R = Et, Ar = *p*-C<sub>6</sub>H<sub>4</sub>Me; DCE = 1,2-dichloroethane)

The final products of kinetic runs were characterized by comparison with the spectra of authentic

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samples prepared independently. As an example, we report in the Experimental section the preparation, elemental analysis, IR and NMR characterization of the derivative with R = Me, Ar = *p*-C<sub>6</sub>H<sub>4</sub>OMe.

Spectral changes in the UV region (380–330 nm) of a 1,2-dichloroethane (DCE) solution of **I** upon addition of excess *N*-methyl-*p*-anisidine show the occurrence of a very fast prior stage followed by much slower formation of the final amidino product **III**.

In analogy with the behaviour of primary amines [4], the first stage is thought to involve rapid formation of a cationic monomeric labile intermediate **II** through breaking of the nitrile bridges in **I** by the entering amine: nucleophilic substitution at the platinum center – a typical feature of platinum(II) chemistry – produces a mixed amino–cyanobenzyl species bearing the uncoordinated nitrile group at the free end of the  $\sigma$  metal-bonded *o*-cyanobenzyl residue:



The observed high rate of opening of the *o*-cyanobenzyl bridges is probably due to i) the easy replacement of organonitrile ligands by even poorly coordinating agents: a feature exploited commonly in the preparation of hard-to-get intermediates [5]; ii) the enhanced lability of nitriles as ligands brought about by the high *trans* effect of triphenylphosphine in **I**; and iii) the relief of steric strain of the cyanobenzyl bridges in the dimeric substrate **I**, as suggested by X-ray structural analysis [6]. Intermediates of type **II** have been isolated with aliphatic amines [3]. Dreiding molecular models indicate that the dangling nitrile group may occupy an axial position at sufficient distance from the central metal to allow a possible 'side-on' interaction with the latter [7]. Such electronic interaction, which might well be established on demand, activates the CN group towards nucleophilic attack which takes place in the second slower step of the reaction. This could be followed kinetically by conventional spectrophotometry under pseudo-first-order conditions with an excess of amine.

The pseudo-first order rate constant for the second step is found to obey the two-term law

$$k_{\text{obs}} = k_2[A] + k_3[A]^2 \quad (1)$$

with overall second- and third-order contributions. Linear plots of  $k_A = k_{\text{obs}}/[A]$  were obtained (Fig. 1) according to a re-formulation of rate eqn. (1):

TABLE I. Rate Data for the Reaction of  $[\text{Pt}(o\text{-CH}_2\text{C}_6\text{H}_4\text{CN})(\text{PPh}_3)_2]_2(\text{BF}_4)_2$  with N-methyl-*p*-anisidine in 1,2-Dichloroethane.

Temperature (°C)	$10^2 [A]$ (M)	$10 k_A^a$ ( $M^{-1} \text{min}^{-1}$ )	$10^2 k_2^b$ ( $M^{-1} \text{min}^{-1}$ )	$k_3^c$ ( $M^{-2} \text{min}^{-1}$ )
25	1.91	0.86	$4.04 \pm 0.2$	$2.34 \pm 0.03$
	2.48	0.98		
	4.45	1.45		
	5.38	1.63		
	5.84	1.78		
	6.71	1.98		
	7.35	2.13		
35	1.76	1.31	$6.67 \pm 0.7$	$3.84 \pm 0.1$
	2.12	1.60		
	4.01	2.18		
	4.84	2.40		
	6.31	3.17		
	7.26	3.37		
	8.37	3.92		
45	10.02	4.54	$10.4 \pm 1$	$6.92 \pm 0.2$
	1.62	2.17		
	2.75	3.00		
	3.12	3.30		
	4.74	4.24		
	5.83	4.97		
	6.78	5.55		
7.86	6.49			
	8.97	7.42		

<sup>a</sup> $k_A = k_{\text{obs}}/[A]$ . <sup>b</sup>Intercept of linear plot of  $k_A$  vs.  $[A]$ . <sup>c</sup>Slope of linear plot of  $k_A$  vs.  $[A]$ .

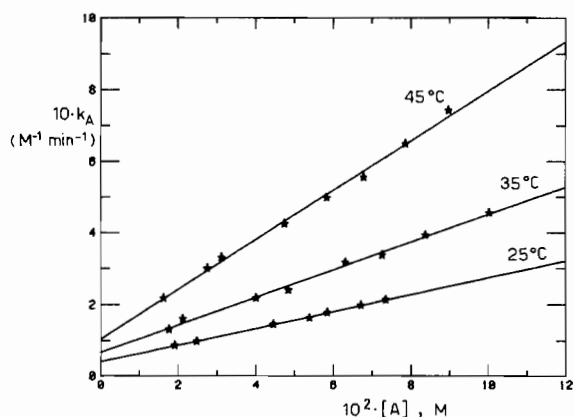
TABLE II. Rate Data for the Reaction of  $[\text{Pt}(o\text{-CH}_2\text{C}_6\text{H}_4\text{CN})(\text{PPh}_3)_2]_2(\text{BF}_4)_2$  with N-ethyl-*p*-toluidine in 1,2-Dichloroethane at 35 °C.

$10^2 [A]$ (M)	$10^2 k_A^a$ ( $M^{-1} \text{min}^{-1}$ )	$10^2 k_2^b$ ( $M^{-1} \text{min}^{-1}$ )	$k_3^c$ ( $M^{-2} \text{min}^{-1}$ )
4.34	2.28	$1.15 \pm 0.1$	$0.26 \pm 0.01$
4.91	2.52		
6.51	2.67		
8.18	3.23		
11.54	4.23		
13.28	4.56		
13.89	4.70		

<sup>a</sup> $k_A = k_{\text{obs}}/[A]$ . <sup>b</sup>Intercept of linear plot of  $k_A$  vs.  $[A]$ . <sup>c</sup>Slope of linear plot of  $k_A$  vs.  $[A]$ .

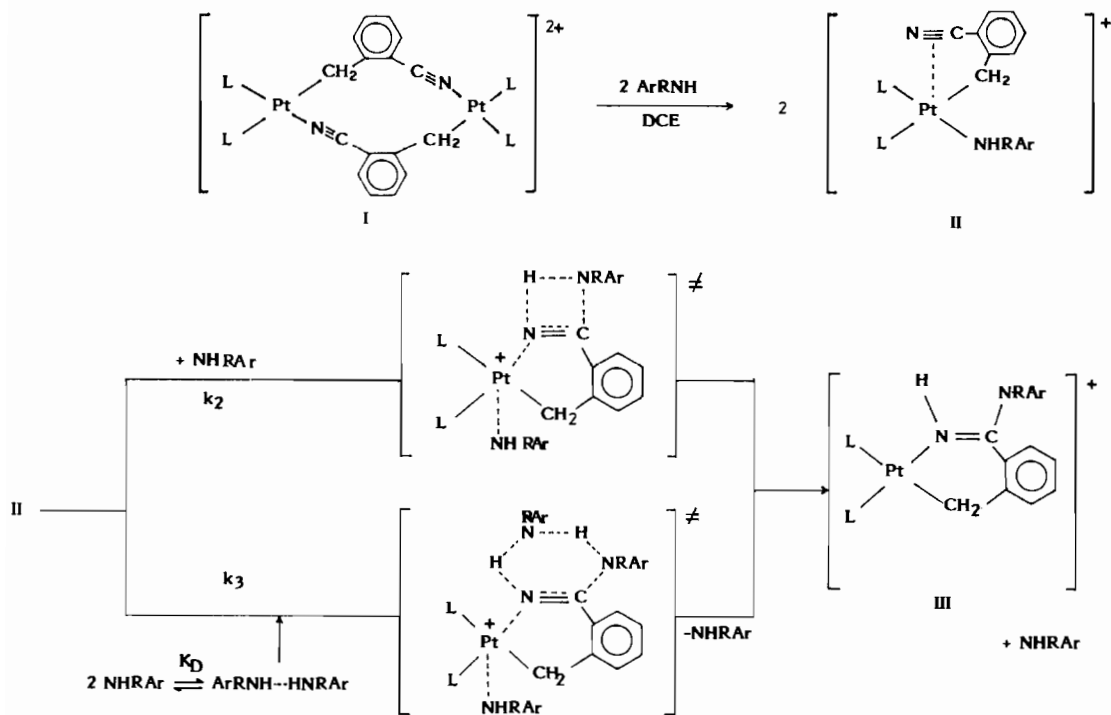
$$k_A = k_2 + k_3[A] \quad (2)$$

The rate parameters  $k_2$  and  $k_3$  for the reactions of I with N-methyl-*p*-anisidine and N-ethyl-*p*-toluidine, as computed by linear regression, are listed in Tables I and II, respectively. Figure 2 shows a typical kinetic run as a 3-D plot of absorbance vs. both wavelength and time. *Abstract Factor Analysis* [8] of spectral

Fig. 1. Plots of  $k_A$  vs. amine concentration  $[A]$  for the reaction of I with N-methyl-*p*-anisidine at some temperatures.

changes indicated that only two independently absorbing species, *i.e.*, II and III, were always present throughout the second stage, as required by the mechanism in Scheme 1.

The first-order amine dependence in rate law (1) is consistent with direct nucleophilic attack of the amine on the 'coordinated' nitrile group in intermediate II *via* a four-center transition state in



Scheme 1

( L = PPh<sub>3</sub>; R = Me, Ar = *p*-C<sub>6</sub>H<sub>4</sub>-OMe; R = Et, Ar = *p*-C<sub>6</sub>H<sub>4</sub>-Me )

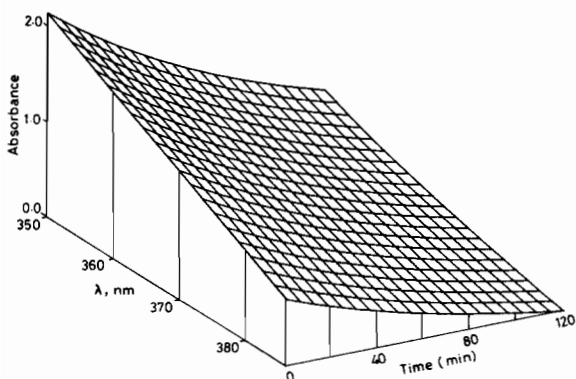


Fig. 2. Plot of absorbance vs. both wavelength and time for the reaction of I with N-methyl-*p*-anisidine. Temp. 45 °C, amine concn.  $2.75 \times 10^{-2}$  M. The absorbance surface is expressed as  $A_{t,\lambda} = A_{\infty,\lambda} + (A_{0,\lambda} - A_{\infty,\lambda}) \exp(-8.3 \times 10^{-3} \cdot t)$  where  $A_{0,\lambda}$  = initial spectrum of second stage,  $A_{\infty,\lambda}$  = spectrum of reaction mixture after 7–8 half-lives.

which intramolecular proton exchange occurs between the amine and nitrile nitrogens. Concomitant formation of a Pt–amidino bond and rupture of the existing Pt–amine bond complete the activation process. Consistently, the  $k_2$  value for N-methyl-*p*-anisidine is ca. 6 times higher than the  $k_2$  term for N-ethyl-*p*-toluidine, since the former has higher nucleophilic ability and lower steric hindrance around the reacting center than the latter. The fact

that the rate of nucleophilic attack by aromatic amines on metal-coordinated unsaturated groups is enhanced by good electron-donor substituents with low steric requirements on the amine had been observed earlier for the formation of carbene derivatives by reaction of isonitrile derivatives with anilines [9]. The low activation enthalpy and the highly negative activation entropy for the reaction with N-methyl-*p*-anisidine ( $\Delta H_2^\ddagger = 8.5 \pm 0.2$  kcal/mol;  $\Delta S_2^\ddagger = -44.6 \pm 0.6$  e.u.) also support the view that the activation process for this stage involves concerted bimolecular formation of a constrained, strongly oriented cyclic transition state. Similar activation parameters have been previously observed for nucleophilic attacks on metal-coordinated carbonyl and isocyanide ligands [10–12] or on carbon–carbon double bonds of activated olefins [13].

The second-order amine dependence in rate law (1) can be simply explained by the involvement of a hydrogen bonded amine dimer – formed in a rapid pre-equilibrium step – wherein proton exchange takes place through a second amine molecule acting as a bifunctional catalyst in a six-membered cyclic activated complex (path  $k_3$  in Scheme 1). Amine dimers as attacking nucleophiles were indicated previously for the aminolysis of metal carbene complexes [14], for the formation of metal carbamoyl complexes from metal carbonyl derivatives and amines

[15], for some ester aminolyses [16] and for the amine acylation by ketenes [17]. We have no data bearing on the merits of possible alternative mechanisms to explain the overall third-order term in rate law (1) and we are also mindful that there is no virtue in choosing a mechanism more complex than that demanded by the experimental evidence. In this context the  $k_3$  parameter should be the product of the amine dimerization equilibrium constant,  $K_D$ , times the second order rate constant for nucleophilic attack and proton exchange,  $k'_3:k_3 = k'_3 \cdot K_D$ . The corresponding activation parameters ( $\Delta H_3^\ddagger = 9.5 \pm 0.5$  kcal/mol,  $\Delta S_3^\ddagger = -33 \pm 2$  e.u. for N-methyl-*p*-anisidine) are therefore composite in nature; nonetheless they are quite in line with the proposed mechanism for the  $k_3$  step. The  $k_3$  value for N-ethyl-*p*-toluidine is much lower than that for N-methyl-*p*-anisidine, showing that steric hindrance in the crowded six-membered transition state is of prime importance.

## Experimental

### Reaction of I with N-methyl-*p*-anisidine

A solution of I (1.59 g, 0.86 mmol, prepared by general methods reported previously [3]) and N-methyl-*p*-anisidine (0.47 g, 3.46 mmol, molar ratio I: amine 1:4) in 100 ml of 1,2-dichloroethane, was stirred for 10 h at  $\approx 70^\circ\text{C}$ , under nitrogen. Concentration of the solution, precipitation with hexane, dissolution in  $\text{CH}_2\text{Cl}_2$ , treatment with charcoal, filtration, and reprecipitation with hexane gave 1.53 g (85%) of the off-white product III. *Anal.* Calcd. for III ( $\text{C}_{52}\text{H}_{47}\text{BF}_4\text{N}_2\text{OP}_2\text{Pt}$ ): C 58.93; H, 4.47; N, 2.64. Found: C, 58.44; H, 4.42; N, 2.38. Ir (Nujol mull)  $\nu(\text{C}=\text{N})$  1545 s, 1580 m;  $\nu(\text{NH})$  3360 w.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$  in ppm, J in Hz):  $\delta(\text{OCH}_3)$ : 3.70 s;  $\delta(\text{N-Me})$ : 2.79 s;  $\delta(o\text{-CH}_2\text{-Ph})$ : broad and obscured by the N-Me signal;  $\delta(\text{N-H})$ : not observed.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2\text{-H}_3\text{PO}_4$  85%):  $\delta_{\text{P}}$  (*trans* to carbon): 24.48 d,  $^1J_{\text{P-Pt}} = 1844$ ,  $^2J_{\text{P-P}} = 15.6$ ;  $\delta_{\text{P}}$  (*cis* to carbon): 16.36 d,  $^1J_{\text{P-Pt}} = 4030$ ,  $^2J_{\text{P-P}} = 15.6$ .

### Infrared and NMR Spectra

Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer, calibrated with polystyrene film. A Varian FT 80 A spectrometer operating in FT mode was used for proton and  $^{31}\text{P}$  NMR spectra.

### Kinetics

The reactions were followed spectrophotometrically by measuring changes in optical density in the range 330–380 nm with time by means of a Cary-219 Varian 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 ( $\pm 0.1^\circ\text{C}$ ) cell compartment of the spectrophotometer. A solution containing the same concentration of the entering amine was used as a reference. The entering 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,  $k_{\text{obs}}$ , and activation parameters were obtained as described elsewhere [18]. The rate parameters in rate law (1) were determined by linear regression.

### Statistical Data Reduction and Handling

All statistical and graphical analyses of kinetic data were performed with a comprehensive software package implemented on a Tektronix 4052 Graphic System (64 kbytes RAM) equipped with a 4907 File Manager-Floppy Disc Driver, a Tektronix 4662 Digital Plotter and an Anadex DP-9500 fast printer. The package was in part derived from the Tektronix Plot 50 Statistical Software and locally tailored to suit the needs of the system under study. Detailed information is available upon request.

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