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Reactions of Coordinated Nitriles. I. Mechanism of Formation of Amidino Complexes by Attack of Primary Anilines on Pt(II) *ortho*-Cyanobenzyl Complexes

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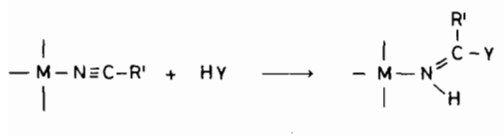
The reaction of the dimeric o*-cyanobenzyl complex* cis-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ *with primary anilines to form monomeric amidino complexes* cis-$[Pt(o\text{-}CH_2C_6H_4C(=NH)(p\text{-}YC_6H_4NH)(PPh_3)_2]BF_4$ *in DCE is a biphasic process. The first, rapid stage involves displacement of the nitrile group by the entering amine leading to a labile mononuclear amino complex bearing a dangling -CN group. This intermediate reacts with the amine in the second slower stage* via *attack of the amine nitrogen on the nitrile carbon to yield the final Pt(II)–amidino species.*

Introduction

The chemistry of transition metal–nitrile complexes has aroused a growing interest in the past few years [1], since organonitrile complexes may act as suitable precursors to a variety of novel organometallic derivatives. In particular, the activation of the nitrile group upon metal coordination has been exploited in addition reactions of nucleophiles such as alcohols, thiols, water and amines yielding imino-ether-, imino-thioether-, amido, or amidino-complexes (eqn. 1):

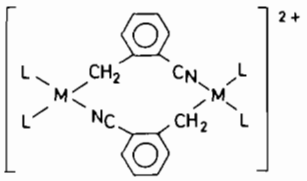


Y = -OR, -SR, -OH, -NR"R"' (1)

Thus, imino-ether complexes were obtained from *trans*-$[Pt(Me)(NCR)L_2]^+$ (L = PMe_2Ph [2]; L_2 = 1,5-Cyclooctadiene [3]; RCN = pentafluorobenzonitrile and 2,3,5,6-tetrafluoroterephthalonitrile) by reaction with an alcohol. It is noteworthy that the nitriles undergoing nucleophilic attack in these reactions are activated by electron-withdrawing substituents.

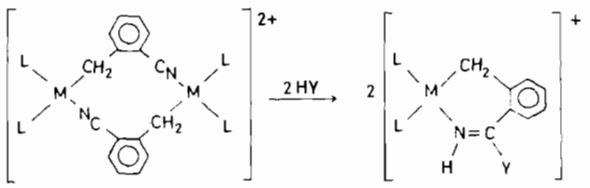
The attack of alcohols on the nitrile group in cyano-pyridines has been shown to be catalyzed by metal ions such as Cu(II) [4]. Most studies of metal-catalyzed reactions on nitriles deal with the hydration of the nitrile group to carboxamide promoted by transition metal–phosphine complexes in low oxidation states [5] or in the presence of Cu(II), Zn(II) and Ni(II) ions [6]. Examples of hydration of nitriles catalyzed by Hg^{2+} in Co(II) complexes have been reported [7]. Recently hydroxo complexes of the type $[Pt(OH)RL_2]$ (R = alkyl or aryl; L = tertiary phosphine) proved also to catalyze the hydration of nitriles [8].

An interesting class of nitrile complexes is represented by dimeric species of the type:



M = Pd(II), Pt(II); L = tertiary phosphine

wherein the nitrile group bonded to one metal ion belongs to an *ortho*-benzyl moiety linked to the other metal ion through a M–C σ-bond [9]. The nitrile groups in these cationic complexes proved markedly susceptible to nucleophilic attack to yield monomeric chelates (eqn. 2):



I II (2)

M = Pd(II), Pt(II); L = PPh_3, 1/2 diphosphine
Y = MeO, EtO, i-PrO, $PhCH_2O$, MeS, EtS, $PhCH_2S$, Me_2N, Et_2N, Me(Ph)N, $C_5H_{10}N$, 4-MeC_6H_4NH, 4-$MeOC_6H_4NH$
Solvent = DCE

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A preliminary mechanistic study for the reaction with alcohols (M = Pt; L = PPh_3) [9b] has proposed a stepwise sequence involving the breaking of the cyanobenzyl bridge followed by intramolecular attack on the nitrile end in the ensuing monomeric intermediate (eqn. 3):

$$cis\text{-}[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2^{2+} + 2HOR \rightleftharpoons$$
$$2\,cis\text{-}[Pt(o\text{-}CH_2C_6H_4CN)(HOR)(PPh_3)_2]^+ \longrightarrow$$
$$\longrightarrow cis\text{-}[Pt(o\text{-}CH_2C_6H_4C(=NH)OR)(PPh_3)_2]^+ \quad (3)$$

An analogous stepwise pattern was also proposed for the reactions with amines [9c], based on the isolation of stable Pt–amino intermediates *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(RNH_2)(PPh_3)_2]BF_4$ (R = H, Et), along with the final amidino derivatives.

Since all attempts to elucidate the mechanism of reaction (2) were so far based solely on the nature of intermediates and final products, we thought that a full kinetic study was required to ascertain the electronic and steric factors determining the reactivity of the various sites of attack in the dimeric substrates **I**. In the following we report on such kinetic studies for the reactions with some primary anilines. A preliminary account of these reactions with secondary anilines has already appeared [10].

Experimental

Materials

1,2-Dichloroethane (DCE) was purified by washing with aqueous NaOH, drying over P_2O_5 and distillation under N_2. Aniline was vacuum distilled. *p*-Anisidine and *p*-toluidine were sublimed under vacuum. All the amines were stored cold under N_2 in the dark.

Preparation of Complexes

The following complexes were prepared according to literature procedures: *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ [9a], *cis*-$[Pt(o\text{-}CH_2C_6H_4C(=NH)NH(p\text{-}YC_6H_4))(PPh_3)_2]BF_4$ (Y = Me, OMe) [9a].

cis-$[Pt(o\text{-}CH_2C_6H_4C(=NH)NHC_6H_5)(PPh_3)_2]BF_4$

To an acetone suspension (50 ml) of *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ (0.87 g, 0.47 mmol) was added aniline (0.3 ml, 3 mmol) and the reaction mixture was heated at 40 °C for 6 hr. After addition of active charcoal, stirring for an additional hour and filtration, the filtrate was concentrated to *ca.* 10 ml under reduced pressure. Dropwise addition of Et_2O (80 ml) caused precipitation of the white product which was recrystallized from CH_2Cl_2/n-pentane. Yield 66%. Mp 248–250 °C dec. *Anal.* Calcd. for $C_{50}H_{43}N_2P_2BF_4Pt$: C, 59.13; H, 4.27; N, 2.76. Found: C, 58.74; H, 4.06; N, 2.68%. IR (Nujol mull, cm^{-1}): νNH 3325w, νC=N 1580m, 1545s; νBF_4 1060s. ^1H NMR (CD_2Cl_2, δppm, J Hz): δCH_2 2.81dd, ^2J(H–Pt) 67, ^3J(H–P) *trans* 8.4, ^3J(H–P) *cis* 6.2. $^{31}P-\{^1H\}$ NMR (CD_2Cl_2, H_3PO_4 85%): δP(*cis* to benzyl carbon): 17.1d, ^1J(P–Pt) 4022, ^2J(P–P) 15.5; δP(*trans* to benzyl carbon) 23.95d, ^1J(P–Pt) 1872, ^2J(P–P) 15.5.

Instrumentation and Kinetics

IR spectra were recorded on a Perkin-Elmer 597 spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a Varian FT 80-A spectrometer. Electronic spectra were recorded on a Varian Cary 219C spectrophotometer. Kinetic data acquisition and computer analysis were performed on a Tektronix 4052 Graphic System equipped with a 4907 floppy disk and a 4662 Digital Plotter.

The reactions were followed by recording changes in optical density in the range 390–320 nm, by using fresh solutions of the substrate and amine reactants (the latter being in excess to provide first order conditions). The reactions were started by mixing known volumes of pre-thermostatted standard solutions in the thermostatted (±0.1 °C) cell compartment of the spectrophotometer.

Plots of absorbance values *versus* time on the recorder strip chart were directly fed to the minicomputer by use of the digitizing facility of the 4662 Digital Plotter. For both consecutive stages observed (see Results and Discussion) the absorbance changes with time were found to fit the pseudo-first order exponential law. Statistical treatment of all kinetic data was carried out as described previously [11].

Results and Discussion

Figure 1 shows spectral changes in the range 370–320 nm of a solution of substrate **I** (10^{-4} *M*) and excess aniline (0.13 *M*) at 25 °C. Spectrum *a* refers to a solution of **I** alone at the same concentration. Spectrum *b* is observed at completion and matches closely the spectrum of an authentic sample of the final amidino product prepared independently, as described above. Intermediate spectra were recorded in the course of reaction 2, indicating that the process takes place in two distinct stages. The first stage, relating to the $a \rightarrow i$ spectral changes, takes place within *ca.* 1–2 min, whereas the subsequent $i \rightarrow b$ conversion takes typically *ca.* 2–3 hr, depending on the amine concentration. Quite analogous spectral changes were also observed for the other two amines examined, *p*-anisidine and *p*-toluidine. Abstract factor analysis [12] of spectral changes $i \rightarrow b$ showed the presence of only two absorbing species, *i* and *b*, throughout the spectral range examined.

The above evidence indicates that the reaction under study involves fast formation of a labile inter-

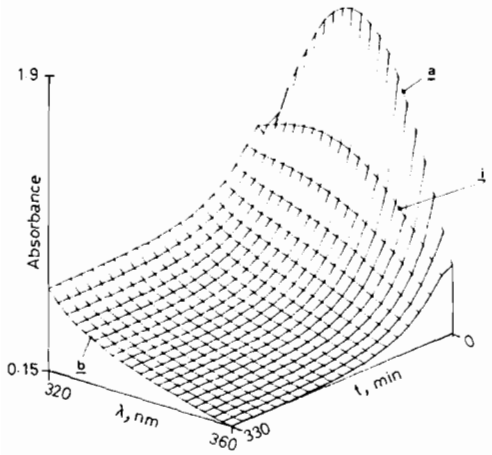


Fig. 1. Plot of absorbance *vs.* both wavelength and time for the reaction of I (10^{-4} *M*) with aniline (0.13 *M*) in DCE at 25 °C. Spectrum *a* refers to a solution of I alone at the same concentration. Spectrum *i* is approximately the spectrum of intermediate I*, spectrum *b* is observed at completion.

mediate which then reacts at a much slower rate to yield the final product.

First Stage

Owing to its rapidity the first stage was followed kinetically at 340 nm, corresponding to the greatest observable spectral changes. The stage proved to be pseudo-first order with respect to substrate **I**, with pseudo first order rate constant k^I_{obs} being a linear function of amine concentration [A], with a statistically significant intercept (95% confidence level):

$$k^I_{obs} = k^I_1 + k^I_2[A] \quad (4)$$

Kinetic data for the first stage with A = *p*-anisidine are listed in Table I (see also Fig. 2).

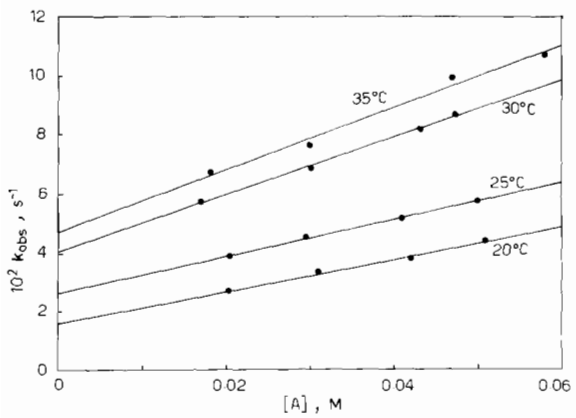


Fig. 2. Plots of k^I_{obs} *vs.* amine concentration (A) for the reaction of *p*-anisidine at various temperatures.

The determination of these rate constants is affected by considerable experimental error, due both

TABLE I. Rate Data for the First Stage of the Reaction of *cis*-[Pt(*o*-$CH_2C_6H_4CN$)$(PPh_3)_2]_2(BF_4)_2$ with *p*-Anisidine (A) in DCE at Various Temperatures. Uncertainties quoted are standard errors of estimate (in parenthesis).

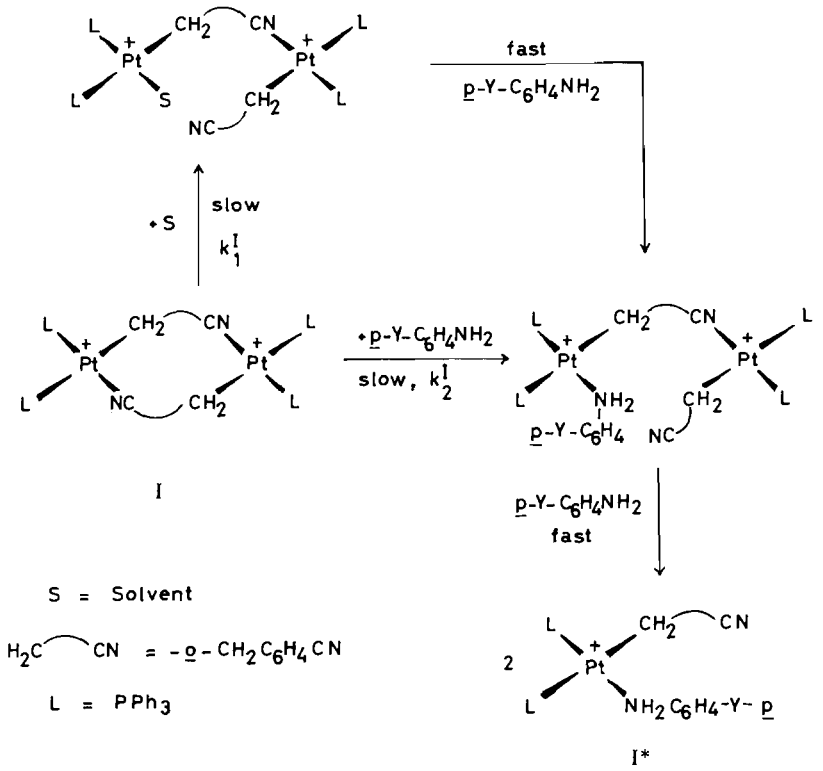
Temp., °C	10^2[A] *M*	$10^2 k^I_{obs}$ s^{-1}	$10^2 k^I_1$ [a] s^{-1}	$10 k^I_2$ [b] $M^{-1} s^{-1}$
20	2.03	2.7	1.7(0.3)	5.3(0.7)
	3.10	3.3		
	4.20	3.8		
	5.08	4.4		
25	2.05	3.9	2.6(0.1)	6.2(0.1)
	2.95	4.5		
	4.10	5.2		
	5.00	5.7		
30	1.71	5.7	4.1(0.1)	9.7(0.4)
	3.02	6.9		
	4.31	8.2		
	4.73	8.7		
35	1.82	6.7	4.7(0.3)	10.4(0.7)
	3.00	7.6		
	4.70	9.9		
	5.81	10.7		

[a] Intercept and [b] Slope of plot of k_{obs} *vs.* [A].

to the high reaction rate (approaching the instrumental limits of conventional spectrophotometric techniques) and to the onset of the subsequent second stage during the later portion of the first one. These conditions make the assessment of infinite time absorbance values difficult, even with iterative non-linear regression computer techniques [11]. These difficulties manifest themselves in the high value of the least-squares function being minimized at convergence and in the high standard error of the fit. Slightly better results were obtained by fitting the combined absorbance *versus* time data for both stages to a consecutive two-step regression model—a procedure favoured by the highly different rates of the stages involved. These alternative fitting methods yielded the same k^I_{obs} values.

The intrinsic uncertainties in k_{obs} are reflected in the k^I_1 and k^I_2 rate parameters. A fit of these parameters to the Eyring equation for the reaction with *p*-anisidine gave the activation parameters $\Delta H^{\neq}_{I,1}$ = 12 ± 2 Kcal/mol, $\Delta S^{\neq}_{I,1} = -25 \pm 5$ e.u., $\Delta H^{\neq}_{I,2} = 8 \pm 2$ Kcal/mol, $\Delta S^{\neq}_{I,2} = -31 \pm 5$ e.u. The analogous k^I_{obs} data for the other amines also appear to obey the two-term rate law (4) but their large standard deviations do not lead to sufficiently reliable k^I_1 and k^I_2 parameters.

In spite of these experimental uncertainties, the observed spectral changes and the form of the rate law (4) indicate that the first stage implies the breaking of the nitrile bridges in the dimeric sub-



Scheme 1

strate **I** by the amine. This takes place by nucleophilic substitution—a typical feature of square-planar Pt(II) chemistry—leading to a monomeric cationic intermediate (**I***, Scheme 1) which bears the uncoordinated nitrile group at the end of the σ-metal-bonded *o*-cyanobenzyl residue. Formation of intermediate **I*** takes place by two parallel steps wherein the solvent and the amine compete favourably for substrate **I**, with first- and second-order kinetics. Displacement of solvent by the amine in the intermediate species of the k_1^I stage is rapid. The ensuing binuclear intermediate contains one single *o*-cyanobenzyl bridge and one amine bound to one single metal center: the subsequent fast reaction of a further amine molecule breaks the nitrile bridge to yield the mononuclear intermediate **I***, which is the reaction product of the first stage. The high reaction rates observed appear to stem from a low activation enthalpy, probably related to a combination of concomitant factors, *viz.*:

(*i*) the tendency of organonitrile ligands in transition metal complexes to undergo displacement by other even weak donor ligands—a feature commonly exploited in synthetic methods to prepare otherwise in accessible derivatives;

(*ii*) the presence of the highly *trans* activating PPh_3 ligand which further enhances the nitrile group lability;

(*iii*) the increased tendency of nitrile bridges toward rupture by nucleophilic substitution due to strain relief in the constrained dimeric substrate **I**. Such a steric strain was clearly shown by single crystal X-ray structure analysis of the analogous dimer $[Pt(o\text{-}CH_2C_6H_4CN)(Ph_2PCH{=}CHPPh_2)]_2(BF_4)_2$ [9d].

The associative nature of the nucleophile-dependent k_2^I term is clearly indicated by the highly negative activation entropy, in agreement with the wealth of evidence gathered so far for nucleophilic displacement in square-planar Pt(II) complexes. The highly *trans* activating PPh_3 reduces the discriminating ability of the substrate by increasing the solvent role in the nucleophile-independent step, despite the poor coordinating ability of DCE. The nature of intermediate **I*** finds precedents in the isolation of the analogous NH_3 species and in the formation of a mixture of **I***- like and **II**- like complexes with $EtNH_2$ [9c]. However, all our attempts to isolate such intermediates with the aromatic amines of this study failed since the reaction mixtures always reverted back to the initial reactants upon addition of precipitating media. Apparently the donor ability of the amine governs the stability of the mononuclear metal–amine intermediate. Only with large excess of the aromatic amine reactant under kinetic conditions is the system driven to complete formation of such an intermediate.

TABLE II. Rate Data for the Second Stage of the Reaction of *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ with *p*-$YC_6H_4NH_2$ (A) in DCE at Various Temperatures.

A	Temp., °C	10^2[A] *M*	$10^4 k_{obs}^{II}$ s^{-1}	$10^3 k_2^{II}$ [a] $M^{-1} s^{-1}$
Aniline	15	39.0	3.7	
		52.0	4.9	
		64.0	6.1	0.94(0.01)
		77.0	7.2	
	20	20.0	3.1	
		33.0	5.2	
		52.0	8.0	1.50(0.02)
		77.0	11.7	
	25	13.0	3.1	
		33.0	7.9	
		52.0	12.0	2.36(0.04)
		77.0	18.4	
	30	10.0	3.7	
		26.0	10.2	
		35.0	13.6	3.84(0.03)
		46.0	17.5	
p-Toluidine	15	7.4	1.9	
		11.1	2.6	
		13.9	3.4	2.43(0.04)
		16.5	4.0	
	20	2.93	1.0	
		4.96	1.7	
		7.96	2.9	3.55(0.06)
		9.85	3.4	
		12.80	4.6	
	25	4.0	2.8	
		7.6	5.2	
		11.8	8.2	6.90(0.03)
		14.5	9.1	
	30	3.0	2.8	
		4.9	4.7	
		8.2	7.7	9.60(0.03)
		12.2	11.8	
p-Anisidine	15	3.10	1.4	
		3.90	1.8	
		5.02	2.2	4.55(0.04)
		6.10	2.8	
	20	1.70	1.4	
		3.00	2.4	
		4.00	3.3	8.20(0.04)
		5.00	4.1	
	25	1.20	1.4	
		2.10	2.5	
		3.00	3.5	11.80(0.07)
		4.00	4.7	
	30	1.70	3.5	
		2.40	4.9	
		3.10	6.3	20.50(0.08)
		3.80	7.8	

[a]Slope of plot of k_{obs} *vs.* [A].

Second Stage

The second, slower stage is also a pseudo-first order process with a one-term linear dependence on amine concentration:

$$k_{obs}^{II} = k_2^{II}[A] \quad (5)$$

thereby ruling out any amine independent path. The values of k_{obs}^{II} and k_2^{II} are listed in Table II for all the three anilines examined (see also Fig. 3). A simple mechanism consistent with this evidence is shown in Scheme 2.

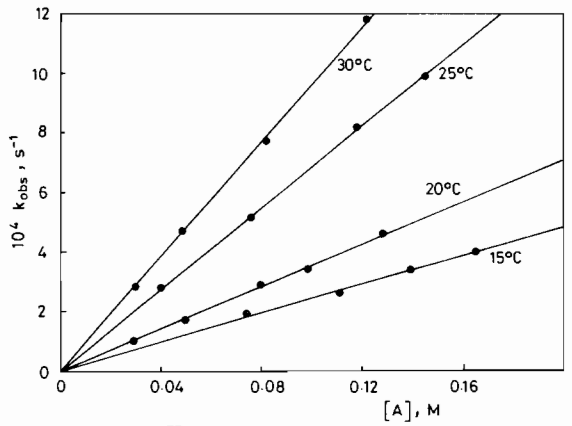
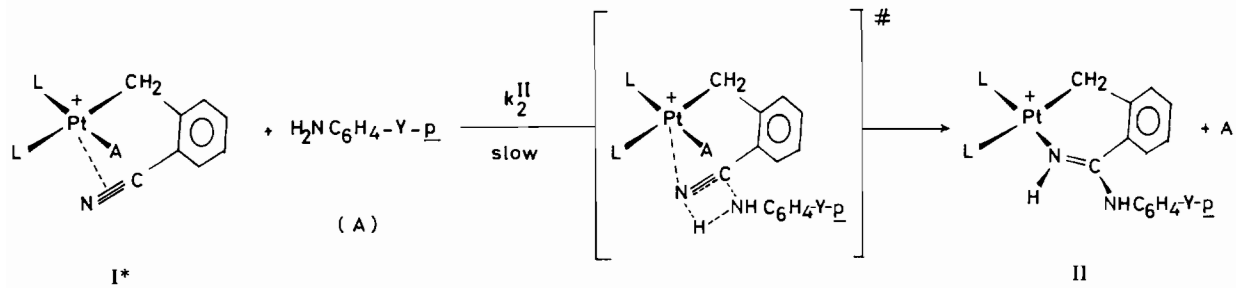


Fig. 3. Plots of k_{obs}^{II} *vs.* amine concentration (A) for the reaction with aniline at various temperatures.



Scheme 2

The nitrile group activated by interaction with the central metal in **I*** reacts with the amine by attack of the amine nitrogen on the nitrile carbon with concomitant concerted proton exchange between the nitrile and amine nitrogens with incipient Pt···N-(imino) bond formation in a cyclic four-center transition state. Elimination of the already-coordinated amine leads to the final monomeric imino derivative **II**. The key feature of this mechanism appears to be tendency of the dangling nitrile group of the *ortho*-cyanobenzyl moiety to undergo nucleophilic attack. Indeed, Dreiding molecular models indicate that it can occupy an axial position at sufficient distance from the central metal to allow a possible 'side-on' interaction with the latter. This electronic interaction, which could well be established on demand, would activate the -CN group by enhancing the electrophilic character of the nitrile carbon.

The intrinsic stability of such configuration is likely to be enhanced by electron donor substituents in the aromatic ring of the coordinated amine. A limiting representation of this π nitrile–metal interaction would be a transition metal-stabilized carbocation, as suggested by Clark *et al.* to explain the formation of imino ether complexes from cationic methyl platinum(II)–nitrile derivatives [2]. Examples of 'side-on' nitrile coordination, as shown by X-ray structural analysis, are the complexes $Pt(PPh_3)_2(N{\equiv}CCF_3)$ [13] and $Ni(CO)(N{\equiv}CNC_5H_{10})$ [14].

The stability of the activated complex is expected to increase with increasing nucleophilic ability of the attacking amine and with decreasing steric hindrance around the reacting sites. The activation process requires considerable restrictions of degrees of freedom since the *ortho*-cyanobenzyl residue must be oriented properly to allow the concerted interaction of reacting centers. The stabilizing role that the amine *para* substituent plays on both the substrate **I*** and the activated complex is clearly shown by the activation parameters for the k_2^{II} stage listed in Table III. As can be seen, the reactivity order

p-anisidine > *p*-toluidine > aniline

which parallels the order of amine nucleophilic ability is essentially due to entropic factors, whereas activation enthalpies are virtually identical within experimental error (see also Fig. 4). Apparently, the larger

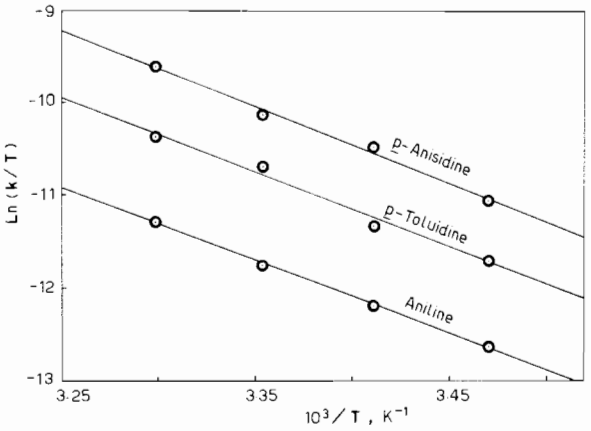


Fig. 4. Eyring plots for the k_2^{II} terms of reaction 2 with *p*-anisidine, *p*-toluidine, and aniline.

stabilization of substrate **I*** caused by a more nucleophilic amine is virtually offset by the greater stabilization of the activated state in which such amine is involved. The negative activation entropies agree with the bimolecular nature of the proposed process and with the steric restrictions mentioned above. However, it is not clear how the *p*-substituent in the amine determines the differences in the activation entropies observed.

We are now carrying out further kinetic studies to determine the electronic and steric influence of substituents on both the amine and cyanobenzyl ring, the role of the central metal, and of the *cis*-ancillary ligands in these reactions.

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TABLE III. Selected Activation Parameters for Both Stages.

Y	1st Stage		1st Stage		2nd Stage	
	$\Delta H_1^{\neq}$, kcal/mol	$\Delta S_1^{\neq}$, e.u.	$\Delta H_2^{\neq}$, kcal/mol	$\Delta S_2^{\neq}$, e.u.	$\Delta H_2^{\neq}$, kcal/mol	$\Delta S_2^{\neq}$, e.u.
p-OMe	12(2)	−25(5)	8(2)	−31(5)	16(1)	−12(3)
p-Me					16(1)	−15(3)
H					15.5(0.3)	−18(1)

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