

ELECTROPHILIC AND NUCLEOPHILIC ATTACKS ON ALKYL, NITRILE, AND ISONITRILE COMPLEXES OF Pd(II) AND Pt(II)

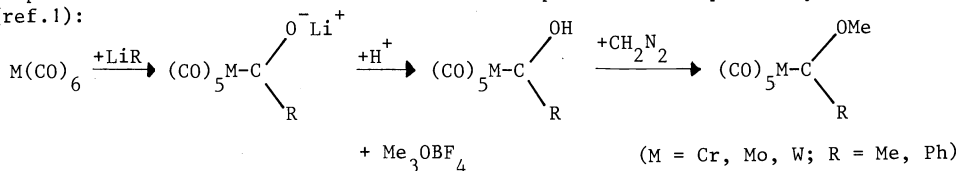
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Abstract

In this paper are reported the results of a comprehensive mechanistic study of nucleophilic attack by amines on coordinated isocyanides in square-planar Pd(II) complexes, leading to amino-carbene complexes. The reactivity pattern that has emerged displays several facets: (i) whatever the details, in this stepwise mechanism the most prominent step always involves direct attack of the amine nitrogen on the isocyanide carbon, followed by the required rearrangements; (ii) this fundamental primary step is affected by the donor ability of the entering amine, the electrophilic character of the isocyanide carbon, and the steric crowding around the reacting centers, with the solvent playing an important role; (iii) the conversion of the intermediate originating from the primary step into the final carbene species is often aided by the entering amine itself which behaves as a bifunctional catalyst; (iv) the relative magnitude of the elementary step rates can be changed with a fair degree of versatility by properly tailoring the reaction system through the choice of the substituents on the amine and isocyanide aromatic rings and of the ancillary ligands in the metal complex; (v) the variety of steric and electronic parameters that can be changed at will makes the system ideally suited as a mechanistic model for elucidating the reactivity of coordinated CO-iso-electronic ligands as precursors of carbene moieties.

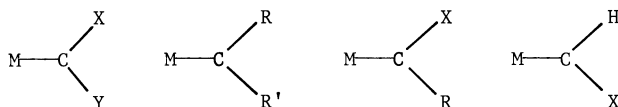
First examples of stable transition metal carbene complexes were reported by E.O. Fisher et al. (ref.1):



Carbene complexes were also prepared in which the heteroatom (X) in the carbene moiety, $\text{M}-\text{C} \begin{array}{l} \text{XR} \\ \text{R}' \end{array}$, can be N, S or Se.

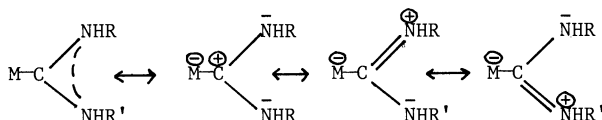
The main preparative routes for amino-carbene derivatives are: (i) nucleophilic attacks on metal coordinated or on preformed carbene groups; (ii) electrophilic attacks on imino-complexes; (iii) reactions of metal complexes with organic carbene precursors, such as electron-rich olefins, gem-dichlorides, imidazolium salts, etc.; (iv) electrophilic attacks on coordinated isocyanides.

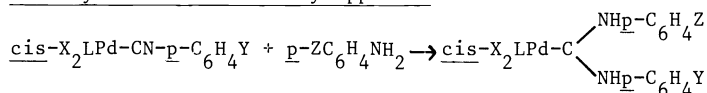
The following types of carbene ligands are known:



X = NHR, OR, SR, SeR;
 Y = NHR, OR;
 R = alkyl, aryl;
 M = transition metal

The products have been alternatively described as metal-carbenes, stabilized carbonium ions or metallated amidinium ions:



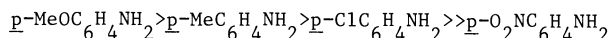
I - Nucleophilic Attacks by Amines on Coordinated Isonitrilesa) Primary Anilines an early approach

L = PPh₃, AsPh₃; X = Cl, Br; Solvent: 1,2-dichloroethane (DCE); Z = MeO, Me, H, Cl, NO₂; Y = MeO, Me, H, NO₂.

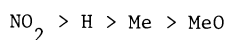
The pseudo-first-order rate constants were found to obey the simple second-order rate law:

$$k_{\text{obs}} = k_2 [\text{Amine}]$$

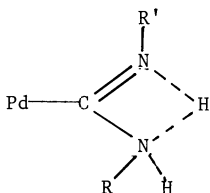
The observed reactivity order for entering amines on cis-PdCl₂(CNPh)(PPh₃) parallels the order of decreasing σ -donor ability of the amine nitrogen:



The rate of attack of a given amine, on the other hand decreases with decreasing electron-withdrawing ability of the p-substituent Y on the isonitrile:



The following mechanism is proposed: direct nucleophilic attack of the amine on the isocyanide carbon atom in a one-step cyclic concerted pathway :



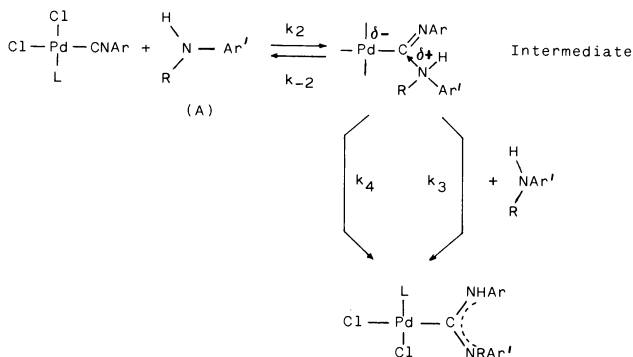
(four-center transition state)

$$\Delta H^\ddagger = 9.4 \pm 0.1 \text{ kcal/mol and } \Delta S^\ddagger = -35 \pm 2 \text{ e.u.}$$

for the reaction of cis-PdCl₂(CNPh)(PPh₃) with p-toluidine.

b) Secondary Anilines: getting a better insight

The general mechanism of the reaction was proven to be as follows:



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

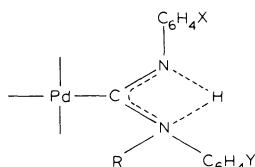
In the steady-state approach, the observed "second order" rate coefficient, $k_A = k_{\text{obs}}/[A]$, fits the general rate law (1).

First step (k_2)

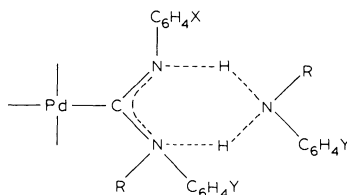
Nucleophilic attack of the entering amine on the isocyanide carbon atom yielding a reactive intermediate or transient

Following steps

path k_{4-} : intramolecular proton transfer through a four-membered cyclic transition state



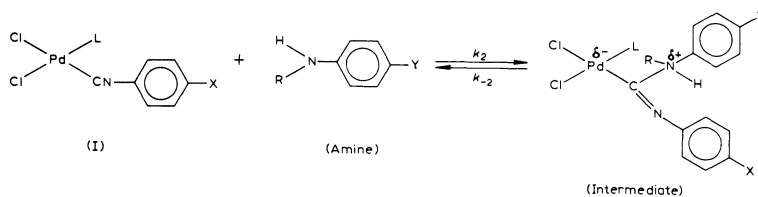
path k_{3-} : proton transfer by the agency of a further amine molecule serving as proton acceptor-donor in a six-membered cyclic transition state (bifunctional catalysis):



The proposed mechanism rests on the following evidence:

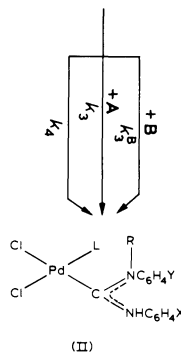
- 1) No catalytic action by N,N-dimethylaniline
- 2) Remarkable catalytic activity of $p\text{-BrC}_6\text{H}_4\text{NH}_2$;

in this case the mechanism becomes:



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

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



In the absence of B, three types of plots of k_A vs. $[A]$ are observed, depending on the relative magnitude of k_{-2} , k_4 and k_3 .

When k_{-2} , k_4 and $k_3 \cdot [A]$ are comparable, the general rate law cannot be simplified and gives rise to a non-linear plot of k_A vs. $[A]$.

When $k_{-2} \gg k_4 + k_3[A]$, k_A becomes a linear function of $[A]$:

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

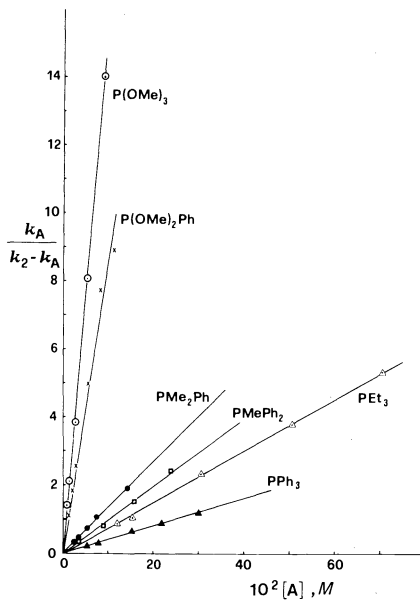
Finally, when $k_{-2} \ll k_4 + k_3[A]$, the rate law becomes:

$$k_A = k_2$$

as observed for primary anilines.

The following general features of the mechanism are noteworthy:

- 1) k_2 increases with increasing electron-withdrawing ability of the para-substituent on the isocyanide and decreases with increasing steric hindrance on the attacking amine.
- 2) k_2 increases with increasing π -accepting ability of the ancillary cis ligand L in the metal complex and with decreasing steric requirements of L.



3) the k_3/k_{-2} ratio is also markedly affected by changes in the properties of the cis ligand L: good π -accepting ligands with lower bulkiness will stabilize the intermediate toward breakdown to starting substrate, while favouring its further reaction with the amine in the catalytic step k_3 .

4) the k_2 step is associated to a comparatively low activation enthalpy, as expected for a direct attack leading to the intermediate adduct without the breaking of any bonds in the reactants. The activation entropy is largely negative in agreement with an associative process where neutral reactants develop some charge separation in the transition state which

probably involves freezing of solvent molecules in the highly ordered region around the constrained, strongly oriented activated complex.

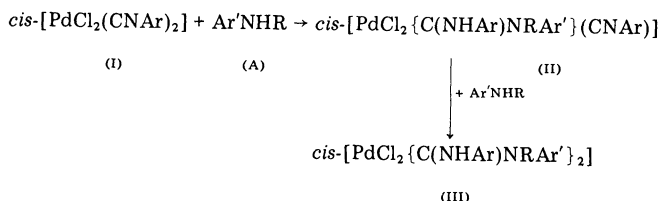
A striking solvent effect has been observed.

The overall second-order rate constant decreases in the order:

benzene > 1,2-dichloroethane > acetone \sim dioxane at comparable amine concentrations.

Such a difference is mainly related to a greater stabilization of the attacking amine by solvation and hydrogen bonding with the solvents acetone and dioxane.

Reactions of bis-isocyanide complexes $cis-PdCl_2(CNAr)_2$



The first step is much faster than the second one. When secondary anilines are used, the second step becomes so slow that it cannot be followed kinetically at ambient temperature and the final product is a mono-carbene species.

The k_2 values of the first step are the highest so far observed for reaction of amines with coordinated isocyanides.

These high values of k_2 relate to the fact that in these bis-isocyanide complexes 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 or phosphines in the vicinity of the reaction center.

The marked sensitivity of carbene formation to steric and electronic factors is also shown by the fact that the second step of reaction is much slower than the first one with primary anilines and does not occur at all with secondary anilines: once the first carbene moiety is formed, its good sigma-donor ability and bulkiness make the remaining isocyanide less susceptible to further attack.

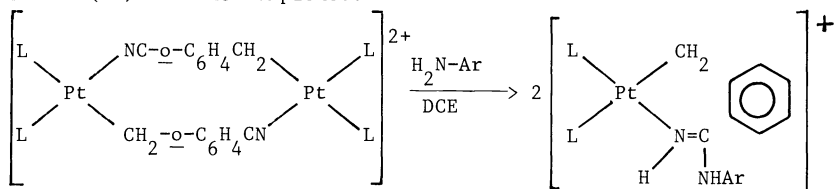
The inability of secondary anilines to react further with mono-carbene isocyanide complexes is mainly related to increased steric repulsion between the reacting centers. Consistently, it is possible to block the second stage of carbene formation even for primary anilines by introducing ortho-substituents in the amine phenyl ring.

In previous studies, the k_3/k_{-2} ratios are also effected by both steric and electronic factors.

It is noteworthy that the use of trans-amino complexes as substrates has allowed us to measure the k_3/k_{-2} values for unhindered primary anilines reacting with unhindered coordinated isocyanides: this was possible due to the fact that the trans amine ligand, lacking π -bonding ability, is less effective in stabilizing the steady-state intermediate toward collapse to the starting reactants, thereby making the k_{-2} term comparable with the $k_3[A]$ value.

II - Nucleophilic Attacks on Coordinated Nitriles

Nucleophilic attacks by aromatic amines on dimeric Pt(II) nitrile complexes involve formation of Pt(II) amidino complexes:



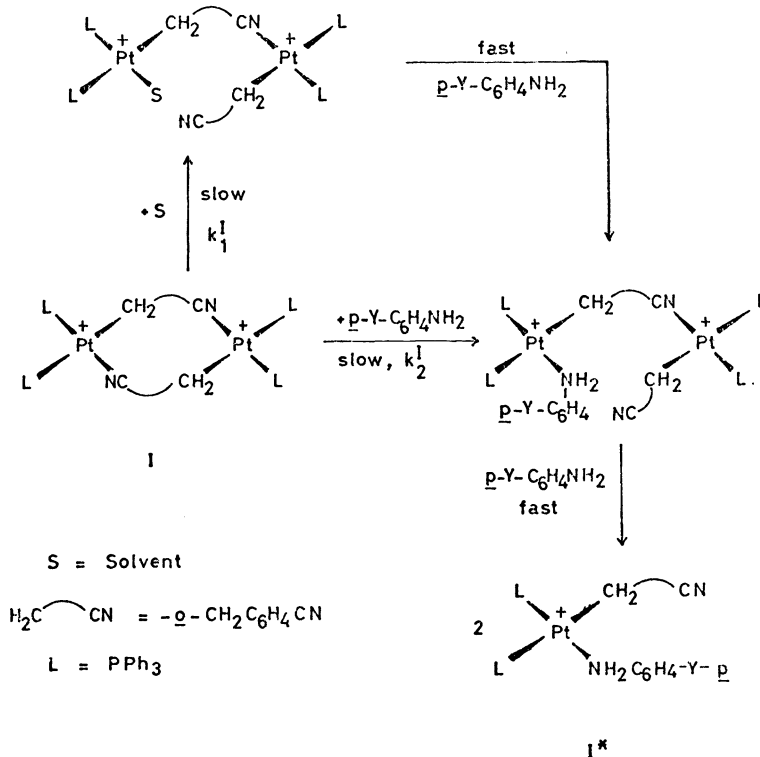
L = PPh₃. Ar = C₆H₅, *p*-CH₃C₆H₄, *p*-CH₃OC₆H₄; DCE = 1,2-dichloroethane

The reaction proceeds in two well separated stages.

The first, faster stage obeys the two-term rate law:

$$k_{\text{obs}}^{\text{I}} = k_1^{\text{I}} + k_2^{\text{I}} [\text{A}] \quad \text{A} = \text{amine}$$

This suggests breaking of the nitrile bridges on the dimeric substrate by nucleophilic substitution by the entering amine, with a nucleophile-independent path (solvent-path). The resulting intermediate contains a free nitrile group with some interaction with the central metal:

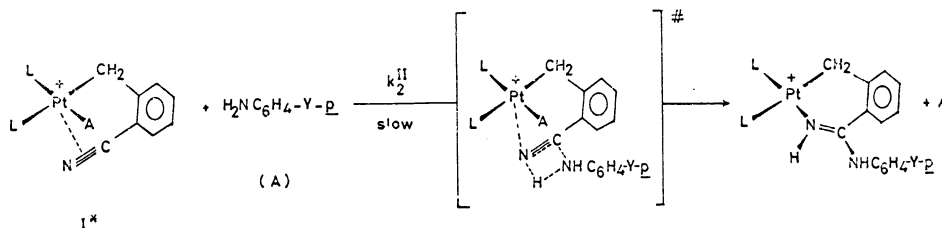


The reaction is favoured by the intrinsic lability of the nitrile group enhanced by the strong trans-effect of the PPh₃ ligand and also by the tendency of the strained nitrile bridges in the substrate to open up.

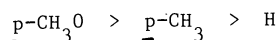
The second, slower stage is first order in amine concentration:

$$k_{\text{obs}}^{\text{II}} = k_2^{\text{II}} [\text{A}]$$

We suggest a direct, second-order bimolecular attack by the amine on the intermediate I: the nitrile group, which is activated by interaction with the central metal, reacts with the amine by attack on the nitrile carbon with parallel concerted proton exchange between the nitrile and amine nitrogens in a cyclic 4-center transition state:



The activation parameters indicate that the amine reactivity order:



is essentially due to entropic effects. The negative activation entropies are in agreement with the bimolecular nature of the activation process.

Activation parameters for both stages are listed in Table I.

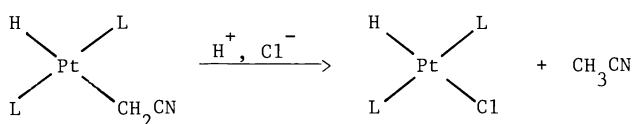
The rate of the second stage is also affected by the nucleophilic power of the amine and by the steric hindrance of ortho-substituents in the aromatic amine ring.

Table I. Activation Parameters

Y	FIRST STAGE				SECOND STAGE	
	ΔH_1^\ddagger	ΔS_1^\ddagger	ΔH_2^\ddagger	ΔS_2^\ddagger	ΔH_2^\ddagger	ΔS_2^\ddagger
OCH ₃	12+2	-25+5	8.3+2	-13+5	16.3+1	-12+3
CH ₃					15.8+1	-15+5
H					15.5+0.3	-18+1

III - Electrophilic Attacks on Pt-C sigma bonded Complexes

The mechanism of the following reaction has been studied:



The protolytic cleavage of the Pt-C σ -bond in trans-PtH(CH₂CN)(PPh₃)₂ in a methanol/1,2-dichloroethane (9/1v/v) solvent mixture takes place smoothly and quantitatively at temperatures in the range 20-60°C.

The pseudo-first order rate constant, k_{obs} sec⁻¹, obeys the following rate law:

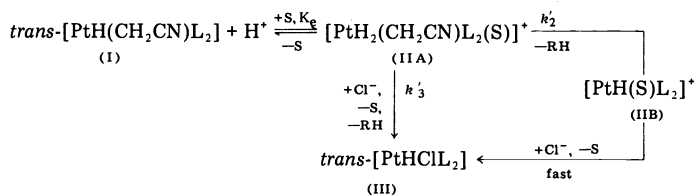
$$k_{\text{obs}} = k_2[\text{H}^+] + k_3[\text{H}^+][\text{Cl}^-]$$

Activation parameters are:

ΔH_2^\ddagger	ΔS_2^\ddagger	ΔH_3^\ddagger	ΔS_3^\ddagger
(kcal/mol)	(e.u.)	(kcal/mol)	(e.u.)
17.5 ± 0.5	-15 ± 2	20.5 ± 0.7	0.5 ± 2

These data are consistent with a step-wise mechanism involving prior oxidative addition of the proton to give an unstable Pt(IV) hydride intermediate, followed by slow

reductive elimination of CH_3CN :



(L = PPh_3 ; S = solvent; R = CH_2CN)

The reductive-elimination takes place both intramolecularly (chloride-independent path) and under the influence of an entering chloride ion. The activation parameters for the single steps in this mechanism are composite quantities of pre-equilibrium and rate-determining components, each one depending on structural features of activated states and solvent participation.

The oxidative addition path as sketched in the scheme is favoured by the small size and high donor ability of the hydride ligand while the electronegative cyanomethyl group helps in stabilizing the platinum(II) substrate toward reductive elimination to platinum(0) species and CH_3CN . When the alkyl group trans to the hydride is not electronegatively substituted (*i.e.*, CH_3) the corresponding alkylplatinum(II) hydride species decomposes to phosphineplatinum(0) complexes with liberation of methane, even at low temperature.

The selectivity of cleavage appears to be strictly related to the type of electrophile and experimental conditions employed; the substrate trans- $\text{PtH}(\text{CH}_2\text{CN})(\text{PPh}_3)_2$ undergoes cleavage of the Pt- CH_2CN bond by hydrogen chloride in ether, whereas the Pt-H bond is involved in the cleavage when HBF_4 in ether is used as the electrophile.

Therefore it appears that both the particular mechanism which is operative and the selectivity of attack are the result of many factors (electronic and steric properties of the groups to be cleaved and of ancillary ligands, steric configuration of the substrate, nature of the electrophile and solvation properties of the medium). Care must thus be exercised in extrapolating mechanistic features of general validity from particular systems:

