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MECHANISMS OF NUCLEOPHILIC AND ELECTROPHILIC ATTACK ON CARBON BONDED PALLADIUM(II) AND PLATINUM(II) COMPLEXES

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Summary

A systematic mechanistic study is reported for the formation of palladium(II) carbene complexes by nucleophilic attack of aromatic amines on isocyanide derivatives. The most prominent step of the reaction involves direct attack of the amine nitrogen on the isocyanide carbon to give an intermediate which then is converted to the final carbene species by the agency of the entering amine itself which behaves as a bifunctional catalyst. The rate of the primary step is affected by the donor ability of the entering amine, by the electrophilic character of the isocyanide carbon, and by steric crowdiness around the reacting centers, with the solvent also playing an important role. The reaction system displays a high versatility through a proper choice of the substituents on the amine and isocyanide aromatic rings and of the ancillary ligands in the metal complex.

A mechanistic study is also described of the cleavage of the platinum–carbon σ-bond by electrophilic attack by the proton on organoplatinum(II) complexes. The particular mechanism which is operative, viz. direct electrophilic attack at the metal–carbon bond or oxidative addition/reductive elimination, appears to be the result of many factors. These include electronic and steric properties of the cleaved group and of ancillary ligands, steric configuration of the substrate, nature of the electrophile and solvating ability of the medium.

Introduction

In this review we deal with the mechanisms of reactions involving the following processes:

I. Nucleophilic attack on coordinated isocyanides in palladium(II) complexes, leading to metal-carbene derivatives;

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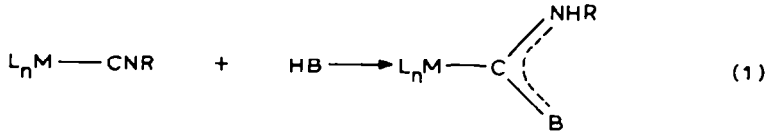
II. Electrophilic attack on alkyl- and aryl-platinum(II) complexes with cleavage of metal–carbon σ bonds.

The first topic has attracted worldwide interest in the past decade following the discovery that metal-carbene complexes could be easily isolated from addition reactions of protic nucleophiles to coordination-activated isocyanide ligands. The great interest in this field has both theoretical and practical aspects, since the metal-carbene species involved a new type of metal–carbon bonds possibly possessing novel reactivity and having implications for organic synthesis. In other words, new, otherwise inaccessible, highly reactive species such as carbenes might be trapped upon a complex metal center. However, such stabilization exceeded expectations since the resulting metal–carbene bond proved, in most cases, to be very stable towards further reactions. Typical metal–carbon bond reactions such as insertion and electrophilic cleavage are rather rare. Thus interest has focused progressively on methods of preparation, bonding properties, and mechanisms of formation rather than on the reactivity. As far as the latter aspect is concerned, however there are possibilities in the widening of the range of metals, use of polyfunctional isocyanides, and variation of the nucleophiles.

The second topic is concerned with the mechanisms of protonolysis of carbon–metal σ bonds in alkyl- and aryl-platinum(II) complexes to give free hydrocarbons. The cleavage may occur via different mechanistic patterns in which the primary steps involve either direct protonation of the arylmetal derivatives, or prior oxidative addition to the central metal followed by reductive elimination. Which site of attack is involved can be unequivocally established only if the relevant intermediates are isolated. Nonetheless, the distinction may be helpful in defining the details of mechanistic patterns on the basis of differing rate laws, which imply different activation processes.

I. Mechanisms of nucleophilic attack on coordinated isocyanides in palladium(II) complexes

Coordination-activated isocyanides undergo 1,2-addition by protic nucleophiles (amines, alcohols and thiols) [1] to give metal-carbene species:



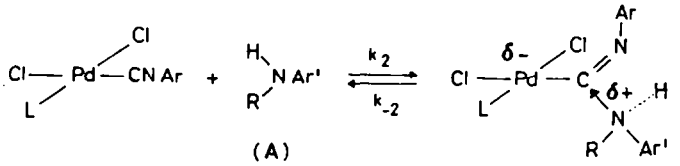
(1)

This reaction, initially studied for M = Hg^{2+}, Pt^{2+}, Pd^{2+}, Fe^{2+}, Au^{+}, was later extended to other transition metal ions and can be considered to be of a general type provided that favourable electronic and steric requirements are met. We carried out

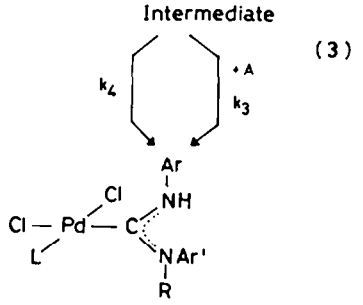
(2)

detailed kinetic studies for the system shown in eq. 2 (Ar and Ar′ = *ortho*- or *para*-substituted aryl groups; R = H, Me, Et; L = phosphorus donor ligand, isocyanide) [2–7].

Reaction 2 is a multi-step process with inter- and intra-molecular stages, as shown in eq. 3 and 4.



(A)

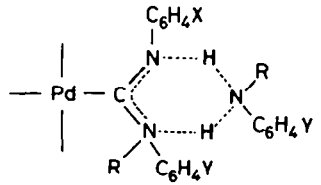


(3)

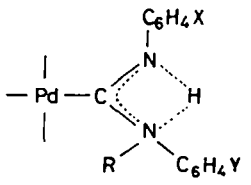
General rate law:

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

The first step (k_2) can be interpreted as a nucleophilic attack of the entering amine on the carbon of coordinated isocyanide to give the intermediate iminopalladium(II) species. The subsequent steps to give the final carbene complex involve proton transfer, which may occur either intramolecularly (reaction k_4) in a four-membered cyclic transition state, or by the intervention of a further amine molecule (reaction k_3) which acts as proton acceptor–donor in a six-membered cyclic transition state (in general, the k_3 reaction predominates over the k_4 one). That is, reaction k_3 represents a catalytic contribution to carbene formation by the entering amine acting as bifunctional catalyst:



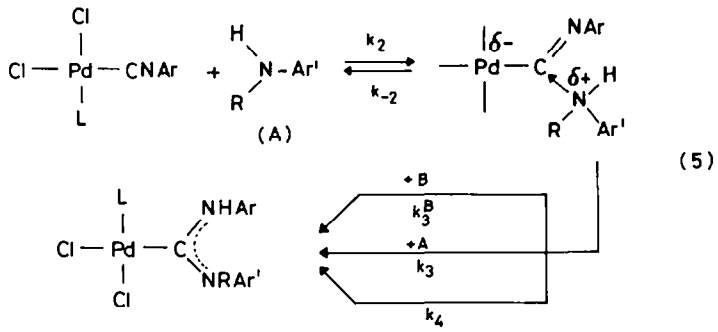
T.S. for k_3



T.S. for k_4

This is confirmed by the fact that tertiary amines, such as *N*,*N*-dimethylaniline, have no appreciable effect on the reaction rates over a wide range of concentration. In other words, the dimethylamino group, though having good basic properties and small steric requirements, is incapable of bifunctional catalysis, since it lacks a transferable proton. On the other hand, the primary amine *para*-$BrC_6H_4NH_2$ (B)

has a remarkable catalytic activity in the proton transfer step, whereas, due to its lower basicity, it is not able to compete with secondary amines in the nucleophilic attack step, k_2 (eqs. 5 and 6).



(5)

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

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} is comparable with $k_4 + k_3$ [A], the general rate law gives rise to a non-linear plot of k_A vs. [A] (Fig. 1).

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

$$k_A = \frac{k_2 k_4}{k_{-2}} + \frac{k_2 k_3}{k_{-2}}[A] \tag{7}$$

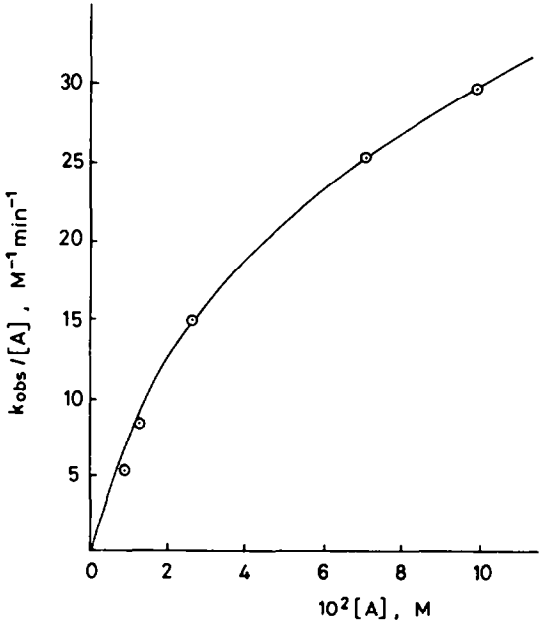


Fig. 1. Dependence of $k_{obs}/[A]$ on amine concentration for the reaction of *cis*-[$PdCl_2(CNC_6H_4Cl$-*p*)(PPh_3)] with $MeHNC_6H_5$ (A) at 25°C.

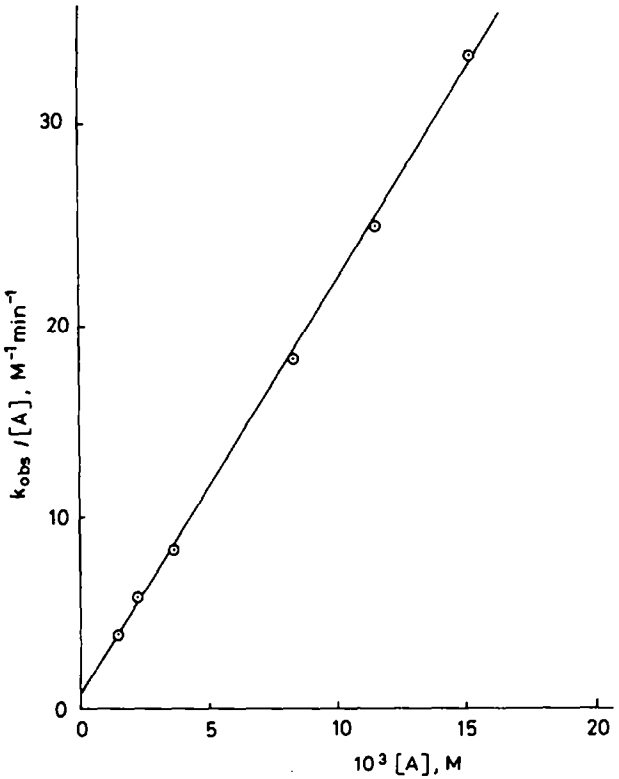
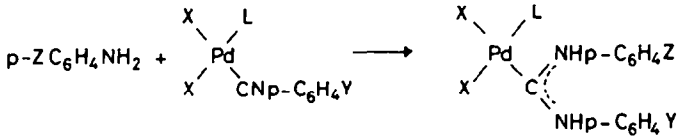


Fig. 2. Dependence of k_{obs}/[A] on amine concentration for the reaction of *cis*-[$PdCl_2(CNC_6H_5)(PPh_3)$] with $MeHNC_6H_4OMe$-*p* (A) at 25°C.

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

$$k_A = k_2 \tag{8}$$

This simplified limiting rate law was first encountered in the system involving the reaction of primary *p*-substituted aromatic amines with palladium(II) complexes of *p*-substituted aromatic isocyanides [2] (eq. 9).



(9)

(L = PPh_3, $AsPh_3$; X = Cl, Br; Solvent = 1, 2-dichloroethane (DCE); Z = MeO, Me, H, Cl, NO_2; Y = MeO, Me, H, NO_2)

In this case, the formation of the intermediate becomes rate-determining.

The observed reactivity order for entering amines on *cis*-[$PdCl_2(CNC_6H_5)(PPh_3)$] as a model substrate was: *p*-$MeOC_6H_4NH_2$ > *p*-$MeC_6H_4NH_2$ > $C_6H_5NH_2$ > *p*-$ClC_6H_4NH_2$ > *p*-$O_2NC_6H_4NH_2$, which is also the order of decreasing electron-donating properties of the *p*-substituent Z (i.e., the order of decreasing σ-donor ability of the amine nitrogen) (Fig. 3).

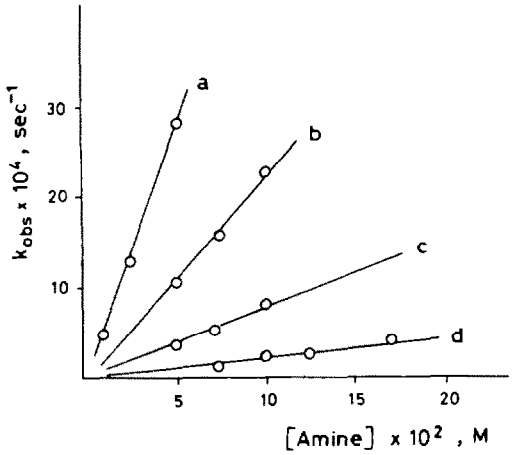


Fig. 3. Plots of k_{obs} vs. the concentration of amine for the reactions of *cis*-[$PdCl_2(CNC_6H_5)(PPh_3)$] with $H_2NC_6H_4Z$-*p* at 30°C; a, Z = OMe: b, Me; c, H; d, Cl.

The rate constants decreased linearly with increasing Hammett's σ-parameter of the amine. The rate of attack by a given amine, on the other hand, decreased with decreasing electron-withdrawing ability of the *p*-substituent Y in the isonitrile: NO_2 > H > Me > MeO. A linear free energy correlation was observed using the Hammett σ-parameters for Y. The activation parameters for the reaction of the phenyl isocyanide complex with *p*-toluidine were $\Delta H^{\ddagger} = 9.4 \pm 0.1$ kcal/mole and $\Delta S^{\ddagger} = -35 \pm 2$ e.u.

These substituent electronic effects and activation parameters fit well into the general mechanistic picture, since the rate of direct attack at the isocyanide carbon is expected to increase with increasing nucleophilic ability of the reacting amine and increasing electrophilic character of the terminal isonitrile carbon atom. The general rate law (eq. 4) was first observed when reaction 2 with secondary anilines was kinetically studied [3]. In this case the alkyl *N*-substituent enhances the k_2 step due to an increased basicity, but at the same time it also increases the value of k_{-2} owing to an increased steric repulsion between the reacting centers, making the reversal of the formation of the intermediate comparable in rate with the subsequent proton transfer steps leading to the final carbene products. In some reactions, the tendency of the intermediate to collapse to the initial reactants becomes so overwhelming that the linear rate law (eq. 7) is observed. The prime importance of steric factors in the mechanism of reaction 2 was further confirmed when *ortho*-substituents were introduced into the phenyl ring of either the primary aniline or the isocyanide molecule [5]. *Ortho*-substitution not only causes a marked decrease in the overall reaction rates relative to those of the analogous *para*-substituted reactants [2], but also yields the same mechanistic pattern as observed for secondary anilines (Fig. 4). Consistently, when *ortho*-substituents were present in both reactants the reaction rates were drastically depressed.

Besides these steric effects, the second order k_2 parameter for secondary anilines depends on the electronic properties of both the entering amine and isocyanide substrate in much the same way as described for primary anilines.

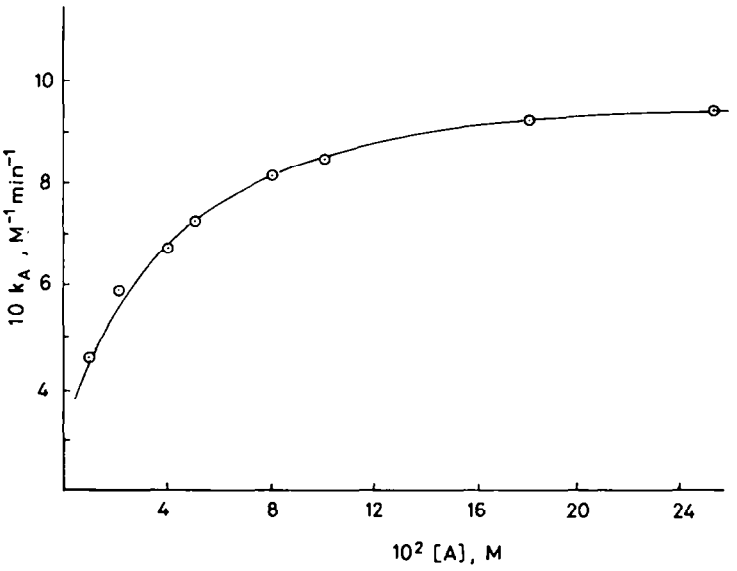


Fig. 4. Dependence of $k_A = k_{obs}/[A]$ on the amine concentration [A] for the reaction of *cis*-$[PdCl_2(CNC_6H_4Me\text{-}o)(PPh_3)]$ with *p*-anisidine at 30°C.

Some selected rate parameters are listed in Table 1.

It appears that there is a complex balance of both electronic and steric factors which determines the particular rate law observed.

A mechanistic study of reaction 2 in which the *cis* group L was a phosphorus ligand of different bulkiness and electronic ability (L = $P(OMe)_3$, $P(OMe)_2$-Ph, PPh_3, $PMePh_2$, PMe_2Ph, PEt_3, PCy_3) clearly shows that for every L the general curvilinear rate law 4 is obeyed, with the k_4/k_{-2} term being statistically insignificant (Table 2) [4].

Figure 5 shows the dependence of $k_A/(k_2-k_A)$ vs. *N*-methyl aniline concentration for the various *cis* ligands examined. The slopes of these linear plots yield the term k_3/k_{-2}, according to eq. 10, which is a reformulation of the general rate law 4:

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

The second order rate constant, k_2, increases in the order: $PEt_3 < PMePh_2 < PPh_3 < PMe_2Ph < P(OMe)_2Ph < P(OMe)_3$ depending on the net balance between the steric requirements of L and its π-acceptor vs. σ-donor abilities: the k_2 term will increase with the π-accepting power of L through a reduced charge density on the metal, resulting in a higher electrophilic character of the isocyanide carbon (reduced Pd-isocyanide $d \rightarrow \pi^*$ back donation). In this closely related series of complexes the electrophilic character of the isocyanide carbon, which is governed by the electronic properties of L, can be fairly well gauged from the stretching frequency of coordinated isocyanide, ν(CN). Figure 6 displays a correlation of k_2 with ν(CN) of the appropriate complex and with the L ligand cone angle, the latter being taken as a measure of the steric requirements of L [8]. As can be seen, k_2 increases regularly with ν(CN), with the exception of L = PMe_2Ph, which appears to have a higher reactivity than expected on purely electronic grounds. This position of PMe_2Ph in

TABLE 1

RATE DATA FOR THE REACTION OF *cis*-[$PdCl_2$(CNAr)(PPh_3)] WITH RHNAr' IN 1,2-DICHLOROETHANE (DCE)

Ar	Ar'	R	Temp (°C)	k_2 (M^{-1} min^{-1})	k_3/k_{-2} (M^{-1})	k_4/k_{-2}	k_2k_3/k_{-2} (M^{-2} min^{-1})	k_2k_4/k_{-2} (M^{-1} min^{-1})
C_6H_5	C_6H_5	H	30	0.49				
C_6H_5	*p*-C_6H_5Me	H	25	0.98				
C_6H_5	*p*-C_6H_5Me	H	30	1.33				
C_6H_5	*p*-C_6H_5OMe	H	30	3.32				
p-C_6H_4Me	*p*-C_6H_4Me	H	30	0.75				
p-C_6H_4Cl	*p*-C_6H_4Me	H	30	4.03				
p-C_6H_4Me	C_6H_5	Me	25	5.8	4.1	~ 0		
C_6H_5	C_6H_5	Me	25	14.8	3.7	~ 0		
p-C_6H_4Cl	C_6H_5	Me	25	49.8	16.1	~ 0		
p-C_6H_4Me	*p*-C_6H_4OMe	Me	25	28.3	36.5	~ 0		
p-C_6H_4Cl	C_6H_5	Et	25	17.0	2.4	~ 0		
C_6H_5	*p*-C_6H_4OMe	Me	25	–	–	–	2100	0.7
p-C_6H_4Cl	*o*-C_6H_4Me	H	30	1.60	48	0.18		
o-C_6H_4Me	*p*-C_6H_4OMe	H	30	1.02	45.3	0.25		
o,o'-$C_6H_3Me_2$	*p*-C_6H_4OMe	H	30	0.40	1.43	~ 0		

TABLE 2

cis-LIGAND EFFECTS ON THE RATES OF REACTION OF *cis*-[$PdCl_2$(CN-*p*-C_6H_4Me)(L)] WITH *N*-METHYLANILINE IN DCE AT 25°C

L	k_2 (M^{-1} min^{-1})	k_3/k_{-2} (M^{-1})
$P(OMe)_3$	10.5	149
$P(OMe)_2Ph$	7.4	82.4
PPh_3	5.8	4.1
$PMePh_2$	3.0	10.1
PMe_2Ph	6.7	13.9
PEt_3	1.2	6.8

the reactivity series stems from the favourably low steric hindrance of this phosphine which acts as the overriding factor (see the correlation with the cone angle in Fig. 6). The predominant importance of electronic factors is borne out by the fact that the PPh_3-containing substrate is much more reactive than the PEt_3 analog in spite of the reverse order of ligand bulk. The highest rates are observed when both electron-withdrawing properties and low steric requirements obtain, as with $P(OMe)_2Ph$ and $P(OMe)_3$. Consistently, when L = PCy_3, the steric bulkiness and poor π-acceptor ability of the ligand reduce the rate below observation limits.

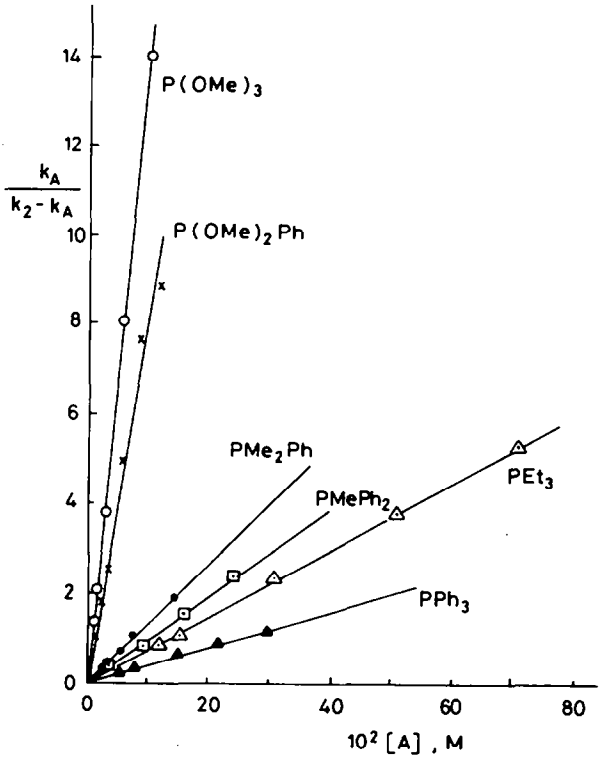


Fig. 5. Plots of $k_A/(k_2 - k_A)$ ($k_A = k_{obs}/[A]$) vs. the concentration of amine for the reaction of *cis*-[$PdCl_2$(CNC_6H_4Me-*p*)(L)] with $MeHNC_6H_5$ in DCE at 25°C.

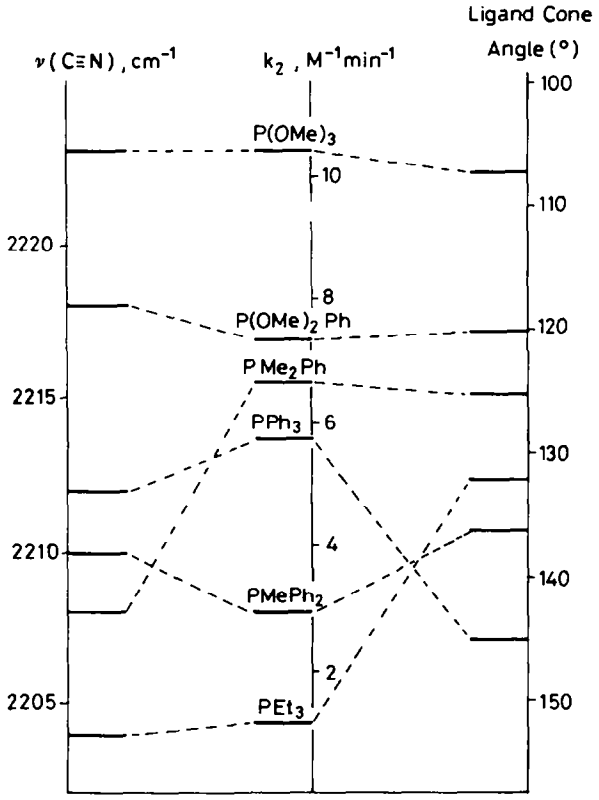


Fig. 6. Correlation of k_2 with ν(CN) of coordinate isocyanide and with ligand cone angle of L for the reaction of *cis*-$[PdCl_2(CNC_6H_4Me\text{-}p)(L)]$ with $MeHNC_6H_5$.

The k_3/k_{-2} ratios derived from the slopes of the linear plots in Fig. 5 are also markedly affected by changes in the properties of the *cis* ligand L: good π-accepting ligands with lower bulk will stabilize the intermediate toward breakdown to starting substrate while favouring its further reaction with the amine in the catalytic step k_3. By contrast, increasing bulkiness of L will simultaneously reduce k_3 and increase k_{-2} by steric crowding and repulsion around the metal atom in the activation processes of these competing steps. The following order of L is observed for the k_3/k_{-2} ratio: $PPh_3 < PEt_3 < PMePh_2 < PMe_2Ph < P(OMe)_2Ph < P(OMe)_3$. In some cases, steric factors may become overwhelming, as is clearly shown by the observed trend, $PPh_3 < PMePh_2 < PMe_2Ph$, which is the reverse order of electron-withdrawing ability. The activation parameters for the k_2 step of the reaction between *cis*-$[PdCl_2(CN\text{-}p\text{-}C_6H_4Me)(PPh_3)]$ and *N*-methylaniline are $\Delta H^{\ddagger} = 9.8 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -30 \pm 2$ e.u., very close to those previously reported for the system *cis*-$[PdCl_2(CNPh)(PPh_3)]$/*p*-toluidine. The comparatively low enthalpies of these reactions are in agreement with a direct bimolecular attack to give the intermediate (eq. 3) without the breaking of any bonds in the reactants. The large negative activation entropies are consistent with an associative process in which neutral reactants develop some charge separation in the transition state with freezing

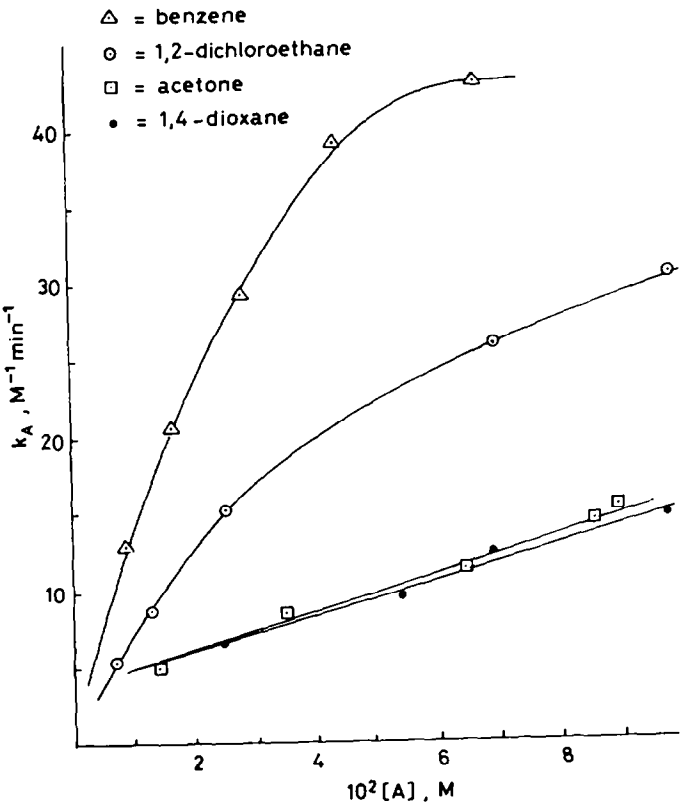


Fig. 7. Dependence of $k_A = k_{obs}/[A]$ on amine concentration in the various solvents for the reaction of *cis*-$[PdCl_2(CNC_6H_4Cl\text{-}p)(PPh_3)]$ with $MeHNC_6H_5$ at 25°C.

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

The solvent effect has been studied for the reaction of *cis*-$[PdCl_2(CN\text{-}p\text{-}C_6H_4Cl)(PPh_3)]$ with *N*-methylaniline [4]. The overall second-order rate constant decreases in the order: benzene > 1,2-dichloroethane > acetone ≃ dioxane at comparable amine concentrations. Further, the dependence of k_A on [A] is curvilinear in benzene and 1,2-dichloroethane, and linear in acetone and dioxane (Fig. 7).

The observed differences in reactivity between these two pairs of solvents are mainly related to a greater stabilization of the attacking amine by solvation and hydrogen bonding with acetone and dioxane. This can be deduced from the lower values of the nitrogen-hydrogen stretching frequencies in such solvents. The resulting deactivation of the amine will bring about a decrease in the overall reaction rates, which will be reflected in both the bimolecular nucleophilic attack (k_2) and in the catalytic path (k_3). A decrease in the latter term will account for the linear dependence of k_A on amine concentration in acetone and dioxane, as expected from the general rate law when $k_{-2} \gg k_4 + k_3$ [A].

Having established the general mechanism of carbene formation, we extended our studies to some particular systems, namely the reactions of the substrates *cis*-$[PdCl_2(CNAr)_2]$ or $[PdCl_2(CNAr)]_2$ with primary and secondary anilines. The

reaction of bis-isocyanide complexes involves two consecutive stages, with the first one being much faster than the second [6].

$$\underset{\text{(I)}}{cis\text{-}[PdCl_2(CNAr)_2]} + \underset{\text{(A)}}{Ar'NHR} \rightarrow \underset{\text{(II)}}{cis\text{-}[PdCl_2\{C(NHAr)NRAr'\}(CNAr)]} \xrightarrow{+Ar'NHR} \underset{\text{(III)}}{cis\text{-}[PdCl_2\{C(NHAr)NRAr'\}_2]} \quad (11)$$

When secondary anilines are used, the second stage becomes so slow that it cannot be followed kinetically at ambient temperature, and the final product is a mono-carbene species.

Bis-isocyanide substrates may be regarded a particular case of *cis*-$[PdCl_2(CNAr)(L)]$ complexes wherein the L ligand *cis* to the isocyanide being attacked is another isocyanide.

In the first stage the limiting value $k_A = k_2$ is quickly reached on increasing the amine concentration, and formation of the intermediate becomes the rate-determining step (Fig. 8). The k_2 values are the highest so far observed for the reactions of amines with coordinated isocyanides (Table 3). In most cases the first stage of reaction 11 could only be followed by stopped-flow techniques. These high values of k_2 relate to the fact that in these complexes the *cis*-isocyanide ligand has good π-acceptor ability giving rise to a much lower steric hindrance than phosphites or phosphines in the vicinity of the reaction center. As in the systems considered previously, the k_2 values increase with increasing basicity of the amine, decreasing bulk of the *N*-substituent, and increasing electron-withdrawing ability of the *para*-groups in the aryl isocyanide. For complexes with *ortho*-substituted isocyanides the

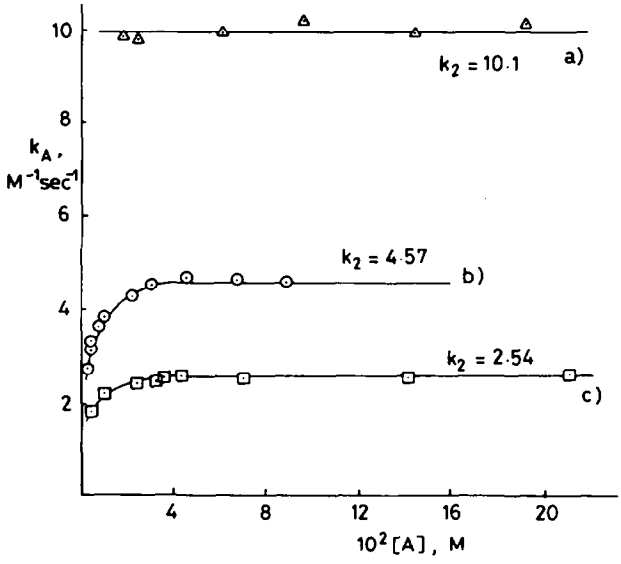


Fig. 8. Dependence of $k_A = k_{obs}/[A]$ on amine concentration for the reaction of *cis*-$[PdCl_2(CNC_6H_4Me\text{-}p)_2]$ with (a) *N*-ethyl-*p*-toluidine, (b) *N*-methylaniline and (c) *N*-ethylaniline at 25°C in DCE.

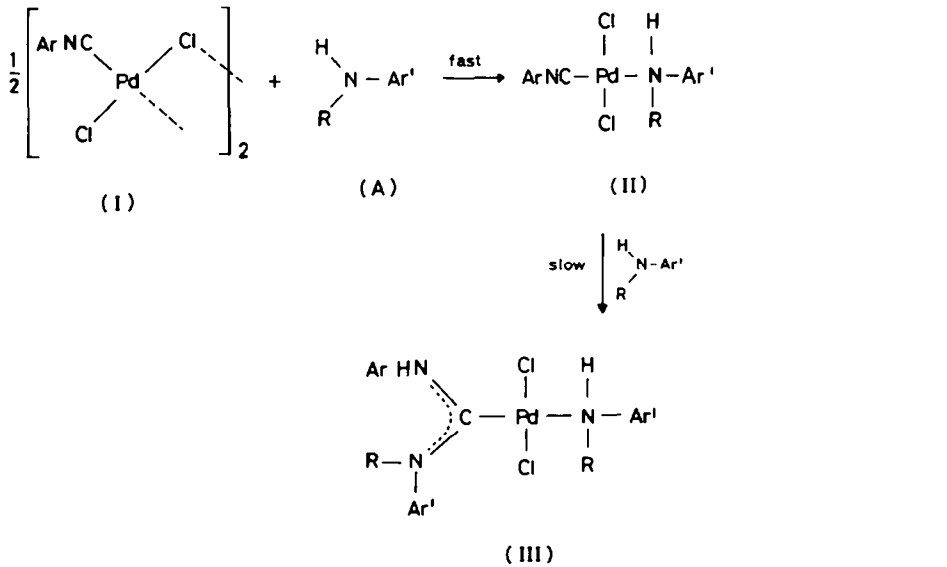
TABLE 3

SELECTED RATE DATA FOR THE FORMATION OF MONO-CARBENE DERIVATIVES FROM THE REACTION OF *cis*-$[PdCl_2(CNAr)_2]$ WITH RHNAr' IN DCE AT 25°C

Ar	Ar'	R	k_2 (M^{-1} min^{-1})	k_3/k_{-2} (M^{-1})
C_6H_5	C_6H_5	Me	570	
C_6H_5	*p*-C_6H_4OMe	Me	2880	
C_6H_5	C_6H_5	Et	342	306
p-C_6H_4Me	C_6H_5	Me	274	529
p-C_6H_4OMe	C_6H_5	Me	174	
o,o'-$C_6H_3Me_2$	C_6H_5	Me	11.4	
p-C_6H_4Me	*o*-C_6H_4Me	H	11.4	
p-C_6H_4Me	*o,o'*-$C_6H_3Me_2$	H	16.2	321
p-C_6H_4Me	*p*-C_6H_4Me	H	72.6	

rates are reduced by one order of magnitude owing to the combined electronic and steric effects.

The marked sensitivity of carbene formation to steric and electronic factors is also shown by the fact that the second stage of reaction 11, that is formation of a bis-carbene species, is much slower than the first in the case of primary anilines and does not occur at all with secondary anilines: once the first carbene moiety is formed, its good σ-donor ability and bulkiness make the remaining isocyanide less susceptible to further attack. Consistent with this trend, we found that it is possible to block the second stage of reaction 11 even for primary anilines by introducing *ortho*-substituents in the amine phenyl ring.



(I) (A) (II) (III)

SCHEME 1

TABLE 4

RATE DATA FOR THE REACTION OF $[PdCl_2(CNAr)]_2$ WITH RHNAr' IN DCE AT 25°C

Ar	Ar'	R	k_2 (M^{-1} min^{-1})	k_3/k_{-2} (M^{-1})
p-C_6H_4Me	p-C_6H_4Me	H	4.00	100
p-C_6H_4Me	p-C_6H_4Cl	H	0.88	32
p-C_6H_4Me	o-C_6H_4Me	H	1.89	50
p-C_6H_4Me	C_6H_5	Me	23.9	12.6
p-C_6H_4Me	C_6H_5	Et	12.5	5.5
p-C_6H_4OMe	p-C_6H_4Me	H	3.18	99
p-C_6H_4OMe	o-C_6H_4Me	H	1.57	42
p-C_6H_4OMe	C_6H_5	Me	22.5	7.6

In the case of binuclear chloride-bridged dimer, $[PdCl_2(CNAr)]_2$, the first step of the reaction with primary and secondary anilines leads immediately and quantitatively to mononuclear *trans* amine complexes $[PdCl_2(CNAr)(Amine)]$ [7] which react further to yield the final carbene product. Therefore, the latter originates from an isocyanide substrate (II in Scheme 1) which, unlike the previous ones, has a *trans* configuration and a nitrogen-donor ancillary ligand.

The final carbene complex also has a *trans* configuration, consistent with what appears to be a general feature of nucleophilic attack on coordinated isocyanides, i.e., retention of configuration around the metal center.

Kinetic measurements of the rate of reaction of the second, slower step showed that in all cases the second order rate parameter k_A fits the general rate law 4 corresponding to the stepwise mechanism 3.

It was possible to make a comparison of rate data for the various amines examined with a fair degree of confidence even though the use of different entering ligands necessarily implies different mononuclear, *trans*-amino substrates: in fact, the C≡N stretching frequencies of coordinated isocyanides in these complexes are virtually the same, and are independent of the *trans*-amine ligand. This fact, taken together with the *trans* configuration, implies that in all these substrates the electrophilic character of the isocyanide carbon and steric requirements around such reacting center are little affected by the nature of the coordinated amine. This was a rather favourable situation, since attempts at studying the attack by different amines on a fixed *trans*-amine substrate were always frustrated by scrambling of these ligands. Once again, k_2 values increase with increasing donor ability, decreasing steric hindrance on the entering amine, and decreasing electron-releasing ability of the substituent in the isocyanide aryl group (Table 4).

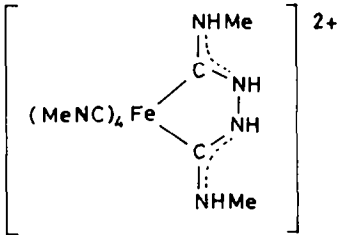
As observed in previous studies, the k_3/k_{-2} ratios are also affected by both steric and electronic factors.

The use of *trans*-amino complexes as substrates allowed us to measure the k_3/k_{-2} values for unhindered primary anilines reacting with unhindered coordinated isocyanides as a consequence of 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 $k_4 + k_3$ [A].

Attempts to study the mechanism of analogous reactions with platinum(II)-iso-

cyanide substrates of type *cis*-$[PtCl_2(CNAr)L]$ and *trans*-$[PtCl(CNAr)L_2]^+$ were unsuccessful because of the much lower reactivity of these systems towards aromatic amines.

In the reaction of $[Fe(CNMe)_6]^{2+}$ with hydrazine a chelate bis-carbene complex of type:



is formed with a kinetic law

$$k_{obs} = \{K_1 k_2 [H^+] + k_3\}[NH_2NH_2] \qquad (12)$$

where the K_1 term is the equilibrium constant for the reaction:

$$N_2H_4 + H^+ \rightleftharpoons N_2H_5^+$$

and the k_2 and k_3 rate constants refer to bimolecular nucleophilic attack of $N_2H_5^+$ and N_2H_4, respectively, on one isocyanide ligand of the substrate, followed by rapid ring closure to yield the final cyclic bis-carbene product [9].

Conclusions. From the body of evidence that has been gathered from these studies, the following features can be defined:

(a) Whatever the details, the dominant step always involves direct attack of the amine nitrogen on the iscyanide carbon, followed by the required rearrangements.

(b) This fundamental primary step is affected by the donor ability of the entering amine, the electrophilic character of the isocyanide carbon, and the degree of steric crowding around the reacting centers, with the solvent playing an important role.

(c) The conversion of the intermediate originating from the primary step into the final carbene species is aided by the entering amine itself which behaves as a bifunctional catalyst.

(d) The relative magnitudes of the elementary step rates can be changed over a fairly wide range by tailoring the reaction system appropriately through the choice of the substituents on the amine and isocyanide aromatic rings and of the ancillary ligands in the metal complex.

II. Electrophilic attack on alkyl- and aryl-platinum(II) complexes with cleavage of metal–carbon σ bonds

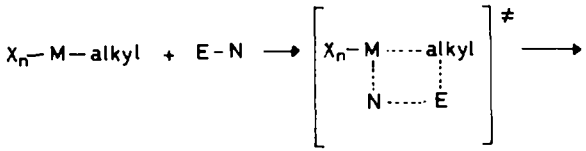
The cleavage of non-transition-metal–carbon bonds (demetalation) has been extensively investigated and its mechanism elucidated in detail [10]. When alkyl groups are being cleaved in a bimolecular process, electrophilic substitution at the saturated carbon may take place via an open transition state (S_E2).

$$X_n\text{–M–alkyl} + \text{E–N–}\left[X_n\text{–}\overset{\delta+}{\text{M}}\ \ldots\overset{\delta-}{\text{alkyl}}\ldots\text{E}\ldots\text{N}\right]^{\ddagger} \rightarrow$$

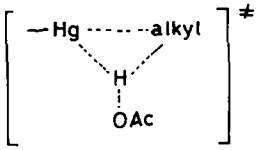
$$\text{alkyl–E} + N^- + MX_n^+ (S_E2)$$

E = electrophilic end and N = nucleophilic end of the reagent.

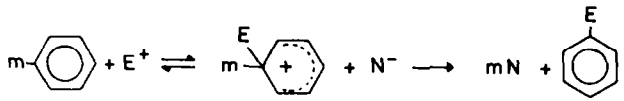
A cyclic process (S_Ei) may also occur via a cyclic transition state involving concurrent attack of the two ends of the reagent on the polarized metal–carbon bond:



These mechanisms apply particularly to the cleavage of the metal–carbon bond in Group IIB and IVB organometallics. In particular, for protonolysis reactions the driving force of the electrophilic attack is always the rate-determining proton transfer to the substrate. The extent of interaction of the proton with the alkyl group and of the nucleophile with the metal will depend on the charge separation being developed on both the cleaved group and the metal moiety, as well as on the solvent polarity. Thus for the protonolysis of alkyl–mercury bonds in acetic acid a three-center transition state has been proposed [11]:



As for the cleavage of non-transition-metal–aryl bonds, there is a body of evidence to show that electrophilic attack on the substrate produces a labile σ complex of the Wheland type:



The proton attack is rate determining; that is, subsequent reaction of the intermediate with the nucleophile is faster than its reversal to starting reactants [10b].

The mechanism of electrophilic cleavage of metal–carbon bonds in transition-metal complexes is especially intriguing since here the problem arises of the selectivity of attack. This may in principle take place by (i) direct attack on the metal–carbon bond, (ii) attack on the aromatic ring in the case of metal–aryl derivatives, and (iii) prior oxidative addition to the central metal followed by reductive elimination. The latter pathway is strictly related, inter alia, by the oxidation state of the metal and its promotional energy.

We have carried out a mechanistic study of the electrophilic cleavage of the platinum–carbon σ-bond by the proton on a variety of alkyl- and aryl-platinum(II)

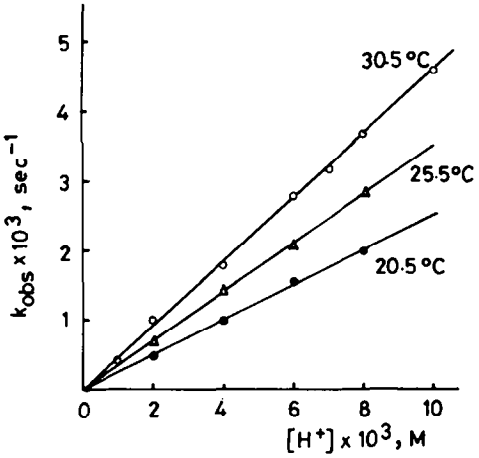


Fig. 9. Plots of k_{obs} vs. [H$^+$] at different temperatures ($I = 5 \times 10^{-2}$ M) for *trans*-[Pt(C_6H_5)$_2$(PEt_3)$_2$] in MeOH.

derivatives. In the case of bis-aryl complexes the reactions involved are shown in eq. 13 [12,13]:

$$\textit{cis}\text{- or } \textit{trans}\text{-}\left[PtAr_2(PEt_3)_2\right] \xrightarrow{H^+,Cl^-} \textit{cis}\text{- or } \textit{trans}\text{-}\left[PtClAr(PEt_3)_2\right] + ArH \qquad (13)$$

(Ar = monosubstituted aryl group; solvent = anhydrous or aqueous methanol).

In the presence of Cl^- ions, the cleavage takes place with retention of configuration around the platinum center.

TABLE 5

SECOND ORDER RATE CONSTANTS FOR THE REACTIONS AT 30°C [a]

cis-[Pt(PEt_3)$_2$(Ar)$_2$] + H$^+$ + Cl$^-$ → *cis*-[Pt(PEt_3)$_2$(Ar)Cl] + ArH

Ar	Methanol $10^2 k_2$ ($M^{-1}s^{-1}$) [b]	90% aqueous methanol $10^2 k_2$ ($M^{-1}s^{-1}$) [b]
p-C_6H_4OMe	180 ±5	11.2 ±0.1
p-C_6H_4Me	36 ±1	4.34 ±0.05
o-C_6H_4Me	0.74 ±0.03	
o-C_6H_4Et	0.24 ±0.003	
C_6H_5	5.66 ±0.04	0.83 ±0.01
m-C_6H_4OMe	5.79 ±0.07	0.510±0.003
p-C_6H_4F	1.64 ±0.02	0.277±0.005
p-C_6H_4Cl	0.28 ±0.01	0.051±0.003
m-C_6H_4F	0.136±0.004	0.022±0.003
m-$C_6H_4CF_3$	0.027±0.001	
p-$C_6H_4CF_3$	0.012±0.003	

[a] Ionic strength 0.3 M ($LiClO_4$). Uncertainties quoted are estimated standard errors. [b] Slopes of plots of k_{obs} vs. [H$^+$].

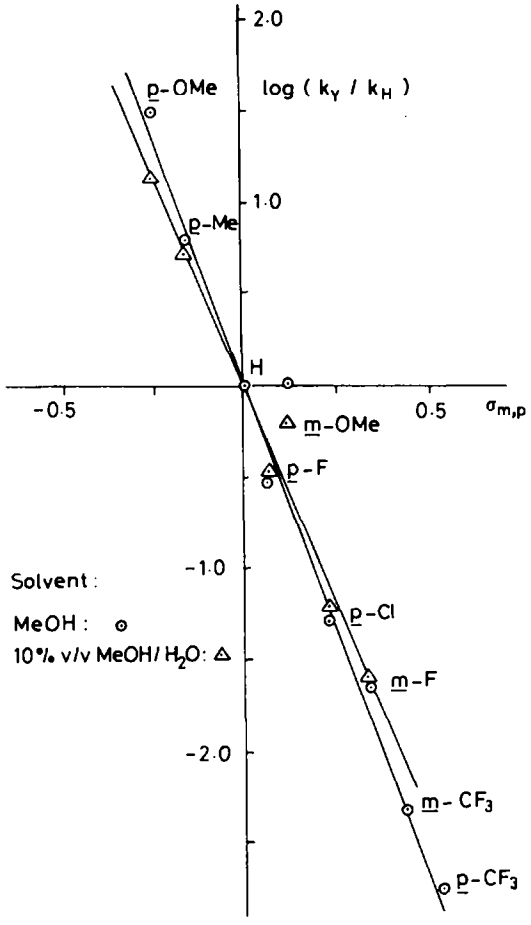


Fig. 10. Plots of $\log(k(C_6H_4Y)/k(C_6H_5))$ vs. Hammett's σ parameter of Y for the protonolysis of *cis*-$[Pt(C_6H_4Y)_2(PEt_3)_2]$ in $MeOH/H_2O$ (9/1 v/v) and in MeOH at 30°C ($I = 0.3$ *M*).

The pseudo-first-order rate constants, k_{obs}, were linearly dependent on the proton concentration but independent of chloride concentration at constant ionic strength:

$$k_{obs} = k_2[H^+] \tag{14}$$

For the substrate *trans*-$[Pt(C_6H_5)_2(PEt_3)_2]$, the plots of k_{obs} vs. $[H^+]$ at three different temperatures are shown in Fig. 9.

The activation parameters are $\Delta H^{\ddagger} = 10.6 \pm 1$ kcal/mol, $\Delta S^{\ddagger} = -24 \pm 3$ e.u.

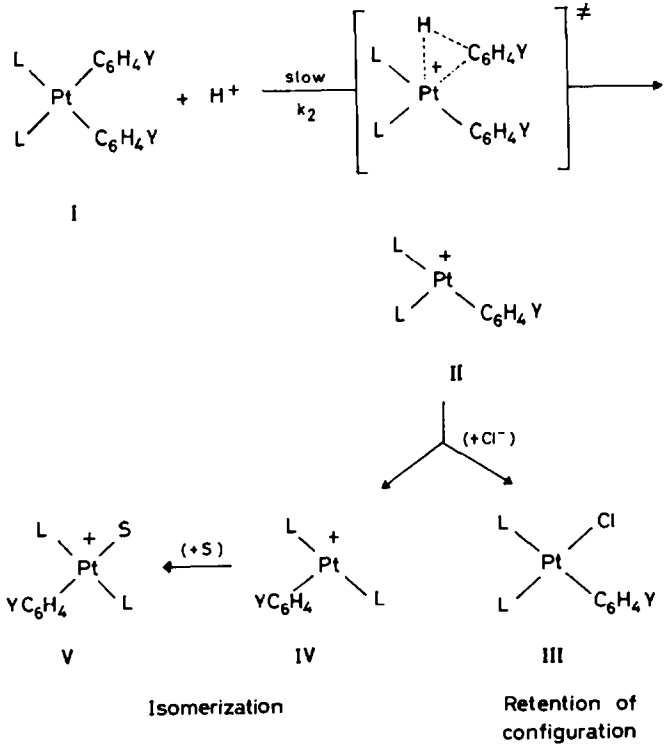
The rate data for the reactions of *cis*-$[Pt(Ar)_2(PEt_3)_2]$ are listed in Table 5.

Addition of water to methanol depresses the rates until a constant level is reached at a water content of ca. 5% v/v. The values of $\log(k(Ar)/k(C_6H_5))$ fit a fairly good linear relationship with the Hammett parameters for the aryl group substituents both in methanol and in 10% v/v aqueous methanol (Fig. 10).

The rates increase markedly with increasing electron-release by the substituents ($\rho = -5.1 \pm 0.3$ in methanol). The k_2 values are also lowered by increased steric hindrance in the proximity of the Pt–C bond.

When protonolysis of *cis*-$[Pt(Ar)_2(PEt_3)_2]$ is carried out in the absence of chloride ions, the cleavage of the first Pt–C σ bond is accompanied by complete isomerization to *trans*-monoaryl products.

A large (ca. 6) overall kinetic isotope effect is observed with DCl in $MeOD/D_2O$ (9/1 v/v) (For $Ar = p\text{-}C_6H_4OMe$ and $p\text{-}C_6H_4Me$, the k_2 values at 30°C are 2.06×10^{-2} and 0.71×10^{-2} M^{-1} sec^{-1}, respectively). A mechanism which is consistent with this body of evidence is shown in Scheme 2. The same mechanism but with the exclusion of the isomerization step, holds for the protonolysis of *trans*-$[Pt(C_6H_5)_2(PEt_3)_2]$. The simplest way of envisaging the attack by the proton is to consider the Pt–aryl bond as the reaction site. The protonation will then involve perturbation of the metal–aryl bonding orbital in a three-center transition state. No nucleophilic assistance is required by the activation process and therefore the rate is independent of chloride ion concentration. The rate will increase with increasing electron density in the Pt–C bond, as determined by the electron-donating ability of the substituents on the aromatic ring. The rate also increases with the ease of electron detachment from platinum, as measured by anodic oxidation potentials of the metal substrates from cyclic voltammetry experiments [14]. Theses arguments support the view that the platinum center is involved in the activation process, although they fall short of establishing a full-fledged oxidative addition to platinum(IV).



SCHEME 2

In this connection it is worth mentioning that cleavage of the first Pt–C bond by protonolysis in *cis*-$[Pt(PEt_3)_2Me_2]$ is ca. 10^6 times faster than in *cis*-$[Pt(PEt_3)_2(aryl)_2]$ under comparable conditions, whereas the same reaction on *cis*-$[Pt(PEt_3)_2(C_6F_5)_2]$ is immeasurably slow; this reactivity order (Me ≫ aryl > C_6F_5) reflects a decreasing electron density at the protonation site combined with an increasing Pt–C bond strength. The large kinetic isotope effect (ca. 6) observed is close to the highest expected for a half transfer of the proton and provides unmistakable evidence that the driving force of protonolysis is the rate-determining transfer to the substrate [15] with the bulk at the protonation site playing an adverse role. The marked decrease in rate on going from methanol to aqueous methanol is mostly due to stabilization of the electrophile H^+ because of the greater solvation by water.

For the steps following the first rate-determining protonolysis, we propose a pathway similar to the mechanism assumed [16] for the uncatalyzed *cis-trans* isomerization in platinum(II) complexes. The intermediate resulting from electrophilic attack is taken to be a three-coordinate species, II, whose fate is governed by the presence of nucleophiles in the system. When chloride ion is present, the vacant coordination site in II is blocked before the intermediate isomerizes to its "*trans*-like" counterpart, IV, thereby leading to retention of configuration in the ensuing monoaryl platinum product, III; in the absence of good nucleophiles, *cis* to *trans* isomerization, II → IV, can take place and the final monoaryl complex has *trans* configuration. However, since we lack direct experimental evidence other than product analysis, we cannot at present rule out the possibility that the intermediate II is a four-coordinate solvento species, *cis*-$[Pt(PEt_3)_2(aryl)S]^+$ (S = solvent) from which chloride ion, if present, will displace the solvent before isomerization to *trans*-$[Pt(PEt_3)_2(aryl)S]^+$ can take place.

The protonolysis of monoalkylplatinum(II) derivatives (eq. 15 and 16) follows a different kinetic pattern [17, 18].

$$trans\text{-}[PtCl(Me)(PEt_3)_2] \xrightarrow{H^+, Cl^-} trans\text{-}[PtCl_2(PEt_3)_2] + CH_4 \qquad (15)$$

$$trans\text{-}[PtH(CH_2CN)(PPh_3)_2] \xrightarrow{H^+, Cl^-} trans\text{-}[PtClH(PPh_3)_2] + CH_3CN \qquad (16)$$

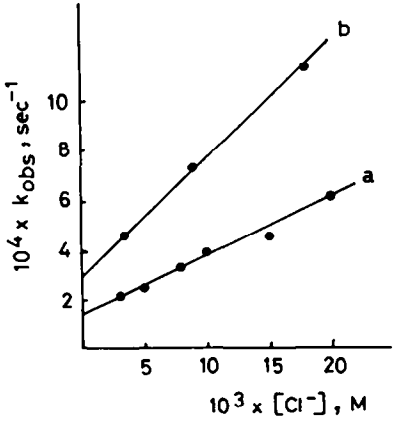


Fig. 11. Dependence of k_{obs} on $[Cl^-]$ for the protonolysis of *trans*-$[PtClMe(PEt_3)_2]$ in MeOH at 40°C ($I = 5.8 \times 10^{-2}$ *M*); (a) $[H^+] = 8 \times 10^{-3}$ *M*; (b) $[H^+] = 16 \times 10^{-3}$ *M*.

TABLE 6

RATE AND ACTIVATION PARAMETERS FOR THE PROTONOLYSIS OF *trans*-[PtH-$(CH_2CN)(PPh_3)_2$] ($I = 0.3$ M)

Temperature (°C)	$10^3 k_2$ (M^{-1} sec^{-1})	$10^2 k_3$ (M^{-2} sec^{-1})	$\Delta H_2^{\ddagger}$ (kcal/mol)	$\Delta S_2^{\ddagger}$ (e.u.)	$\Delta H_3^{\ddagger}$ (kcal/mol)	$\Delta S_3^{\ddagger}$ (e.u.)
25	0.37 ± 0.03	0.66 ± 0.02	17.5 ± 0.5	−15 ± 2	20.5 ± 0.7	0.5 ± 2
30	0.63 ± 0.01	1.26 ± 0.02				
40	1.79 ± 0.04	3.39 ± 0.05				
45	2.62 ± 0.02	6.46 ± 0.04				

In both cases the rate law includes a chloride dependent term:

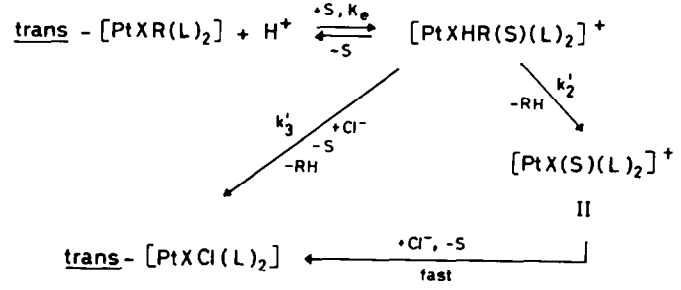
$$k_{obs} = k_2[H^+] + k_3[H^+][Cl^-] \quad (17)$$

The values of k_2 and k_3 constants for reaction 15 in methanol at 40°C ($I = 5.8 \times 10^{-2}$ M) are 1.78×10^{-2} M^{-1} sec^{-1} and 3.0 M^{-2} sec^{-1}, respectively. The linear dependence of k_{obs} on chloride concentration at constant acid concentration is shown in Fig. 11.

Once again, the reaction rates decrease with increasing water content of the medium.

The rate data and activation parameters for reaction 16 in methanol/1,2-dichloroethane (9/1 v/v) are shown in Table 6.

Rate law 17 is consistent with a stepwise mechanism involving prior oxidative addition of the proton to give a transient labile platinum(IV) hydride followed by slow reductive elimination of alkane (Scheme 3).



(X = Cl, R = Me, L = PEt_3 ; X = H, R = CH_2CN, L = PPh_3)

SCHEME 3

The reductive elimination takes place both intramolecularly (chloride-independent path) and under the influence of an entering chloride ion. The latter may well be exerted via the intermediacy of an unstable six-coordinate platinum(IV) hydride-chloride species. Complexes of the type $PtH_2Cl_2(L)_2$ have, in fact, been isolated following oxidative addition of anhydrous HCl on *trans*-[PtHCl(L)$_2$] [19]. The above mechanism reminds that proposed for the deuterium-hydrogen exchange on *trans*-[PtHCl(PEt_3)$_2$] [20]:

$$[PtHCl(PEt_3)_2] + DCl \rightleftharpoons [PtHDCl_2(PEt_3)_2] \rightleftharpoons [PtDCl(PEt_3)_2] + HCl$$

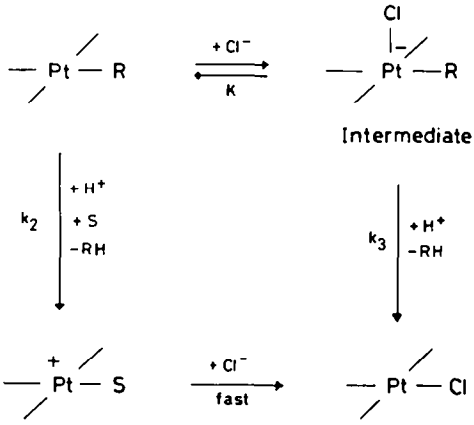
$$k_{obs} = k_1[D^+] + k_2[D^+][Cl^-]$$

Protonolysis of dialkylaurate(I) was also suggested to proceed via oxidative addition to form an hydrido gold(III) intermediate [21].

However, when the substrate of reaction 15 is changed to *trans*-$[PtI(Me)(PEt_3)_2]$ or *cis*-$[PtCl(Me)(PEt_3)_2]$ no dependence on the chloride ion is observed and the kinetics follow the simple one-term rate law 14.

These results indicate that the particular mechanism which is operative viz. the direct electrophilic attack at the metal-carbon bond (Scheme 2) or the oxidative addition/reductive elimination process (Scheme 3) is the result of many factors, such as the electronic and steric properties of the group to be cleaved and of ancillary ligands, the steric configuration of the substrate, the nature of the electrophile and the solvating ability of the medium.

Thus care must be exercised in extrapolating general mechanistic features from particular systems. In fact, the experimental evidence gathered so far does not rule out other alternative mechanisms, such as one in which direct proton attack is accompanied by a parallel two-step route involving initial chloride attack on the platinum center to give an anionic five-coordinate platinum(II) intermediate followed by protonolysis to the final cleavage product (Scheme 4).



SCHEME 4

We are now seeking experimental evidence for such a mechanism by a proper choice of ancillary ligands and R groups with a wide range of electronic and steric properties.

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