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Mechanism of aminocarbene formation by nucleophilic attack on isocyanide ligands in platinum(II) 2-pyrazyl and 4-pyridyl complexes

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Abstract

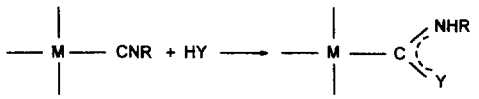
The reactions of 2-pyrazyl and 4-pyridyl isocyanide complexes $[Pt(CNC_6H_{11})(C_4H_3N_2\text{-}C^2)(dppe)]ClO_4$ and $[Pt(CNC_6H_{11})(C_5H_4N\text{-}C^4)(dppe)]ClO_4$ (**1**) with amines involving the formation of aminocarbene derivatives have been studied kinetically in 1,2-dichloroethane by UV–VIS techniques. The kinetics obey the simple second-order rate law rate = k_2[**1**][amine]. Low activation enthalpies and highly negative activation entropies for the k_2 term are observed.

A mechanism is proposed involving direct nucleophilic attack of the amine on the isocyanide carbon with concomitant proton transfer from the amine to the isocyanide nitrogen assisted by the heterocyclic nitrogen in position 1 of the 2-pyrazyl ligand. © 1997 Elsevier Science S.A.

Keywords: Kinetics and mechanism; Platinum complexes; Isocyanide complexes; Carbene complexes; Nucleophilic attacks

1. Introduction

Coordinated unsaturated ligands in organotransition metal complexes, such as carbon monoxide [1,2], olefins [3], nitriles (for a recent review see Ref. [4]), and isocyanides [5], undergo easy attack by a variety of nucleophiles. In particular, the reactions of isocyanide complexes with protic nucleophiles such as amines or alcohols yield metal–carbene derivatives through attack at the terminal carbon atom:



(1)

A systematic study is available on the mechanism of the reaction in Eq. (1) with M = Pd and HY = primary and secondary aromatic amines [5,6]. It has been established that the reaction proceeds via a stepwise mechanism involving prior nucleophilic attack to form an amidino intermediate which subsequently yields the final carbene species by proton transfer between the nitrogen atoms. The latter step is promoted either by the entering amine itself or by other amines carrying a nitrogen-bonded proton. Evidence for such a mechanism was based on a wealth of experimental data regarding the effects of amine basicity, steric requirements, electrophilic character of the isocyanide carbon, electronic and steric properties of ancillary ligands, and nature of the solvent. The associative step is governed by low activation enthalpies and highly negative activation entropies. Under comparable conditions, isocyanide complexes of platinum(II) are far less reactive toward amines, thereby preventing any kinetic study [7]. However, isocyanide Pt(II) complexes containing the highly basic 2-pyridyl ligand in cis-position, of type $[Pt(CNR)(C_5H_4N\text{-}C^2(dppe)]^+$, are markedly reactive toward protic nucleophiles [8]. In these complexes the coordinated isocyanide is readily attacked by water, alcohols, and primary amines. It is hydrolysed to CO and RNH_2 by trace amounts of water in the solvent and also reacts with the ethanol present in chloroform as stabilizer to give an (ethoxy)-aminocarbene species. Fast reaction with *p*-anisidine yields a di-aminocarbene

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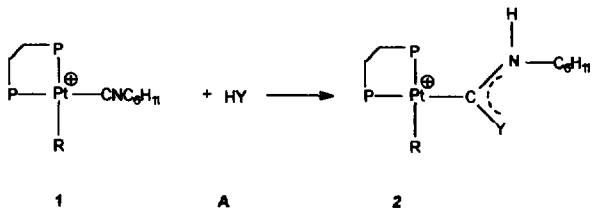
derivative. Such enhanced reactivity has been ascribed to the highly basic 2-pyridyl group in the favourable cis position which assists the nucleophilic attack at the isocyanide carbon through hydrogen bonding with the incoming protic nucleophile and possibly promotes the proton transfer step. The 2-pyridyl complex proved too reactive to allow a kinetic study of the reaction by customary techniques. However, the analogous 2-pyrazyl complex, containing the much less basic $C_4H_3N_2$-C^2 ligand, reacted much more slowly, admittedly due to its being less effective in assisting the process.

We have therefore undertaken a kinetic and mechanistic study of the reaction of nucleophilic attack on $[Pt(CNC_6H_{11})(R)(dppe)]^+$ ($R = C_4H_3N_2$-C^2 (2-pyz); C_5H_4N-C^4 (4-py)) by aliphatic and alicyclic amines HY in 1,2-dichloroethane (DCE) yielding the amino-carbene derivatives $[Pt\{C(NHC_6H_{11})(Y)\}(R)(dppe)]^+$. We expected that a lower reactivity of the 4-pyridyl complex relative to the 2-pyrazyl analogue might reflect the inability of the former to assist the rate-determining proton transfer, owing to the unfavourable position of the heterocyclic nitrogen in the 4-py derivative.

2. Results and discussion

2.1. Mechanism of nucleophilic attack by amines

The isocyanide complexes $[Pt(CNC_6H_{11})(R)(dppe)]^+$ (R = 2-pyz, 4-py) undergo nucleophilic attack by aliphatic and alicyclic amines HY to give amino-carbene derivatives in DCE at ambient temperature according to Eq. (2):



(2)

R = 2-pyz (**1a**); 4-py (**1b**)

A = morpholine (R = 2-pyz, 4-py); diethylamine, *n*-butylamine, t-butylamine, di-isopropylamine, piperidine (R = 2-pyz)

R = 2-pyz, Y = NEt_2 (**2a**), (**2b**),  (**2c**);

R = 4-py, Y =  , (**2d**)

The reactions proceed smoothly to completion in the presence of an excess of amine over the metal substrate. The kinetics were studied by spectrophotometrically monitoring the spectral changes in the UV–VIS region (400–250 nm) of reaction mixtures of **1** and **A** with time ($[Pt]_{tot} \approx 1 \times 10^{-4}$, $[A] = 1 \times 10^{-3}$ to $0.9\ mol\ dm^{-3}$). The spectra of reaction mixtures at completion agreed well with those of carbene complexes prepared independently (see Section 3). Under these conditions the kinetics followed a pseudo first-order rate law of type

$$-d[\mathbf{1}]/dt = k_{obs}[\mathbf{1}] \quad (3)$$

from which the values of k_{obs} could be obtained by non-linear regression of absorbance to time data (see Section 3). The dependence of k_{obs} on amine concentration was found to obey a linear relationship with a statistically insignificant intercept:

$$k_{obs} = k_2[\mathbf{A}] \quad (4)$$

(see Fig. 1 as an example). The values of the second-order rate constants k_2 for the reaction of **1a** are listed in Table 1. The rate law in Eq. (4) had been already observed for the attack of primary aromatic amines on coordinated isocyanides in mono- [9] and bisisocyanide [10] Pd(II) complexes and had been taken as a particular case of the general rate law

$$k_{obs} = k_2\left(k_4[\mathbf{A}] + k_3[\mathbf{A}]^2\right)/\left(k_{-2} + k_4 + k_3[\mathbf{A}]\right) \quad (5)$$

pertaining to this type of reaction [5,6,11], with $k_3 = 0$, $k_{-2} \ll k_4$. The rate law in Eq. (5) corresponded to a stepwise mechanism involving the direct attack of the amine on the isocyanide carbon (k_2), followed by proton transfers to the final carbene product. These would take place both intramolecularly in a four-membered cyclic transition state (k_4) and by the agency of one

Table 1
Rate constants and activation parameters for the reaction of $[Pt(CNC_6H_{11})(2\text{-}Pyz)(dppe)]ClO_4$ with amine in DCE

Amine	$10^2 k_2$ (25 °C) ($mol^{-1}\ dm^3\ s^{-1}$)	$\Delta H^{\ddagger}$ ($kcal\ mol^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)	pK_a [a]
Morpholine	0.69 ± 0.02	11.0 ± 0.4	−31 ± 2	8.33
Diethylamine	1.87 ± 0.03	7.0 ± 0.8	−43 ± 3	10.49
n-Butylamine	6.63 ± 0.04	7.2 ± 0.1	−39.8 ± 0.4	10.77
t-Butylamine	0.0119 ± 0.0002			10.83
Di-isopropylamine	0.0081 ± 0.0002			10.96
Piperidine	5.58 ± 0.08	10.0 ± 0.3	−30 ± 1	11.12

[a] In water.

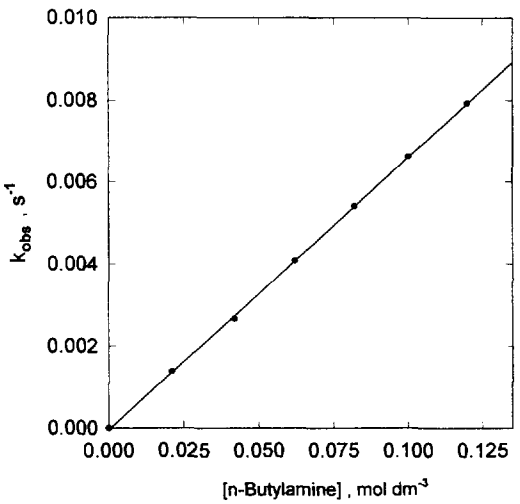
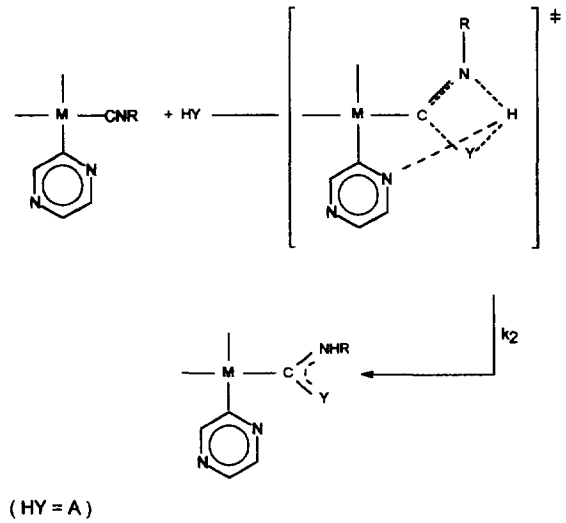


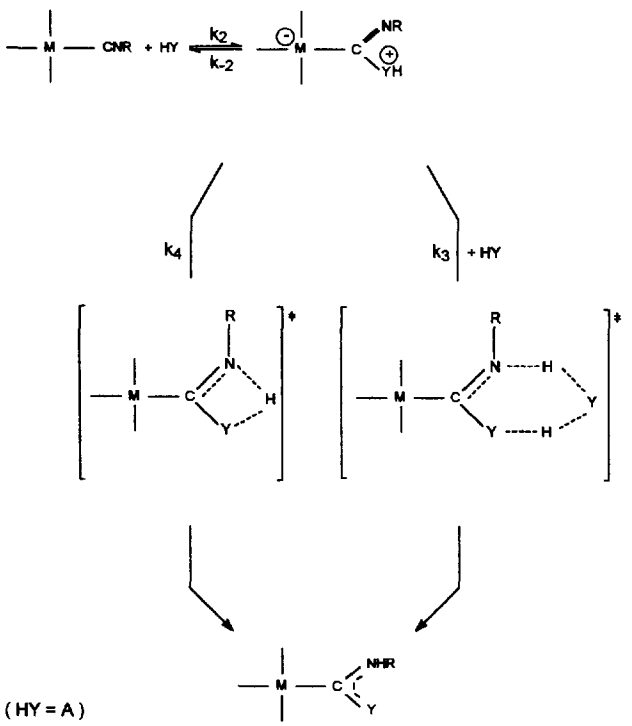
Fig. 1. Dependence of k_{obs} on amine concentration for the reaction of **1a** with *n*-butylamine at 25 °C.



Scheme 2.

further amine molecule serving as a proton acceptor–donor in a six-membered transition state (k_3) (Scheme 1).

Our linear rate law (Eq. (4)) is consistent with a simplified one-step mechanism involving concomitant amine attack and proton transfer in a cyclic transition state (Scheme 2). The same type of mechanism had been suggested for the attack of aromatic amines on coordinated nitriles in Pt(II) complexes leading to amidino species [12]. The absence of the higher order k_3 term in Eq. (4) clearly indicates that the activation process does not involve a second amine molecule in the proton transfer step nor, alternatively, a hydrogen-bonded amine dimer in the direct attack to the isocyanide carbon, as previously suggested for the formation of carbamoyl derivatives from metal–carbonyl complexes reacting with amines [1].



Scheme 1.

If we assume the mechanism in Scheme 2, we may expect the rate of the bimolecular process to increase with increasing basicity and decreasing steric requirements of the attacking amine. As a matter of fact, the k_2 values in Table 1 fulfil these expectations, since they increase with increasing pK_a of the amine in water and decrease markedly for sterically crowded amines, other things being equal. This is clearly evident in Fig. 2, in which log k_2 is plotted vs. pK_a. As can be seen, a linear free energy relationship is extant for the less bulky amines, whereas the values for the more crowded t-butylamine and di(*i*-propyl)amine fall off the line by more than two orders of magnitude, despite their good basicity.

The proposed mechanism is supported by the activation parameters listed in Table 1. Their determination

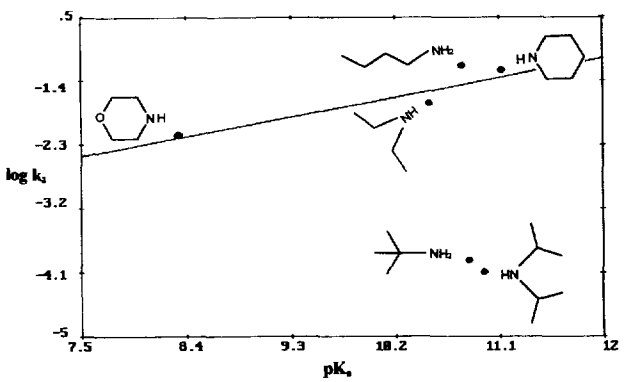


Fig. 2. Dependence of log k_2 (in DCE) on the amine pK_a (in water) for the reactions of **1a** at 25 °C.

requires some comments. Activation parameters are usually derived from the dependence of rate constants on temperature, according to the absolute reaction rate theory (Eq. (6)):

$$k_2/T = \exp(23.76)\exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT) \quad (6)$$

If the temperature range explored is narrow, as is commonly the case for reactions in solution, non-linear regression of k_2/T vs. T according to Eq. (6) is plagued by a high correlation between the parameters $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$, such that convergence of the iterative process becomes a problem and the guessing of initial parameter estimates is critical [13]. One way to circumvent the difficulty is to re-parametrize the model Eq. (6) to be fitted by a transformation of the independent variable according to Eq. (7) [14]:

$$k_2/T = A\exp(23.76)\exp(-B/T^{*}) \quad (7)$$

where: $A = \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT_0)$, $B = \Delta H^{\ddagger}/R$, $1/T^{*} = 1/T - 1/T_0$ and T_0 is the harmonic mean of temperatures.

Weighted linear regression of $\ln(k_2/T)$ vs. $1/T^{*}$ according to Eq. (7) for the data in Table 2 (which lists k_2 values for the amines investigated at some temperatures in the range 15–45 °C) yielded the activation parameters in Table 1. The weighting scheme was $w_i = (k_i/\sigma_i)^2$, where σ_i is the standard error of estimate of k_i, to maintain the original distribution of errors

Table 2
Second-order rate constants k_2 for the reaction of $[Pt(CNC_6H_{11})(2\text{-}Pyz)(dppe)]ClO_4$ with amines in DCE at various temperatures

Amine	t (°C)	$10^2 k_2$ ($mol^{-1}\,dm^3\,s^{-1}$)
Morpholine	15	0.33 ± 0.01
	25	0.69 ± 0.02
	35	1.29 ± 0.03
	45	2.33 ± 0.03
Diethylamine	15	1.24 ± 0.05
	25	1.87 ± 0.03
	35	3.28 ± 0.02
	45	4.15 ± 0.02
n-Butylamine	15	4.20 ± 0.02
	25	6.63 ± 0.04
	32	8.91 ± 0.03
	40	12.60 ± 0.01
Piperidine	15	3.10 ± 0.03
	25	5.58 ± 0.08
	35	10.10 ± 0.06
	45	18.20 ± 0.03
t-Butylamine	25	0.0119 ± 0.0002
Di-isopropylamine	25	0.0081 ± 0.0002

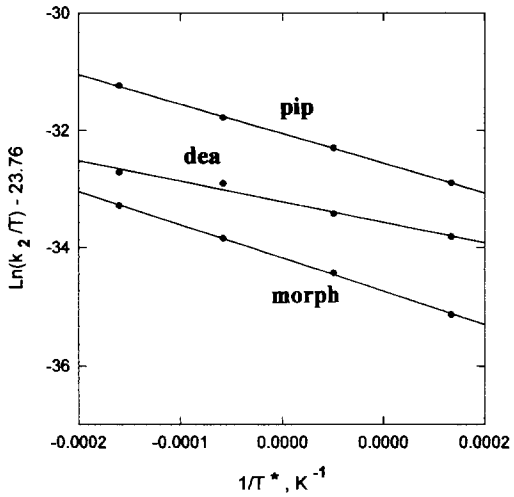


Fig. 3. Re-parametrized Eyring plots for the reactions of **1a** with piperidine (pip), diethylamine (dea), and morpholine (morph).

[13]. The results of the fit for A = piperidine, diethylamine, and morpholine are shown in Fig. 3.

As can be seen, the attack of amines on the coordinated isocyanide involves low activation enthalpies and highly negative activation entropies. A low activation enthalpy is in agreement with a direct nucleophilic attack in an associative step involving incipient formation of a carbon–nitrogen bond. A largely negative activation entropy further supports our view of a rigid, strongly oriented, multicentre transition state whose formation entails a marked loss of degrees of freedom. Similar values of activation parameters were observed previously for nucleophilic attacks on coordinated isocyanides [5,15], nitriles [4,12,16], and carbon monoxide [17]. In this context it is noteworthy that the more rigid, cyclic amines morpholine and piperidine display less negative activation entropies than *n*-butyl- and diethylamine, in agreement with the associative, concerted nature of the transition state.

It is most likely that the heterocyclic nitrogen in favourable position in the 2-pyz ligand will assist the proton transfer from the amine nitrogen to the isocyanide nitrogen, thereby providing some sort of anchimeric assistance which would be consistent with the low activation enthalpies observed while contributing to the decrease in the degrees of freedom of the activation process. There would then be no need for the intervention of a further amine molecule, in agreement with the absence of higher order terms in amine concentration in the rate law in Eq. (4). Supporting evidence for the operation of such anchimeric assistance comes from kinetic data for the reaction of morpholine with the 4-pyridyl complex $[Pt(CNC_6H_{11})(4\text{-py})(dppe)]^+$ (**1b**). The k_2 value for this reaction, $(7.76 \pm 0.09) \times 10^{-4}\ mol^{-1}\,dm^3\,s^{-1}$, is about one order of magnitude lower than that for the analogous reaction of the 2-pyz complex. Apparently, the lower reactivity of the 4-

pyridyl derivative can be traced back to the unfavourable position of the heterocyclic nitrogen which can hardly provide any assistance to proton transfer. On the other hand, such difference in reactivity cannot be accounted for by any difference in electrophilic power of the coordinated isocyanide in the two metal substrates, since they display very close $\nu(C{\equiv}N)$ values (see Section 3) [5,15]. It is fitting to recall in this context that the 2-pyridyl complex [Pt(CNR)(2-py)(dppe)]$^+$ (R = C_6H_4OMe-4) is extremely reactive toward amines, whereas blocking of the 2-pyridyl nitrogen by methylation causes a consistently marked decrease in the reactivity of the 1-methyl-2-pyridylium complex [Pt(CNR){C_5H_4(1-Me)N-C^2}(dppe)]$^{2+}$ toward formation of the aminocarbene [8].

It could be objected that the lower reactivity of the 4-py derivative might at least in part be related to a lower basicity of the 4-pyridyl ligand since, although pyrazine itself is a much weaker base than pyridine [18], substitution of a complexed metal moiety in position 2 of pyridine brings about a marked increase in basicity due to inductive effects [8,19]. As a matter of fact, the pK_a values of **1a** and **1b** in methanol–DCE (19/1 v/v) which we determined as detailed in the Section 2.2, are 3.69 ± 0.01 and 6.3 ± 0.3 respectively, indicating that the latter cannot exploit its higher basicity, lacking a favourable position for anchimeric assistance.

2.2. Determination of pK_a of 1a and 1b

The measurement of pK_a values related to protonation of the heterocyclic nitrogen in position 1 in **1a** and **1b** was carried out in a mixed solvent mixture, MeOH–DCE 19/1 v/v, owing to solubility problems. Low solubility also dictated the use of a spectrophotometric technique which allowed working with highly diluted metal complex solutions ($[Pt]_{tot} \approx 1 \times 10^{-4}$ mol dm^{-3}). The spectrophotometric titration involved adding aliquots of solutions of triflic acid (CF_3SO_3H, HX) of known concentration to known volumes of organometallic base ($B^+ClO_4^-$) solutions and monitoring the ensuing spectral changes in the range 220–310 nm. Absorbance vs. titrant concentration c_X data were fitted by the following model:

$$BH^{2+} + MeOH \rightleftharpoons B^+ + MeOH_2^+$$

$$2MeOH \rightleftharpoons MeOH_2^+ + MeO^-$$

$$[X^-] = c_x$$

$$[BH^{2+}] + [B^+] = [Pt]_{tot} = [ClO_4^-]$$

$$2[BH^{2+}] + [B^+] + [MeOH_2^+] = [MeO^-] + [ClO_4^-] + [X^-]$$

$$[B^+][MeOH_2^+]/[BH^{2+}] = K_a$$

$$[MeO^-][MeOH_2^+] = K_s$$

$$A_\lambda = \varepsilon_B[B^+] + \varepsilon_{BH}[BH^{2+}]$$

The parameters K_a, K_s, and ε_B were optimized by minimizing the object function $\Sigma(A_{obs} - A_{calcd})^2$ in the least squares sense by non-linear regression. The value of ε_{BH} in the wavelength range chosen was determined from spectra of highly acidic solutions by the Lambert–Beer relationship. The value of ε_B was not accessible from spectra in a basic medium since the MeO^- species present under such conditions acted as a nucleophile toward the coordinated isocyanide in the metal substrate, thereby causing unwanted changes in the absorbance [8]. The parameter K_s (the autoprotolysis constant of methanol in the medium) proved to be hardly influential on the fitting, probably due to the acid concentration range examined in which the MeO^- species is negligible. Therefore, its value could either be held constant or allowed to float in the refining process. In the latter case, the resulting optimized value (pK_s = 16.9 ± 0.2) was in good agreement with the literature value for pure methanol [20]. During each iterative cycle of the Gauss–Newton–Marquardt algorithm employed [21] the concentrations of all species involved were determined by solving the equilibrium and mass balance equation system at the current parameter values by means of a Newton system solver based on an LU decomposition/back substitution scheme [22].

Spectral changes for the titration of **1a** (R = 2-pyz) are shown in Fig. 4. The result of the fitting at 290 nm for **1a** is shown in Fig. 5. The 2-pyz group behaves as a monoprotic base up to the highest c_x explored, i.e. 1×10^{-3} mol dm^{-3}.

The resulting pK_a values were 3.69 ± 0.01 for R = 2-pyz and 6.3 ± 0.3 for R = 4-py. For comparison pur-

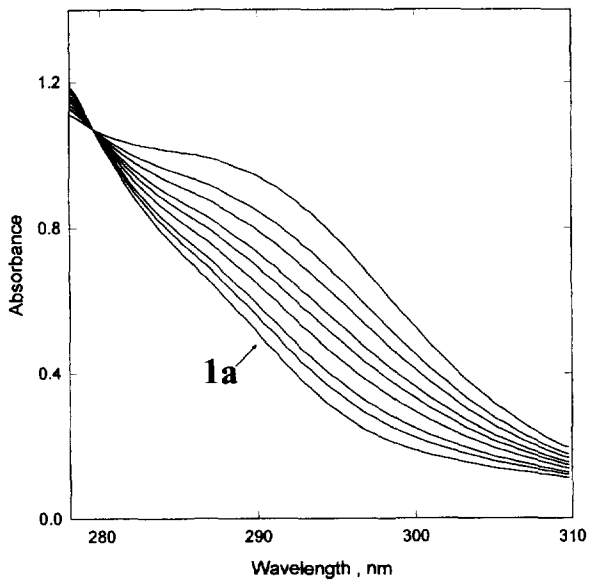


Fig. 4. Spectral changes for the spectrophotometric titration of **1a** with triflic acid in MeOH–DCE at 25 °C (from bottom).

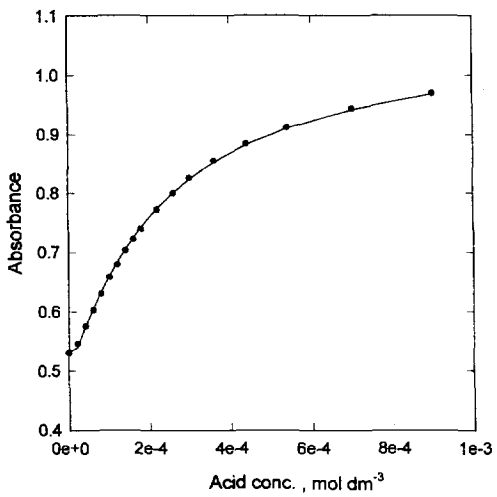


Fig. 5. Fit of absorbance at 290nm to acid concentration for the spectrophotometric titration of **1a** with triflic acid.

poses and also as a means of validating the method, we also determined the pK_a of pyridine in the same medium, which turned out to be 5.42 ± 0.02, in very good agreement with the value calculated by semiempirical extrapolation methods in the literature [20]. As can be seen, the order of basicity for the heterocyclic nitrogen is

4-py > Pyridine > 2-pyz

in line with previous studies on complexes containing these heterocyclic ligands in various coordination environments. In fact, the basicity of complexes in homologous series of type $[PtL_2(R)X]$ (L = PPh_3; X = Cl, Br; R = 2-py, 4-py, 2-pyz) [8,23] is in the order 2-py > 4-py ≫ Pyridine > 2-pyz ≫ Pyrazine.

3. Experimental

The complexes [PtCl(2-pyz)(dppe)] [8] and [PtBr(4-py)(dppe)] [24] were prepared by published methods. The amines were purified by distillation over K_2CO_3 under nitrogen. DCE was purified by refluxing over $LiAlH_4$ for 4 h and distilled. All other chemicals were reagent grade and were used without further purification. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

3.1. Preparation and characterization of the isocyanide and carbene complexes

The cationic cyclohexylisocyanide complexes $[Pt(CNC_6H_{11})(R)(dppe)]ClO_4$ [R = 2-pyz (**1a**), 4-py (**1b**)] were prepared in the same way as described previously for the analogue $[Pt(CNC_6H_4OMe\text{-}4)(2\text{-}pyz)(dppe)]ClO_4$ [8].

The carbene derivatives $[Pt\{C(NHC_6H_{11})Y\}(R)(dppe)]ClO_4$ [R = 2-pyz, Y = NEt_2 (**2a**),  (**2b**),  (**2c**); R = 4-py, Y =  (**2d**)] were prepared by the following general method.

1 mmol of [PtCl(R)(dppe)] (R = 2-pyz, 4-py) and 1 mmol of CNC_6H_{11} were dissolved in $CHCl_3$ (100 cm^3) and then treated with an excess of the amine H–Y (ca. 40 mmol). The progress of the reaction was monitored by IR spectroscopy following the decrease in intensity of the ν(C≡N) band of the coordinated isocyanide at 2220 cm^{-1} in the cationic intermediate $[Pt(CNC_6H_{11})(R)(dppe)]^+$. The reaction went to completion in 1–1.5 h. 2 h after mixing, 2 mmol of $NaClO_4 \cdot H_2O$ in ca. 10 cm^3 of acetone were added. The solvents were evaporated to dryness and the solid residue taken

Table 3
Selected analytical, conductivity, IR, and $^{31}P\text{-}\{^1H\}$ NMR data

Compound	Analysis (%) [a]			Λ_M [b] (Ω^{-1} cm^2 mol^{-1})	IR bands (cm^{-1}) [c]		^{31}P NMR [d]
	C	H	N		ν(N–H)	ν(CN)	
1a	50.6	4.3	4.6	91.2		2228	43.5 d [e] (^2J 8.1, ^1J 1582)
	(50.43)	(4.35)	(4.77)				42.5 d [e] (^1J 3163)
1b	52.0	4.3	3.2	89.0		2239	45.7 d [e] (^2J 7.5, ^1J 1625)
	(51.85)	(4.47)	(3.18)				43.2 d [e] (^1J 3093)
2a	51.5	5.3	5.7	94.9	3317	1555	40.2 d (^2J 6.5, ^1J 1668)
	(51.60)	(5.18)	(5.87)				37.8 d (^1J 2284)
2b	52.1	5.0	5.7	98.6	3317	1560	40.2 d (^2J 6.5, ^1J 1665)
	(52.20)	(5.11)	(5.80)				37.6 d (^1J 2271)
2c	50.8	4.9	5.6	88.9	3310	1560	40.3 d (^2J 6.5, ^1J 1654)
	(50.85)	(4.89)	(5.79)				37.7 d (^1J 2277)
2d	52.3	5.1	4.4	87.8	3310	1563	41.3 d (^2J 6.4, ^1J 1695)
	(52.15)	(5.00)	(4.35)				39.0 d (^1J 2258)

[a] Calculated values in parentheses.
[b] For 10^{-3} mol dm^{-3} methanol solution at 25 °C.
[c] As Nujol mulls.
[d] In $CDCl_3$ solution, unless otherwise stated; chemical shifts (δ ppm) from 85% H_3PO_4 external standard; $^1J = {}^1J(^{195}Pt\text{–}P)$, $^2J = {}^2J(P\text{–}P)$ in hertz.
[e] In CD_2Cl_2 solution.

up with CH_2Cl_2 (ca. 50 cm^3). After addition of activated charcoal and filtration, the resulting solution was concentrated to small volume and the carbene products were precipitated by addition of Et_2O. Purification was achieved by reprecipitation from a CH_2Cl_2–Et_2O solvent mixture (yields in the range 65–76% based on the theoretical amount).

The new compounds were characterized by elemental analysis, conductivity measurements, IR spectra in the solid, ^1H and ^{31}P–{^1H} NMR spectra (Table 3).

3.2. Apparatus and instrumentation

The UV–VIS spectra were recorded on a Perkin–Elmer Lambda 5 instrument equipped with a Peltier effect (Perkin–Elmer) thermostatting device, IR spectra on Nicolet 750 or Bio-Rad FTR 40 spectrophotometers, and NMR spectra on a Bruker AC 200 spectrometer. Conductivities were measured with a CDM83 conductivity meter.

3.3. Data reduction and analysis

The mathematical and statistical analysis of equilibrium and kinetic data was carried out by the use of a locally adapted version of Marquardt's algorithm written in TURBOBASIC™ (Borland).

Acknowledgements

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[24] Prepared in the same way as its palladium analog as described in Ref. [23].