# Mechanism of formation of (methoxy)(amino)- and bis(amino)carbene complexes by nucleophilic attack of methoxide ion and amines on platinum(II)-coordinated isocyanide in anhydrous methanol

Luciano Canovese [a,*], Fabiano Visentin [a], Paolo Uguagliati [a], Bruno Crociani [b]

[a] *Dipartimento di Chimica, Universita' di Venezia, Venezia, Italy*
[b] *Dipartimento di Scienze e Tecnologie Chimiche, II Universita' di Roma, Roma, Italy*

## Abstract

The isocyanide complexes $[Pt(CNC_6H_{11})(R)(dppe)]ClO_4$ ($R = C_4H_3N_2-C^2$, 2-pyz; $C_5H_4N-C^4$, 4-py) undergo nucleophilic attack on the coordinated isocyanide by methoxide ion in acid–base equilibrium with triethylamine in anhydrous methanol, leading to the (methoxy)(amino)carbene species $[Pt\{C(NHC_6H_{11})OMe\}(R)(dppe)]^+$ by a bimolecular, second-order path. When a primary or secondary amine is used instead of triethylamine, concomitant formation of (methoxy)(amino)- and bis(amino)carbene complexes takes place via parallel, second-order paths involving nucleophilic attack by both methoxide and amine on the isocyanide. A marked solvent effect depressing the rates in comparison to those of the corresponding reactions of amines in chlorinated solvents is observed. No substantial difference in reactivity between the two metal substrates can be detected, indicating the lack of anchimeric assistance to proton transfer from the entering amine to the isocyanide nitrogen, possibly replaced by a solvent mediated pathway. The methoxide ion proves a much better nucleophile than amines in this type of reaction. The interconversion of (methoxy)(amino)- with bis(amino)carbene species via methoxy–amine exchange is extremely slow. © 1997 Elsevier Science S.A.

## 1. Introduction

We have recently described a kinetic study of the mechanism of nucleophilic attack of aliphatic and alicyclic amines $(HNR_1R_2)$ on the isocyanide carbon in 2-pyrazyl (2-pyz) and 4-pyridyl (4-py) complexes $[Pt(CNC_6H_{11})(R)(dppe)]ClO_4$ ($R = C_4H_3N_2-C^2$, 2-pyz; $R = C_5H_4N-C$, 4-py)[4] 1,2-dichloroethane, leading to the bis(amino)carbene derivatives $[Pt\{C(NHC_6H_{11})(NR_1R_2)\}(R)(dppe)]ClO_4$ [1]. The results, based on activation parameters and the influence of the entering amine and of the heterocyclic group R on the rates, indicate a mechanism involving direct bimolecular attack of the amine on the coordinated isocyanide in a rigid, multi-center transition state with concomitant proton transfer from the amine to the isocyanide nitrogen. In the case of the more reactive 2-pyrazyl complex, such proton transfer is assisted by

the heterocyclic ligand through some sort of anchimeric assistance involving hydrogen-bridging with the nitrogen atom in position 1 of the 2-pyrazyl group. The amines investigated in this preliminary study were diethylamine, piperidine, morpholine, diisopropylamine, n-butylamine and ter-butylamine for $R = 2$-pyz, whereas with the much less reactive 4-pyridyl complex only the less basic morpholine could be examined, since the more basic amines react via $S_N2$ substitution at the saturated carbon of the dichloroethane solvent. Such undesired side reactions had no effect on the kinetics of the faster 2-pyz substrate but became comparable in rate with the main carbene-forming reactions in the case of the 4-py derivative.

We then decided to extend this mechanistic study to using methanol as the solvent. This would also provide an opportunity to detect solvent effects (this type of reaction is indeed known to display marked solvent effects [2,3]) and to study the mechanism of nucleophilic attack on the coordinated isocyanide by methanol itself, leading to (methoxy)(amino)carbene complexes [4,5].

---

[*] Corresponding author.

## 2. Results and discussion

### 2.1. Attack of methanol on the coordinated isocyanide

Methanol can act as a nucleophile attacking the isocyanide ligand in **1** according to the following reaction:



**1a,1b**                                        **2a,2b**
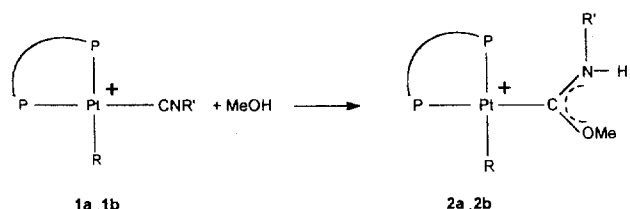
**1a** : R = 2-pyz , R' = C$_6$H$_{11}$

**1b** : R = 4-py , R' = C$_6$H$_{11}$

$$\text{(1)}$$

Preliminary investigations showed that this reaction is extremely slow; only 25% conversion can be detected for **1a** after four weeks at room temperature, as indicated by $^{31}$P NMR spectra of the reaction mixture recorded in CD$_3$OD (selected $^{31}$P signals in CD$_3$OD for **1** and **2** are listed in Table 1).

Consistently, solutions of the isocyanide substrate **1** in methanol appear quite stable when monitored by UV/vis spectrophotometry ([**1**] = $10^{-4}$ mol dm$^{-3}$, 1 day at reflux temperature). Apparently, methanol is a poor nucleophile toward attack on the isocyanide carbon of **1**. One way to increase the rate of reaction was to use the much more reactive methoxide anion generated in solution by the acid–base equilibrium (2):

$$\text{NEt}_3 + \text{MeOH} \overset{K_b}{\rightleftharpoons} {}^+\text{HNEt}_3 + \text{MeO}^- \qquad (2)$$
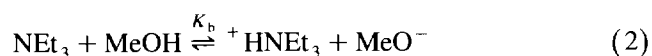
Triethylamine was chosen as a strong enough base lacking the ability to form bis(amino)carbene groups through attack on the coordinated isocyanide, since it has no transferable protons. The ensuing methoxide concentration is not sufficiently high to cause deprotonation of the (methoxy)(amino)carbene **2** to its conjugated base, the methoxy-imino species **3**:
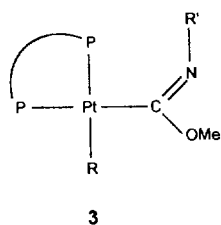


**3**

Alkoxy-imino complexes can be obtained by reaction of isocyanide platinum(II) complexes with sodium alkoxide [3,4] or by deprotonation of (alkoxy)(amino)carbene species by tertiary amines in the presence of zinc chloride which shifts the equilibria through precipitation of a ZnCl$_2$ adduct with the alkoxy-imino group [6].

Reaction (1) was studied kinetically by following spectral changes with time in the 220–300 nm range of solutions of **1** (ca. $5 \times 10^{-5}$ mol dm$^{-3}$) containing an excess of NEt$_3$ (in the range 0.02–0.3 mol dm$^{-3}$). Under these conditions, the disappearance of the metal isocyanide substrate **1** followed the pseudo-first-order rate law

$$-\text{d}[\mathbf{1}]/\text{d}t = k_{\text{obs}}[\mathbf{1}] \qquad (3)$$

The spectrum of the reacting mixture after seven to eight half-lives was virtually identical to that of an authentic sample of **2** independently prepared (see Section 3). The $k_{\text{obs}}$ values showed a curvilinear dependence on NEt$_3$ concentration, according to the stepwise mechanism of Scheme 1, Fig. 1 where (see Eq. (2))

$$[\text{MeO}^-] = 0.5\left\{\left(K_b^2 + 4K_b[\text{NEt}_3]_0\right)^{1/2} - K_b\right\} \qquad (4)$$

and

$$k_{\text{obs}} = k_{\text{MeO}}[\text{MeO}^-] \qquad (5)$$

Even at the lowest NEt$_3$ concentration employed, the MeO$^-$ concentration given by Eq. (4) is sufficiently higher than that of **1** to ensure pseudo-first-order conditions. In any case, its constancy is ensured by the constancy of [NEt$_3$]$_0$ in excess and the operation of equilibrium (2). The values of $k_{\text{MeO}}$, the second-order rate constant for the attack of methoxide anion on the metal isocyanide substrates **1a,b**, were determined by non-linear regression of $k_{\text{obs}}$ to [NEt$_3$]$_0$ data by assuming a fixed literature value of $4.47 \times 10^{-5}$ for $K_b$ of NEt$_3$ in anhydrous methanol [7].

The resulting $k_{\text{MeO}}$ parameters are $(5.55 \pm 0.02) \times 10^{-2}$ (**1a**) and $(7.16 \pm 0.03) \times 10^{-2}$ mol$^{-1}$ dm$^3$ s$^{-1}$ (**1b**). These rather close values indicate that the electrophilic ability of the coordinated isocyanide carbon in the two substrates is about the same, in agreement with the close $\nu(\text{C}\equiv\text{N})$ values for **1a** and **1b** in methanol (2226 and 2234 cm$^{-1}$ respectively) [2,3]. On the other hand, the methoxide anion, lacking a transferable proton, needs no anchimeric assistance by the heterocyclic nitrogen in favorable position in the 2-pyz complex **1a**, which would otherwise be reflected by a higher reactivity of such metal substrate [1]. As shown in Scheme 1, proton transfer from the solvent to the methoxy-imino intermediate **3** takes place in a subsequent, fast acid–base equilibrium which is likely to be completely driven over to the right.

In this mechanistic picture, the only source of nucleophile MeO$^-$ is the acid–base behavior of the tertiary amine NEt$_3$, since the concentration of the other base

Table 1
Selected analytical, conductivity, IR, and $^{31}$P NMR data

| Compound | Analysis (%) [d] | | | $\Lambda_M$ [e] (ohm$^{-1}$ cm$^2$ mol$^{-1}$) | IR bands (cm$^{-1}$) [f] | | $^{31}$P NMR [g] |
|---|---|---|---|---|---|---|---|
| | C | H | N | | $\nu$(N–H) | $\nu$(CN) | |
| [Pt(CNC$_6$H$_{11}$)(C$_4$H$_3$N$_2$–$C^2$)(dppe)]ClO$_4$ (1a) | 50.6 (50.43) | 4.3 (4.35) | 4.6 (4.77) | 91.2 | | 2228 | 45.0 d ($^2J$ 7.4 $^1J$ 3077) 44.3 d ($^1J$ 1649) |
| [Pt(CNC$_6$H$_{11}$)(C$_5$H$_4$N–$C^4$)(dppe)]ClO$_4$ (1b) | 52.0 (51.85) | 4.3 (4.47) | 3.2 (3.18) | 89.0 | | 2239 | 46.2 d ($^2J$ 7.3 $^1J$ 3015) 45.4 d ($^1J$ 1687) |
| [Pt{C(NHC$_6$H$_{11}$)OMe}(C$_4$H$_3$N$_2$–$C^2$)(dppe)]ClO$_4$ (2a) | 50.1 (49.98) | 4.7 (4.64) | 4.6 (4.60) | 96.0 | 3274 (br) | 1566 | 42.9 d ($^2J$ 5.7 $^1J$ 2268) 39.8 d ($^1J$ 1719) |
| [Pt{C(NHC$_6$H$_{11}$)OMe}(C$_5$H$_4$N–$C^4$)(dppe)]ClO$_4$ (2b) | 51.2 (51.35) | 4.7 (4.75) | 3.0 (3.07) | 93.7 | 3279 (br) | 1563 | 43.8 d ($^2J$ 5.2 $^1J$ 2270) 42.3 d ($^1J$ 1714) |
| [Pt{C(NHC$_6$H$_{11}$)Y}(C$_4$H$_3$N$_2$–$C^2$)(dppe)]ClO$_4$ [a] | 50.8 (50.85) | 4.9 (4.89) | 5.6 (5.79) | 94.9 | 3317 | 1555 | 41.9 d ($^2J$ 4.7 $^1J$ 1702) 39.0 d ($^1J$ 2265) |
| [Pt{C(NHC$_6$H$_{11}$)Y}(C$_4$H$_3$N$_2$–$C^2$)(dppe)]ClO$_4$ [b] | 52.1 (52.20) | 5.0 (5.11) | 5.7 (5.80) | 98.6 | 3317 | 1560 | 41.4 d ($^2J$ 4.7 $^1J$ 1692) 38.7 d ($^1J$ 2258) |
| [Pt{C(NHC$_6$H$_{11}$)Y}(C$_4$H$_3$N$_2$–$C^2$)(dppe)]ClO$_4$ [c] | 51.3 (51.60) | 5.3 (5.18) | 5.7 (5.87) | 88.9 | 3310 | 1560 | 41.6 d ($^2J$ 4.7 $^1J$ 1690) 38.8 d ($^1J$ 2272) |
| [Pt{C(NHC$_6$H$_{11}$)Y}(C$_5$H$_4$N–$C^4$)(dppe)]ClO$_4$ [a] | 52.7 (52.93) | 5.4 (5.29) | 4.1 (4.42) | 90.1 | 3316 | 1556 | 42.1 d ($^2J$ 4.8 $^1J$ 1750) 40.4 d ($^1J$ 2246) |
| [Pt{C(NHC$_6$H$_{11}$)Y}(C$_5$H$_4$N–$C^4$)(dppe)]ClO$_4$ [b] | 53.1 (53.51) | 5.3 (5.23) | 4.3 (4.36) | 105.7 | 3316 | 1558 | 42.4 d ($^2J$ 4.7 $^1J$ 1741) 40.2 d ($^1J$ 2240) |
| [Pt{C(NHC$_6$H$_{11}$)Y}(C$_5$H$_4$N–$C^4$)(dppe)]ClO$_4$ [c] | 52.0 (52.73) | 5.1 (4.94) | 4.1 (4.29) | 87.8 | 3310 | 1563 | 42.5 d ($^2J$ 4.7 $^1J$ 1728) 40.2 d ($^1J$ 2261) |

[a] Y = NEt$_2$. [b] Y = N◯. [c] Y = N◯O.

[d] Calculated values in parentheses.

[e] For 10$^{-3}$ mol dm$^{-3}$ methanol solution at 25°C.

[f] As Nujol mulls.

[g] In CD$_3$OD solution; chemical shifts ($\delta$) in ppm from 85% H$_3$PO$_4$ external standard; $^1J = {}^1J(^{195}$Pt–P), $^2J = {}^2J$(P–P) in Hz.
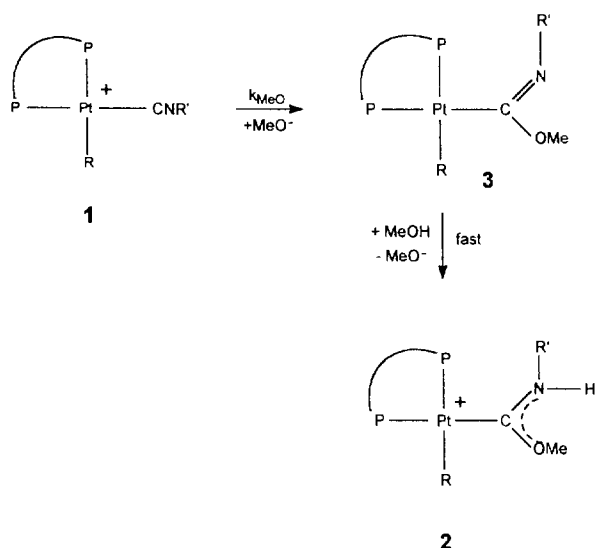
Scheme 1.



Scheme 2.

present, i.e. the metal substrate **1**, and its basicity $\{pK_a = 3.69$ (**1a**), 6.3 (**1b**) in MeOH/DCE 19/1 v/v [1]} would provide a negligible contribution to the $MeO^-$ concentration given by Eq. (4), as can easily be proved. When the source of $MeO^-$ is a primary or secondary amine (HY), which is also able to attack the isocyanide carbon, the $k_{obs}$ rate constant will also comprise a second-order term $(k_2)$ corresponding to nucleophilic attack by the amine:

$$k_{obs} = k_{MeO}[MeO^-] + k_2\{[HY]_o - [MeO^-]\} \qquad (6)$$

where $[MeO^-]$ is given by

$$[MeO^-] = 0.5\left\{\left(K_{bHY}^2 + 4K_{bHY}[HY]_o\right)^{1/2} - K_{bHY}\right\} \qquad (7)$$

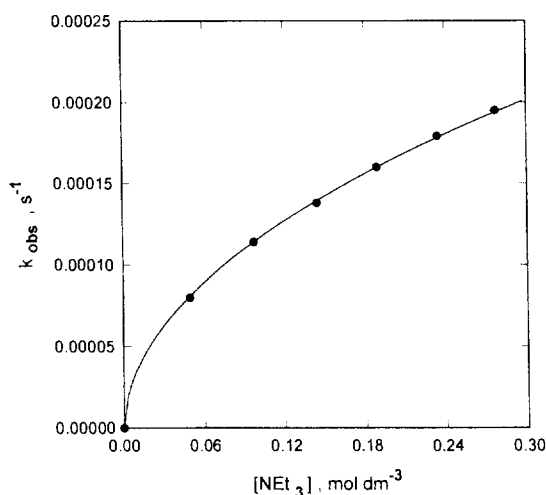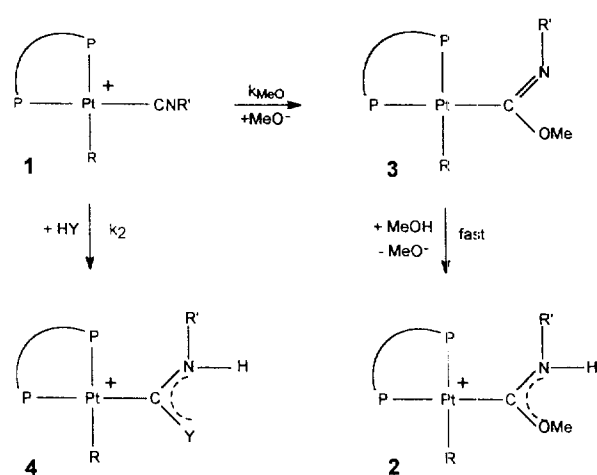$[HY]_o$ is the analytical amine concentration and $K_{bHY}$



Fig. 1. Dependence of $k_{obs}$ on the analytical amine concentration for the reaction of **1a** with triethylamine in anhydrous methanol at 25 °C. The solid line is the fit to Eqs. (4) and (5).

is the literature value chosen for the entering amine under study [7]. The corresponding mechanistic scheme is the following (Scheme 2):

$$HY + MeOH \overset{K_{bHY}}{\rightleftharpoons} H_2Y^+ + MeO^- \qquad (8)$$

As can be seen, the metal substrate **1** reacts with the nucleophiles $MeO^-$ and HY via two parallel bimolecular steps, leading to a mixture of (methoxy)(amino)carbene (**2**) and bis(amino)carbene (**4**) species, which do not interconvert at an appreciable rate, at variance with the methoxy–amine exchange observed in aryl–carbene complexes of chromium for which a mechanistic study has been reported [8]. Under these conditions it is easy to show that conversion of substrate **1** still obeys pseudo-first-order kinetics. In fact, the following relationships will hold, HY being in large excess over the metal substrate:

$$[Pt]_o = [1] + [2] + [4] \qquad (9)$$

$$d[2]/dt = k_{MeO}[MeO^-][1] \qquad (10)$$

$$d[4]/dt = k_2[HY][1] \qquad (11)$$

$$-d[1]/dt = [1]\{k_{MeO}[MeO^-] + k_2[HY]\} \qquad (12)$$

whence

$$[1] = [Pt]_o \exp(-k_{obs}t) \qquad (13)$$

with $k_{obs} = k_{MeO}[MeO^-] + k_2[HY]$, where $[HY] = [HY]_o - [MeO^-]$ and $[MeO^-]$ is given by Eq. (7). Eq. (6) will follow immediately.

Integration of Eqs. (10) and (11) will give

$$[2] = [Pt]_o k_{MeO}[MeO^-]\{1 - \exp(-k_{obs}t)\}/k_{obs} \qquad (14)$$

$$[4] = [Pt]_o k_2[HY]\{1 - \exp(-k_{obs}t)\}/k_{obs} \qquad (15)$$

so that

$$[2]/[4] = k_{MeO}[MeO^-]/k_2[HY] \qquad (16)$$

Table 2
Second-order rate constants for the reaction of $[Pt(CNC_6H_{11})(R)(dppe)]ClO_4$ with amines HY in methanol at 25 °C

| R | HY | $10^3 k_2$ (mol$^{-1}$ dm$^3$ s$^{-1}$) | $10^2 k_{MeO}$ (mol$^{-1}$ dm$^3$ s$^{-1}$) [a] | $10^5 K_b$ [b] |
|---|---|---|---|---|
| 2-Pyz | Diethylamine | 1.85 ± 0.02 | 5.55 ± 0.02 | 5.5 |
| | Piperidine | 3.13 ± 0.05 | 5.55 ± 0.02 | 10.5 |
| | iso-Propylamine | 4.87 ± 0.03 | 5.55 ± 0.02 | 3.39 |
| | Morpholine | 0.75 ± 0.02 | 5.55 ± 0.02 | 0.0251 |
| 4-Py | Diethylamine | 2.49 ± 0.04 | 7.16 ± 0.03 | 5.5 |
| | Piperidine | 1.94 ± 0.04 | 7.16 ± 0.03 | 10.5 |
| | iso-Propylamine | 2.95 ± 0.02 | 7.16 ± 0.03 | 3.39 |
| | Morpholine | 0.27 ± 0.04 | 7.16 ± 0.03 | 0.0251 |

[a] Determined from the kinetics of reaction with $NEt_3$ in methanol.
[b] From Ref. [7].

The absorbance at time $t$ will be

$$A_t = \epsilon_1[\mathbf{1}] + \epsilon_2[\mathbf{2}] + \epsilon_4[\mathbf{4}]$$
$$= \beta + \{\epsilon_1[Pt]_o - \beta\}\exp(-k_{obs}t) \qquad (17)$$

where $\beta = [Pt]_o\{\epsilon_2 k_{MeO}[MeO^-] + \epsilon_4 k_2[HY]\}/k_{obs}$, and will then also follow a mono-exponential first-order dependence on time. Non-linear regression of $k_{obs}$ vs. $[HY]_o$ according to Eqs. (6) and (7) was carried out with $k_2$ as the parameter to be refined. In the fitting process the $k_{MeO}$ values were held fixed at those previously determined from the kinetics of **1a** and **1b** in the presence of $NEt_3$, whereas $K_b$ for each amine was fixed at the literature value [7]. The resulting values are collected in Table 2. As can be seen in Table 2, the protic dipolar solvent brings about a substantial levelling off of rate constants for the various amines for both metal substrates. Moreover, on comparing the $k_2$ values with those for the corresponding reactions in DCE [1], a general decrease of about one order of magnitude is observed in methanol. These facts can be accounted for by extensive solvation of the reactants in this solvent accompanied by stabilization of the ground state of the attacking amine by hydrogen bonding with methanol. A similar solvent effect has been observed for the reactions of amines on unsaturated organic [9,10] and organotransition metal substrates [11]. This is also reflected in the virtually identical reactivity of the two metal complexes with the same amine, indicating that anchimeric assistance to proton transfer from the entering amine to the isocyanide nitrogen, if any, is overshadowed by a more favored solvent-mediated pathway.

The only exception to the above-mentioned levelling off is given by morpholine (R = 2-pyz), probably owing to its much lower nucleophilic power which parallels its lower basicity. The latter also allows a very low MeO$^-$ equilibrium concentration (Eq. (7)) such that Eq. (6) tends virtually to the linear relationship $k_{obs} = k_2[morpholine]_o$. However, for the sake of internal consistency, the $k_{obs}$ values for morpholine were fitted to Eq. (6) by the same non-linear regression procedure as for the other amines. The $k_2$ value in Table 2 is the result of such fitting.

The marked solvent effect observed for these reactions prevents an analysis of $k_2$ values in Table 2 in terms of nucleophilic power of the amine vs. steric hindrance around the reacting centers, as could be disentangled in previous work on nucleophilic attacks by amines on coordinated isocyanides in Pd(II) complexes [1,2,12–15].

The most prominent feature arising from the rate data in Table 2 is the much higher reactivity of methoxide anion compared to that of the amines under study, indicating a higher nucleophilic ability of such ion related to its high basicity and comparatively low steric requirements. However, the rates of formation of products **2** and **4** are of the same order of magnitude due to compensation effects of the much lower equilibrium concentration of MeO$^-$ relative to the analytical amine concentration prevailing during each kinetic run (cf. Eqs. (6), (7) and (16) and Fig. 2). The only precedent to this study reported so far involves the kinetics of reversible formation of alkoxycarbonyl complexes of Pt(II) by reaction of alcohols with *trans*-chlorocarbonylbis(triphenylphosphine)platinum(II) in mixed solvents, for
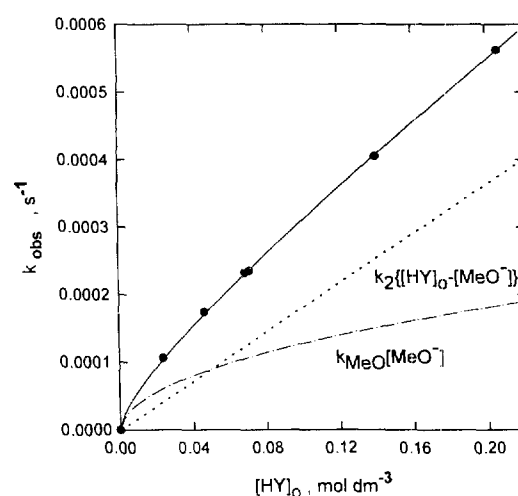


Fig. 2. Dependence of $k_{obs}$ on the analytical concentration of the amine for the reaction of **1a** with diethylamine (HY) in anhydrous methanol. Dotted and dot-dashed lines are the amine and methoxide contributions to the overall rate respectively (Eq. (6)).

which nucleophilic attack by the alcohol on the coordinated carbonyl carbon has been proposed [16]. Methoxy-arylimino complexes of Pt(II) have been obtained by reaction of methanol with isocyanides in the presence of potassium hydroxide and of chelate Pt(II) halide complexes [17], but no mechanistic studies were carried out.

Attempts at studying kinetically the interconversion of the (methoxy)(amino)carbene derivative 2 with its bis(amino)carbene analog 4 were hampered by the extreme slowness of the process, the occurrence of which could, however, be detected qualitatively by $^{31}$P NMR spectrometry (see further).

### 2.2. NMR studies

The course of reactions in Schemes 1 and 2 can be easily monitored by $^{31}$P NMR spectrometry. In Table 1 are listed the chemical shifts and coupling constants of isocyanide substrates 1 and of (methoxy)(amino)- and bis(amino)carbene derivatives 2 and 4 described in the present work. The bis(amino)carbene species 4 display a typical AX spectrum with $^{2}J$(P–P) around 4.7 Hz and $^{1}J$(Pt–P) around 1700 and 2250 Hz for $^{31}$P nuclei *trans* to heterocyclic and carbene carbons respectively. In the case of the (alkoxy)(amino)carbene complex 2, an AB spectrum is observed for 2a with a doublet centered at 42.9 ppm ($^{2}J = 5.7$, $^{1}J = 2278$ Hz) and a doublet centered at 42.7 ppm ($^{1}J = 1719$ Hz), whereas 2b displays an AX spectrum with a doublet centered at 42.3 ppm ($^{2}J = 5.2$, $^{1}J = 2270$ Hz) and a doublet centered at 43.8 ppm ($^{1}J = 1714$ Hz).

In any case, the carbene ligand assumes only one of the possible configurations resulting from restricted rotation around the C=N and C=O bonds. Since no $\delta$(NH) signal could be detected in the $^{1}$H NMR spectra in CDCl$_3$ even at low temperature ($-40$ °C), the carbene configuration could not be assessed [18]. However, a Z, E arrangement of N- and O-substituents is most likely on steric grounds [3].

Reaction (1) was also followed by the $^{31}$P spectra, by adding sufficient triethylamine to a ca. $10^{-2}$ mol dm$^{-3}$ solution of 1a or 1b in CD$_3$OD to produce a ca. 0.2 mol dm$^{-3}$ base concentration. The formation of (alkoxy)(amino)carbenes 2a, 2b was then monitored through the time evolution of the relevant $^{31}$P signals and comparison with those of authentic samples independently prepared (see Section 3). In the case of the reaction of 1a, the rates grossly estimated by this technique were in satisfactory agreement with the much more precise ones determined by UV/vis. The reaction of 1b appears to be fairly slow at the higher concentrations required by $^{31}$P NMR experiments, for reasons that are presently under further study (a possible explanation could be given by concentration-dependent association equilibria of the cation 1b through labile Pt(4-py)–Pt bridges, which would increase the steric demands around the platinum-bound isocyanide carbon).

For the reactions in Scheme 2, the concomitant formation of (methoxy)(amino)- and bis(amino)carbene species 2 and 4 was found to occur in a concentration ratio fairly consistent with that computed from Eq. (15) and an overall rate comparable with that determined by UV/vis kinetics.

The spectra of reaction mixtures indicated that an extremely slow conversion of the (methoxy)(amino)carbene 2 to the bis(amino)carbene derivative 4 takes place, which was more conveniently studied by reacting a solution of an authentic sample of 2 with the appropriate amine in methanol. Under these conditions, a half-life of about 30 h was measured with HY = NHEt$_2$ and piperidine, corresponding to a second-order rate constant for the conversion of ca. $10^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$ (ca. two orders of magnitude lower than the values in Table 2). These findings lend further support to the mechanism proposed in Scheme 2 and fit well within the kinetic pattern described above.

## 3. Experimental

### 3.1. Preparation of the complexes

The isocyanide substrates 1a and 1b and the bis(amino)carbene products [Pt{C(NHC$_6$H$_{11}$)(Y)}(R)(dppe)]ClO$_4$ (R = 2-pyz, Y = NEt$_2$, N◯, N◯o; R = 4-py, Y = N◯o) were prepared by published methods [1]. The complex [Pt{C(NHC$_6$H$_{11}$)( N◯)}(4-py)(dppe)]ClO$_4$ was prepared by the following procedure: cyclohexylisocyanide (0.109 g, 1 mmol) was added to a solution of [PtBr(4-py)(dppe)] [19] (0.751 g, 1 mmol) in 100 cm$^3$ of CHCl$_3$. After 10 min neat piperidine (4 cm$^3$, ca. 40 mmol) was added and the solution was stirred at r.t. for ca. 1 h, up to complete disappearance of the $\nu$(C≡N) band of the cation [Pt(CNC$_6$H$_{11}$)(4-py)(dppe)]$^+$ at 2240 cm$^{-1}$. The reaction mixture was treated with a solution of NaClO$_4$ · H$_2$O (0.280 g, 2 mmol) in 10 cm$^3$ of acetone and taken to dryness at reduced pressure on a rotary evaporator. The crude solid residue was extracted with CH$_2$Cl$_2$ (2 × 50 cm$^3$) in the presence of activated charcoal. After filtration the extract was concentrated to small volume and diluted with Et$_2$O to precipitate white crystals of the pure product.

The [Pt{C(NHC$_6$H$_{11}$)NEt$_2$}(4-py)(dppe)]ClO$_4$ analog was prepared in a similar way (yields 62 and 64% respectively based on the theoretical amount).

The complex [Pt{C(NHC$_6$H$_{11}$)OMe}(2-pyz)(dppe)]ClO$_4$ (2a) was prepared by reacting

$[Pt(CNC_6H_{11})(2-pyz)(dppe)]ClO_4$ (0.176 g, 0.2 mmol), dissolved in the minimum amount of methanol, with 1 cm$^3$ of neat NEt$_3$. After being stirred overnight, the solution was concentrated to small volume and diluted with Et$_2$O to precipitate **2a** as a white solid. The crude product was purified by recrystallization from CH$_3$OH/Et$_2$O. The analogous complex $[Pt\{C(NHC_6H_{11})OMe\}(4-py)(dppe)]ClO_4$ (**2b**) was prepared similarly. In this case a longer reaction time of two days was required for completion (yields 60.5% for **2a** and 61% for **2b**).

### 3.2. Materials and chemicals

The amines were purified by distillation over $K_2CO_3$ under nitrogen. Anhydrous methanol was prepared by distillation over magnesium methoxide. All other chemicals were reagent grade and were used without further purification. The solvents were evaporated to small volume or to dryness on a rotary evaporator under reduced pressure.

### 3.3. Apparatus and instrumentation

The UV/vis spectra were recorded on a Perkin–Elmer Lambda 5 instrument equipped with a Peltier effect thermostatting device (Perkin–Elmer), 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.

### 3.4. Data reduction and analysis

The mathematical and statistical analysis of kinetic data was carried out with an in-house general purpose non-linear regression program written in TURBOBA-SIC™ (Borland) and implemented on a personal computing system.

## Acknowledgements

## References

[1] L. Canovese, F. Visentin, P. Uguagliati, B. Crociani, F. Di Bianca, J. Organomet. Chem. (in press).

[2] P. Uguagliati, B. Crociani, U. Belluco, L. Calligaro, J. Organomet. Chem. 112 (1976) 111.

[3] B. Crociani, in Reactions of Coordinated Ligands, vol. 1, Plenum, New York, 1986, p. 553 and references cited therein.

[4] P.M. Treichel, W.J. Knebel, R.W. Hess, J. Am. Chem. Soc. 93 (1971) 5424.

[5] B. Crociani, in Reactions of Coordinated Ligands, vol. 1, Plenum, New York, 1986, p. 576.

[6] B. Crociani, F. Di Bianca, A. Fontana, E. Forsellini, G. Bombieri, J. Chem. Soc., Dalton Trans. (1994) 407.

[7] O. Budevsky, Talanta 36 (1989) 1209.

[8] C.F. Bernasconi, M.W. Stronach, J. Am. Chem. Soc. 115 (1993) 1341 and references cited therein.

[9] N. Sbarbati-Nudelman, D. Palleros, J. Chem. Soc., Perkin Trans. II (1984) 1277.

[10] J.E. Del Bene, J. Am. Chem. Soc. 95 (1973) 5460.

[11] L. Canovese, F. Visentin, P. Uguagliati, B. Crociani, F. Di Bianca, Inorg. Chim. Acta 235 (1995) 45.

[12] L. Calligaro, P. Uguagliati, B. Crociani, U. Belluco, J. Organomet. Chem. 92 (1975) 399.

[13] B. Crociani, P. Uguagliati, U. Belluco, J. Organomet. Chem. 117 (1976) 189.

[14] E. Rotondo, M. Cusumano, B. Crociani, P. Uguagliati, U. Belluco, J. Organomet. Chem. 134 (1977) 249.

[15] L. Calligaro, P. Uguagliati, B. Crociani, U. Belluco, J. Organomet. Chem. 142 (1977) 105.

[16] J.E. Byrd, J. Halpern, J. Am. Chem. Soc. 93 (1971) 1634.

[17] G. Minghetti, F. Bonati, G. Banditelli, Inorg. Chem. 15 (1976) 2649.

[18] B. Crociani, R.L. Richards, J. Chem. Soc., Dalton Trans. (1974) 693.

[19] Prepared in the same way as the Pd analog as described in L. Canovese, F. Visentin, P. Ugualiati, F. Di Bianca, B. Crociani, J. Organomet. Chem., 525 (1996) 43.