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Solution Behaviour and Relative Stability of the Complexes $[MCl_2(RN{=}CH{-}CH{=}NR)]$ and $[MCl_2(py\text{-}2\text{-}CH{=}NR)]$ (M = Pd, Pt; R = C_6H_4OMe-*p*)

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Abstract

Even though the α-diimino complexes $[MCl_2(RN{=}CH{-}CH{=}NR)]$ and $[MCl_2(py\text{-}2\text{-}CH{=}NR)]$ (M = Pd, Pt; R = C_6H_4OMe-*p*) are poorly soluble in chlorinated solvents, such as chloroform and 1,2-dichloroethane, or in acetonitrile, the electronic and ^1H NMR spectra indicate that these compounds are generally present as undissociate monomers with σ, σ'-*N,N'* chelate N-ligands in dilute solutions. Only for $[PdCl_2(RN{=}CH{-}CH{=}NR)]$, some dissociation of the α-diimine occurs in acetonitrile. In dimethylsulfoxide, where the solubility is much higher, no dissociation is observed for the pyridine-2-carbaldimine complexes $[MCl_2(py\text{-}2\text{-}CH{=}NR)]$, whereas the 1,2-bis(imino) ethane derivatives $[MCl_2(RN{=}CH{-}CH{=}NR)]$ are extensively dissociated through a step-wise process involving intermediates with a σ-*N* monodentate α-diimino group. As is shown by the course of substitution reactions with 2,2'-bipyridine, the higher stability of $[MCl_2(py\text{-}2\text{-}CH{=}NR)]$ in dimethylsulfoxide is mainly due to thermodynamic factors (ground state stabilization for the presence of stronger M–N bonds) rather than by kinetic factors (higher activation energy for steric strain in the activation states or transients).

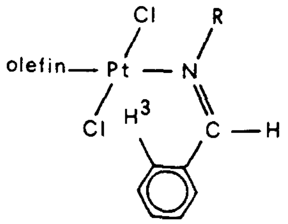
Introduction

In the past few years, the coordination chemistry of 1,2-bis(imino)ethanes, RN=CH–CH=NR, has been extensively investigated because of the versatile bonding properties of the flexible N=CH–CH=N unit [1]. It was also shown by theoretical and spectroscopic studies that 1,2-bis(imino)ethanes have better π-accepting abilities than pyridine-2-carbaldimines, py-2-CH=NR, and 2,2'-bipyridine (bipy) [2–4]. Despite the large interest in this class of α-diimino ligands, only a few comparative studies concerning the relative stabilities of their metal adducts have been reported in the literature [5–7]. In particular, for the σ,σ'-*N,N'* chelate complexes $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(N{-}N')]^+$ and $[SnCl_2Me_2(N{-}N')]$, the stability (towards ligand dissociation) was found to increase in the order:

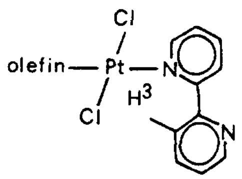
$$N{-}N' = RN{=}CH{-}CH{=}NR < py\text{-}2\text{-}CH{=}NR < bipy$$

$$(R = C_6H_4OMe\text{-}p)$$

On the other hand, the incapability of 1,2-bis(imino)-ethanes to replace the σ,σ'-*N,N'* chelate pyridine-2-carbaldimines or bipy in the five-coordinate complexes $[PtCl_2(\eta^2\text{-olefin})(N{-}N')]$ was interpreted in terms of kinetic stabilization of the five-membered metallacycle $Pt(N{-}N')$ resulting from an increased activation energy to form the four-coordinate transients **A** or **B**, for steric repulsion between the pyridyl ^3H and the Pt atoms [8]:



A



B

Due to our interest in this field and particularly in the chemistry of imino-carbon palladate α-diimino ligands, RN=C(R')–C(R'')=NR and py-2-C(R')=NR [R = C_6H_4OMe-*p*; R' = *trans*-$PdCl(L)_2$ (L = tertiary phosphine); R'' = H, Me] [9, 10], we have investigated the solution behaviour of the complexes $[MCl_2(RN{=}CH{-}CH{=}NR)]$ and $[MCl_2(py\text{-}2\text{-}CH{=}NR)]$ (M = Pd, Pt; R = C_6H_4OMe-*p*) in solvents of different polarity and donor ability, in order to obtain more information about the factors which

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influence the stability of these α-diimino adducts towards M–N bond breaking.

Experimental

The ligands RN=CH–CH=NR [11], py-2-CH=NR [5] ($R = C_6H_4OMe$-*p*) and the starting complexes $[PdCl_2(MeCN)_2]$, $[PdCl_2(CH_2{=}CHPh)]_2$ [12], and $K[PtCl_3(CH_2{=}CH_2)]\cdot H_2O$ [13] were prepared by standard methods. All other chemicals and solvents were reagent grade, and were used without further purification. All reactions were carried out at room temperature, unless otherwise stated. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparation of [PdCl₂(RN=CH–CH=NR)] (Ia)

The acetonitrile compound $[PdCl_2(MeCN)_2]$ (0.13 g, 0.5 mmol) or the styrene dimer $[PdCl_2(CH_2{=}CHPh)]_2$ (0.14 g, 0.25 mmol) was added to a stirred solution of the α-diimine (0.135 g, 0.5 mmol) in CH_2Cl_2 (100 ml). An orange colour appeared immediately. Concentration to small volume and dilution with Et_2O gave the product as a brick red precipitate, which was purified by reprecipitation from the same solvents. (Yield, based on the theoretical amount: 0.19 g, 85.3%).

Preparation of [PtCl₂(CH₂=CH₂)(RN=CH–CH=NR)]

A solution of the complex $K[PtCl_3(CH_2{=}CH_2)]\cdot H_2O$ (0.19 g, 0.5 mmol) in 5 ml of methanol was added dropwise to a stirred solution of the α-diimine (0.135 g, 0.5 mmol) in CH_2Cl_2 (50 ml). The colour of the mixture changed immediately to dark red and a white precipitate of KCl was quickly formed. After treatment with charcoal and filtration, the clear solution was evaporated to dryness (without heating) and the brick red solid was extracted with CH_2Cl_2 (2 × 30 ml). After filtration, the analytically pure product was precipitated by diluting the concentrated CH_2Cl_2 solution with Et_2O (0.24 g, 85.3%).

Preparation of [PtCl₂(RN=CH–CH=NR)] (Ib)

A solution of $[PtCl_2(CH_2{=}CH_2)(RN{=}CH{-}CH{=}NR)]$ (0.20 g) in 1,2-dichloroethane (100 ml) was heated at 60 °C for 2 h and the solvent was then evaporated, leaving a dark red solid residue, which was extracted with boiling CH_2Cl_2 (6 × 100 ml). The extracts were reunited, treated with charcoal and filtered off. Concentration of the solution caused some precipitation of the dark red product, which was completed by adding Et_2O (0.10 g, 52.6%).

Preparation of [PdCl₂(py-2-CH=NR)] (IIa)

A suspension of $[PdCl_2(MeCN)_2]$ (0.13 g, 0.5 mmol) in 80 ml of CH_2Cl_2 was treated with the pyridine-2-carbaldimine (0.11 g, 0.52 mmol). The colour changed from orange to yellow and a yellow solid began to precipitate in a few minutes. The solvent was evaporated to *ca.* 20 ml and the precipitation was completed by adding Et_2O. The crude product was purified by reprecipitation from the same solvents. (A large volume of CH_2Cl_2, *ca.* 300 ml, was required for the poor solubility of the compound; 0.15 g, 77%).

Preparation of [PtCl₂(py-2-CH=NR)] (IIb)

A solution of $K[PtCl_3(CH_2{=}CH_2)]\cdot H_2O$ (0.19 g, 0.5 mmol) in 5 ml of methanol was added dropwise to a solution of py-2-CH=NC_6H_4OMe-*p* (0.11 g, 0.52 mmol) in CH_2Cl_2 (50 ml). After stirring for 10 min, an orange precipitate appeared. The solvents were evaporated to dryness and the residue was extracted with boiling CH_2Cl_2 (3 × 100 ml). The extracts were worked up in the same way as for the preparation of **Ib** to yield the product **IIb** as a yellow–brown solid (0.14 g, 58.5%).

Substitution Reactions in (CD₃)₂SO

The complexes $[MCl_2(RN{=}CH{-}CH{=}NR)]$ (**I**), $[MCl_2(\text{py-2-CH{=}NR})]$ (**II**), and $[MCl_2(\text{bipy})]$ (M = Pd, Pt; $R = C_6H_4OMe$-*p*), dissolved in 1 ml of $(CD_3)_2SO$ in the required amount for a 4×10^{-2} M concentration were treated with an equimolar quantity of the entering α-diimino ligands. The ^1H NMR spectra of the mixtures at different times showed that the replacement of the chelate ligand RN=CH–CH=NR by py-2-CH=NR or bipy is fast for both the palladium and platinum substrates **I**, and leads quantitatively to the final products $[MCl_2(\text{py-2-CH{=}NR})]$ or $[MCl_2(\text{bipy})]$. The chelate pyridine-2-carbaldimine of **II** was also replaced by bipy at different rates depending on the central metal: for **IIa** the reaction is complete in a few minutes after mixing of the reactants at room temperature, whereas for **IIb** it takes about 2 days at 40 °C for completion. No substitution was observed in the systems **II**/RN=CH–CH=NR and $[MCl_2(\text{bipy})]$/RN=CH–CH=NR.

Physical Measurements

Infrared spectra were recorded with a Perkin-Elmer 983G instrument, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}. The electronic spectra in solution were recorded with a Bausch-Lomb Spectronic 210UV and with a Cary 219 spectrophotometer in the range 700–250 nm at 25 °C, using quartz cells of 1 cm path length. The ^1H NMR spectra were recorded on a Varian FT80A spectrometer by A. Berton of the Centro Chimica Tecnologia Composti Metallorganici C.N.R., Padova, Italy.

Analytical data and characteristic IR bands of the compounds are given in Table I. ^1H NMR spectral data are given in Table II.

TABLE I. Analytical Data and Characteristic IR Bands

Compound (R = C_6H_4OMe-*p*)	C[a]	H	N	Cl	ν(C=N)	ν(M–Cl)
$[PdCl_2(RN{=}CH{-}CH{=}NR)]$	43.0 (43.12)	3.6 (3.62)	6.2 (6.29)	16.1 (15.91)	1564m	337ms; 330sh
$[PtCl_2(RN{=}CH{-}CH{=}NR)]$	36.2 (35.96)	3.0 (3.02)	5.1 (5.24)	13.4 (13.27)	1552m	343ms; 335sh
$[PtCl_2(CH_2{=}CH_2)(RN{=}CH{-}CH{=}NR)]$	38.2 (38.44)	3.5 (3.58)	4.9 (4.98)	12.6 (12.61)	1571ms	338s
$[PdCl_2(py\text{-}2\text{-}CH{=}NR)]$	39.9 (40.08)	3.1 (3.11)	7.1 (7.19)	18.2 (18.20)	1617mw	350m; 338ms
$[PtCl_2(py\text{-}2\text{-}CH{=}NR)]$	32.8 (32.65)	2.6 (2.53)	5.8 (5.86)	15.0 (14.83)	1614mw	345ms; 335sh

[a] Calculated values in parentheses.

Results and Discussion

The reactions of the *N*-aryl 1,2-bis(imino)ethane, *p*-$MeOC_6H_4N{=}CH{-}CH{=}NC_6H_4OMe$-*p* with $[PdCl_2(MeCN)_2]$ or $[PdCl_2(CH_2{=}CHPh)]_2$, and with $K[PtCl_3(CH_2{=}CH_2)]$ yield the 1/1 adducts **Ia** and **Ib**, respectively, according to eqn. (1) of Scheme 1. As in the case of the analogous *N*-alkyl α-diimino ligands [14], the reaction with $K[PtCl_3(CH_2{=}CH_2)]$ gives initially a five-coordinate complex, containing the σ,σ'-*N,N'* chelate α-diimine and η^2-bonded ethylene, characterized in the ^1H NMR spectrum ($CDCl_3$) by a δ(N=CH) signal at 8.92 ppm (^3J(Pt–H) = 35 Hz) and by an olefin proton resonance at 3.87 ppm with a ^{195}Pt coupling constant of 70.5 Hz. On standing in $CDCl_3$ solution, this compound undergoes a slow olefin dissociation, as is shown by the appearance of the signal of free ethylene at 5.40 ppm and those of the four-coordinate species $[PtCl_2(RN{=}CH{-}CH{=}NR)]$ (see Table II). After 2 h from dissolution, the integration of the ^1H NMR spectrum indicates that dissociation has proceeded to *ca.* 40%. Accordingly, the final product **Ib** is obtained by prolonged heating of the five-coordinate complex in 1,2-dichloroethane. The IR spectrum of $[PtCl_2(CH_2{=}CH_2)(RN{=}CH{-}CH{=}NR)]$ in the solid state shows a strong ν(Pt–Cl) band at 338 cm^{-1} and a ν(C=N) of the coordinate α-diimine at 1571 cm^{-1}, whereas the spectra of **I** show two ν(M–Cl) bands in the range 343–330 cm^{-1}, and a ν(C=N) absorption at 1564 cm^{-1} for **Ia** and at 1552 cm^{-1} for **Ib**. In each compound, the ν(C=N) band is detected at lower frequencies than the IR active ν(C=N) vibration of the free ligand (1609 cm^{-1}).

Both compounds **I** are scarcely soluble in 1,2-dichloroethane for molecular weight measurements. However, the electronic spectra in the same solvent obey the Lambert–Beer law in the concentration range 2×10^{-4}–3×10^{-5} M and are characterized by a set of metal to ligand charge-transfer (MLCT) bands in the range 600–300 nm (Figs. 1 and 2), typical of the five-membered metallacyclic chromophores involving α-diimino groups σ,σ'-*N,N'* chelate to palladium(II) and platinum(II) centers [6, 9b]. Furthermore, the ^1H NMR spectra of diluted $CDCl_3$ solutions show the 1,2-bis(imino)ethane to be symmetrically N-bonded to the central metal: only one sharp singlet is observed for the imino protons at 8.08 ppm for **Ia** and at 8.59 ppm for **Ib** (0.27 ppm upfield and 0.24 ppm downfield relative to the free ligand, respectively), the latter signal being flanked by ^{195}Pt satellites (^3J(Pt–H) = 88 Hz).

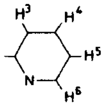
Thus, the combined electronic and ^1H NMR spectral data strongly suggest that both complexes **Ia** and **Ib** exist as undissociate monomers in chlorinated solvents.

A different solution behaviour is observed in more donor solvents, such as acetonitrile or dimethylsulfoxide, where some dissociation of the α-diimino ligand occurs. In acetonitrile, no appreciable dissociation is detected for the platinum compound **Ib** down to a 10^{-4} M concentration: the electronic spectra are time-independent and very similar to those in 1,2-dichloroethane, except for a solvatochromic high-frequency shift of the MLCT bands (Fig. 2). Correspondingly, the ^1H NMR spectrum of a saturated CD_3CN solution closely matches that in $CDCl_3$ (see Table II), without any evidence of Pt–N bond breaking. In contrast, the electronic spectrum of **Ia** in acetonitrile, recorded immediately after dissolution (spectrum 1 of Fig. 1), is markedly different from that in 1,2-dichloroethane and changes progressively with time, indicating a slow dissociation of the ligand. After 90 min, a strong absorption at 375 nm characteristic of the free α-diimine is clearly observable (spectrum 2 of Fig. 1).

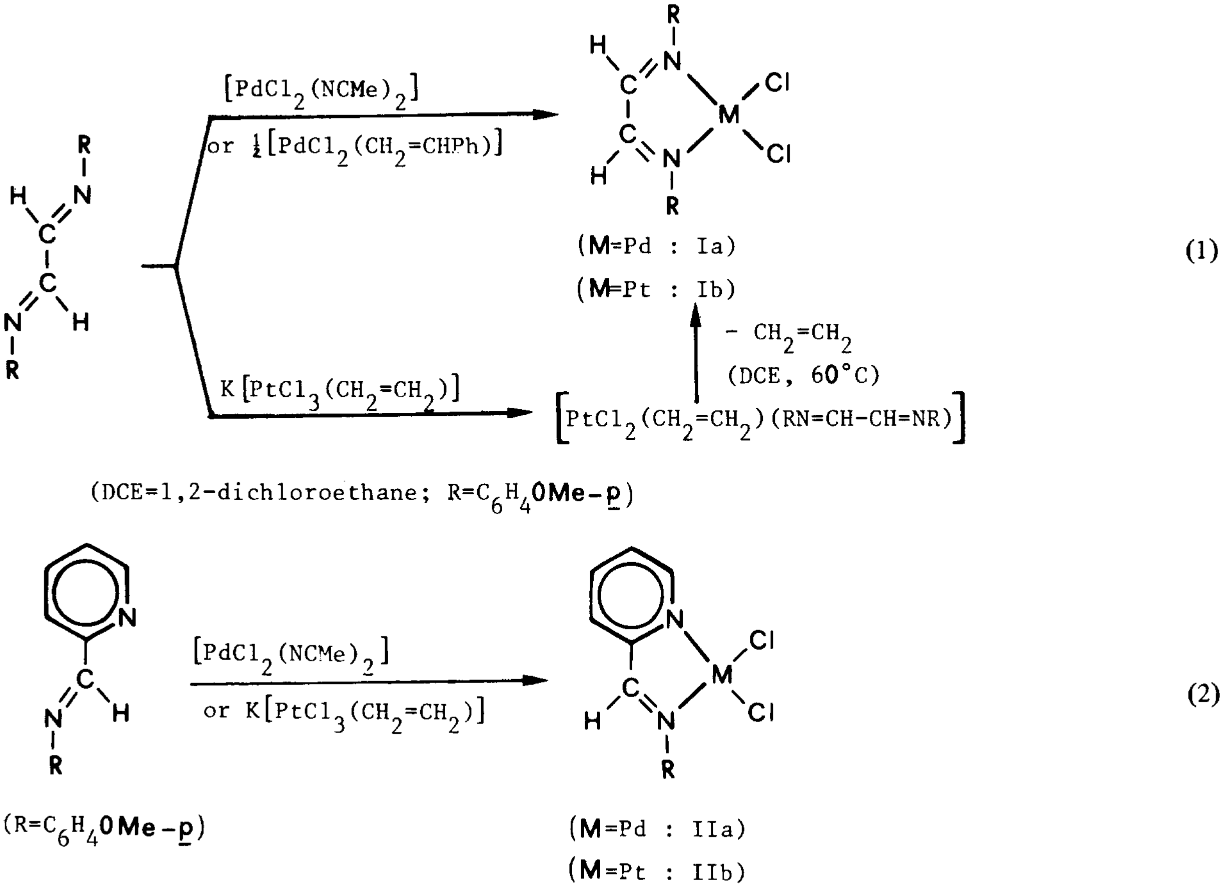
TABLE II. ^1H NMR Spectral Data[a]

Compound (R = C_6H_4OMe-*p*)	Solvent	Imino proton N=C–H	2-Pyridyl protons[b]				*p*-Methoxyphenyl protons[c]		
			H^3	H^4	H^5	H^6	AA′	BB′	OCH_3
RN=CH–CH=NR	$CDCl_3$	8.35s					7.30m	6.71m	3.77s
	$(CD_3)_2SO$	8.44s					7.42m	6.99m	3.78s
[$PdCl_2$(RN=CH–CH=NR)]	$CDCl_3$	8.08s					7.58m	6.70m	3.82s
[$PtCl_2$(RN=CH–CH=NR)]	CD_3CN	8.79t ^3J(Pt–H) = 88					7.50m	7.01m	3.83s
[$PtCl_2$(CH_2=CH_2)(RN=CH–CH=NR)][d]	$CDCl_3$	8.92t ^3J(Pt–H) = 35					7.98m	7.02m	3.89s
		8.59t[e] ^3J(Pt–H) = 88					7.60m[e]	6.75m[e]	3.84s[e]
py-2-CH=NR	$(CD_3)_2SO$	8.60s	8.15m	7.92m	7.48m	8.71m	7.38m	6.98m	3.78s
[$PdCl_2$(py-2-CH=NR)]	$(CD_3)_2SO$	8.66s	8.15m	8.39m	7.89m	9.05m	7.40m	6.98m	3.79s
[$PtCl_2$(py-2-CH=NR)]	$(CD_3)_2SO$	9.24t ^3J(Pt–H) = 94	8.16m	8.41m	7.92m	9.45m ^3J(Pt–H) = 38.5	7.45m	7.02m	3.81s

[a] ^1H chemical shifts (δ) in ppm from $SiMe_4$ at 30 °C; coupling constants in Hz; s = singlet, t = triplet, m = multiplet; satisfactory integration values were obtained. [b] Second-order spectra in which each proton appears as a multiplet of characteristic pattern; pyridyl proton labelling:



[c] The *ortho* AA′ and *meta* BB′ protons of the C_6H_4OMe-*p* substituent appears as a symmetrical AA′BB′ system. [d] This compound undergoes partial dissociation of the olefin in solution: the protons of the coordinate ethylene resonate at 3.87 ppm with a ^{195}Pt coupling constant of 70.5 Hz, whereas those of free ethylene appear as a singlet at 5.40 ppm. [e] Resonances of the four-coordinate complex [$PtCl_2$(RN=CH–CH=NR)].



Scheme 1.

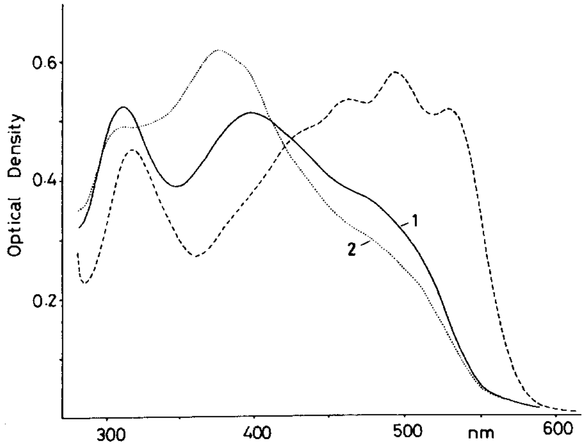


Fig. 1. Electronic spectra of 5×10^{-5} M solutions of $[PdCl_2(RN{=}CH{-}CH{=}NR)]$ (**Ia**) in 1,2-dichloroethane (- - - -) and in acetonitrile: (1) immediately after dissolution (——), (2) 90 min after dissolution (·······); at 25 °C.

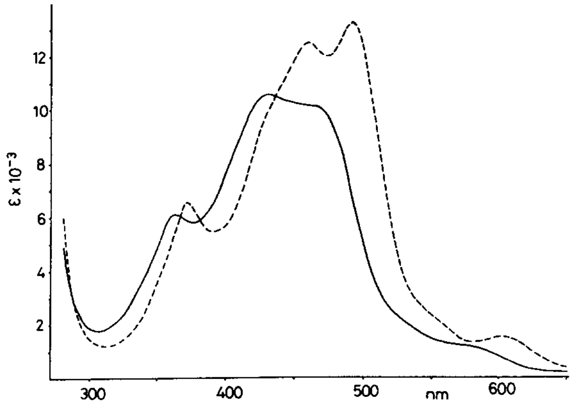


Fig. 2. Electronic spectra (ε (cm^{-1} M^{-1})) of $[PtCl_2RN{=}CH{-}CH{=}NR)]$ (**Ib**) in 1,2-dichloroethane (- - - -) and in acetonitrile (——), at 25 °C.

In $(CD_3)_2SO$, both compounds **Ia** and **Ib** undergo extensive dissociation, as is shown by the ^1H NMR spectra of their 3×10^{-2} M solutions, reported in Figs. 3 and 4, respectively. For the palladium derivative **Ia**, the dissociation is fast and leads quickly to an equilibrium position with *ca.* 60% of free α-diimine. The spectrum of Fig. 3 (recorded 15 min after dissolution) shows no further changes with time

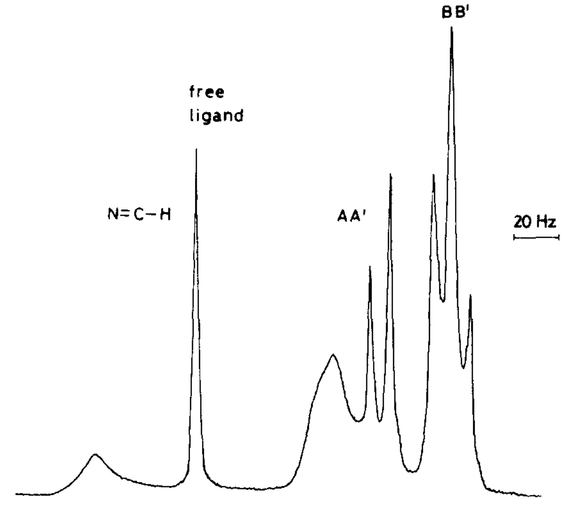


Fig. 3. ^{1}H NMR spectrum of a 3 × 10^{-2} M solution of [$PdCl_2$-(RN=CH–CH=NR)] (**Ia**) in $(CD_3)_2SO$ at 30 °C, in the range 9.5–7.5 ppm.

in the relative intensities of the broad signal at 9.0 ppm and of the sharp singlet at 8.44 ppm, due to the imino proton resonances of coordinate and free ligand, respectively. For the platinum derivative **Ib**, the dissociation is much slower, and the spectrum of Fig. 4 (recorded 15 min after dissolution) shows the presence of the free (singlet at 8.44 ppm, *ca.* 15%) and coordinate α-diimine in three different species. On the basis of δ(N=C–H) resonance patterns and ^{195}Pt coupling constants for platinum(II) α-diimino complexes with different coordination environments, the singlet at 9.02 ppm (^3J(Pt–H) = 91 Hz) is assigned to the square-planar undissociate adduct **Ib** (*cf.* the coupling constant of 88 Hz for **Ib** in CD_3CN and $CDCl_3$ in Table II), the slightly broader singlet at 9.23 ppm (^3J(Pt–H) = 33 Hz) to a five-coordinate solvent species [$PtCl_2$(RN=CH–CH=NR)(Solvent)] with a σ,σ′-*N,N′* chelate ligand (*cf.* the ^{195}Pt coupling constants of *ca.* 40 Hz reported for the five-coordinate complexes [$PtCl_2$(RN=CH–CH=NR)-(olefin)] [14]), and finally the AB system at 9.64 and 8.78 ppm (J_{AB} = 8 Hz) to a solvent species containing a σ-N monodentate ligand [$PtCl_2$(RN=CH–CH=NR)-(Solvent)] (*cf.* the AX resonance pattern with J_{AX} of *ca.* 8 Hz reported for the complexes [$PtCl_2$(RN=CH–CH=NR)(L)] (L = tertiary phosphine or arsine) with a σ-N monodentate α-diimine in the slow exchange limit [15]). Even though the ^{195}Pt satellites for the δ(N=C–H) signal at 9.02 ppm are somewhat masked by other resonances, they are clearly observed upon addition of CD_2Cl_2 to the $(CD_3)_2SO$ solution, because of different changes in chemical shifts. For **Ib**, the relative amount of free α-diimine increases progressively with time until an equilibrium value of *ca.* 80% is reached after 3 h (without disappearance of any of the coordinate species).

The dissociation process of both **Ia** and **Ib** in $(CD_3)_2SO$ may therefore be interpreted in terms of a step-wise mechanism of Scheme 2. According to the ^{1}H NMR spectral features, the successive equilibria (i), (ii) and (iii) are all slow (on the NMR time scale) for the platinum complex **Ib**. For the palladium complex **Ia**, the different half-band width of δ(N=C–H) signals in Fig. 3 suggests that only the final dissociation step (iii) is slow, whereas the coordinate α-diimine undergoes much faster dynamic processes

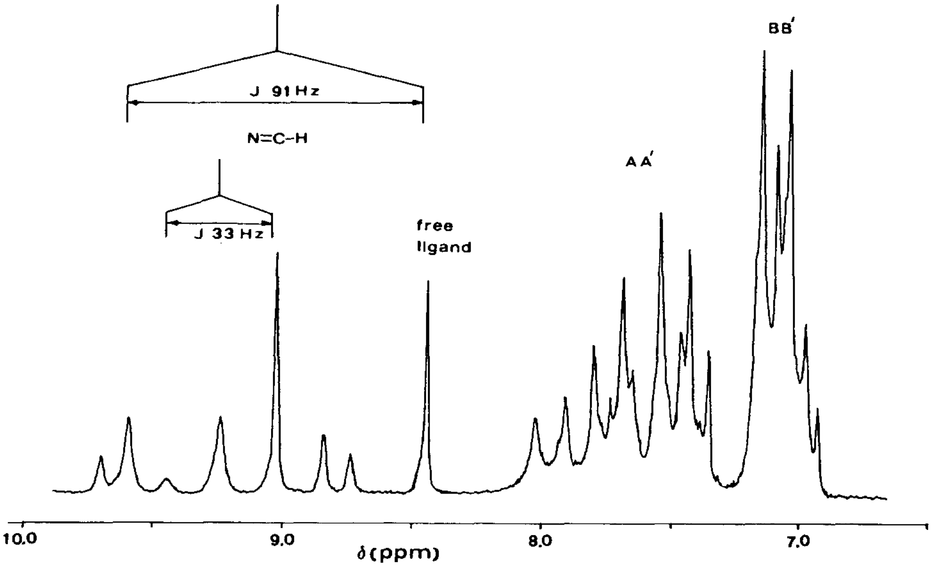
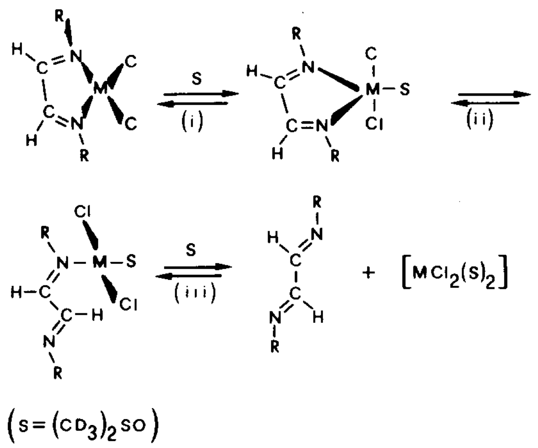


Fig. 4. ^{1}H NMR spectrum of a 3 × 10^{-2} M solution of [$PtCl_2$(RN=CH–CH=NR)] (**Ib**) in $(CD_3)_2SO$ at 30 °C, in the range 10.0–7.5 ppm.



(3)

Scheme 2.

(i) and (ii), which give rise to averaged broad resonances for the imino protons (9.0 ppm) and also for the *ortho* protons of the C_6H_4OMe-*p* group (7.7 ppm).

The reactions of the pyridine-2-carbaldimine with $[PdCl_2(MeCN)_2]$ or $K[PtCl_3(CH_2{=}CH_2)]$ yield the 1/1 adducts **II** (eqn. (2) of Scheme 1). The IR spectra in the solid (Table I) are characterized by two ν(M–Cl) bands in the range 350–335 cm^{-1}, and by a ν(C=N) band at 1617 cm^{-1} for **IIa** and at 1614 cm^{-1} for **IIb**, at slightly lower frequencies than ν(C=N) of the free ligand (1626 cm^{-1}). The spectral data of these compounds show no evidence of M–N bond dissociation in solution. In the electronic spectra of **IIa** and **IIb** (Figs. 5 and 6, respectively), the Lambert–Beer law is obeyed down to the lowest explored concentration, 5×10^{-5} M, in both 1,2-dichloroethane and acetonitrile. On the other hand, no trace of free pyridine-2-carbaldimine is detected in the ^{1}H NMR spectra in $(CD_3)_2SO$ (Table II). The σ,σ'-*N,N'* chelating mode of this ligand is indicated by the downfield shift of both the imino and the 2-pyridyl H^6 protons upon coordination to the MCl_2 group: for **IIb**, this is further supported by the observation of ^3J(Pt–H) couplings of 94.0 Hz for δ(N=C–H) and of 38.5 Hz for δ(H^6) [16]. Although the aggregation state of complexes **II** cannot be established by molecular weight measurements because of the poor solubility in 1,2-dichloroethane, from the above data it appears that both complexes **II** are present as monomeric undissociate species in dilute solution, with a *cis* geometry around the central metal, as in the case of the more soluble binuclear complexes $[MCl_2\{py\text{-}2\text{-}C(R'){=}NR\}]$ (R = C_6H_4OMe-*p*; R' = *trans*-$PdCl(PPh_3)_2$) [17]. The increased stability of the MCl_2 adducts **II** can arise either from thermodynamic (presence of stronger M–N bonds in **II**) or from kinetic factors (higher activation energy to reach a transition state or transient of type (**C**) because of steric repulsion between the pyridyl H^3 proton and the central metal, if the M–N(pyridyl) bond is initially broken in the dissociation process).

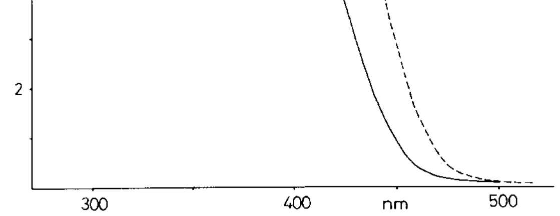


Fig. 5. Electronic spectra (ε (cm^{-1} M^{-1})) of $[PdCl_2(py\text{-}2\text{-}CH{=}NR)]$ (**IIa**) in 1,2-dichloroethane (- - - -) and in acetonitrile (——), at 25 °C.

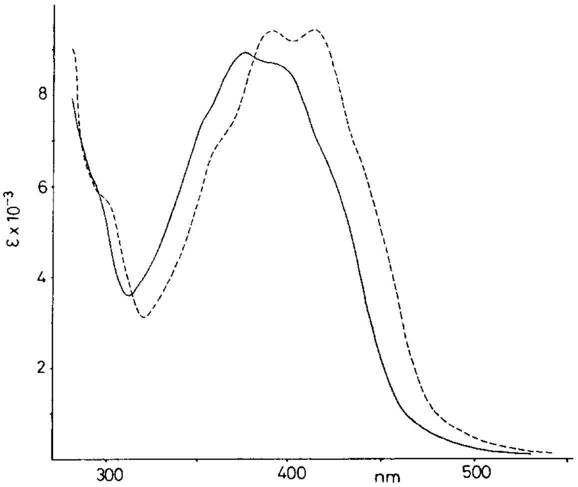
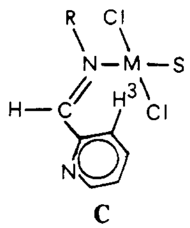


Fig. 6. Electronic spectra (ε (cm^{-1} M^{-1})) of $[PtCl_2(py\text{-}2\text{-}CH{=}NR)]$ (**IIb**) in 1,2-dichloroethane (- - - -) and in acetonitrile (——), at 25 °C.

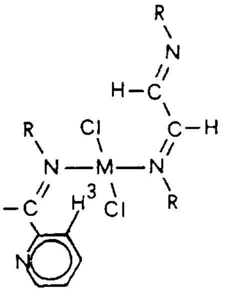


C

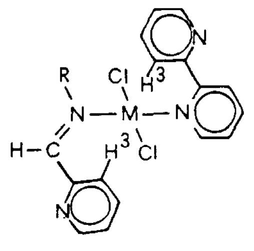
(S = solvent)

$$\begin{tikzcd}[column sep=large] \underset{\mathbf{I}}{[MCl_2(RN{=}CH{-}CH{=}NR)]} \arrow[r, "\text{py-2-CH=NR}", "\text{(fast)}"'] \arrow[rr, bend left, "\substack{\text{bipy}\\ \text{(fast)}}"] & \underset{\mathbf{II}}{[MCl_2(\text{py-2-CH=NR})]} \arrow[r, "\text{bipy}", "\substack{(M = Pd,\ \text{fast})\\ (M = Pt,\ \text{slow})}"'] & [MCl_2(\text{bipy})] \end{tikzcd} \qquad (4)$$

In this connection, we have studied the substitution reactions of eqn. (4), with equimolar amounts of entering ligands in $(CD_3)_2SO$. The ^1H NMR spectra of the reaction mixtures show that the 1,2-bis(imino)ethane of **I** is quantitatively and irreversibly displaced by pyridine-2-carbaldimine or 2,2'-bipyridine, whereas the pyridine-2-carbaldimine of **II** is quantitatively and irreversibly displaced only by 2,2'-bipyridine. Since these reactions occur through four-coordinate transients containing both the entering and the leaving ligands simultaneously σ-*N* bonded to the central metal, the lack of substitution of the chelate py-2-CH=NR by RN=CH–CH=NR cannot be ascribed to steric strain in the intermediate (**D**) because (i) the same intermediate is involved in the ready substitution of the chelate RN=CH–CH=NR by py-2-CH=NR, and (ii) in the irreversible substitution of the chelate py-2-CH=NR by bipy an even more sterically hindered transient (**E**) is traversed:



D



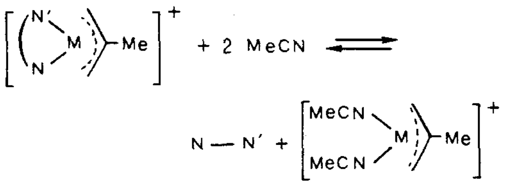
E

Thus, the course of the substitution reactions (4) appears to be controlled essentially by electronic factors, such as the formation of stronger M–N bonds with the entering ligands, which lead to the formation of thermodynamically more stable five-membered metallocycles in the order:

bipy > py-2-CH=NR > RN=CH–CH=NR

($R = C_6H_4OMe$-*p*)

This is in a good agreement with the stability order found for the cationic complexes $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(N\text{–}N')]^+$ (M = Pd, Pt; *N–N'* = RN=CH–CH=NR, py-2-CH=NR, bipy; $R = C_6H_4OMe$-*p*) from dissociation constant measurements of equilibrium (5) in acetonitrile [6, 7]:



(5)

Since the π-accepting abilities of the α-diimino ligands were found to increase in the reverse order (for a given R) [2–4]:

RN=CH–CH=NR > py-2-CH=NR > bipy

the observed stability trend suggests that σ contribution plays a major role in stabilizing the M–N bonds in $[MCl_2(N\text{–}N')]$ and $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(N\text{–}N')]^+$. This is further confirmed by the higher stabilities towards dissociation of the σ,σ'-*N,N'* chelate RN=CH–CH=NR and py-2-CH=NR adducts when the nitrogen substituent R is changed from an aryl to a better electron-releasing alkyl group. For the complexes $[MCl_2(RN{=}CH{-}CH{=}NR)]$ (M = Pd, Pt; R = $CHMe_2$, CMe_3, CMe_2Et) no dissociation was actually reported in $(CD_3)_2SO$ [14, 15]. On the other hand, the equilibrium constant of reaction (6) in acetonitrile at 25 °C was found to increase considerably on going from $R = C_6H_4OMe$-*p* ($\log K = 2.60$) to R = Me ($\log K > 5$) [5]:

$$SnCl_2Me_2 + \text{py-2-CH=NR} \rightleftarrows [SnCl_2Me_2(\text{py-2-CH=NR})] \qquad (6)$$

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