Reactions of Pyridine-2-carbaldimines with Chloro-bridged Palladium(II) and Platinum(II) 2-Methylallyl Dimers. Solution Behaviour of the Cationic Complexes [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]$^+$

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Abstract

The reactions of pyridine-2-carbaldimines, py-2-CH=NR (R = C$_6$H$_4$OMe-*p*, Me), with allylic dimers [MCl(η^3-2-MeC$_3$H$_4$)]$_2$ give rise to stoichiometry, concentration, solvent and temperature dependent equilibria, in which the cationic complexes [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]$^+$ and the anion [MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ or Cl$^-$ are involved. In general, the ligand/dimer reaction (1/1 molar ratio) yields the ionic products [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]-[MCl$_2$(η^3-2-MeC$_3$H$_4$)], which can be isolated as solids, whereas the same reaction in a 1/0.5 molar ratio yields the species [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]Cl, which can be studied only in solution, but are easily converted into [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]X in the presence of an excess of NaX (X = ClO$_4$, BF$_4$, BPh$_4$). In the cationic complexes, the α-diimino ligand is σ,σ'-*N,N'* chelate to the central metal. The combined conductivity measurements and electronic, IR, and ^{1}H NMR spectral data show that (i) the cationic complexes are greatly stabilized in methanol solution; (ii) extensive ion-pairing occurs in chlorinated solvents, such as dichloromethane, chloroform, and 1,2-dichloroethane; (iii) the complexes with X = ClO$_4$ are slightly dissociated in acetonitrile, with the following order of dissociation constants; Pd $\gg$ Pt and py-2-CH=NC$_6$H$_4$OMe-*p* > py-2-CH=NMe; (iv) various dynamic processes take place in solution at different rates depending on the temperature, solvent, central metal, and counteranion. In general, a low-energy process involving *syn–syn, anti–anti* exchange of the allylic protons occurs, which in some cases cannot be frozen out and which is interpreted in terms of formation of stereochemically non-rigid five-coordinate intermediates by association of the cationic complexes with the solvent

or the counteranion. Cation–anion interactions and, probably, formation of five-coordinate species with the more coordinating anions, Cl$^-$ and [MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$, are responsible for the solvent and anion dependent ^{1}H NMR chemical shifts of the chelate py-2-CH=NC$_6$H$_4$OMe-*p* ligand. For [Pd(η^3-2-MeC$_3$H$_4$)-(py-2-CH=NC$_6$H$_4$OMe-*p*)][PdCl$_2$(η^3-2-MeC$_3$H$_4$)], but not for the platinum analogue, a rather fast scrambling of the Pd(η^3-2-MeC$_3$H$_4$) unit between the cation and anion is observed at ambient temperature in CDCl$_3$. This and other differences in the solution behaviour between palladium and platinum derivatives can be rationalized on the basis of a higher stability (toward dissociation) of the five-membered metallacycle M(py-2-CH=NR) on going from M = Pd to M = Pt.

Introduction

In recent years, the coordination chemistry of the α-diimines RN=C(R^1)–C(R^2)=NR has been extensively studied because of the versatile bonding properties of the flexible N=C–C=N group [1]. In particular, with Pd and Pt d^8 metal centers these compounds may act as either σ-*N* monodentate [2], or σ,σ'-*N,N'* bridging bidentate [3], or σ,σ'-*N,N'* chelating bidentate ligands [4], the latter being the most common ligating mode.

In previous papers, we have described the reactions of ligands RN=C(R^1)–C(R^2)=NR (R = alkyl or aryl group; R^1 = H, Me) [5] and their imino-carbon metallated analogues RN=C(R^1)–C(MClL$_2$)=NR [M = Pd, Pt; L$_2$ = *trans* tertiary phosphines or 1,2-bis(diphenylphosphino)ethane] [6–9] with chloro-bridged allyl dimers [PdCl(η^3-2-YC$_3$H$_4$)]$_2$ (Y = H, Me). These reactions yield different products depending on the experimental conditions and the nature of the imino-carbon substituents, as is summarized in Scheme 1 for R = C$_6$H$_4$OMe-*p*.

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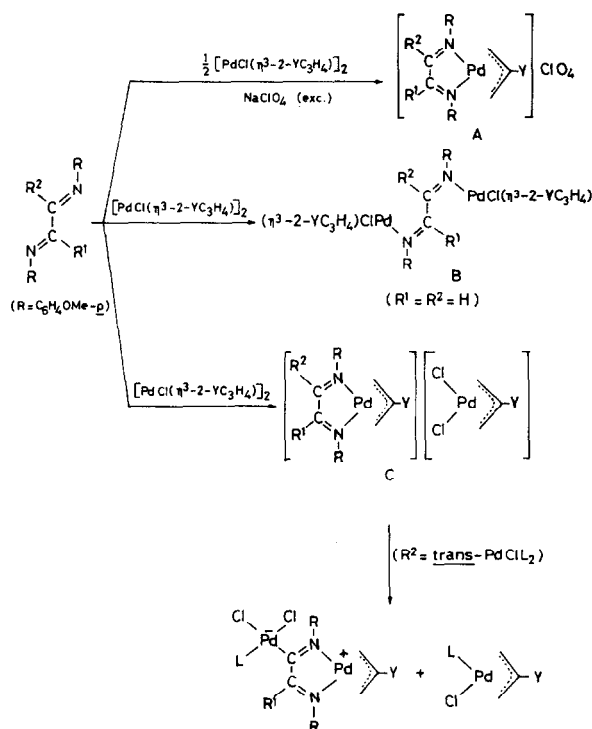
Scheme 1.

The cationic complexes **A** with the asymmetric α-diimine (R^1 = H, R^2 = Me) undergo a fast dynamic process at ambient temperature, which involves *syn—syn, anti—anti* exchange of the allylic protons. Such a process is absent (or occurs at markedly reduced rate) in the corresponding compounds with metallated α-diimines (R^1 = H, Me; R^2 = $MCIL_2$), under comparable conditions. The binuclear complexes **B** are obtained only for R^1 = R^2 = H in benzene or chlorinated solvents, and are converted almost quantitatively into the ionic derivatives **C** in methanol or ethanol. The latter complexes are generally formed with bulkier R^1 and R^2 substituents. For R^2 = *trans*-$PdClL_2$ (L = tertiary aryl phosphine), the cation—anion interaction in the ionic intermediates **C** brings about a phosphine—chloride exchange with formation of the products **D** and **E** at rates which are markedly influenced by the solvent and decrease in the order:benzene > 1,2-dichloroethane ≫ ethanol.

As an extension of this line of research, we report here the reactions of the system py-2-CH=NR/[MCl-(η^3-2-MeC$_3$H$_4$)]$_2$ (M = Pd, Pt) in various solvents and with different ligand/dimer molar ratios. The presence of an asymmetric α-diimino unit (with two different *N*-donor sites) in pyridine-2-carbaldimines makes these ligands particularly suitable for a variable temperature ^{1}H NMR investigation of the solution behaviour of the cationic species in complexes of type **A** and **C**.

This work is also a preliminary step toward the study of similar reactions involving palladated ligands, such as py-2-C(R^1)=NR [R = C$_6$H$_4$OMe-*p*, Me; R^1 = *trans*-PdCl(PPh$_3$)$_2$], the synthesis of which has recently been reported [10].

Experimental

The pyridine-2-carbaldimines py-2-CH=NR (R = C$_6$H$_4$OMe-*p*, Me) and the complexes [MCl(η^3-2-MeC$_3$H$_4$)]$_2$ were prepared by published methods [11–13]. All other chemicals and solvents were reagent grade, and were used without further purification. All reactions were carried out at room temperature. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

[M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]X (M = Pd, Pt; R = C$_6$H$_4$OMe-p, Me; X = ClO$_4$, BF$_4$)

A solution of the dimer [MCl(η^3-2-MeC$_3$H$_4$)]$_2$ (0.5 mmol) in *ca.* 30 ml of CH$_2$Cl$_2$ was treated with py-2-CH=NR (1 mmol) and then with an excess of NaX (*ca.* 2 mmol) dissolved in 10 ml of methanol. A white precipitate of NaCl was immediately formed. The reaction mixture was stirred for 15 min and the solvents were evaporated to dryness. The solid residue was redissolved in CH$_2$Cl$_2$, treated with charcoal and filtered off to give a clear solution. After concentration, the product was precipitated by adding diethylether, and purified by reprecipitation from the same solvents. The yield based on the theoretical amount was in the range 85–90%, and the colour varied from yellow—brown for the platinum(II) to yellow for the palladium(II) derivatives.

[Pd(η^3-2-MeC$_3$H$_4$)(py-2-CH=NC$_6$H$_4$OMe-p)]BPh$_4$

The complex [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ (0.20 g, 0.5 mmol) and the ligand (0.21 g, 1 mmol) were mixed together in methanol. Dropwise addition of NaBPh$_4$ (0.34 g, 1 mmol), dissolved in 20 ml of MeOH/H$_2$O (2/1 *v/v*), caused the immediate precipitation of a yellow solid which was stirred for 20 min and filtered off. Repeated washings with H$_2$O, with MeOH/H$_2$O (1/1 *v/v*) and finally with MeOH gave the pure product, which was dried *in vacuo* (0.62 g, 89%).

[M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NC$_6$H$_4$OMe-p)][MCl$_2$-(η^3-2-MeC$_3$H$_4$)] (M = Pd, Pt)

A solution of [MCl(η^3-2-MeC$_3$H$_4$)]$_2$ (0.5 mmol) in 40 ml of benzene was treated with py-2-CH=NC$_6$H$_4$-OMe-*p* (0.5 mmol) dissolved in 20 ml of CH$_2$Cl$_2$. Evaporation of the more volatile CH$_2$Cl$_2$ solvent and dilution with Et$_2$O gave the product as a yellow solid for M = Pd, or as a yellow—orange oil for M = Pt, which crystallized on stirring. Each compound was reprecipitated from a CH$_2$Cl$_2$/C$_6$H$_6$ solution (1/1 *v/v*), following the same procedure (yield 81%, M = Pd; 77%, M = Pt).

Attempted Preparation of [M(η³-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]Cl

Attempted Preparation of $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CH=NC_6H_4OMe\text{-}p)]Cl$

In an attempt to isolate these cationic complexes with chloride as counteranion, the reactants [MCl(η^3-2-MeC₃H₄)]₂ (0.5 mmol) and py-2-CH=NC₆H₄OMe-p (1 mmol) were dissolved in 20 ml of CH₂Cl₂. The solution was concentrated to *ca.* 2 ml and then diluted with benzene to precipitate a yellow solid (M = Pd) or an oily material (M = Pt), which crystallized upon addition of Et₂O and stirring. Elemental and spectral analysis showed that the product was [Pd(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)] [PdCl₂-(η^3-2-MeC₃H₄)], starting from the palladium dimer, or a mixture of [Pt(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄-OMe-p)] [PtCl₂(η^3-2-MeC₃H₄)] and presumably [Pt-(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]Cl, starting from the platinum dimer.

AsPh₄[MCl₂(η³-2-MeC₃H₄)]

AsPh₄[MCl₂(η^3-2-MeC₃H₄)]

These anionic complexes were obtained from the reaction of [MCl(η^3-2-MeC₃H₄)]₂ with AsPh₄Cl·H₂O (1/2 molar ratio), as was described for the preparation of [NEt₃(CH₂Ph)] [PdCl₂(η^3-2-MeC₃H₄)] [8] (yield 81%, M = Pd; 62%, M = Pt).

[PtCl(η³-2-MeC₃H₄)(py-2-CH=O)]

[PtCl(η^3-2-MeC₃H₄)(py-2-CH=O)]

The complex was prepared by bridge-splitting reaction of [PtCl(η^3-2-MeC₃H₄)]₂ (0.28 g, 0.5 mmol) with pyridine-2-carbaldehyde (0.12 g, 1.1 mmol) in 20 ml of CH₂Cl₂. Concentration of the solution, followed by addition of Et₂O, gave the analytically pure product (0.30 g, 75%).

Physical Measurements

The conductivity measurements were carried out with a CDM 83 conductivity meter at 20 °C. 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. The electronic spectra in solution were recorded with a Bausch-Lomb Spectronic 21OUV and with a Cary 219 spectrophotometer in the range 550–250 nm at 25 °C, using quartz cells of 1 cm path length. Infrared spectra were recorded with a Perkin-Elmer 983G instrument, using Nujol mulls and CsI windows in the range 4000–200 cm⁻¹, and CaF₂ cells of 0.5 mm width for CH₂Cl₂ solution in the range 1800–1400 cm⁻¹.

Results and Discussion

Preparation and Characterization of the Cationic Complexes [M(η³-2-MeC₃H₄)(py-2-CH=NR)]⁺

Preparation and Characterization of the Cationic Complexes $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CH=NR)]^+$

The reactions of the system [MCl(η^3-2-MeC₃H₄)]₂/ py-2-CH=NR are reported in Scheme 2. In the absence of the sodium salt NaX (which causes the precipitation of the insoluble NaCl), the formation of
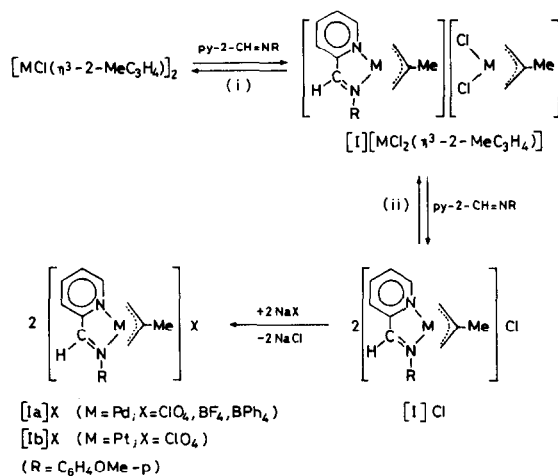
Scheme 2.

the ionic intermediates [I] [MCl₂(η^3-2-MeC₃H₄)] or the final product [I]Cl (where [I]⁺ refers to the cationic species [M(η^3-2-MeC₃H₄)(py-2-CH=NR)]⁺) appears to be controlled by the stoichiometry and concentration of the reactants. Electronic, IR and ¹H NMR spectra of the reaction mixtures [MCl(η^3-2-MeC₃H₄)]₂/py-2-CH=NR (1/1 or 1/2 molar ratio) show that the position of the equilibria (i) or (ii) in Scheme 2 is much in favour of complexes [I] [MCl₂-(η^3-2-MeC₃H₄)] or [I]Cl, both in methanol (at initial concentration of allylic dimer higher than 5 × 10⁻⁵ mol dm⁻³) and in chlorinated solvents (at initial concentration of allylic dimer higher than 5 × 10⁻³ mol dm⁻³).

The IR spectra of [I] [MCl₂(η^3-2-MeC₃H₄)] in CH₂Cl₂ (4–8 × 10⁻² mol dm⁻³) show no evidence of free pyridine-2-carbaldimine, whereas the IR spectra of [I]Cl under the same experimental conditions indicate that a small amount of free ligand, characterized by a ν(C=N) band at 1626 cm⁻¹, is present and that the intensity ratio ν(C=N)_free/ν(C=N)_coord increases with increasing dilution. Accordingly, the complexes [I] [MCl₂(η^3-2-MeC₃H₄)] can be easily obtained from the 1/1 reaction in benzene, whereas the products [I]Cl cannot be isolated as solids, since equilibrium (ii) shifts completely (M = Pd) or partially (M = Pt) toward the less soluble compound [I] [MCl₂(η^3-2-MeC₃H₄)] in the attempted precipitation (see 'Experimental'). The cationic species [I]⁺ are better isolated with bulkier and less coordinating anions, such as ClO₄⁻, BF₄⁻, and BPh₄⁻. In the same way, the reaction of [PdCl(η^3-2-MeC₃H₄)]₂ with py-2-CH=NMe (1/2 molar ratio) in the presence of an excess of NaClO₄ yields [Pd(η^3-2-MeC₃H₄)(py-2-CH=NMe)]-ClO₄, which will be indicated hereafter as [Ic]ClO₄.

Elemental analyses, molar conductivities, and selected IR and electronic spectral data are listed in Table I. The infrared spectra of the cationic complexes [I]ClO₄ and [Ia]BF₄ show the typical bands

TABLE I. Analyses, Conductivity, and Selected IR and Electronic Spectral Data

Compound	Analyses[a]				Molar conductivity (ohm⁻¹ cm² mol⁻¹)[b]	Infrared bands (cm⁻¹)[c]				Electronic spectra (nm)[d] λ_{max} (ε, mol⁻¹ dm³ cm⁻¹)
	C (%)	H (%)	N (%)	Cl (%)		ν(C=N)	ν(Cl–O)	δ(Cl–O)	ν(M–Cl)	
[Pd(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]ClO₄ ([Ia]ClO₄)	43.2 (43.15)	4.1 (4.05)	5.9 (5.92)	7.5 (7.49)	92.0 [29.2]	1618m	1090vs	625s		387(10600) [418sh, 398(12000), 380sh]
[Pd(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]BF₄ ([Ia]BF₄)	44.1 (44.33)	4.1 (4.16)	6.0 (6.08)		100.2 [29.7]	1616m	1060vs[e]	522ms[f]		387(10600)
[Pd(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]BPh₄ ([Ia]BPh₄)	70.9 (71.06)	5.7 (5.67)	4.0 (4.04)		[23.0][g]	1615m				[415sh, 397(10600), 390sh][g]
[Pd(η^3-2-MeC₃H₄)(py-2-CH=NMe)]ClO₄ ([Ic]ClO₄)	34.5 (34.66)	4.0 (3.97)	7.3 (7.35)	9.4 (9.30)	106.5	1634mw	1090vs	624s		296sh, 294(7000), 268sh [300sh, 294(7200), 268(5300)]
[Pd(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]-[PdCl₂(η^3-2-MeC₃H₄)]	41.5 (41.61)	4.3 (4.32)	4.7 (4.62)	11.5 (11.70)	86.1 [14.5]	1615m [1617m][i]			268m, 255m	387(11400)
[Pd(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]Cl[h] ([Ia]Cl)					84.8 [10.3]	[1619m][i]				387(10800)
[Pt(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]ClO₄ ([Ib]ClO₄)	36.5 (36.34)	3.5 (3.41)	5.0 (4.99)	6.3 (6.31)	84.5	1621mw	1080vs	623s		395sh, 379(9800) [435sh, 408sh, 390(10000)]
[Pt(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]-[PtCl₂(η^3-2-MeC₃H₄)]	32.3 (32.19)	3.3 (3.34)	3.5 (3.58)	9.1 (9.05)	75.0 [13.7]	1616m [1615sh][i]			294m, 265m	395sh, 379(9800) [435sh, 408sh, 390(9800)]
[Pt(η^3-2-MeC₃H₄)(py-2-CH=NC₆H₄OMe-p)]Cl[h] ([Ib]Cl)					73.8 [12.0]	[1618m][i]				395sh, 379(10000)
AsPh₄[PtCl₂(η^3-2-MeC₃H₄)]	48.0 (47.74)	3.9 (3.86)		10.2 (10.06)	83.7				298m, 266m	
[PtCl(η^3-2-MeC₃H₄)(py-2-CH=O)]	30.4 (30.58)	3.1 (3.08)	3.5 (3.57)	8.9 (9.03)		1712s[j] [1712][i,j]			297ms	

[a]Calculated values in parenthesis. [b]In 10⁻³ mol dm⁻³ MeOH solution at 20 °C; molar conductivities in square brackets refer to 10⁻³ mol dm⁻³ 1,2-dichloroethane solution at 20 °C. [c]As Nujol mulls. [d]Absorption maxima in MeOH solution at 25 °C; the absorption maxima in square brackets refer to 1,2-dichloroethane solution at 25 °C. [e]ν(B—F) band. [f]δ(B—F) band. [g]Measured immediately after dissolution (see text). [h]Prepared in solution from the reaction [MCl(η^3-2-MeC₃H₄)]₂/py-2-CH=NC₆H₄OMe-p (1/2 molar ratio). [i]In CH₂Cl₂ solution. [j]ν(C=O) band of the uncoordinate aldehyde.

of the uncoordinate tetrahedral anions. For the compounds [I] [MCl$_2$(η^3-2-MeC$_3$H$_4$)], two ν(M—Cl) vibrations are detected at 268 and 255 cm^{-1} for M = Pd, and at 294 and 265 cm^{-1} for M = Pt, which suggest the presence of the anions [MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$, also in the solid state [In AsPh$_4$[MCl$_2$(η^3-2-MeC$_3$H$_4$)], the ν(M—Cl) bands occur at 270 and 256 cm^{-1} for M = Pd, and at 298 and 266 cm^{-1} for M = Pt].

In general, all the studied complexes behave as uni-univalent electrolytes in methanol. In solvents of lower dielectric constant, such as 1,2-dichloroethane, however, the molar conductivities for 10^{-3} mol dm^{-3} solutions depend markedly on the counteranion and decrease in the order; ClO$_4^-$ ~ BF$_4^-$ > BPh$_4^-$ > [MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ > Cl$^-$. Furthermore, in the same solvent, the Λ_M values decrease considerably with increasing concentration: e.g., the molar conductivity of [Ia]ClO$_4$ drops from 29.2 to 16.7 ohm^{-1} cm^2 mol^{-1} when the concentration is increased from 10^{-3} to 10^{-2} mol dm^{-3}. A similar concentration dependence is observed for [Ia]BF$_4$ in dichloromethane at 20 °C, for which the Λ_M values are found to increase from 10.8 to 17.5 and to 45.6 ohm^{-1} cm^2 mol^{-1}, when the concentration is progressively lowered from 5 X 10^{-2} to 10^{-2} and to 10^{-3} mol dm^{-3}, respectively. In the light of electronic and ^{1}H NMR spectral results (see further), such anion and concentration influence appears to result essentially from extensive ion-pairing in chlorinated solvents, even though the lower mobility of some ions (particularly for the bulky BPh$_4^-$) and the formation of non-conducting species with the more coordinating [MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ and Cl$^-$ anions may also contribute to the observed changes in conductivities.

Electronic Spectra

The electronic spectra of the cationic complexes [I]$^+$ in the range 500—250 nm are characterized by a series of overlapping bands, which give rise to a main maximum surrounded by one or more shoulders. In this range, the free ligands py-2-CH=NR exhibit intense $\pi \rightarrow \pi^*$ transitions at 339 and 286 nm for R = C$_6$H$_4$OMe-p or at 272 nm for R = Me, in 1,2-dichloroethane. The spectral changes observed when the ligand is σ,σ'-N,N' chelate to a M(η^3-2-MeC$_3$H$_4$) group are shown in Fig. 1 (for R = C$_6$H$_4$OMe-p), and can be interpreted in terms of low-frequency shifts of the ligand $\pi \rightarrow \pi^*$ bands, which largely overlap with metal-to-ligand charge-transfer (MLCT) d$_M \rightarrow \pi^*$ transitions.

Similar red-shifts of ligand $\pi \rightarrow \pi^*$ bands upon σ,σ'-N,N' chelation to transition metal ions in positive oxidation states were reported for complexes of 2,2'-bipyridine [14] and 1,2-bis(imino)ethanes, RN=CH—CH=NR [15]. On the other hand, the occurrence of MLCT transitions is suggested by solvatochromic effects, as most of the bands undergo higher frequency shifts on going from 1,2-dichloro-
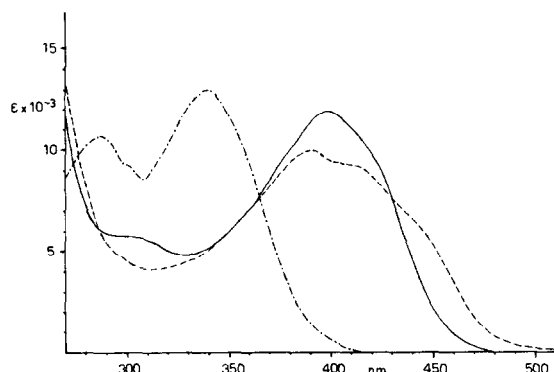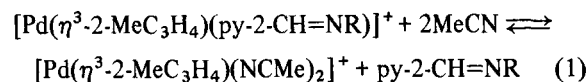

Fig. 1. Electronic spectra of py-2-CH=NC$_6$H$_4$OMe-p (—·—), [Ia]ClO$_4$ (——), and [Ib]ClO$_4$ (———) in 1,2-dichloroethane at 25 °C.

ethane to more polar solvents, such as methanol (see Table I) or acetonitrile.

In methanol, the Lambert—Beer law is obeyed in the concentration range 5 X 10^{-4}—5 X 10^{-5} mol dm^{-3} for all the complexes, independent of the nature of the central metal and the counteranion. In very dilute acetonitrile solution, the palladium derivatives [Ia]ClO$_4$ and [Ic]ClO$_4$ undergo a dissociation equilibrium according to eqn. (1)

$$[Pd(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{py-2-CH=NR})]^+ + 2\text{MeCN} \rightleftharpoons$$
$$[Pd(\eta^3\text{-2-MeC}_3\text{H}_4)(\text{NCMe})_2]^+ + \text{py-2-CH=NR} \quad (1)$$

(R = C$_6$H$_4$OMe-p, Me)

The occurrence of this equilibrium can be checked by adding appropriate amounts of free ligand to acetonitrile solutions of the independently prepared [Pd(η^3-2-MeC$_3$H$_4$)(NCMe)$_2$]ClO$_4$ [13]. The electronic spectra of the resulting solutions closely reproduce those corresponding to the dissociation of [Ia]ClO$_4$ at the same concentration and temperature conditions.

Non-linear regression analysis of the spectral changes with dilution [5] at 25 °C gives dissociation constants (K_D) of (5.6 ± 1.8) X 10^{-6} mol dm^{-3} for [Ia]ClO$_4$ and (9.0 ± 3) X 10^{-7} mol dm^{-3} for [Ic]ClO$_4$. No dissociation is observed for the platinum derivative [Ib]ClO$_4$. If compared with the corresponding dissociation constants in acetonitrile at 25 °C for [M(η^3-2-YC$_3$H$_4$)(RN=CH—CH=NR)]-ClO$_4$ (R = C$_6$H$_4$OMe-p; M = Pd, Y = H K_D = (3.0 ± 0.4) X 10^{-4} mol dm^{-3}, Y = Me (3.4 ± 0.5) X 10^{-4}; M = Pt, Y = H (3.0 ± 0.8) X 10^{-6}) [5], the present results indicate that the ligand py-2-CH=NC$_6$H$_4$OMe-p gives more stable chelate adducts than the ligand RN=CH—CH=NR (R = C$_6$H$_4$OMe-p). Furthermore, since no dissociation was detected for the complex [Pd(η^3-2-MeC$_3$H$_4$)(bipy)]BF$_4$ (bipy = 2,2'-bipyridine) [5], the stability of the five-membered metallacycle in the cationic complexes [Pd(η^3-2-MeC$_3$H$_4$)-(N–N')]$^+$ containing a σ,σ'-N,N' chelate α-diimino

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

Compound	Solvent (mol dm^{-3})	Temperature (°C)	Pyridine-2-carbaldimine protons[b]				OMe	NMe	Allyl protons[c]		
			N=CH	H^3	H^6	AA'			H$_{syn}$	H$_{anti}$	C–Me
[1a]ClO$_4$	CD$_2$Cl$_2$ (4 × 10^{-2})	30	8.78 S	8.22 M	8.83 M	7.48 M	3.85 S		3.95(vbr)	3.39 S(br)	2.21 S
	CD$_2$Cl$_2$ (4 × 10^{-2})	−50	8.71 S	8.20 M	8.74 M	7.45 M	3.79 S		4.04 S / 3.73 S	3.38 S / 3.27 S	2.12 S
[1a]ClO$_4$	CDCl$_3$ (3 × 10^{-2})	30	8.87 S	8.34 M	8.83 M	7.50 M	3.83 S		3.95 S	3.38 S	2.21 S
	CDCl$_3$ (3 × 10^{-2})	−40	8.91 S	8.40 M	8.85 M	7.52 M	3.85 S		3.96 S	3.40 S	2.22 S
[1a]BF$_4$	CDCl$_3$ (3 × 10^{-2})	30	8.89 S	8.37 M	8.79 M	7.50 M	3.84 S		3.94 S	3.36 S	2.21 S
	CDCl$_3$ (3 × 10^{-2})	−40	8.92 S	8.42 M	8.82 M	7.52 M	3.86 S		3.94 S	3.38 S	2.22 S
[1a]BPh$_4$	CD$_2$Cl$_2$ (3 × 10^{-2})	30	7.87 S	m[d]	8.43 M	m[d]	3.86 S		3.81 S(br)	3.24 S	2.15 S
[1a][PdCl$_2$(η^3-2-MeC$_3$H$_4$)]	CDCl$_3$ (3 × 10^{-2})	30	9.58 S	8.97 M	8.81 M	7.65 M	3.83 S		3.85(sh)	3.08 S(br)	2.11 S
	CDCl$_3$ (3 × 10^{-2})	−40	9.70 S	9.10 M	8.74 M	7.68 M	3.82 S[e]		3.88 S[f]	3.36 S[f] / 2.76 S[g]	2.15 S[f] / 2.03 S[g]
[1a][PdCl$_2$(η^3-2-MeC$_3$H$_4$)]	CD$_3$OD (2.5 × 10^{-2})	30	8.89 S	8.16 M	8.92 M	7.55 M	3.87 S		4.05 S[f] / 3.79 S[g]	3.46 S[f] / 2.82 S[g]	2.21 S[f] / 2.09 S[g]
[1a]Cl	CD$_2$Cl$_2$ (8 × 10^{-2})	30	9.15 S(br)	8.51 M	8.75 M	7.50 M	3.82 S		3.5(vbr)[h]	3.5(vbr)[h]	2.09 S
	CD$_2$Cl$_2$ (8 × 10^{-2})	−50	9.75 S	8.78 M	8.71 M	7.57 M	3.75 S		3.86 S	3.33 S	2.10 S
[1a]Cl	CD$_3$OD (5 × 10^{-2})	30	8.90 S	8.17 M	8.94 M	7.55 M	3.87 S		4.06 S	3.46 S	2.22 S
[1c]ClO$_4$	CD$_2$Cl$_2$ (4 × 10^{-2})	30	8.70 Q ^4J(H–Me) = 1.6	8.04 M	8.76 M			3.89 D	4.00 S	3.25 S	2.18 S
	CD$_2$Cl$_2$ (4 × 10^{-2})	50	8.64 Q ^4J(H–Me) = 1.6	7.98 M	8.69 M			3.86 D	3.95 S / 3.93 S	3.24 S / 3.11 S	2.12 S
[1b]ClO$_4$	CD$_2$Cl$_2$ (4 × 10^{-2})	30	9.34 S J(Pt–H) = 72.5	8.41 M	9.10 M J(Pt–H) = 34.0	7.57 M	3.86 S		3.94 J(Pt–H) = 26 / 3.56 / J(Pt–H) = 28	3.03 J(Pt–H) = 74 / 2.88 / J(Pt–H) = 76	2.30 S J(Pt–H) = 84.0

Compound	Solvent	T (°C)								
[1b]ClO₄	CDCl₃ (2.5 × 10⁻²)	30	9.53 S J(Pt–H) = 73.0	8.57 M	9.12 M J(Pt–H) = 34.0	7.60 M	3.85 S	3.8(br)i	2.94 (br) J(Pt–H) = 76	2.31 S J(Pt–H) = 84.5
	CDCl₃ (2.5 × 10⁻²)	–40	9.54 S J(Pt–H) = 73.0	8.60 M	9.14 M J(Pt–H) = 34.0	7.64 M	3.87 S	3.95 J(Pt–H) = 26 3.55 J(Pt–H) = 26	3.05 J(Pt–H) = 76 2.90 J(Pt–H) = 74	2.33 S J(Pt–H) = 85.0
[1b][PtCl₂(η³-2-MeC₃H₄)]	CDCl₃ (4 × 10⁻²)	30	10.20 S J(Pt–H) = 74.5	9.18 M	9.04 M J(Pt–H) = 34.0	7.75 M	3.85 S	3.8(br)f,i	2.92(br)f J(Pt–H) = 75	2.30 Sf J(Pt–H) = 83.5
	CDCl₃ (4 × 10⁻²)	–40	10.30 S J(Pt–H) = 74.5	9.26 M	9.03 M J(Pt–H) = 34.0	7.78 M	3.87 S	3.48 Sg J(Pt–H) = 38.0 3.9(sh)f,i 3.49f J(Pt–H) = 25 3.55 Sg J(Pt–H) = 37.5	1.81 Sg J(Pt–H) = 81.5 2.98f J(Pt–H) = 75 2.84f J(Pt–H) = 75 1.88 Sg J(Pt–H) = 82.0	2.06 Sg 2.06 Sg J(Pt–H) = 78.5 2.32 Sf J(Pt–H) = 84.0 2.10 Sg J(Pt–H) = 79.5
[1b]Cl	CD₂Cl₂ (8 × 10⁻²)	30	10.56 S J(Pt–H) = 73.0	9.03 M	9.07 M J(Pt–H) = 34.0	7.72 M	3.84 S	3.71 J(Pt–H) = 27	2.90 J(Pt–H) = 74	2.28 S J(Pt–H) = 85.5
	CD₂Cl₂ (8 × 10⁻²)	–50	10.44 S J(Pt–H) = 74.0	8.92 M	9.01 M J(Pt–H) = 34.0	7.64 M	3.77 S	3.85 J(Pt–H) = 28 3.47 J(Pt–H) = 26	2.94 J(Pt–H) = 74 2.83 J(Pt–H) = 74	2.21 J(Pt–H) = 84.0
AsPh₄[PtCl₂(η³-2-MeC₃H₄)]	CDCl₃	30						3.37 J(Pt–H) = 37.0	1.71 J(Pt–H) = 80.0	1.99 S J(Pt–H) = 76.5
[PtCl(η³-2-MeC₃H₄)(py-2-CH=O)]	CD₂Cl₂	30	10.90 Sj	8.0 M	9.03 M J(Pt–H) = 33.0			3.65 J(Pt–H) = 28.0 3.51 J(Pt–H) = 34.0	2.26 J(Pt–H) = 72.0 2.10 J(Pt–H) = 81.5	2.21 S J(Pt–H) = 82.0

a ¹H chemical shifts in ppm from TMS; S = singlet, D = doublet, Q = quartet, M = multiplet, sh = shoulder, br = broad, vbr = very broad; coupling constants in Hz; satisfactory integration values are obtained. b The 2-pyridyl protons give rise to second-order spectra, in which each proton appears as a multiplet of characteristic pattern; the ^{4}H and ^{5}H protons resonate in the narrow ranges 8.0–8.3 and 7.5–7.8 ppm, respectively; the *ortho* and *meta* protons of the C_6H_4OMe-*p* group appear as a symmetrical AA'BB' system; numbering scheme:
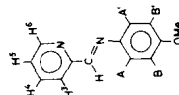
c In general, the allyl proton spectra are typical of η^3-2-MeC_3H_4 ligands, with distinct signals for *syn* and *anti* protons; the spectra are rather simple for palladium(II) compounds, since no coupling between *syn* and *anti* protons is observed within the resolution limit of the instrument; for platinum(II) derivatives, the η^3-2-MeC_3H_4 resonances are more complicated by coupling with ^{195}Pt isotope and by small *syn–syn* and geminal *syn–anti* couplings of ca. 1–2 Hz. d Masked by the intense phenyl proton resonances of BPh_4^- in the range 7.6–6.5 ppm. e This signal masks the δ(H$_{syn}$) resonance of the anion [$PdCl_2$(η^3-2-MeC_3H_4)]⁻. f Allyl signals of the cationic complex. g Allyl signals of the anion [MCl_2(η^3-2-MeC_3H_4)]⁻. h Broad absorption due to *syn–anti* proton exchange (see Text). i Unresolved ^{195}Pt satellites. j δ(O=CH) of the aldehydic proton.
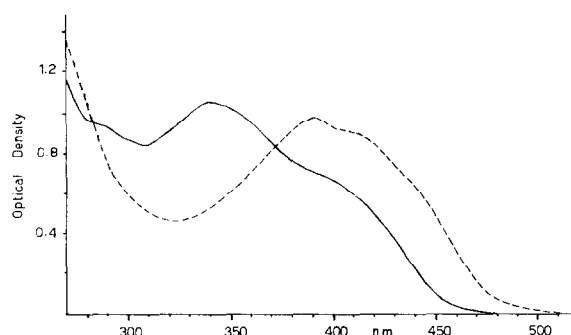
Fig. 2. Electronic spectra of 10^{-4} mol dm^{-3} solutions of [Ia][PdCl$_2$(η^3-2-MeC$_3$H$_4$)] (———), and of [Ib][PtCl$_2$(η^3-2-MeC$_3$H$_4$)] (— — —) in 1,2-dichloroethane at 25 °C.
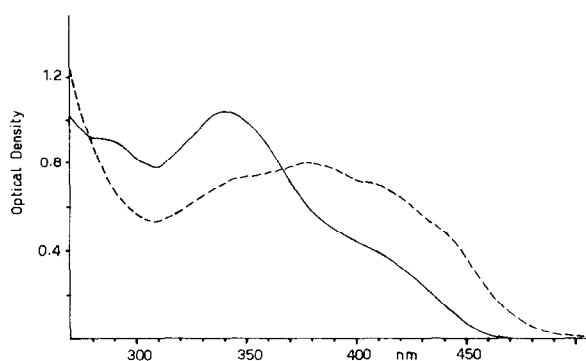
Fig. 3. Electronic spectra of 10^{-4} mol dm^{-3} solutions of [Ia]Cl (———), and of [Ib]Cl (— — —) in 1,2-dichloroethane at 25 °C.

ligand appears to increase with increasing number of 2-pyridyl groups in *N–N'*, in the order:

RN=CH–CH=NR < py-2-CH=NR < bipy
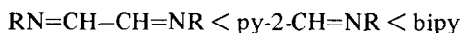
(R = C$_6$H$_4$OMe-*p*)

In line with previous observations, an increased stability is observed for complexes [M(η^3-2-MeC$_3$H$_4$)-(py-2-CH=NC$_6$H$_4$OMe-*p*)]ClO$_4$ when the central metal is changed from palladium to platinum [5], and for complexes [Pd(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]-ClO$_4$ when the C$_6$H$_4$OMe-*p* imino nitrogen substituent is replaced by a better electron-releasing Me group [11].

The different stability of the cationic complexes [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]$^+$ (M = Pd, Pt; R = C$_6$H$_4$OMe-*p*) toward dissociation of the pyridine-2-carbaldimine is also reflected in the electronic spectra of [I][MCl$_2$(η^3-2-MeC$_3$H$_4$)] (Fig. 2) and [I]Cl (Fig. 3) in 1,2-dichloroethane. Whereas for [Ib][PtCl$_2$(η^3-2-MeC$_3$H$_4$)] the spectrum is identical to that of [Ib]-ClO$_4$ at the same concentration, and the Lambert–Beer law is obeyed down to the lowest explored concentration (5 × 10^{-5} mol dm^{-3}), for [Ia][PdCl$_2$(η^3-2-MeC$_3$H$_4$)] a substantial dissociation according to

equilibrium (i) of Scheme 2 occurs, as can be inferred from the intense band at 340 nm of the uncoordinate py-2-CH=NC$_6$H$_4$OMe-*p* ligand in Fig. 2. For the complexes [I]Cl at concentrations lower than 5 × 10^{-3} mol dm^{-3}, the higher coordinating ability of the chloride anion causes a rather extensive dissociation for the palladium derivative [Ia]Cl [equilibria (i) and (ii) of Scheme 2] and a slight dissociation for the platinum analogue [Ib]Cl according to equilibrium (ii). In the latter case, the formation of a small amount of free ligand is revealed by a shoulder at *ca.* 340 nm on the high-energy side of the main absorption at 390 nm of the cationic species [Ib]$^+$ in Fig. 3.

The electronic spectrum of [Ia]BPh$_4$ in 1,2-dichloroethane must be recorded immediately after dissolution, since this compound undergoes a slow reaction in chlorinated solvents, as is shown by the progressive colour change from yellow to red of the solution and the eventual formation of palladium metal. The course of such reaction is presently under investigation. Preliminary results suggest that a phenyl transfer from BPh$_4^-$ to the palladium center of the cation [Ia]$^+$ is probably involved, followed by reductive elimination of allylbenzene. This behaviour is in accordance with the good phenylating properties of the tetraphenylborate anion toward palladium(II) complexes [16] and the reactivity of compounds of the type [Pd(η^3-C$_3$H$_5$)(Ar)(L)] and *cis*-[Pd(η^1-C$_3$H$_5$)-(Ar)(L)$_2$] (Ar = aryl group, L = tertiary phosphine) [17].

^{1}H NMR Spectra

The variable temperature ^{1}H NMR spectra have been studied in CDCl$_3$ (−50–30 °C), in CD$_2$Cl$_2$ (−80–30 °C), and for some soluble compounds also in CD$_3$OD (−50–30 °C), in the concentration range 5 × 10^{-3}–8 × 10^{-2} mol dm^{-3}. Some selected data are listed in Table II. A comparison with the ^{1}H NMR spectra of the free ligands py-2-CH=NR [18] shows that the resonances of the 2-pyridyl, the imino N=CH, and the phenyl *ortho* AA' protons (R = C$_6$H$_4$OMe-*p*) or the N-methyl protons (R = Me) are generally shifted downfield in the cationic complexes [I]$^+$. This effect and the observation of ^{195}Pt couplings for δ(N=CH) and δ(H^6) signals in the platinum derivatives point to a σ,σ'-*N,N'* chelating mode for the pyridine-2-carbaldimine ligands [19].

The N=CH and H^3 resonances are markedly affected by the central metal, the solvent, the counteranion and, for [Ia]Cl, also by the temperature. In the platinum complexes, the N=CH and H^3 protons resonate at a lower field of *ca.* 0.7 and 0.3 ppm, respectively, than in the corresponding palladium analogues. A comparable downfield shift of δ(N=CH) was previously noted for the cationic α-diimine derivatives [M(η^3-C$_3$H$_5$)(RN=CH–CH=NR)]ClO$_4$ (R = C$_6$H$_4$OMe-*p*) on going from M = Pd to M = Pt [5]. The counteranion and solvent

influence is particularly evident in the series of palladium compounds of Table II. Whereas $\delta(N=CH)$ and $\delta(H^3)$ are detected at rather close chemical shifts in both [Ia]ClO$_4$ and [Ia]BF$_4$ [$\delta(N=CH)$ in the range 8.9–8.7 ppm, and $\delta(H^3)$ in the range 8.4–8.2 ppm], the same signals are shifted upfield in [Ia]BPh$_4$, and downfield in [Ia] [PdCl$_2(\eta^3$-2-MeC$_3$H$_4)$] or [Ia]Cl, in chlorinated solvents. However, when CD$_3$OD is used as solvent for [Ia] [PdCl$_2(\eta^3$-2-MeC$_3$H$_4)$] or [Ia]Cl, the downfield shifts are removed and the N=CH and H^3 resonances appear at chemical shift values comparable to those of [Ia]ClO$_4$ or [Ia]BF$_4$. A parallel trend is observed for the platinum compounds. In our opinion, these changes are essentially due to specific cation–anion interactions in tight ion pairs, extensively formed in solvents of low dielectric constant, such as CDCl$_3$ or CD$_2$Cl$_2$. The upfield shifts for [Ia]BPh$_4$ can be interpreted in terms of shielding effects of the phenyl ring currents when the BPh$_4^-$ anion approaches the planarly chelate py-2-CH=NR ligand with one phenyl group above and one below the coordination plane, as is shown in Fig. 4. The downfield shifts for [I] [MCl$_2(\eta^3$-2-MeC$_3$H$_4)$] and [I]Cl are probably due to partial (or complete) bonding of the more coordinating anions to the central metal of the cation [I]$^+$, with formation of labile five-coordinate species.
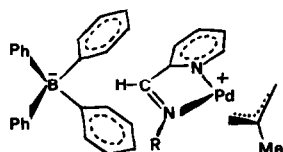

Fig. 4. Proposed interaction of the anion BPh$_4^-$ with the cationic complex [Pd(η^3-2-MeC$_3$H$_4$)(py-2-CH=NC$_6$H$_4$OMe-p)]$^+$.

Five-coordination has been well established for α-diimine complexes of Rh(I) and Pt(II) of the type [RhCl(L^1)(L^2)(RN=CH–CH=NR)]   (L^1 = L^2 = CO or PF$_3$; L^1 = CO, L^2 = C$_2$H$_4$) [20], [PtCl$_2(\eta^2$-olefin)-(RN=CH–CH=NR)]   [4], and [PtCl$_2(\eta^2$-olefin)-(py-2-CH=NR)] [19].

An alternative explanation for the downfield shifts of $\delta(N=CH)$ and $\delta(H^3)$ on going from [I]ClO$_4$ to [I] [MCl$_2(\eta^3$-2-MeC$_3$H$_4)$] or [I]Cl may be given by the occurrence of equilibria (2) and (3) in chlorinated solvents, with substantial amounts of the neutral species II, III and IV.

The imino proton N=CH in the species II and IV, and the H^3 proton in III and IV, residing at close proximity to d^8 metal centers above or below the coordination plane, would experience large downfield shifts, as in the case of the N=CH$_\beta$ or both the N=CH protons of 1,2-bis(imino) ethanes when these ligands are σ-N monodentate or σ, σ'-N,N' bridging bidentate in the complexes [21]:
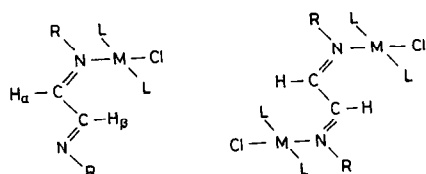
(M = Pd, Pt; L = tertiary phosphine or arsine)

(2)

(X$^-$= Cl$^-$, [MCl$_2 (\eta^3$-2-MeC$_3$H$_4)$]$^-$)

(3)
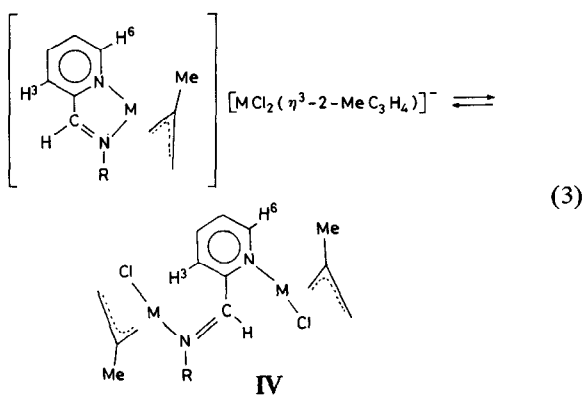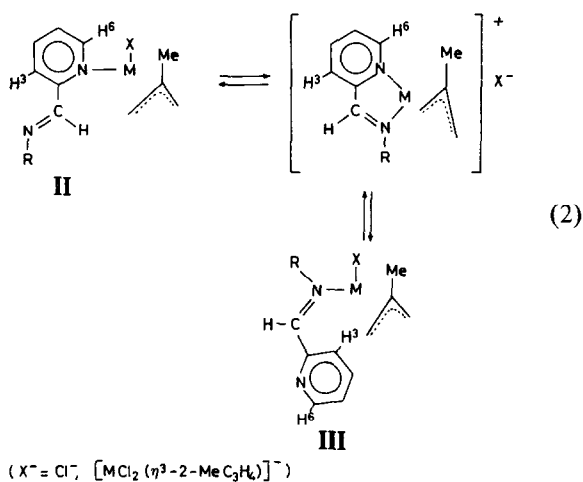
Such an explanation, however, is not consistent with other experimental results, at least for the platinum complexes. The equilibria (2) and (3) should be fast on the NMR time scale even at the lowest explored temperatures, since only one signal for the imino proton and one for each pyridyl proton are always observed in all the compounds examined. Under these conditions, the equilibrium (2) for [Ib]Cl and [Ib] [PtCl$_2(\eta^3$-2-MeC$_3$H$_4)$] would lead to averaged J(Pt–H^6) and J(Pt–NCH) coupling constants at significantly lower values than those in the complex [Ib]ClO$_4$, because of the small long-range ^4J(Pt–NCH) coupling in II and ^6J(Pt–H^6) in III. In the related compound [PtCl(η^3-2-MeC$_3$H$_4$)(py-2-CHO)], containing the σ,N bonded pyridine-2-carboxalde-hyde, no appreciable ^4J(Pt–OCH) coupling is actually

observed. On the other hand, the J(Pt—NCH) coupling constants were reported to decrease from a value of 86 Hz for the σ,σ'-N,N' chelate α-diimine in [PtCl$_2$(RN=CH—CH=NR)] (R = CMe$_3$) [4] to 29 Hz for the same σ-N monodentate ligand in *trans*-[PtCl$_2$-(RN=CH—CH=NR)(PPh$_3$)] under conditions of fast $\sigma,N \rightleftarrows \sigma',N'$ interconversion, *i.e.*, when the ligand changes rapidly its point of attachment to the metal [21].

A fast equilibrium (3) would also yield averaged values for J(Pt—H^6) and J(Pt—NCH) with concomitant averaged proton resonances for the differently bonded Pt(η^3-2-MeC$_3$H$_4$) unit.

In contrast, the complexes [Ib]ClO$_4$, [Ib][PtCl$_2$-(η^3-2-MeC$_3$H$_4$)] and [Ib]Cl exhibit J(Pt—H^6) and J(Pt—NCH) couplings at almost constant values of 34 and 74 Hz, respectively, and distinct allyl proton signals for [Ib]$^+$ and for [PtCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ are observed in the ^{1}H NMR spectra of [Ib][PtCl$_2$(η^3-2-MeC$_3$H$_4$)] in the temperature range -50–30 °C.

A complex of type **II** is indeed obtained in the bridge-splitting reaction of [PtCl(η^3-2-MeC$_3$H$_4$)]$_2$ with pyridine-2-carboxaldehyde (see 'Experimental'):
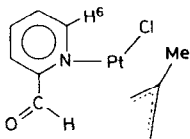

The coordination occurs only through the pyridine nitrogen, as is shown by the J(Pt—H^6) coupling of 33 Hz and by the absence of ^{195}Pt satellites for the O=CH resonance, which is considerably deshielded (0.8 ppm) relative to the free ligand [22]. In agreement with the proposed formulation, the IR spectra of the complex exhibit a ν(C=O) vibration at 1712 cm^{-1} (at the same frequency as for the uncoordinate pyridine-2-carboxaldehyde in CH$_2$Cl$_2$ solution) and a ν(Pt—Cl) band at 297 cm^{-1}. However, the solution behaviour of this compound is quite different from that of [Ib]Cl, since no fast *syn–syn, anti–anti* exchange of allylic protons is observed in CD$_2$Cl$_2$ at 30 °C. A fast rotation around the Pt—N bond probably occurs, as for the 2-methylpyridine complex [PdCl(η^3-crotyl)(py-2-Me)] [23], but this point was not further investigated.

Dynamic Behaviour in Solution

The ^{1}H NMR spectra of Table II also show that the cationic complexes [I]$^+$ undergo dynamic processes in solution, which generally involve a *syn–syn, anti–anti* exchange of allylic protons at different rates depending on the temperature, the central metal (Pd > Pt), the solvent (CDCl$_3$ > CD$_2$Cl$_2$ and CD$_3$OD > CD$_2$Cl$_2$), the counteranion ([MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ > ClO$_4$$^-$ and Cl$^-$ > ClO$_4$$^-$), and in some case ([Ia]-ClO$_4$ in CD$_2$Cl$_2$) also on the concentration. Only for the platinum derivative [Ib]ClO$_4$, such exchange is

slow at 30 °C in CD$_2$Cl$_2$: two separate resonances are in fact observed for the *syn* protons, at 3.94 and 3.56 ppm, and two for the *anti* protons, at 3.03 and 2.88 ppm. However, when CDCl$_3$ is used as solvent and when the ClO$_4$$^-$ anion is replaced by Cl$^-$ in CD$_2$Cl$_2$, the rate of exchange at 30 °C is markedly increased so as to give an averaged signal for H$_{syn}$ (at 3.8 ppm for [Ib]ClO$_4$ in CDCl$_3$ and at 3.71 ppm for [Ib]Cl in CD$_2$Cl$_2$) and an averaged signal for H$_{anti}$ (at 2.94 ppm for [Ib]ClO$_4$ in CDCl$_3$ and at 2.90 ppm for [Ib]Cl in CD$_2$Cl$_2$). On cooling, the dynamic processes are slowed down and at -30 °C for [Ib]ClO$_4$ in CDCl$_3$, or at -50 °C for [Ib]Cl in CD$_2$Cl$_2$, the observed ^{1}H NMR spectra are consistent with a 'static' η^3-2-MeC$_3$H$_4$ group in the cationic complex with a chelate py-2-CH=NC$_6$H$_4$OMe-p ligand:
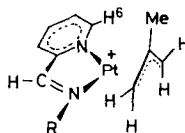
No significant changes in J(Pt—NCH) and J(Pt—H^6) are detected when the temperature is lowered from the fast to the slow exchange limit, and also when the solvent or the counteranion are changed. On the other hand, if py-2-CH=NC$_6$H$_4$OMe-p is added to a CDCl$_3$ solution of [Ib]ClO$_4$ or to a CD$_2$Cl$_2$ solution of [Ib]Cl, no exchange between free and coordinate ligand takes place at appreciable rate at 30 °C.

These observations appear to rule out any dissociative mechanism for the dynamic behaviour of the platinum complexes, involving either complete dissociation of the α-diimine (as in equilibrium (1)) or breaking of only one of the Pt—N bonds (as in equilibrium (2)). Alternative processes for the *syn–syn, anti–anti* exchange may be found either in an intramolecular rotation of the allyl (or the pyridine-2-carbaldimine) about the metal—ligand axis, or in an intermolecular association of the cation with the solvent (or the counteranion) to give stereochemically non-rigid five-coordinate intermediates, which can undergo Berry pseudorotation.

The rate of *syn–syn, anti–anti* exchange for the palladium complex [Ia]ClO$_4$ is higher than for the platinum analogue [Ib]ClO$_4$ under the same experimental conditions. For example, such process is still fast for [Ia]ClO$_4$ in CDCl$_3$ at -40 °C. A rapid exchange between coordinate and free pyridine-2-carbaldimine is observed at 30 °C upon addition of py-2-CH=NC$_6$H$_4$OMe-p to a 2.5×10^{-2} mol dm^{-3} CDCl$_3$ solution of [Ia]ClO$_4$ (molar ratio [Ia]$^+$/free ligand 1/0.5). For this system, the ^{1}H NMR spectrum shows averaged δ(N=CH), δ(OMe), δ(H$_{syn}$), and δ(H$_{anti}$) signals as sharp singlets at 8.80, 3.84, 3.94, and 3.38 ppm, respectively. The rate of the latter process decreases rapidly on cooling and becomes
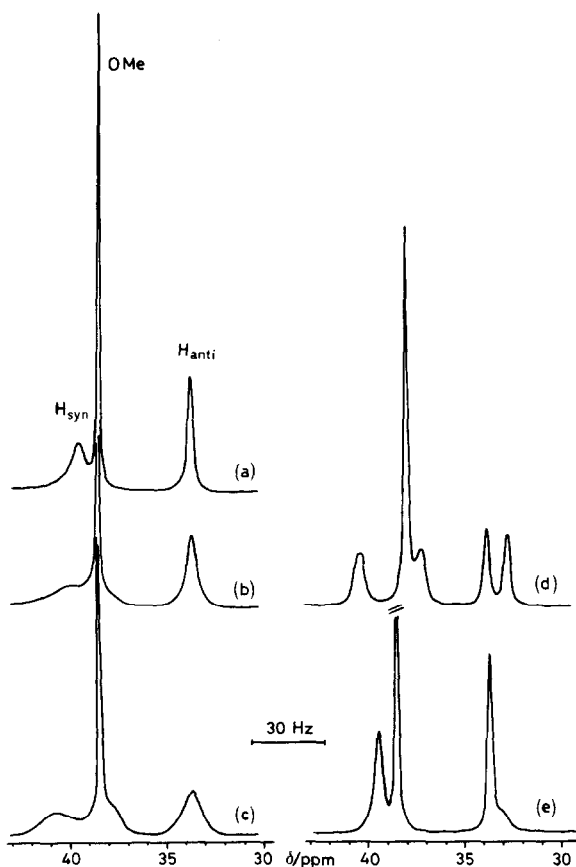
Fig. 5. ^{1}H NMR spectra at 30 °C of [Ia]ClO$_4$ in CD$_2$Cl$_2$ solution at different concentration: (a) 8×10^{-2} mol dm^{-3}; (b) 4×10^{-2} mol dm^{-3}; (c) 8×10^{-3} mol dm^{-3}. (d) ^{1}H NMR spectrum of [Ia]ClO$_4$ in 4×10^{-2} mol dm^{-3} CD$_2$Cl$_2$ solution at -40 °C. (e) ^{1}H NMR spectrum of [Ia]ClO$_4$ in 8×10^{-3} mol dm^{-3} CD$_2$Cl$_2$ solution at 30 °C, upon addition of a small amount of CD$_3$OD.

very slow at -35 °C, whereas at the same temperature a much faster *syn–syn, anti–anti* exchange is still observed. At -35 °C, the ^{1}H NMR spectrum shows two sharp singlets for δ(N=CH) at 8.92 and 8.64 ppm, and two sharp singlets for δ(OMe) at 3.86 and 3.83 ppm, corresponding to the coordinate and free α-diimine, whereas the allylic protons H$_{syn}$ and H$_{anti}$ appear as somewhat broader singlets at 3.95 and 3.38 ppm, respectively. These results clearly demonstrate that the exchange between free and coordinate pyridine-2-carbaldimine, which requires the initial breaking of at least one of the Pd—N bonds of the σ,σ'-N,N' chelate ligand [probably through a short-lived intermediate or transition state in which both the entering and leaving α-diimine is σ-N mono-dentate to the palladium center (see Scheme 3)] occurs at higher energy than the process which causes the *syn–syn, anti–anti* exchange of the allyl protons.

For [Ia]ClO$_4$, the *syn–syn, anti–anti* exchange is much faster in CDCl$_3$ than in CD$_2$Cl$_2$ under com-

parable temperature and concentration conditions. Furthermore, dilution studies in CDCl$_3$ at 30 °C show no appreciable changes in line-shape of the H$_{syn}$ and H$_{anti}$ resonances on lowering the concentration from 3×10^{-2} to 5×10^{-3} mol dm^{-3}, whereas similar studies in CD$_2$Cl$_2$ at 30 °C show a progressive broadening of H$_{syn}$ and H$_{anti}$ signals with increasing dilution from 8×10^{-2} to 5×10^{-3} mol dm^{-3}, and even a splitting of the H$_{syn}$ resonance into two broad absorptions at concentrations lower than 10^{-2} mol dm^{-3} (see Fig. 5).

As can be seen when the temperature is lowered from 30 °C to -40 °C for the 4×10^{-2} mol dm^{-3} CD$_2$Cl$_2$ solution, the rate of exchange is considerably depressed and a spectrum typical of a rigid η^3-2-MeC$_3$H$_4$ ligand is observed (spectrum (d) of Fig. 5). In contrast, addition of a small amount of CD$_3$OD to the 8×10^{-3} mol dm^{-3} solution brings about a marked increase in rate, and two averaged sharp singlets are observed for the H$_{syn}$ and H$_{anti}$ protons (spectrum (e) of Fig. 5).

A comparison of the dynamic behaviour in 4×10^{-2} mol dm^{-3} CD$_2$Cl$_2$ solutions for the palladium complexes [Pd(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]ClO$_4$ (R = C$_6$H$_4$OMe-p, Me) and [Pd(η^3-2-MeC$_3$H$_4$)(py-2-CR'=NC$_6$H$_4$OMe-p)]ClO$_4$ [R' = *trans*-PdCl(PPh$_3$)$_2$] [24] shows that the rate of *syn–syn, anti–anti* exchange is little changed when the C$_6$H$_4$OMe-p substituent in [Ia]ClO$_4$ is replaced by the Me group in [Ic]ClO$_4$, whereas it is very much reduced when the imino proton in [Ia]ClO$_4$ is replaced by the bulky *trans*-PdCl(PPh$_3$)$_2$ unit in the binuclear complex. The ^{1}H NMR spectra of the latter compound and of its platinum analogue are consistent with rigidly bound η^3-allyl groups both in CD$_2$Cl$_2$ and CDCl$_3$ at 30 °C, according to the following structure:
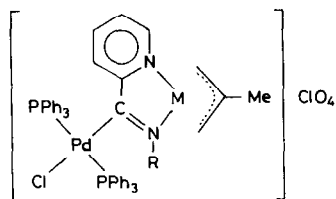
(M = Pd, Pt ; R = C$_6$H$_4$OMe-p)

Thus, steric factors may also play an important role in the process of *syn–syn, anti–anti* exchange of allylic protons in cationic complexes with σ,σ'-N,N' chelate pyridine-2-carbaldimine ligands.

All these results can be accommodated into a mechanism involving association equilibria of the cationic substrates with the solvent, the counter-anion and, if present, also with the free ligand to give five-coordinate intermediates of sufficient life-time to undergo low-energy stereochemical changes through Berry pseudorotation (Scheme 3)

(M = Pd, Pt, N–N' = py-2-CH=NR ; L = S (solvent), X⁻(counteranion), N-N')
(iii) : M = Pd, L = N-N'
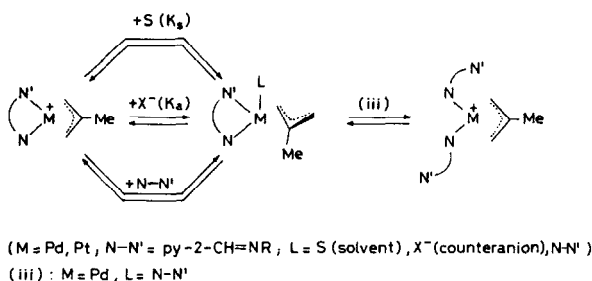
Scheme 3.

The rate of *syn–syn*, *anti–anti* exchange will depend on the magnitude of the equilibrium constants, and both K_s (association with solvent) and K_a (association with anion) will increase with increasing ligating ability of S and X⁻, respectively, and decrease with increasing steric bulkiness of the N–N' ligand, whereas K_a will become smaller in solvents of higher dielectric constants. In this context, the higher rates of exchange for [Ia]ClO₄ in CDCl₃ or CD₂Cl₂/CD₃OD and the lack of concentration dependence in CDCl₃ can be rationalized by a predominant association with solvent (CDCl₃ or CD₃OD), with relative K_s values much higher than that with CD₂Cl₂. In the latter solvent, a significant contribution is given by association with the anion, as suggested by the concentration dependence of the exchange rate for [Ia]ClO₄.

Similar solvent or anion promoted dynamic processes, involving *cis–trans* isomerization through five-coordinate intermediates, have been reported for the cationic complexes [Pd(η^3-allyl)(η^4-diene)]PF₆ [13] or [Pt(PNH₂)₂]X₂ [PNH₂ = (*o*-aminophenyl)-diphenylphosphine] [25].

The equilibrium (iii) of Scheme 3 is proposed to account for the exchange between free and chelate pyridine-2-carbaldimine, which is found to occur at an appreciable rate only for the palladium system [Ia]⁺/py-2-CH=NC₆H₄OMe-*p* at higher temperatures. The lack of this exchange for the analogous platinum cation [Ib]⁺ can be related to a greater inertness of the five-membered metallacycle in [Ib]⁺ to undergo rupture of the Pt–N bonds, in line with the greater stability of the complex toward dissociation in chlorinated solvents [equilibria (i) and (ii) of Scheme
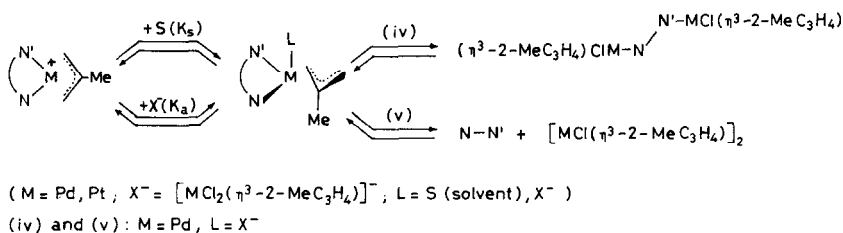
2] and in acetonitrile (equilibrium (1)). This gives a rationale also to the different dynamic behaviour of the systems [I] [MCl₂(η^3-2-MeC₃H₄)] and [I]Cl when the metal is changed from palladium to platinum. In contrast to [Ib] [PtCl₂(η^3-2-MeC₃H₄)], a rather fast exchange of the Pd(η^3-2-MeC₃H₄) unit between the cationic and anionic species of [Ia] [PdCl₂(η^3-2-MeC₃H₄)] is observed at 30 °C in CDCl₃. The rate of exchange decreases at lower temperatures, and also in CD₃OD. At −40 °C in CDCl₃ or at 30 °C in CD₃OD, no exchange occurs at an appreciable rate. It is worth noting that under these conditions a fast *syn–syn*, *anti–anti* exchange of the allylic protons of [Ia]⁺ is still present. For [Ib] [PtCl₂(η^3-2-MeC₃H₄)], only the latter process is found to occur rapidly at 30 °C in CDCl₃. This behaviour can be interpreted on the basis of the mechanism proposed in Scheme 4.

The scrambling of the Pd(η^3-2-MeC₃H₄) group in [Ia] [PdCl₂(η^3-2-MeC₃H₄)] may take place through two different pathways: step (iv), involving the formation of a short-lived binuclear intermediate (or transition state) with a σ,σ'-N,N' bridging ligand, and/or step (v), involving dissociation to the free ligand N–N' and the dimer [PdCl(η^3-2-MeC₃H₄)]₂.

A third possible mechanism, involving exchange of η^1-allyl groups between the cationic and anionic species, as was proposed for the ionic complexes [Pd(η^3-all)(TMEDA)] [PdCl₂(η^3-all)] (TMEDA = tetramethylethylenediamine) [26], is not consistent with previously reported ¹H NMR data on the related system RN=CH–CH=NR/[PdCl(η^3-2-MeC₃H₄)]₂, which showed the typical features of η^3-bound allyl ligands in the fast exchange limit [5], and on the complexes:

[R = C₆H₄OMe-*p*; R' = PdCl(dppe), *trans*-PdCl(PPh₃)₂; R" = H, Me]
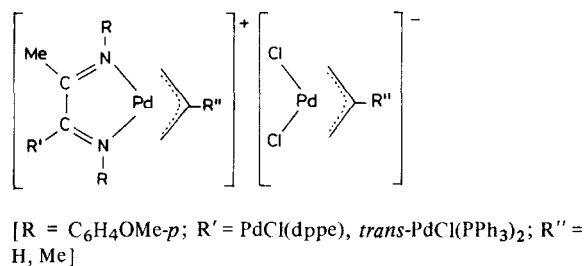
in which the cation–anion interaction caused a fast *syn–anti* exchange of the allylic protons of the

(M = Pd, Pt ; X⁻ = [MCl₂(η^3-2-MeC₃H₄)]⁻ ; L = S (solvent), X⁻)
(iv) and (v) : M = Pd, L = X⁻

Scheme 4.

(M = Pd, Pt ; L = S (solvent), Cl⁻)

(vi) : M = Pd , L = Cl⁻
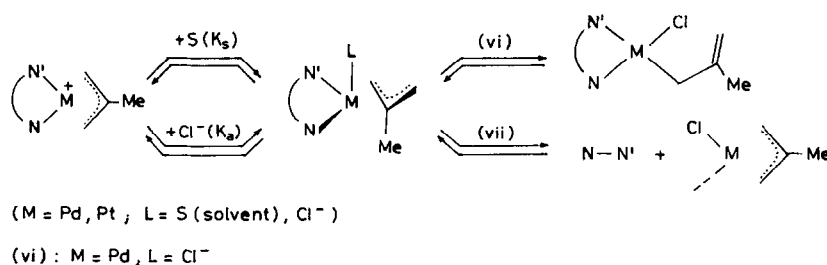
Scheme 5.

cation without any concomitant fast scrambling of allyl groups between the cation and the anion [7].

According to the proposed mechanism, the marked decrease in rate of exchange of the Pd(η^3-2-MeC$_3$H$_4$) unit for [Ia][PdCl$_2$(η^3-2-MeC$_3$H$_4$)] in CD$_3$OD solution can be understood in terms of the expected changes in the association equilibria (larger K_s and smaller K_a value in a solvent of higher dielectric constant and better coordinating properties, such as CD$_3$OD).

The combined ^{1}H NMR, IR and electronic spectral data for the compounds [I]Cl are in accordance with the dynamic behaviour shown in Scheme 5. The $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ process (vi) occurs only for the palladium complex [Ia]Cl in CD$_2$Cl$_2$ at 30 °C, as suggested by the appearance of a broad resonance for the allylic protons at 3.5 ppm. The rate of such process decreases markedly when the temperature is lowered, and also in CD$_3$OD solution. At −30 °C in CD$_2$Cl$_2$ or at 30 °C in CD$_3$OD, no appreciable *syn–anti* exchange is observed. However, under these conditions a fast *syn–syn*, *anti–anti* exchange is still apparent for the allylic protons of [Ia]$^+$, which is not frozen out even at lower temperatures (−50 °C). For the platinum derivative [Ib]Cl, only the latter process occurs rapidly at 30 °C in CD$_2$Cl$_2$.

In agreement with IR data in CH$_2$Cl$_2$ solution, a dissociation equilibrium (vii) is observed in CD$_2$Cl$_2$ for both systems [Ia]Cl and [Ib]Cl, which shifts progressively to the left (towards the coordinate species) on cooling. The rate of dissociation is low (on the NMR time scale) for [Ib]Cl, as indicated by the presence of a small δ(N=CH) resonance at 8.6 ppm for the free py-2-CH=NC$_6$H$_4$OMe-p ligand in the ^{1}H NMR spectrum at 30 °C, and fast for [Ia]Cl, for which an averaged δ(N=CH) signal at 9.15 ppm is detected. At lower temperatures, the weak signal of the free ligand disappears in the spectrum of [Ib]Cl, while the averaged δ(N=CH) signal of [Ia]Cl shifts progressively to lower field, until a limiting value of 9.8 ppm is reached at −60 °C. Neither process (vi) for [Ia]Cl nor process (vii) for both [Ia]Cl and [Ib]Cl are observed in CD$_3$OD at 30 °C, in line with the previously discussed stabilization of the cationic species [I]$^+$ in this solvent.

Conclusions

From dissociation equilibria studies, it appears that the pyridine-2-carbaldimine py-2-CH=NC$_6$H$_4$-OMe-p is a better σ,σ'-N,N' chelating ligand than the α-diimine p-MeOC$_6$H$_4$N=CH–CH=NC$_6$H$_4$OMe-p in the cationic complexes [M(η^3-2-MeC$_3$H$_4$)(N–N')]$^+$ (M = Pd, Pt). For the palladium derivatives [Pd(η^3-2-MeC$_3$H$_4$)(N–N')]$^+$, the stability of the five-membered metallacycle increases with increasing number of 2-pyridyl groups in N–N', in the order:

RN=CH–CH=NR < py-2-CH=NR < 2,2′-bipyridine
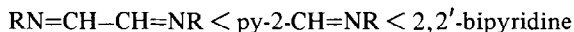
(R = C$_6$H$_4$OMe-p)

In contrast to the coordination behaviour of RN=CH–CH=NR [5], the pyridine-2-carbaldimines show no tendency to act as σ,σ'-N,N' bridging bidentate ligands in the reaction with [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ in benzene or chlorinated solvents (ligand/dimer molar ratio 1/1).

For the complexes [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NC$_6$H$_4$OMe-p)]$^+$X$^-$ (X$^-$ = ClO$_4^-$, [MCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$, Cl$^-$), an increased stability (toward dissociation) of the five-membered metallacycle M(py-2-CH=NR) is observed on going from M = Pd to M = Pt, which can also account for some significant differences in the solution behaviour between palladium and platinum derivatives. Thus, the processes involving either exchange between free and chelate pyridine-2-carbaldimine in the system [M-(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]$^+$/py-2-CH=NR (R = C$_6$H$_4$OMe-p) or exchange of the M(η^3-2-MeC$_3$H$_4$) unit between the cationic and anionic species of [M-(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)][MCl$_2$(η^3-2-MeC$_3$H$_4$)] are relatively fast (on the NMR time scale) for M = Pd at 30 °C in chlorinated solvents, whereas they do not occur at any appreciable rate for M = Pt under the same experimental conditions.

Acknowledgement

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