Coordination Properties of Imino(2-pyridyl)methylpalladium(II) Compounds. Reactions with the Chloride-bridged Allyl Dimers $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (M = Pd, Pt)

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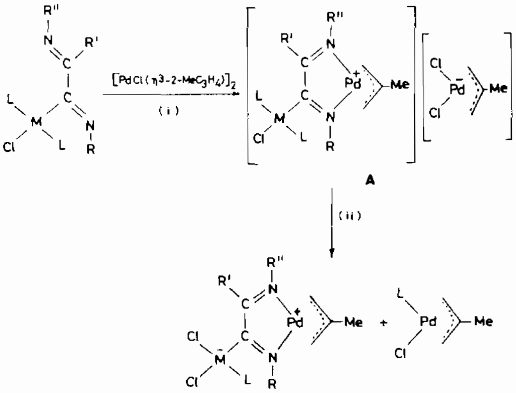
(Received June 17, 1989)

Abstract

The imino(2-pyridyl)methylpalladium(II) compounds py-2-CR_1=NR [R_1 = *trans*-$PdCl(PPh_3)_2$, R = C_6H_4OMe-*p* (**Ia**), Me (**Ib**), CMe_3 (**Ic**); R_1 = Pd(dmtc)(PPh_3), R = C_6H_4OMe-*p* (**Id**)] react with $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (M = Pd, Pt) in a molar ratio 1/0.5 and in the presence of $NaClO_4$ to yield the binuclear cationic complexes **II**, $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(\text{py-2-}CR_1\text{=}NR)]ClO_4$, where the α-diimino group acts as σ,σ-*N,N'* chelating ligand. In the absence of $NaClO_4$ and with a molar ratio 1/1, the reaction leads initially to formation of a ionic intermediate **A**, $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(\text{py-2-}CR_1\text{=}NR)]\,[MCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]$, which subsequently undergoes exchange of ancillary ligands between the cationic and anionic species to give the zwitterionic binuclear complexes **III**, $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(\text{py-2-}CR_2\text{=}NR)]$ (R_2 = *cis*-$PdCl_2(PPh_3)$) and $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ or $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(dmtc)]$. The rates of ligand migration are strongly dependent on the substituents R_1 and R. The great increase in reactivity when the substituent R is changed from C_6H_4OMe-*p* (**Ia**) to Me (**Ib**) or CMe_3 (**Ic**) is due to a predominant mechanism involving PPh_3 dissociation from the *trans*-$PdCl(PPh_3)_2$ unit of the cationic species in the intermediates **A**. This is supported by the fast formation of Ph_3PS in the reaction of **IIb** (R = Me) with an excess of sulphur. No trace of Ph_3PS is formed in the corresponding reaction with **IIa** (R = C_6H_4OMe-*p*), even after prolonged time. An increased reactivity is also observed when the R_1 group is changed from *trans*-$PdCl(PPh_3)_2$ to Pd(dmtc)(PPh_3). For the reaction **Id**/$[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, a mechanism is proposed in which ligand migration occurs by direct interaction of $[PtCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]^-$ with the Pd(dmtc)(PPh_3) unit of the cationic species of **A**. The ^1H and ^{31}P NMR spectra of **III** indicate only a diastereoisomer to be initially present in solution. With time, a second diastereoisomer is formed at different rates, depending on the metal M (Pd > Pt), until an equilibrium mixture of *c*. 1/1 molar ratio is obtained.

Introduction

In the past few years, we have studied the coordination properties of 1,2-bis(imino)alkylpalladium(II) and -platinum(II) compounds [1, 2]. By σ,σ-*N,N'* chelation of the organic moiety to a second metal center it was possible to prepare a variety of binuclear complexes with a C,N-bridging α-diimino group. In particular, the reaction of RN=CR_1–CR'=NR'' (R_1 = *trans*-$MClL_2$) with the allyl dimer $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (1/1 molar ratio) was found to proceed in two steps, as is shown in eqn. (1) [1a, 2].



(1)

(L = triarylphosphine; R = C_6H_4OMe-*p*, R' = R'' = Me, M = Pd, Pt; R = R'' = C_6H_4OMe-*p*, R' = H, Me, Ph, M = Pd).

The second step (ii), involving an exchange of the ancillary ligands L and Cl^- between the cation and anion of the ionic intermediate **A**, was observed only for M = Pd. On the basis of a kinetic investigation [3], a mechanism was proposed in which the ligand exchange occurs predominantly in an intramolecular way through a trinuclear transition state **B**.

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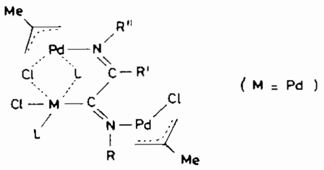


B

The rate of step (ii) was found to increase with decreasing stability (towards Pd–N bond dissociation) of the α-diimino five-membered ring in the cationic species of A, with decreasing steric requirements of R′ substituent, and with increasing lability of the M–L bond.

More recently, we have shown that pyridine-2-carbaldimines, py-2-CH=NR, give σ,σ-*N,N′* chelate adducts $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CH{=}NR)]^+$ and $[MCl_2(py\text{-}2\text{-}CH{=}NR)]$ (M = Pd, Pt) [4, 5], which are much more stable (towards M–N bond breaking involved either in ligand dissociation or in ligand substitution) than the corresponding complexes with 1,2-bis(imino)ethanes, RN=CH–CH=NR, carrying the same N-substituent ($R = C_6H_4OMe$-*p*). This observation prompted us to study the reactions of imino(2-pyridyl)methylpalladium(II) compounds py-2-CR_1=NR (R_1 = *trans*-$PdCl(PPh_3)_2$, $R = C_6H_4$-OMe-*p*, Me, CMe_3; $R_1 = Pd(dmtc)(PPh_3)$, $R = C_6H_4$-OMe-*p*, dmtc = dimethyldithiocarbamate), containing a related α-diimino group [6, 7], with the dimers $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (M = Pd, Pt) in order to assess if a ligand exchange similar to that of step (ii) in eqn. (1) occurs also in these systems, and possibly to get further information about the migration mechanism.

Experimental

The α-diimino derivatives py-2-CR_1=NR (R_1 = *trans*-$PdCl(PPh_3)_2$, $R = C_6H_4OMe$-*p* (**Ia**), R = Me (**Ib**), $R = CMe_3$ (**Ic**); $R_1 = Pd(dmtc)(PPh_3)$, $R = C_6H_4OMe$-*p* (**Id**)) and RN=CR_1–CMe=NR′ (R_1 = $Pd(dmtc)(PPh_3)$, $R = R' = C_6H_4OMe$-*p* (**Ie**); R_1 = *trans*-$PdCl(PPh_3)_2$, $R = R' = C_6H_4OMe$-*p* (**If**); $R = C_6H_{11}$, $R' = C_6H_4OMe$-*p* (**Ig**)) were prepared by published methods [6–9]. The allyl complexes $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (M = Pd, Pt) were prepared by standard procedures [10, 11]. 1,2-Dichloroethane was purified by distillation on anhydrous K_2CO_3. All other chemicals and solvents were reagent grade, and were used without further purification. The 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 the Binuclear Cationic Complexes II

The dimer $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.10 g, 0.25 mmol) and the imino(2-pyridyl)methylpalladium(II) compound **Ia**, **Ib** and **Id** (0.5 mmol) were dissolved in CH_2Cl_2 (50 ml). Upon addition of $NaClO_4 \cdot H_2O$ (0.14 g, 1 mmol), dissolved in 5 ml of methanol, a white precipitate of NaCl was immediately formed. After stirring for 15–20 min the solvents were evaporated to dryness and the residue was treated with CH_2Cl_2 and charcoal. After filtration, the clear solution was concentrated to small volume and the product was precipitated by addition of Et_2O. The complex was purified by reprecipitation from CH_2Cl_2/Et_2O. (Yields based on theoretical amount: **IIa** 73.0; **IIb** 79.1; **IId** 79.0%.)

The same procedure was followed for the preparation of complex **IIa′** from **Ia** (0.44 g, 0.5 mmol) and $[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.145 g, 0.25 mmol) (Yield: 0.45 g, 73.3%). Under the same experimental conditions, the reaction of **Ic** (0.41 g, 0.5 mmol) with $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.10 g, 0.25 mmol) gave no good result because the initial adduct decomposed too quickly, as was shown by a fast colour change of the solution from yellow to deep red. Any attempt to prepare this cationic complex either at 0 °C or in a different solvent, such as acetone, was unsuccessful.

Preparation of the Binuclear Zwitterionic Complexes III

(a) The complex py-2-CR_1=NR (**Ia**–**Ic**, 0.5 mmol) was added to a solution of $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.5 mmol) in benzene (40 ml). After stirring for a few minutes, a clear yellow solution was obtained, which was set aside for 6–7 h. During this time the product **III** separated as a yellow or pale yellow solid. The precipitation was eventually completed by dilution with Et_2O (20 ml). After filtration, the product was reprecipitated from CH_2Cl_2/Et_2O (Yields: 70–90%).

The mother liquor from the first precipitation was concentrated to small volume. Upon addition of n-hexane, a pale yellow solid was obtained and recrystallized from 1,2-dichloroethane/n-hexane to give $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (0.16–0.19 g for M = Pd; 0.18–0.22 g for M = Pt). These compounds were identified by comparing their IR and ^{31}P NMR spectra [ν(Pd–Cl) at 276 cm^{-1} and $\delta(^{31}P)$ at 23.4 ppm in CD_2Cl_2 for M = Pd; ν(Pt–Cl) at 290 cm^{-1} and $\delta(^{31}P)$ at 23.1 ppm in CD_2Cl_2 with ^1J(Pt–P) of 4311 Hz for M = Pt] with those of authentic samples prepared by the bridge-splitting reaction of $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ with PPh_3 [12, 13].

Because of the low ligand migration rate, the platinum(II) complex **IIIa′** could not be prepared in a sufficiently pure state from the above procedure, even after prolonged reaction times. Complex **IIIa′** and the palladium(II) analogue **IIIa** were readily obtained from the reaction of the dimethyldithiocarbamate derivative **Id** with $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$.

(b) The compound **Id** (0.35 g, 0.5 mmol) was added to a solution of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.20 g, 0.5 mmol) in benzene (40 ml). After stirring for 6 h, the reaction mixture was worked up as described above for method (a) to yield the products **IIIa** (0.32 g, 78.8%) and $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(dmtc)]$ (**Va**, 0.05 g). The latter compound was characterized by elemental analysis, IR and ^1H NMR (CD_2Cl_2) spectra. [Found: C, 30.0; H, 4.6; N, 4.9. Calc. for $C_7H_{13}NS_2Pd$: C, 29.84; H, 4.65; N, 4.97%. $\nu(C\overset{...}{-}N) = 1574s(br)$, $\nu(Pd{-}S) = 365ms$ cm^{-1}; $\delta(N{-}Me) = 3.31$ S, $\delta(H_{syn}) = 3.77$ S, $\delta(H_{anti}) = 2.60$ S, $\delta(C{-}Me) = 1.90$ S, ppm].

(c) The compound **Id** (0.35 g, 0.5 mmol) was added to a stirred solution of $[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.29 g, 0.5 mmol) in benzene (40 ml). The reaction mixture was set aside for 24 h, and then Et_2O was added to complete the precipitation of **IIIa'** (0.36 g, 79.9%, after recrystallization from CH_2Cl_2/Et_2O). The second reaction product $[Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(dmtc)]$ (**Va'**) could not be precipitated from the mother liquor (after filtration of **IIIa'**) because of its high solubility even in hydrocarbon solvents. However, the ^1H NMR spectra of an equimolar mixture **Id**/$[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in CD_2Cl_2, recorded at different times, showed **Va'** to be readily and almost quantitatively formed, together with **IIIa'**.

Preparation of $[Pt(\eta^3\text{-}2\text{-}MeC_3H_4)(dmtc)]$ (Va')

A pure sample of Va' was prepared as follows. The complex $[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.29 g, 0.5 mmol) was added to a stirred solution of $Na[dmtc]\cdot 2H_2O$ (0.27 g, 1.5 mmol) in acetone (30 ml). After 2 h, the solvent was evaporated to dryness and the solid was treated with benzene and charcoal. After filtration, the clear solution was concentrated to small volume and diluted with n-pentane/Et_2O (3/1 vol./vol., *c.* 30 ml) to precipitate a small amount of a yellow–orange solid, which was discarded as it consisted mainly of impurities present in the starting dimer. The filtrate was again concentrated to small volume, as to remove the more volatile Et_2O solvent. During concentration, some pale yellow product began to precipitate. The mixture was diluted with n-pentane and stored at −20 °C for 2 days. The solid was eventually filtered, washed with cold n-pentane and dried *in vacuo* (0.13 g, 35.1%). It was identified as complex Va' by elemental analysis, IR and ^1H NMR (CD_2Cl_2) spectra. [Found: C, 23.0; H, 3.5; N, 3.7. Calc. for $C_7H_{13}NS_2Pt$: C, 22.70; H, 3.54; N, 3.78%. $\nu(C\overset{...}{-}N) = 1545s(br)$, $\nu(Pt{-}S) = 380m, 364m$ cm^{-1}; $\delta(N{-}Me) = 3.23$ S, $\delta(H_{syn}) = 3.53$ ($J(Pt{-}H) = 27.0$ Hz), $\delta(H_{anti}) = 1.90$ ($J(Pt{-}H) = 73.0$ Hz), $\delta(C{-}Me) = 1.95$, ppm ($J(Pt{-}H) = 63.5$ Hz)].

Preparation of the Binuclear Zwitterionic Complexes VI

The palladium(II) complex **VIa** and the platinum(II) analogue **VIa'** were prepared from the reaction of the dimethyldithiocarbamate derivative **Ie** (0.385 g, 0.5 mmol) with $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.5 mmol) in benzene, following the same procedure as for the preparation of **IIIa** and **IIIa'** from **Id**. For the system **Ie**/$[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, both products **VIa** (0.34 g, 77.0%) and **Va** (0.04 g) could be isolated, whereas from the reaction **Ie**/$[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ only product **VIa'** was obtained as an orange microcrystalline solid (0.39 g, 80.3%).

The complex **VIa** was identified by comparison of its spectral data with those previously reported for an authentic sample [1a].

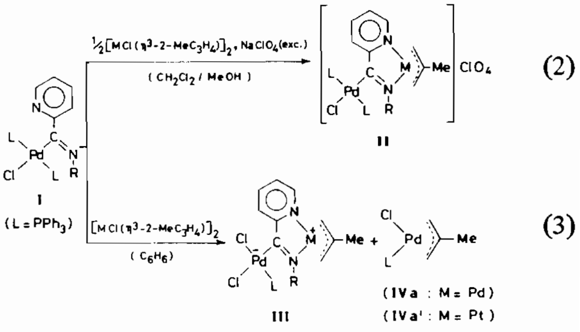
Physical Measurements

The conductivity measurements were carried out with a CDM 83 conductivity meter. Molecular weights were determined with a Knauer osmometer at 37 °C in 1,2-dichloroethane. Infrared spectra were recorded with Perkin-Elmer 1430 and 983G instruments, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian FT 80A spectrometer. The $^{31}P\{^1H\}$ NMR spectra in 1,2-dichloroethane solution were run with external lock on D_2O. The electronic spectra were recorded with a Bausch-Lomb Spectronic 210UV and with a Perkin-Elmer Lambda 15 spectrophotometer in the range 550–250 nm, using quartz cells of 1 cm path length.

Results and Discussion

Reaction of the α-Diimino Compounds Ia–Ie with $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$

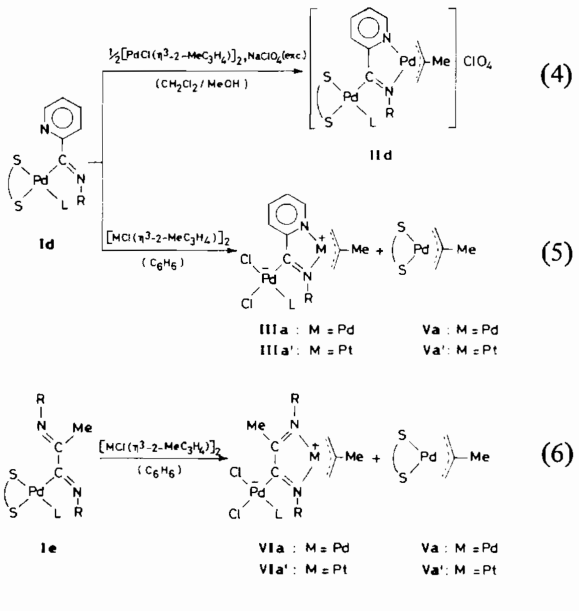
The reactions of imino(2-pyridyl)methylpalladium(II) derivatives **Ia–Id** with $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (M = Pd, Pt) are reported in eqns. (2)–(6).



R = C_6H_4OMe-p : **Ia**; M = Pd : **IIa**, **IIIa**; M = Pt : **IIa'**, **IIIa'**

R = Me : **Ib**; M = Pd : **IIb**, **IIIb**; M = Pt : **IIIb'**

R = CMe_3 : **Ic**; M = Pd : **IIIc**



(L = PPh_3 ; R = C_6H_4OMe-p ; S⌒S = dimethyldithiocarbamate)

In the presence of $NaClO_4$ and with a molar ratio I/dimer of 1/0.5 [eqn. (2) and (4)], the cationic binuclear complexes **II** are generally obtained, with the exception of compound **Ic** (see 'Experimental'). With a molar ratio of 1/1 in benzene [eqn. (3) and (5)], the reaction involves both coordination of the α-diimino group of **I** and migration of ancillary ligands [PPh_3/Cl^- in eqn. (3) or dmtc/$2Cl^-$ in eqn. (5)] between the Pd center of **I** and an M center of the allylic dimer, to yield the zwitterionic binuclear complexes **III** and the mononuclear products **IV** or **V**. The complex **IIIa'** is more conveniently prepared from reaction (5), because it forms too slowly in reaction (3). Accordingly, the reaction of the 1,2-bis(imino)propylpalladium(II) compound **Ie** with $[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ [eqn. (6)] readily gives the product **VIa'**, which could not be isolated in the previous attempts from a similar reaction involving $RN{=}CR_1{-}CMe{=}NR$ (R_1 = *trans*-$PdCl(PPh_3)_2$, R = C_6H_4OMe-*p*). Only a closely related complex $[Pt(\eta^3\text{-}C_3H_5)\{RN{=}CR_2{-}CH{=}NR\}]$ (R_2 = *cis*-$PdCl_2(PPh_3)$, R = C_6H_4OMe-*p*) was obtained from the reaction

TABLE 1. Analyses, conductivity and selected IR spectral data

Compound	M	R_1 or R_2	R	Analyses[a] (%) C	H	N	Cl	Molar conductivity[b] ($ohm^{-1}\,cm^2\,mol^{-1}$)	Infrared bands (cm^{-1})[c] ν(C=N)	ν(Pd–Cl)
$[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CR_1{=}NR)]ClO_4$										
IIa	Pd	$PdCl(PPh_3)_2$	C_6H_4OMe-*p*	56.1 (55.91)	4.3 (4.25)	2.5 (2.46)	6.3 (6.23)	89.3 [31.9]	1510sh	323m
IIa'	Pt	$PdCl(PPh_3)_2$	C_6H_4OMe-*p*	51.5 (51.87)	3.9 (3.94)	2.3 (2.28)	5.9 (5.78)	94.0 [28.0]	1510sh	331mw
IIb	Pd	$PdCl(PPh_3)_2$	Me	53.6 (53.94)	4.3 (4.24)	2.7 (2.68)	6.9 (6.78)	98.3 [26.7]	1557ms	291m
IId	Pd	$Pd(dmtc)(PPh_3)$	C_6H_4OMe-*p*	47.3 (47.49)	4.0 (4.09)	4.3 (4.37)	3.8 (3.69)	83.7 [33.7]	mk[d,e]	
$[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CR_2{=}NR)]$										
IIIa	Pd	$PdCl_2(PPh_3)$	C_6H_4OMe-*p*	51.4 (51.75)	4.0 (4.09)	3.5 (3.45)	8.8 (8.73)	44.7 [0.10]	1525ms	297ms, 267m
IIIa'	Pt	$PdCl_2(PPh_3)$	C_6H_4OMe-*p*	46.8 (46.65)	3.6 (3.69)	3.1 (3.11)	7.8 (7.87)	37.7 [0.19]	1512ms	298ms, 273m
IIIb	Pd	$PdCl_2(PPh_3)$	Me	48.1 (48.36)	4.0 (4.06)	3.9 (3.89)	9.8 (9.84)	37.1	1558ms	293ms, 272m
IIIb'	Pt	$PdCl_2(PPh_3)$	Me	42.9 (43.06)	3.5 (3.61)	3.5 (3.46)	8.9 (8.76)	35.6	1552ms	295ms, 277m
IIIc[f]	Pd	$PdCl_2(PPh_3)$	CMe_3	48.7 (48.50)	4.6 (4.51)	3.4 (3.48)	13.1 (13.21)	46.7	1540ms	292ms, 265m
$[M(\eta^3\text{-}2\text{-}MeC_3H_4)(RN{=}CR_2{-}CMe{=}NR)]$										
VIa'	Pt	$PdCl_2(PPh_3)$	C_6H_4OMe-*p*	48.0 (48.23)	3.9 (4.05)	2.8 (2.88)	7.4 (7.30)	37.5 [0.25]	mk[d]	298ms, 276m

[a] Calculated values in parentheses. [b] In 10^{-3} mol dm^{-3} MeOH solution at 25 °C; molar conductivities in square brackets refer to 10^{-3} mol dm^{-3} 1,2-dichloroethane solution at 25 °C. [c] As Nujol mulls. [d] Masked by the intense absorption of the C_6H_4OMe-*p* group at *c.* 1500 cm^{-1}. [e] In this compound, the dmtc ligand is characterized by a strong $\nu(C\overset{\cdots}{-}N)$ band at 1540 cm^{-1}, and by a medium-strong ν(Pd–S) band at 366 cm^{-1}. [f] This compound contains 1/2 CH_2Cl_2 molecule of crystallization.

$RN{=}CR_1{-}CH{=}NR/[PtCl(C_3H_5)]_4$ (1/0.5 molar ratio) [1b]. The analyses, conductivities, and selected IR data of **II** and **III** are listed in Table 1, while the ^1H and $^{31}P\{^1H\}$ NMR spectra are reported in Table 2.

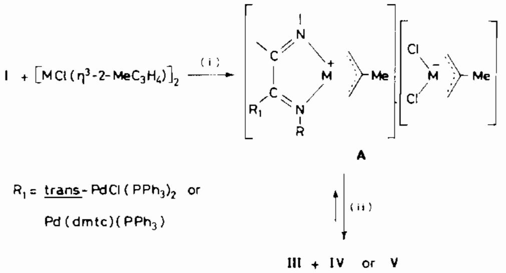
Complexes **II** are uni-univalent electrolytes in methanol and in 1,2-dichloroethane. Some electrical conductivity is observed also for **III** in methanol, probably due to partial ionic dissociation of the Pd–Cl bonds of the *cis*-$PdCl_2(PPh_3)$ unit. In 1,2-dichloroethane, however, complexes **III** are non-conducting monomers: for the most soluble compound **IIIb**, the experimental molecular weight (725) is very close to the calculated value of 720.2. The IR spectra of **II** show the typical bands of uncoordinated ClO_4^- anion [ν(Cl–O) at *c.* 1090 cm^{-1} and δ(Cl–O) at *c.* 624 cm^{-1}], and a ν(C=N) band of the coordinated imino group at lower frequencies (50–60 cm^{-1}) than in the free ligand (ν(C=N) = 1572 (**Ia**), 1606 (**Ib**), 1599 (**Ic**), 1574 (**Id**) cm^{-1}) [6a, 7]. Such a large shift is indicative of an appreciable $d \rightarrow \pi^*$ back-donation in the Pd–C_{imino} bond of **II**. For the related ligands py-2-CH=NR ($R = C_6H_4OMe$-*p*, Me), a smaller low-frequency shift of 10–15 cm^{-1} was actually observed upon chelation in the cationic complexes $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CH{=}NR)]^+$ [4]. The *cis*-$PdCl_2(PPh_3)$ unit of **III** is characterized by two ν(Pd–Cl) bands in the ranges 298–292 and 277–267 cm^{-1}, respectively [1].

In the ^1H NMR spectra of the platinum(II) derivatives, ^{195}Pt couplings are observed for resonances of the 2-pyridyl H^6 proton (34–35 Hz) and of the *N*-imino substituent R ($R = C_6H_4OMe$-*p*, 5.4–6 Hz for the *ortho* protons; R = Me, *c.* 35 Hz), which suggest a σ,σ-*N,N'* coordination mode for the α-diimino ligand, in line with previous findings for the pyridine-2-carbaldimine complexes $[M(\eta^3\text{-}2\text{-}MeC_3H_4)(py\text{-}2\text{-}CH{=}NR)]^+$ [4]. Upon chelation, the imino(2-pyridyl)methyl group undergoes a conformational change (E-*trans* → E-*cis*) which brings the 2-pyridyl H^3 proton close to the palladium atom of the *trans*-$PdCl(PPh_3)_2$ or the *cis*-$PdCl_2(PPh_3)$ unit, and causes a remarkable downfield shift for the H^3 resonance, due to the magnetic anisotropy of the d^8 metal center [6].

In general, the reactions of compounds **Ia**–**Id** and the nature of the resulting products closely parallel those of the related 1,2-bis(imino)alkylpalladium(II) derivatives [1]. However, substantial differences are observed in the rates and mechanism of ligand exchange.

Mechanism of Ligand Migration

The course of reactions (3), (5) and (6) can be monitored by ^1H and ^{31}P NMR spectra in $CDCl_3$ or by electronic spectra and conductivity measurements in 1,2-dichloroethane at different temperatures. The combined data indicate that a ionic intermediate **A** is formed almost immediately and quantitatively upon mixing of the reactants [step (i) of eqn. (7)].



As an example, for the systems **Ia**/$[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in 1,2-dichloroethane, the initial values of specific conductivity are 25.4×10^{-6} and 24.6×10^{-6} ohm^{-1} cm^{-1} for M = Pd and Pt, respectively, and for 10^{-3} mol dm^{-3} solutions in both reactants at 25 °C; the initial electronic spectra closely match those of the cationic complexes **IIa** and **IIa'** (for M = Pd); the ^1H NMR spectra in CD_2Cl_2 clearly indicate the presence of the anionic species $[MCl_2(\eta^3\text{-}2\text{-}MeC_3H_4)]^-$ (see Table 2 and refs. 4 and 14).

The final products **III** and **IV** or **V** are formed in the subsequent and slower step (ii) from ligand exchange between the cationic and anionic species of **A**, at different rates depending on the metal M, the ancillary ligands on the palladium center of R_1, and the imino nitrogen substituent R. In general, step (ii) gives an equilibrium mixture where the final products predominate. For R_1 = *trans*-$PdCl(PPh_3)_2$, the equilibrium is almost completely shifted towards **III** and **IV** in all cases, but for reaction **Ic**/$[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, which leads to an equilibrium mixture **A**/**IIIc'** of *c.* 1/4 (based on integration of the NMR spectra). For $R_1 = Pd(dmtc)(PPh_3)$, the equilibrium position depends on the solvent, the metal M, and the nature of the α-diimino moiety. The products **III** and **V** are formed in higher quantity in 1,2-dichloroethane, for M = Pt and for the 1,2-bis(imino)propyl group, as can be seen from the following equilibrium mixtures at 25 °C: **Id**/$[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, **A**/**IIIa** *c.* 1/9 in 1,2-dichloroethane, **A**/**IIIa** *c.* 2/3 in $CDCl_3$; **Id**/$[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, **A**/**IIIa'** *c.* 0.5/9.5 in $CDCl_3$; **Ie**/$[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, **A**/**VIa** *c.* 1/4 in $CDCl_3$.

In order to compare the reaction rates at least qualitatively, we have determined the reaction times for *c.* 95% completion (R_1 = *trans*-$PdCl(PPh_3)_2$) and *c.* 90% completion ($R_1 = Pd(dmtc)(PPh_3)$) from changes with time in the electronic or ^{31}P NMR spectra, and in electrical conductivities in 1,2-dichloroethane at 40 °C (Table 3). In these conditions, the equilibrium step (ii) is generally shifted towards the final products to an extent of *c.* 100% for R_1 = *trans*-$PdCl(PPh_3)_2$, and of *c.* 95% for $R_1 = Pd(dmtc)(PPh_3)$.

TABLE 2. Selected ^{1}H and ^{31}P NMR data[a]

Compound	2-Pyridyl protons[b]		N–R protons				Allyl protons[c]			^{31}P resonances
	H^3	H^6	AA′[d]	O–Me[d]	N–Me	N–CMe$_3$	H_{syn}	H_{anti}	C–Me	
IIa	8.91M	8.30M	7.02M	3.90S			3.70D 2.90D	2.98S 2.69S	2.04S	20.4S
IIa[e]	9.02M	8.19M	7.18M	3.89S			3.62S(br) 2.92S(br)	2.92S(br) 2.78S(br)	2.12S	
IIa[f]	9.04M	8.22M	7.19M	3.90S			3.35(vbr)	2.86S(br)	2.05S	
IIa′	8.81M	8.61M J(Pt–H) = 35.0	7.08M J(Pt–H) = 5.5	3.91S			3.50DD J(Pt–H) = 25.0	2.58D J(Pt–H) = 74.0	2.13S J(Pt–H) = 78.0	20.6S
							2.68DD J(Pt–H) = 28.0	2.25D J(Pt–H) = 76.0		
IIb	8.80M	8.24M			3.57S		3.64D 3.23D	2.83S 2.57S	2.01S	21.8S
IId	9.21M	8.60M	mk[g]	3.89S	3.34S[h] 3.24S[h]		3.75S, 3.16S, 3.03S, 2.83S 3.72S, 2.99S, 2.96(sh), 2.76S		2.14S[i] 1.97S[i]	28.8S[i] 28.7S[i]
IIIa	9.64M	8.37M	mk[g]	3.92S			3.57S, 3.52S, 2.97S, 2.93S 3.48S, 3.0(sh), 2.82S, 2.67S		2.07S[i] 1.97S[i]	27.7S[i] 27.5S[i]
IIIa′[j]	9.57M	8.70M J(Pt–H) = 35.0	mk[g]	3.93S			3.35DD J(Pt–H) = 26.0	2.55D J(Pt–H) = 74.0	2.18S J(Pt–H) = 77.0	27.9S J(Pt–P) = 22.0
							2.77DD J(Pt–H) = 28.0	2.35D J(Pt–H) = 77.0		
									2.06S[k] J(Pt–H) = 73.0	27.7S[k] J(Pt–P) = 10.0
IIIb	9.31M	8.22M			3.95S[i] 3.93S[i]		3.51[l] 3.38[l]	2.94S, 2.85S 2.81S, 2.67S	2.05S[i] 2.01S[i]	27.5S[i] 27.4S[i]
IIIb′[j]	9.24M	8.52M J(Pt–H) = 34.0			4.22S J(Pt–H) = 34.5		3.36DD J(Pt–H) = 24.0	2.43D J(Pt–H) = 72.5	2.14S J(Pt–H) = 74.0	27.3S
							3.25DD J(Pt–H) = 27.0	2.27D J(Pt–H) = 78.0		
					4.19S[k] J(Pt–H) = 35.0				2.16S[k] J(Pt–H) = 73.0	27.6S[k]

IIIc	10.04M	8.13M			1.71S^{i} 1.70S^{i}	3.75^{l} 3.47^{l}	3.08S, 3.05S 2.98S, 2.85S	2.13S^{i} 2.05S^{i}	22.7S^{i} 22.6(sh)^{i}
VIa′^{j}			7.51M^{m} J(Pt–H) ~ 6	3.92S 3.83S		2.80DD 2.67DD	2.38D 2.33D J(Pt–H) = 77.0	2.08S J(Pt–H) = 78.0	27.9S J(Pt–P) = 23.0
			7.67M^{m,k} J(Pt–H) ~ 6					1.93S^{k} J(Pt–H) = 76.0	27.6S^{k} J(Pt–P) = 11.5
Ia/[PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ (1/1 molar ratio)	8.77M	8.92M	6.99M	3.91S		3.5(vbr) 3.80S^{n}	2.8(sh) 2.81S^{n}	2.09S 2.05S^{n}	20.4S
Ia/[PtCl(η^3-2-MeC$_3$H$_4$)]$_2$ (1/1 molar ratio)	8.80M	8.71M J(Pt–H) = 35.0	7.05M J(Pt–H) = 5.5	3.91S		3.59DD J(Pt–H) = 26.0	2.59D	2.14S J(Pt–H) = 78.0	20.6S
						2.67DD J(Pt–H) = 26.0	2.24D J(Pt–H) = 76.0		
						3.30S^{o} J(Pt–H) = 36.5	1.66S^{o} J(Pt–H) = 79.0	2.01S^{o} J(Pt–H) = 76.0	

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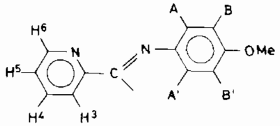
[a] Spectra recorded at 30 °C in CD$_2$Cl$_2$; δ(^{1}H) values in ppm from TMS as internal standard; δ(^{31}P) values in ppm from external 85% H$_3$PO$_4$, downfield shifts being taken as positive; coupling constants in Hz; S = singlet, D = doublet, DD = doublet of doublets, M = multiplet; satisfactory 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 H^4 proton resonates in the narrow range 7.8–8.1 ppm, whereas the H^5 signal is generally masked by the intense PPh$_3$ resonance; the *ortho* and *meta* protons of the C$_6$H$_4$PMe-*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$_3$H$_4$ ligands, with distinct signals for *syn* and *anti* protons; for palladium(II) compounds, a small *syn–syn* coupling of *c.* 2 Hz is generally observed; for platinum(II) derivatives, the allyl prpton resonances are complicated by coupling with the ^{195}Pt isotope and by small *syn–syn* and geminal *syn–anti* couplings of *c.* 2 Hz. [d] Signals of C$_6$H$_4$OMe-*p* N-substituent. [e] In CD$_3$CN at 30 °C. [f] In CD$_3$CN at 50 °C. [g] Masked by the intense phenyl proton resonances in the range 7.7–7.0 ppm. [h] Signals of dmtc ligand. [i] Two diastereoisomers are present. [j] The initial spectrum, recorded immediately after dissolution, shows only a diastereoisomer to be present, probably of type **D** (see text). [k] Signals of the second diastereoisomer, which forms slowly with time. [l] Unresolved multiplets due to overlapping signals and to *syn–syn* couplings. [m] *ortho* protons of the C=NC$_6$H$_4$OMe-*p* imino group at position 1 on the 1,2-bis(imino)propyl moiety; in complex **VIa′**, the δ(C–Me) signal of the chelated α-diimino ligand is observed as two singlets at 2.87 ppm (J(Pt–H) = 7.0) for the initially predominant diastereoisomer, and at 2.85 ppm (J(Pt–H) = 7.0) for the second one. [n] Signals of the [PdCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ anion. [o] Signals of the [PtCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ anion.

TABLE 3. Completion times for reactions I + $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (1/1 molar ratio)[a]

Compound	$[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$	
	M = Pd	M = Pt
R_1 = *trans*-$PdCl(PPh_3)_2$		
Ia	9 h	240 h[b]
Ib	0.8 h	1.2 h
Ic	0.5 h	
If[c]	0.9 h	72 h[b]
Ig[c]	2 h	
R_1 = Pd(dmtc)(PPh_3)		
Id	3 h	2 h
Ie	0.3 h	2 h

[a] Approximate values (±10%) for *c.* 95% completion (R_1 = *trans*-$PdCl(PPh_3)_2$) or *c.* 90% completion (R_1 = Pd(dmtc)(PPh_3)), in 1,2-dichloroethane at 40 °C. [b] For *c.* 90% completion. [c] 1,2-Bis(imino)propyl compounds $RN{=}CR_1{-}CMe{=}NR'$: $R = R' = C_6H_4OMe\text{-}p$ (**If**); $R = C_6H_{11}$, $R' = C_6H_4\text{-}OMe\text{-}p$ (**Ig**).

For R_1 = *trans*-$PdCl(PPh_3)_2$, the rates of reactions with py-2-CR_1=NR (**Ia**–**Ic**) are compared to those of the corresponding reactions with $RN{=}CR_1{-}CMe{=}NR'$ ($R = R' = C_6H_4OMe\text{-}p$ (**If**); $R = C_6H_{11}$, $R' = C_6H_4OMe\text{-}p$ (**Ig**)). For the latter compounds, the ligand migration rate is found to decrease considerably on going from $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ to $[PtCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in the reaction with **If**, and, to a lesser extent, on changing the N-substituent from $R = C_6H_4OMe\text{-}p$ (**If**) to $R = C_6H_{11}$ (**Ig**) in the reaction with $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$. A marked reduction in rate, relative to **If**, is also observed in the reactions of the imino(2-pyridyl)methyl complex **Ia**. These changes can be rationalized on the basis of the previously proposed mechanism involving a trinuclear transition state of type **B** (see 'Introduction') [3], and can be related to an increasing stabilization (towards Pd–N bond dissociation) of the α-diimino five-membered ring in the cationic species of **A**, on going from **If** to **Ig** and to **Ia**, and from M = Pd to M = Pt [4, 14].

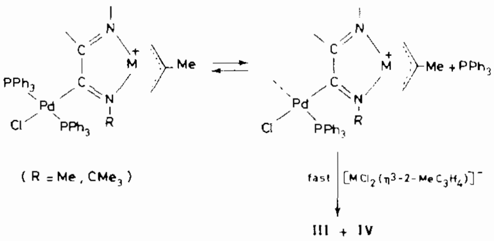
In contrast, when the $C_6H_4OMe\text{-}p$ N-substituent of **Ia** is replaced by an alkyl group (Me in **Ib**; CMe_3 in **Ic**), the reactivity is greatly enhanced and, furthermore, the reaction of **Ib** with $[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ proceeds at comparable rate for both M = Pd and Pt. To investigate such an unexpected behaviour, we have examined the reactions of **Ia**–**If** and of their derivatives **IIa**, **IIb** and $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(RN{=}CR_1{-}CMe{=}NR)]ClO_4$ (R_1 = *trans*-$PdCl(PPh_3)_2$, $R = C_6H_4OMe\text{-}p$ (**IIf**)) [1a] with an excess of sulphur, as to ascertain whether the *trans*-$PdCl(PPh_3)_2$ unit in these complexes has any tendency to release free triphenylphosphine (rapidly oxidized by S_8 to Ph_3PS) [15]. The ^{31}P NMR spectra in CD_2Cl_2 at 25 °C show that Ph_3PS is indeed formed in the reactions of **Ia**–**If** [eqn. (8)].

$$\mathbf{Ia}\text{–}\mathbf{If} \xrightarrow{S_8} Ph_3PS + \text{unidentified products} \qquad (8)$$

The $\delta(^{31}P)$ signals of the starting compounds progressively decrease and the Ph_3PS resonance at 43.0 ppm concomitantly increases, with the following reactivity trend (completion times in parentheses):

$$\begin{array}{ccccccc} \mathbf{Ic} & > & \mathbf{Ib} & \gg & \mathbf{Ia} & \sim & \mathbf{If} \\ (0.5\text{ h}) & & (1.2\text{ h}) & & (8\text{ h}) & & \end{array}$$

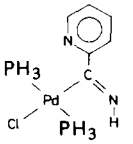
The rate of Ph_3PS formation is greatly reduced when the α-diimino group is *σ,σ-N,N'* chelated in the complexes **II**. For **IIa** and **IIf**, no trace of Ph_3PS is detected even after prolonged time both in CD_2Cl_2 at 25 °C and in 1,2-dichloroethane at 40 °C. For **IIb**, however, Ph_3PS is formed slowly in CD_2Cl_2 at 25 °C (6 h for completion), but more rapidly in 1,2-dichloroethane at 40 °C (*c.* 1.3 h, i.e. at comparable rate with that of ligand migration for the reactions **Ib**/$[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in the same experimental conditions). Since the most reasonable explanation for the release of free PPh_3 from **IIb** is a dissociation equilibrium involving the Pd–PPh_3 bond, we propose the following mechanism for the reactions of **IIb** and **IIc** [eqn. (9)].

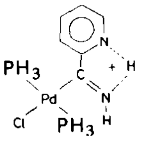


(9)

A fast PPh_3 dissociation from a cationic complex of type **II** ($R = CMe_3$, M = Pd) would also account for the failure to prepare this compound in reaction (2), starting from **Ic** (see 'Experimental'). The reactivity data with S_8 suggest that (a) mechanism (9) is not operating (or gives only a negligible contribution) in the reactions **Ia**/$[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ and **If**/$[MCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$; (b) the lability of the Pd–PPh_3 bond is greater in the uncoordinated α-diimino derivatives **I** than in their binuclear adducts **II**; (c) for the imino(2-pyridyl)methyl compounds **Ia**–**Ic**, the lability of the Pd–PPh_3 bond increases with increasing electron-donating properties of the N-substituent R in the order $CMe_3 > Me \gg C_6H_4\text{-}OMe\text{-}p$.

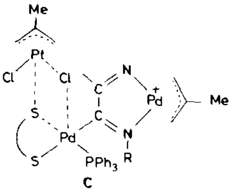
In accord with observation (b), theoretical calculations on the model compounds **VII** and **VIII** have shown an increased overlap population of the Pd–P bond upon protonation of the α-diimino group, as a consequence of an increased ratio of π/σ contributions to the Pd–C_{imino} bond [16].


VII


VIII

Changes in the Pd–C bond π/σ ratio (and consequently in Pd–P bond overlap population) are probably responsible for the observed reactivity of imino(2-pyridyl)methyl derivatives **Ia**–**Ic**, to such extent that, when the π/σ ratio is strongly depressed (as in **Ib** and **Ic** where the α-diimino moieties have low π-accepting properties), a different ligand migration mechanism may become operative. In this context, the π-accepting abilities of α-diimino ligands were reported to decrease in the order RN=CH–CH=NR > py-2-CH=NR (for the same substituent R), and R = aryl > alkyl (for the same ligand) [17].

As can be seen in Table 3, compounds **Id** and **Ie**, with R_1 = Pd(dmtc)(PPh$_3$), exhibit a rate dependence on the metal M and on the α-diimino group which is different from that of the analogous compounds **Ia** and **If**, with R_1 = *trans*-PdCl(PPh$_3$)$_2$. In the system **Id**/[MCl(η^3-2-MeC$_3$H$_4$)]$_2$, ligand migration occurs more rapidly for M = Pt than for M = Pd, while it proceeds at about the same rate in the reactions of [PtCl(η^3-2-MeC$_3$H$_4$)]$_2$ with either **Id** or **Ie**. Furthermore, the latter reactions are much faster than the corresponding ones with **Ia** and **If**. These findings clearly indicate a different reaction pathway to be involved in the systems **Id** or **Ie**/[PtCl(η^3-2-MeC$_3$H$_4$)]$_2$, and we suggest a mechanism in which ligand exchange takes place through direct interaction of the anion [PtCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$ with the Pd(dmtc)(PPh$_3$) group of the cationic species of **A**, probably in a transition state of type **C**.


C

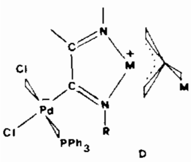
As shown by models, such interaction hardly occurs when R_1 = *trans*-PdCl(PPh$_3$)$_2$ for steric crowding around the Pd center, due to the bulky PPh$_3$ ligands and the close proximity to the metal of C- and N-imino substituents (above and below the coordination plane).

A more detailed kinetic investigation is obviously required to confirm this mechanism and to see if it takes place also in the reactions of [PdCl(η^3-2-MeC$_3$H$_4$)]$_2$ with **Id** and **Ie**.

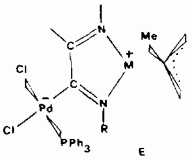
Solution Behaviour of the Binuclear Complexes

In contrast to the fluxional behaviour of [M(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)]ClO$_4$, which exhibits a fast *syn–syn, anti–anti* exchange of the allylic protons at ambient temperature [4], the binuclear complexes **IIa**, **IIa′** and **IIb** do not undergo such a dynamic process at an appreciable rate (on the NMR time scale) under comparable conditions. For **IIa**, the *syn* and *anti* proton resonances coalesce into broad signals at 3.35 and 2.86 ppm, respectively, only when the compound is dissolved in CD$_3$CN and the temperature is raised to 50 °C (see Table 2). The increased activation energy may be due to both steric and electronic factors, such as the bulkiness of the *trans*-PdCl(PPh$_3$)$_2$ unit (which prevents the attack at the M(η^3-2-MeC$_3$H$_4$) metal center by incoming ligands) and the higher σ donor ability of the α-diimino group (which increases the stability of the five-membered ring and reduces the net positive charge on the metal M). Theoretical calculations on the model compounds py-2-CH=NH and py-2-CR$_1$=NH (R_1 = *trans*-PdCl(PH$_3$)$_2$) showed an increased electron density on both pyridine and imino nitrogen atoms when the imino hydrogen is replaced by the R_1 group [16]. Steric factors seem to play a minor role since no significant increase in *syn–syn, anti–anti* exchange rate is observed on going to complexes **IId** and **III**, with the less sterically hindered Pd(dmtc)(PPh$_3$) and *cis*-PdCl$_2$(PPh$_3$) units, respectively. On the other hand, when the perchlorate anion of **IIa** is replaced by the more coordinating anion [PdCl$_2$(η^3-2-MeC$_3$H$_4$)]$^-$, as in the intermediate **A** initially formed in the reaction **Ia**/[PdCl(η^3-2-MeC$_3$H$_4$)]$_2$, a fast *syn–syn, anti–anti* and a slow *syn–anti* proton exchange take place in the cationic species (see Table 2). The simultaneous presence of the latter process is demonstrated by saturation transfer experiments, the intensity of the *syn* protons resonance at 3.5 ppm being considerably enhanced upon irradiation of the *anti* protons signal at 2.8 ppm in the difference spectrum. However, the cation–anion interaction in **A** does not involve scrambling of the Pd(η^3-2-MeC$_3$H$_4$) group between the two ionic species, in contrast to what observed for the compound [Pd(η^3-2-MeC$_3$H$_4$)(py-2-CH=NR)][PdCl$_2$(η^3-2-MeC$_3$H$_4$)] (R = C$_6$H$_4$-OMe-*p*) [4].

The ^{1}H and ^{31}P NMR spectra of **IId**, **III** and **VI** indicate the presence of two diastereoisomers in slow interconversion (on the NMR time scale) at 30 °C. For **III** and **VI**, the diastereoisomers are of type **D** and **E**, each one with an enantiomeric form [1a]. The interconversion rate depends on the metal M in the order Pd > Pt. In the spectra of platinum(II) derivatives **IIIa′**, **IIIb′** and **VIa′**, only a diastereoisomer is initially observed, the second one being slowly formed with time, until an equilibrium mixture of *c.* 1/1 molar ratio is eventually obtained (after *c.* 24 h at room temperature). Similar spectral changes occur for the palladium(II) analogues **IIIa**, **IIIb** and **VIa**, but at much higher rate. In this case, a **D**/**E** equilibrium mixture of *c.* 1/1 molar ratio is obtained after *c.* 1 h from dissolution.



D



E

On the basis of previous studies concerning the X-ray structural analysis of **VIa** [1a] and the solution behaviour of the cationic complexes [M(η^3-2-Me-C_3H_4)(py-2-CH=NR)]$^+$ [4], the above results can be rationalized in terms of (a) a single structure being assumed by the zwitterionic complexes in the solid state (probably of type **D**, as was found for **VIa**), and (b) a dynamic process of the M(η^3-2-MeC_3H_4) group being involved in the **D** $\rightleftarrows$ **E** interconversion (rearrangement at different rates (M = Pd > Pt) of stereochemically non-rigid five-coordinate intermediates, formed by association of the positively charged metal center M with solvent and/or Cl^- anions, dissociated in trace amount from the *cis*-$PdCl_2(PPh_3)$ unit).

Acknowledgement

Financial support from Ministero della Pubblica Istruzione (Research Fund 40%) is gratefully acknowledged.

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