Insertion of Isocyanides into the Palladium–Carbon Bond of C^2-Palladated Heterocycles. Synthesis of *trans*-[PdCl{C(R_N)=NR}(PPh_3)$_2$] Complexes (R_N = 2-Pyridyl, 2-Pyrazyl; R = Alkyl or Aryl Group)

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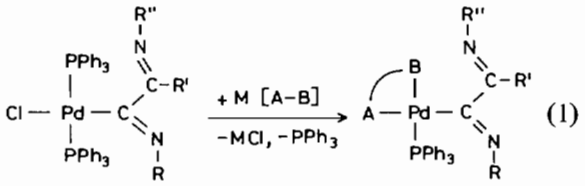
Abstract

The title complexes *trans*-[PdCl{C(R_N)=NR}(PPh_3)$_2$] (R_N = 2-pyridyl (2-py), R = *p*-C_6H_4OMe, Me; R_N = 2-pyrazyl (2-pyz), R = *p*-C_6H_4OMe) can be prepared by reaction of the N-protonated compounds, *cis*-[$PdCl_2$(R_NH)(PPh_3)] (R_NH = 2-pyridylium (2-pyH) or 2-pyrazylium (2-pyzH) group), with PPh_3, followed by addition of the isocyanide CNR and deprotonation with triethylamine, in a molar ratio Pd/PPh_3/CNR/NEt_3 of 1/1/1/1.1. The reaction sequence involves the successive formation of the cationic intermediates *trans*-[PdCl(R_NH)(PPh_3)$_2$]$^+$, *trans*-[Pd(R_NH)(CNR)(PPh_3)$_2$]$^{2+}$ and *trans*-[Pd(R_N)(CNR)(PPh_3)$_2$]$^+$, which were isolated and characterized as perchlorate salts for R_N = 2-pyridyl. In the final step the coordinated isocyanide of *trans*-[Pd(R_N)(CNR)(PPh_3)$_2$]$^+$ undergoes migratory insertion into the Pd–R_N σ bond, promoted by the chloride ions progressively displaced by the entering neutral ligands from *cis*-[$PdCl_2$(R_NH)(PPh_3)]. The resulting products were characterized by conventional spectroscopic techniques and, for R_N = 2-pyridyl and R = *p*-C_6H_4OMe, also by ligand substitution reaction at the palladium center and by protonation and coordination of the *p*-methoxyphenylimino(2-pyridyl)methyl group with strong mineral acids ($HClO_4$, HCl) and $ZnCl_2$, respectively.

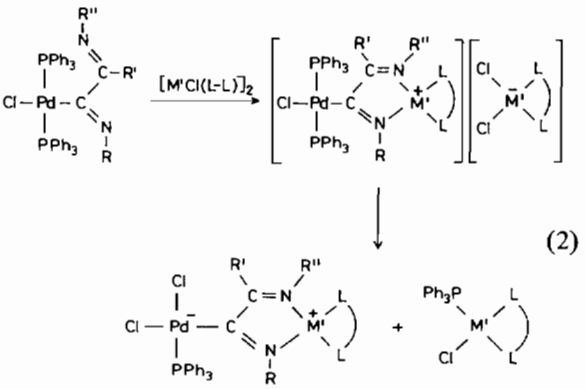
Introduction

In previous papers we have shown that due to the lability of the mutually *trans* PPh_3 ligands, the 1,2-bis(imino)alkyl derivatives of the type *trans*-[PdCl{C(=NR)CR′=NR″}(PPh_3)$_2$] (R = *p*-C_6H_4OMe; R′ = H, Me, Ph; R″ = *p*-C_6H_4OMe, Me) are versatile substrates either for substitution reactions at the palladium center (*e.g.*, with bidentate anionic ligands [1]) or for reactions involving exchange of ancillary ligands between different metal centers [2]:



(1)

(M^+ = Na^+, Tl^+; A–B$^-$ = dimethyldithiocarbamate, 2,4-pentanedionate, N-methylsalicylaldiminate)



(2)

(M′ = Rh, L–L = η^4-1,5-cyclooctadiene; M′ = Pd, Pt, L–L = η^3-allyl)

Because of our interest in the chemistry of such imino-carbon palladated α-diimino compounds with a *trans*-PdCl(PPh_3)$_2$ unit, we recently tried to prepare

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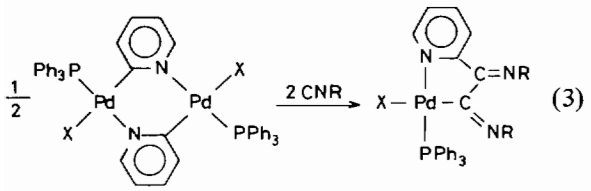
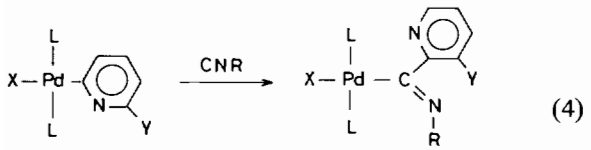
complexes of the type *trans*-[PdX{C(2-py)=NR}-$(PPh_3)_2$] (X = Cl, Br; 2-py = 2-pyridyl; R = alkyl or aryl group), containing an imino(2-pyridyl)methyl group, via migratory insertion of an isocyanide molecule into the Pd–C σ bond of binuclear derivatives $[PdX(\mu\text{-}2\text{-py})(PPh_3)]_2$. The reaction, however, yields a 'double' insertion product, as shown in eqn. (3), even when a Pd/CNR molar ratio of 1/1 is used and in the presence of an excess of free triphenylphosphine [3]:



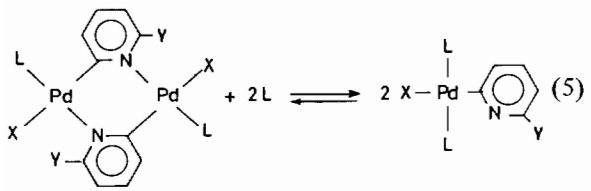
(3)



(4)

(L = $PMePh_2$, Y = H; L = PPh_3, Y = Cl)

The 'mono' insertion products (eqn. (4)) are obtained only when the reaction is carried out on mononuclear compounds with terminal 2-pyridyl ligands [3, 4], which can be isolated from reaction 5:



(5)

since the equilibrium shifts considerably to the right upon increasing the coordinating ability of L (*e.g.*, with the more basic $PMePh_2$ phosphine) or, for L = PPh_3, upon reducing the ligating properties of the pyridine nitrogen with a 6-chloro substituent (Y = Cl), whereas it is completely in favour of the binuclear species for Y = H and L = PPh_3 [5].

The desired imino(2-pyridyl)methylpalladium(II) complexes with a *trans* PPh_3–Pd–PPh_3 arrangement can be conveniently prepared by a new synthetic route involving the formation of a *trans*-$[Pd(2\text{-}pyH)(CNR)(PPh_3)_2]^{2+}$ species as a key intermediate (2-pyH = 1-H-2-pyridylium group). This method can also be extended to related palladium substrates with a C^2 bonded heterocyclic system, such as the 2-pyrazyl group.

Experimental

The complex *cis*-$[PdCl_2(2\text{-}pyH)(PPh_3)]$ (**Ia**) was prepared by a published method [6], which was followed also for the preparation of the analogues *cis*-$[PdCl_2(2\text{-}pyzH)(PPh_3)]$ (**Ic**) and *cis*-$[PdCl_2(2\text{-}pymH)(PPh_3)]$ (**Id**), containing an N-protonated 2-pyrazylium and 2-pyrimidylium ligand, respectively [7]. The isocyanides $CNC_6H_4OMe\text{-}p$ and CNMe were prepared by literature procedures [8, 9]. The preparation and characterization of the 2-(iminomethyl)-pyridines, 2-(RN=CH)–C_5H_4N (R = $p\text{-}C_6H_4OMe$, Me), and their $ZnCl_2$ adducts will be reported in a forthcoming paper [10]. All other chemicals and solvents were reagent grade, and were used without further purification. All reactions were carried out at room temperature, unless otherwise stated. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparation of trans-[PdCl(2-pyH)$(PPh_3)_2$]ClO_4 (IIa)

The complex *cis*-$[PdCl_2(2\text{-}pyH)(PPh_3)]$ (0.52 g, 1 mmol), suspended in CH_2Cl_2 (30 ml), was treated with PPh_3 (0.265 g, 1 mmol). The mixture was stirred until complete dissolution (*ca.* 30 min), then a methanolic solution of $NaClO_4 \cdot H_2O$ (0.28 g, 2 mmol in 5 ml of MeOH) was added. After 5 min the solvents were evaporated to dryness and the solid residue was extracted with CH_2Cl_2 in the presence of charcoal. After filtration of the extract and concentration, the white product **IIa** was precipitated by dropwise addition of Et_2O. (Yield, based on the theoretical amount: 0.70 g, 83%).

The analogous derivatives, *trans*-$[PdCl(2\text{-}pyzH)(PPh_3)_2]ClO_4$ (**IIc**) and *trans*-$[PdCl(2\text{-}pymH)(PPh_3)_2]ClO_4$ (**IId**), were obtained by similar methods [7].

Preparation of trans-[Pd(2-pyH)(CNR)$(PPh_3)_2$]-$(ClO_4)_2$ (R = p-C_6H_4OMe, IIIa; R = Me, IIIb)

The complex *cis*-$[PdCl_2(2\text{-}pyH)(PPh_3)]$ (0.52 g, 1 mmol), suspended in CH_2Cl_2 (30 ml) was treated with PPh_3 (0.265 g, 1 mmol) under stirring. When dissolution was complete, $NaClO_4 \cdot H_2O$ (0.56 g, 4 mmol in 10 ml of MeOH) and the isocyanide CNR (1 mmol in 5 ml of CH_2Cl_2) were successively added. The reaction mixture was worked up as described above for the preparation of **IIa** to give the crude product, which was purified by reprecipitation from a CH_2Cl_2/Et_2O mixture (Yield: 76% **IIIa**; 82% **IIIb**).

The complexes *trans*-$[Pd(2\text{-}pyzH)(CNC_6H_4OMe\text{-}p)(PPh_3)_2](ClO_4)_2$ (**IIIc**) and *trans*-$[Pd(2\text{-}pymH)(CNC_6H_4OMe\text{-}p)(PPh_3)_2](ClO_4)_2$ (**IIId**) were prepared by the same procedure from the parent compounds **Ic** and **Id**, respectively (Yield: 78% **IIIc**, $\nu(C{\equiv}N)$ 2215 cm^{-1}; 84% **IIId**, $\nu(C{\equiv}N)$ 2210 cm^{-1}).

Preparation of trans-[Pd(2-py)$(CNC_6H_4OMe\text{-}p)$-$(PPh_3)_2$]ClO_4 (IVa)

The complex **IIIa** (1.04 g, 1 mmol), dissolved in 50 ml of CH_2Cl_2 was deprotonated with NEt_3 (0.11 g, 1.1 mmol). The solution was quickly taken to dryness,

as the product **IVa** tends to decompose in CH_2Cl_2. The oily residue was stirred with 50 ml of 0.1 M aqueous NaOH until a yellowish solid was obtained, which was filtered off, washed 3–4 times with water and dried *in vacuo*. Two successive precipitations from CH_2Cl_2/Et_2O gave an analytically pure sample of **IVa** (0.63 g, 67%).

Preparation of Complexes V

a) A stirred suspension of *cis*-[$PdCl_2$(2-pyH)(PPh_3)] (1.04 g, 2 mmol) in CH_2Cl_2 (50 ml) was treated with PPh_3 (0.53 g, 2 mmol) until complete dissolution. The isocyanide CNC_6H_4OMe-*p* (0.27 g, 2 mmol, in 5 ml of CH_2Cl_2) was then added to the clear solution. The IR spectrum of the reaction mixture showed an intense $\nu(C\vdots\equiv N)$ band of the coordinated isocyanide at 2200 cm^{-1}, typical of the cationic species *trans*-[Pd(2-pyH)(CNC_6H_4OMe-*p*)(PPh_3)$_2$]$^{2+}$, and a weak $\nu(C\vdots\equiv N)$ band of the free isocyanide at 2125 cm^{-1}. Upon addition of NEt_3 (0.22 g, 2.2 mmol), the $\nu(C\vdots\equiv N)$ of the coordinated isocyanide shifts to 2185 cm^{-1}, indicating the presence of the deprotonated intermediate *trans*-[Pd(2-py)(CNC_6H_4OMe-*p*)(PPh_3)$_2$]$^+$, and rapidly disappears as a consequence of the migratory insertion which yields the final product **Va** (*ca.* 15 min).

After deprotonation, the orange solution was set aside for 1 h. The solvent was evaporated to dryness and the yellow-orange solid was stirred with 90 ml of 0.1 M aqueous NaOH, filtered off, washed 3–4 times with water and dried *in vacuo*. It was redissolved in a C_6H_6/CH_2Cl_2 mixture (1/1, v/v) and treated with charcoal. After filtration the solution was concentrated to small volume and diluted with Et_2O to give the complex **Va** as a yellow powder, which was further purified by reprecipitation from CH_2Cl_2/Et_2O (1.3 g, 72%). This compound contains $1/3CH_2Cl_2$ molecule of crystallization, as shown by elemental analysis (Found: C, 65.1; H, 4.6; N, 3.1; Cl, 6.5. Calcd. for $C_{49}H_{41}ClN_2OP_2Pd \cdot 1/3CH_2Cl_2$: C, 65.40; H, 4.64; N, 3.09; Cl, 6.52), by ^1H NMR spectra in $CDCl_3$ and by GLC experiments. The crystallization solvent is lost when a solution of **Va**·$1/3CH_2Cl_2$ in CH_2Cl_2/MeOH (3/1, v/v) is concentrated to small volume. The evaporation of the more volatile CH_2Cl_2 solvent brings about the almost quantitative precipitation of the analytically pure product **Va** from methanol. This complex is a monomer in 1,2-dichloroethane (Mol. weight found, 881; calcd., 877.6).

b) The preparation of *trans*-[PdCl{C(2-py)=NMe}(PPh_3)$_2$] (**Vb**) was carried out by the same method as described above for **Va**, using CNMe instead of CNC_6H_4OMe-*p*. Upon deprotonation, the $\nu(C\vdots\equiv N)$ band shifts from 2245 cm^{-1} for *trans*-[Pd(2-pyH)(CNMe)(PPh_3)$_2$]$^{2+}$ to 2228 cm^{-1} for *trans*-[Pd(2-py)(CNMe)(PPh_3)$_2$]$^+$. The insertion step takes a longer time to be complete (*ca.* 1 h) (Yield 62%).

c) A similar procedure was followed also for the preparation of *trans*-[PdCl{C(2-pyz)=NC_6H_4OMe-*p*}(PPh_3)$_2$] (**Vc**) from the parent compound **Ic**, with a 68% yield. In this case, the insertion step was complete in *ca.* 30 min, and the crude product recovered from the treatment with aqueous NaOH was dissolved in a C_6H_6/CH_2Cl_2 mixture (1/4, v/v) because of the lower solubility of **Vc** in benzene.

Ligand Substitution Reactions on Va

a) Preparation of [Pd(dmtc){C(2-py)=NC_6H_4OMe-p}(PPh_3)] (VI)

The complex **Va** (0.44 g, 0.5 mmol) in 40 ml of CH_2Cl_2 was treated with sodium dimethyldithiocarbamate, Na[dmtc]·$2H_2O$ (0.11 g, 0.6 mmol), dissolved in 10 ml of MeOH. After stirring for 15 min, the mixture was taken to dryness and the solid residue was extracted with benzene. Addition of charcoal and filtration gave a clear solution, which was concentrated to small volume and slowly diluted with Et_2O for precipitation of **VI** as a yellow microcrystalline solid. The product was purified by reprecipitation from the same solvent mixture (0.26 g, 74%).

b) Preparation of [PdCl{C(2-py)=NC_6H_4OMe-p}(dppe)] (VII)

Complex **Va** (0.44 g, 0.5 mmol) was dissolved in CH_2Cl_2 (50 ml) and treated with 1,2-bis(diphenylphosphino)ethane (0.24 g, 0.6 mmol). After 4 h, the solution was treated with charcoal, filtered, and concentrated to small volume. Dropwise addition of Et_2O gave the yellow product **VII** which was purified by reprecipitation from the same solvents (0.32 g, 85%).

Protonation and Coordination Reactions

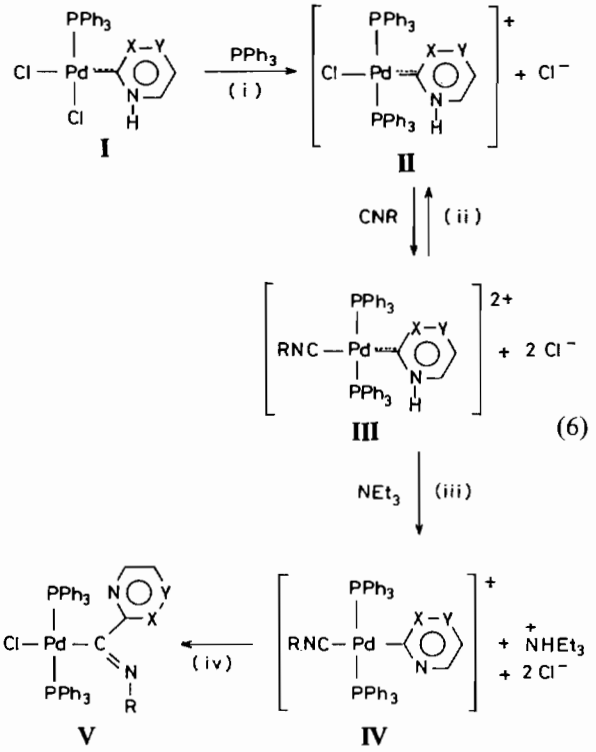
The reaction of **Va** with $HClO_4$ and those of **Va** and **Vc** with $ZnCl_2$ were carried out in the same way as earlier reported for *trans*-[PdCl{C(=NR)CMe=NR}(PPh_3)$_2$] (R = *p*-C_6H_4OMe) [11] (Yield: 63% [(**Va**)H]ClO_4; 91% [$ZnCl_2$(**Va**)]; 85% [$ZnCl_2$(**Vc**)]). The adduct [$ZnCl_2$(**Va**)] is a monomer in 1,2-dichloroethane solution (Mol. weight found, 1060; calcd., 1013.9).

Physical Measurements

Molecular weights were determined in 1,2-dichloroethane at 37 °C with a Knauer osmometer. The conductivity measurements were carried out with a Philips PR 9500 bridge at 20 °C. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian FT80A spectrometer operating at 79.542 and 32.203 MHz, respectively. Infrared spectra were recorded with a Perkin-Elmer 983G instrument, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}.

Results and Discussion

The imino(2-pyridyl)methyl complexes **Va** and **Vb**, and the imino(2-pyrazyl)methyl analogue **Vc** are prepared in satisfactory yields by the reaction sequence reported in Scheme 1.



Ia–Va: X = Y = CH; R = *p*-C_6H_4OMe
IIIb–Vb: X = Y = CH; R = Me
Ic–Vc: X = CH, Y = N; R = *p*-C_6H_4OMe
Id–IVd: X = N, Y = CH; R = *p*-C_6H_4OMe

Scheme 1.

The reactions (i) and (ii) involve the successive formation of the cationic complexes **II** and **III**, which can be isolated as perchlorate salts (see Table I and II, and experimental). As shown by IR spectra in solution, the equilibrium (ii) is almost completely shifted towards the formation of **III** for 2-pyH and 2-pyzH derivatives, whereas for the 2-pymH system, a substantial amount of free isocyanide is present in the reaction mixture. The deprotonation step (iii) yields the cationic species **IV**, which undergoes the subsequent insertion reaction (iv) in the presence of the chloride ions previously displaced from the starting compound **I**. The essential role of Cl^- ions in promoting reaction (iv) is shown by deprotonation of the perchlorate salts **[III]** $(ClO_4)_2$ in the presence of variable amounts of $[AsPh_4]Cl$. The insertion rate, monitored by IR spectroscopy, decreases with decreasing Cl^- concentration to the extent that in the absence of Cl^- the insertion (if any) proceeds very slowly, probably because of the unfavourable steric orientation of the reacting centers (*trans* configuration of the deprotonated product **IV**). In the latter case, a slow decomposition of **IV** is observed, which however does not prevent the isolation of an analytically pure sample of the 2-pyridyl derivative **[IVa]** ClO_4. The insertion rate is also markedly affected by the isocyanide substituent R (*p*-C_6H_4OMe > Me) and by the σ-bonded heterocyclic ligand (2-py > 2-pyz ≫ 2-pym). For the 2-pyrimidyl intermediate **IVd**, the slow insertion step (iv) is accompanied by extensive decomposition of **IVd** itself, so that a mixture of at least three different products is eventually obtained, two of which are identified as $[PdCl(\mu\text{-}2\text{-pym})(PPh_3)]_2$ [7] and the expected compound of type **V**, *trans*-$[PdCl\{C(2\text{-pym})=NC_6H_4OMe\text{-}p\}(PPh_3)_2]$ (ν(Pd–Cl) 293 cm^{-1}; ν(C=N) 1560 cm^{-1}; δ(OMe) 3.83 ppm; $\delta(^{31}P)$ 21.0 ppm).

The influence of halide ions on the migratory insertion of isocyanides into the metal–carbon bond, when cationic intermediates are involved, and the higher reactivity of aryl isocyanides have been already recognised [12, 13]. The observed reactivity trend for the different C^2-bonded heterocycles can be interpreted in terms of a decreased nucleophilic character of the C^2 carbon atom of the migrating ligand on going from the 2-py to the 2-pym system.

The formation of the bis-cationic intermediate **III** appears to be the key step in the preparation of **V**, since deprotonation of **II** regenerates the binuclear complexes with C,N-bridging heterocyclic ligands of the type $[PdCl(\mu\text{-}2\text{-py})(PPh_3)]_2$, which would react with the isocyanide to give a 'double' insertion product, as shown in eqn. (3), independently of the Pd/CNR molar ratio.

The cationic compounds of Table I are characterized by molar conductivity measurements, by IR spectra (which show the presence of typical ClO_4^- bands and of N–H stretching vibrations for the N-protonated species), and by ^1H and ^{31}P NMR spectra. The *trans* PPh_3–Pd–PPh_3 geometry is retained from complex **II** to **V**, as suggested by the occurrence of only one singlet in the ^{31}P spectrum of each compound.

In the IR spectra of **V**, the ν(Pd–Cl) bands are detected in the range 296–286 cm^{-1}, indicative of a rather high *trans* influence of the σ-bonded imino moiety, in agreement with previously reported data for 1,2-bis(imino)alkylpalladium(II) compounds [2b, 11]. The ν(C=N) vibration of the imino group can be unambiguously attributed to a strong absorption at 1606 cm^{-1} only for **Vb** (R = Me), whereas for **Va** and **Vc** the assignment of this band is complicated by the presence of strong ν(C····C) and ν(C····N) absorptions of the C_6H_4OMe and of the heterocyclic groups in the range 1600–1500 cm^{-1}. In **Va** and **Vb**, however, the ν(C=N) of the palladated imino group appears at markedly lower frequency (*ca.* 40–50

TABLE I. Analitycal and Physical Data. Characteristic IR Band (cm^{-1}).

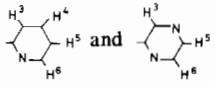
Compound	C[a]	H	N	Cl	Molar conductivity[b] (ohm^{-1} cm^2 mol^{-1})	ν(N–H)	ν(Cl–O)	δ(Cl–O)	ν(C=N)	ν(Pd–Cl)	Other Bands
trans-[PdCl(2-pyH)(PPh$_3$)$_2$]ClO$_4$ ([IIa] ClO$_4$)	58.1 (58.28)	4.2 (4.18)	1.7 (1.66)	8.5 (8.39)	76.8	3210 w, br; 3180 sh, 3130 w	1110 vs, 1095 vs, 1055 s	627 s, 615 s		319 m	
trans-[Pd(2-pyH)(CNC$_6$H$_4$OMe-*p*)(PPh$_3$)$_2$](ClO$_4$)$_2$ ([IIIa] (ClO$_4$)$_2$)	56.4 (56.47)	4.1 (4.06)	2.7 (2.69)	6.9 (6.80)	135.2	3230 w, br; 3190 sh, 3140 w	1090 vs	623 s			2208 ms [ν(C≡N)][c]
trans-[Pd(2-py)(CNC$_6$H$_4$OMe-*p*)(PPh$_3$)$_2$](ClO$_4$) ([IVa] ClO$_4$)	61.9 (62.50)	4.2 (4.39)	3.0 (2.97)	3.9 (3.76)	91.9		1095 vs	622 s			2185 ms [ν(C≡N)][c]
trans-[PdCl{C(2-py) = NC$_6$H$_4$OMe-*p*}(PPh$_3$)$_2$] (Va)	66.8 (67.05)	4.7 (4.71)	3.2 (3.19)	4.2 (4.04)					1572 s[d]	296 m	
trans-[Pd(2-pyH)(CNMe)(PPh$_3$)$_2$](ClO$_4$)$_2$ ([IIIb] (ClO$_4$)$_2$)	54.2 (54.36)	4.0 (4.03)	2.9 (2.95)	7.4 (7.46)	135.1	3230 w, br; 3195 sh, 3145 w	1095 vs	623 s			2246 ms [ν(C≡N)][c]
trans-[PdCl{C(2-py) = NMe}(PPh$_3$)$_2$] (Vb)	65.2 (65.74)	4.6 (4.75)	3.7 (3.57)	4.7 (4.51)					1606 s	286 m	
trans-[PdCl{C(2-pyz) = NC$_6$H$_4$OMe-*p*}(PPh$_3$)$_2$] (Vc)	65.9 (65.61)	4.6 (4.59)	4.8 (4.78)	4.1 (4.03)					1567 s[d]	288 m	
[Pd(dmtc){C(2-py) = NC$_6$H$_4$OMe-*p*}(PPh$_3$)$_2$] (VI)	58.6 (58.32)	4.7 (4.61)	5.9 (6.00)						1574 s[d]		1527 s [ν(C···N)][e] 359 m [ν(Pd–S)]
[PdCl{C(2-py) = NC$_6$H$_4$OMe-*p*}(dppe)] (VII)	62.1 (62.33)	4.8 (4.69)	3.6 (3.73)	4.9 (4.72)					1574 s[d]	293 m	
[(Va) H]ClO$_4$	60.4 (60.17)	4.3 (4.33)	2.8 (2.86)	7.3 (7.25)	72.8[g]	3240 sh, 3195 w, 3135 w	1118 s, 1093 vs, 1070 s	624 s, 615 s	n.o.[f]	316 m	
[ZnCl$_2$(Va)]	57.9 (58.04)	4.1 (4.08)	2.7 (2.76)	10.2 (10.49)					1518 m[d]	n.o.[h]	334 ms; 314 ms [ν(Zn–Cl)]
[ZnCl$_2$(Vc)]	56.4 (56.80)	3.9 (3.97)	4.0 (4.14)	10.6 (10.48)					1510 sh[d]	n.o.[h]	334 ms; 314 ms [ν(Zn–Cl)]

[a]Calcd. values in parenthesis. [b]In methanol solution 10^{-3} M at 20 °C. [c]Vibration of the coordinated isocyanide. [d]Vibration of the imino group (Tentative assignment, see text). [e]Vibration of the dmtc ligand. [f]Not observed, probably masked by the intense absorption of the *p*-C$_6$H$_4$OMe group at 1513 cm^{-1}. [g]In nitromethane solution 10^{-3} M at 20 °C. [h]Masked by the ν(ZnCl) bands.

TABLE II. ^{1}H and $^{31}P\{^{1}H\}$ NMR Data[a].

Compound	Phenyl Protons		Heterocyclic Ring Protons					$O-CH_3$	$N-CH_3$	$\delta(^{31}P)$	Solvent
	$P-C_6H_5$	$-C_6H_4-$	H^3	H^4	H^5	H^6	N–H				
[IIa] ClO_4	7.9–7.2 M		m[b]	m	7.1–6.8 M	m	n.o.			22.7 S	$CDCl_3$
[IIIa] $(ClO_4)_2$	7.8–7.1 M	6.7–6.5 M[c] 6.2–6.0 M[d]	m	m	7.0–6.8 M	7.9–7.7 M	12.8 M, br	3.74 S		20.5 S	$CDCl_3$
[IVa] ClO_4	7.7–7.1 M	6.7–6.5 M[c] 6.3–6.1 M[d]	m	m	6.9–6.7 M	7.7–7.5 M		3.73 S		21.7 S	$CDCl_3$
Va	7.7–7.1 M	m 6.9–6.7 M[d]	m	7.1–6.9 M[e]	7.1–6.9 M[e]	8.5–8.4 M		3.89 S		20.8 S	CD_2Cl_2
[IIIb] $(ClO_4)_2$	7.8–7.1 M		m	m	7.0–6.8 M	7.9–7.7 M	11.2 M, br		2.56 S	20.5 S	$CDCl_3$
Vb	7.9–7.1 M		m	7.1–6.9 M	6.8–6.6 M	8.6–8.4 M			3.51 S	20.9 S	$CDCl_3$
Vc	7.7–7.0 M	m 6.8–6.6 M[d]	7.96 D $J(H^3-H^6) = 1.5$		8.08 D $J(H^5-H^6) = 2.6$	8.39 D_D		3.85 S		21.2 S	CD_2Cl_2
VI	7.7–7.2 M	m 6.9–6.7 M[d]	m	m	7.2–7.0 M	8.7–8.5 M		3.85 S	3.26 S[f] 3.18 S[f]	19.4 S	CD_2Cl_2
VII	8.2–6.9 M	m 6.7–6.5 M[d]	m	m	m	8.6–8.5 M		3.76 S		38.6 D 17.0 D $J(P-P) = 38.9$	CD_2Cl_2
[(Va) H]ClO_4	7.8–7.0 M	8.1–7.9 M[c] 7.0–6.8 M[d]	8.3–8.1 M	m	m	8.4–8.3 M	n.o.	3.88 S		19.7 S	CD_2Cl_2
[$ZnCl_2$ (Va)]	7.7–7.0 M	7.7–7.5 M[c] 6.8–6.6 M[d]	8.5–8.3 M	m	m	8.2–8.0 M		3.87 S		20.1 S	CD_2Cl_2
[$ZnCl_2$ (Vc)]	7.7–7.1 M	7.8–7.6 M[c] 6.8–6.6 M[d]	9.70 D $J(H^3-H^6) = 1.5$		8.45 D $J(H^5-H^6) = 2.5$	8.01 D_D		3.88 S		19.7 S	CD_2Cl_2
2-(RN=CH)–C_5H_4N[g]		7.5–7.2 M[c,e] 7.1–6.9 M[d]	8.3–8.1 M	7.9–7.7 M	7.5–7.2 M[e]	8.7–8.6 M		3.81 S			CD_2Cl_2
[$ZnCl_2$ {2-(RN=CH)–C_5H_4N}][h]		7.8–7.6 M[c,e] 7.1–6.9 M[d]	8.0–7.8 M	8.3–8.1 M	7.8–7.6 M[e]	8.8–8.7 M		3.87 S			CD_2Cl_2

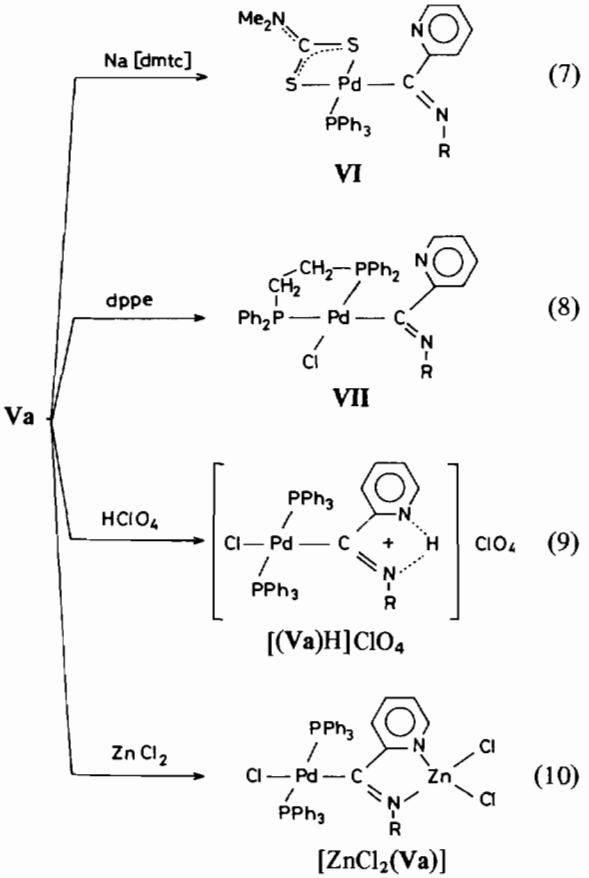
[a] ^{1}H chemical shifts (δ) in ppm from TMS at 30 °C; ^{31}P chemical shifts (δ) in ppm from external 85% H_3PO_4 (down-field shifts taken as positive); coupling constants in Hz; S = singlet; D = doublet; D_D = doublet of doublets; M = multiplet, br = broad; satisfactory integration values have been obtained; heterocyclic proton labelling:



[b] Masked by the intense phenyl proton resonances of the PPh_3 ligands. [c] Symmetrical side of an AA'BB' multiplet, corresponding to the *ortho* protons of the p-C_6H_4OMe group. [d] Symmetrical side of an AA'BB' multiplet corresponding to the *meta* protons of the p-C_6H_4OMe group. [e] Overlapping multiplets. [f] Resonances of dmtc ligand. [g] R = p-C_6H_4OMe, δ(N=C–H) 8.61 ppm. [h] R = p-C_6H_4OMe, δ(N=C–H) 8.71 ppm.

cm^{-1}) than in the corresponding 2-(iminomethyl)-pyridines 2-(RN=CH)–C_5H_4N (R = *p*-C_6H_4OMe, 1628 cm^{-1}; R = Me, 1653 cm^{-1}).

The formulation of **Va** is further supported by ligand substitution reactions at the palladium center and by protonation and coordination of the imino(2-pyridyl)methyl group, as reported in Scheme 2.



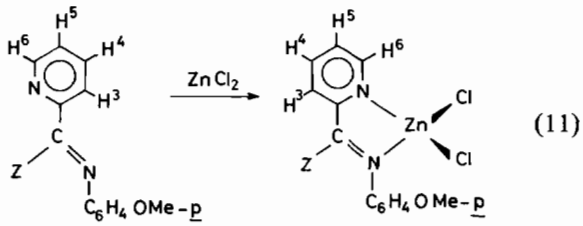
(R = *p*-C_6H_4OMe; dmtc = dimethyldithiocarbamate; dppe = 1,2-bis(diphenylphosphino)ethane)

Scheme 2.

The substitution reactions 7 and 8 yield complexes **VI** and **VII** with chelating dmtc and dppe ligands, respectively, as indicated by their IR and NMR spectra. The reaction with an aqueous solution of strong mineral acid HX (X^- = Cl^-, ClO_4^-) involves only monoprotonation of the α-diimino moiety (eqn. (9)), without cleavage of the Pd–C σ-bond or hydrolysis of the palladated imino group. In the reaction with HCl, the cationic substrate $[(Va)H]^+$ does not undergo displacement of PPh_3 by chloride ligands, even in the presence of an excess of Cl^- ions.

Both complexes **Va** and **Vb** give 1/1 adducts with $ZnCl_2$ through σ,σ′-N,N′ chelation of the α-diimino group. Upon coordination, the ν(Pd–Cl) band of **Va** and **Vc** shits to higher frequencies and is masked by the more intense ν(Zn–Cl) vibrations in the range 334–314 cm^{-1}. A high-frequency shift (20 cm^{-1}) of ν(Pd–Cl) is also observed in the protonation of **Va**. Conversely, upon protonation or coordination the imino group ν(C=N) band is lowered by *ca.* 60 cm^{-1}.

The ^{1}H NMR spectra of the iminomethylpyridine 2-(*p*-$MeOC_6H_4N$=CH)–C_5H_4N and those of **V**, **VI** and **VII** suggest that in solution the α-diimino unit N=C–C=N assumes only one of the possible configurations, which can arise from *cis* or *trans* arrangement of the conjugated double bond system and from the different position of the imino-nitrogen substituent R, rather than a time averaged one. Furthermore, because of the shielding effect of phenyl ring currents of the mutually *trans* PPh_3 ligands, the proton resonances of the 2-pyridyl group of **Va** are generally shifted to higher field compared to the corresponding signals of 2-(*p*-$MeOC_6H_4N$=CH)–C_5H_4N. Such a shift depends on the position of the proton on the heterocyclic ring and varies from 0.2 ppm for H^6 to 0.6–0.8 ppm for H^3 and H^4. In the formation of $ZnCl_2$ adducts, the N=C–C=N unit is forced to assume a *cis* configuration with an E (*anti*) imino-nitrogen substituent:



For Z = H, the coordination brings about a down-field shift of H–C=N, H^4, H^5, H^6 and C_6H_4OMe *ortho* protons, which is typical for imino C- and N-substituents of σ,σ′-N,N′ chelating α-diimines [14], and an up-field shift of 0.3 ppm for the H^3 proton. For Z = *trans*-$PdCl(PPh_3)_2$, similar down-field shifts are observed for H^4, H^5 and C_6H_4OMe *ortho* protons, whereas the H^3 and H^6 resonances change in the opposite way, with a marked deshielding of the H^3 proton (which now appears at 8.5–8.3 ppm) and a shielding of 0.35 ppm for H^6.

The coordination effects on the heterocyclic ring proton resonances are better illustrated by the **Vc**/$ZnCl_2$ system, because the H^3, H^5 and H^6 protons are all clearly observed in the low-field range of the ^{1}H NMR spectra, and because the three-spin system of the 2-pyrazyl group, which should be analyzed as an ABX spectrum, can be reasonably interpreted under a first-order approximation due to the low J_{AB}/δ_{AB} value (Fig. 1). Also in this case, the formation of the $ZnCl_2$ adduct involves a large down-field shift of 1.74 ppm for the H^3 proton and an up-field shift of 0.38 ppm for H^6.

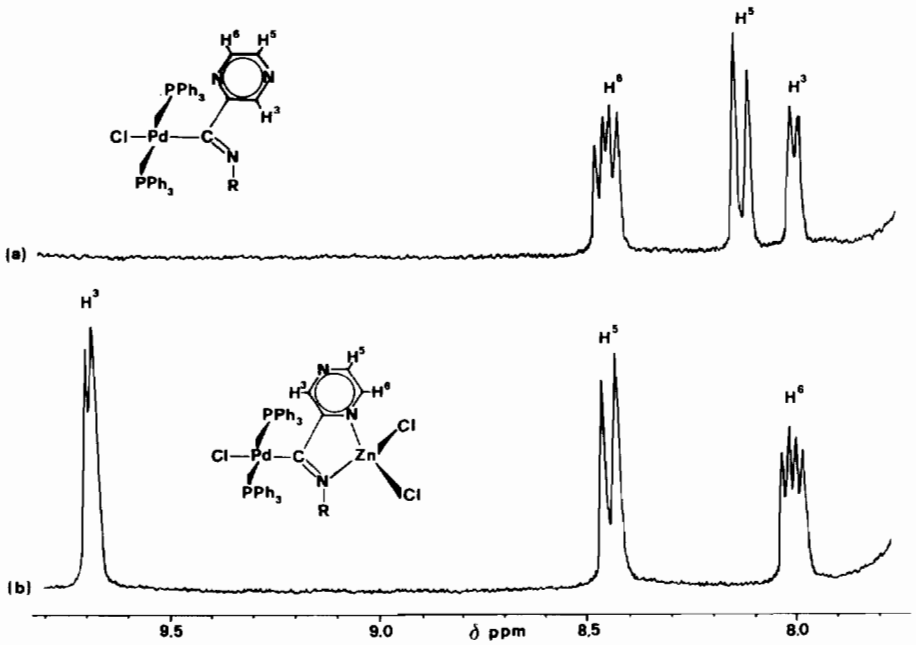
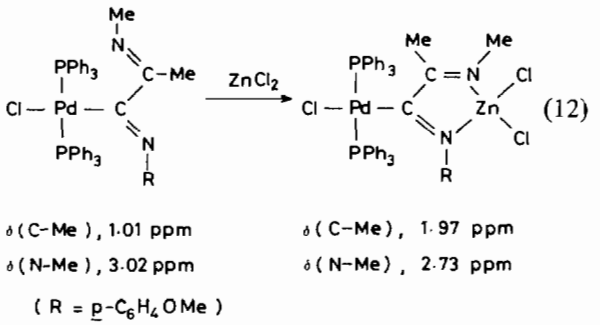


Fig. 1. ^{1}H NMR spectra in the range 9.8–7.8 ppm of Vc (a) and [$ZnCl_2$(Vc)] (b) in CD_2Cl_2.

The different coordination effects on H^3 and H^6 resonances of **Va** and **Vc**, relative to those of 2-(*p*-$MeOC_6H_4N$=CH)–C_5H_4N, can be rationalized by assuming a *trans* N=C–C=N skeleton for the uncoordinate α-diimino group (which is the preferential configuration of α-diimines RN=CR′–CR″=NR [15] and of the palladated analogue *trans*-[PdCl{C(=NR)-CMe=NR}(PPh_3)$_2$] (R = *p*-C_6H_4OMe) [16] in the solid and in solution) and by taking into account the electronic and steric properties of the *trans*-PdCl-(PPh_3)$_2$ unit. The *trans* to *cis* configuration change upon chelation (eqn. (11) and Fig. 1) brings the H^3 proton rather close to the d^8 metal center above its coordination plane, with a consequent deshielding effect on H^3, while the H^6 proton moves into a position (formerly occupied by H^4 in the case of **Va**) for which the shielding influence of phenyl ring currents of the *trans* PPh_3 ligands is the greatest (see spectra of **Va** and 2-(*p*-$MeOC_6H_4N$=CH)–C_5H_4N in Table II).

This interpretation is also supported by the parallel down-field shift of C–Me and up-field shift of N–Me resonances observed in reaction 12 [17]:



In accord with this picture, a *cis* hydrogen-bridged structure is assigned to the protonated imino(2-pyridyl)methyl group of [(**Va**)H]ClO_4 (eqn. 9 of Scheme 2), for which δ(H^6) and δ(H^3) are detected at 8.4–8.3 and 8.3–8.1 ppm, respectively.

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