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PREPARATION AND PROTONATION OF 2-PYRIMIDYL- AND 2-PYRAZYLPALLADIUM(II) COMPLEXES

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Summary

The oxidative addition of 2-chloropyrimidine or 2-chloropyrazine to $[Pd(PPh_3)_4]$ yields a mixture of *trans*-$[PdCl(C_4H_3N_2\text{-}C^2)(PPh_3)_2]$ (I) and $[PdCl(\mu\text{-}C_4H_3N_2\text{-}C^2,N^1)(PPh_3)]_2$ (II) ($C_4H_3N_2$ = 2-pyrimidyl or 2-pyrazyl group). The mononuclear complexes I are quantitatively converted into the binuclear species II upon treatment with H_2O_2. The reaction of II with HCl gives the *N*-monoprotonated derivatives *cis*-$[PdCl_2(C_4H_4N_2\text{-}C^2)(PPh_3)]$ (III), from which the cationic complexes *trans*-$[PdCl(C_4H_4N_2\text{-}C^2)(L)_2]ClO_4$ (L = PPh_3, IV; PMe_2Ph, V; PEt_3, VI) can be prepared by ligand substitution reactions. Reversible proton dissociation occurs in solution for III–VI. The low-temperature ^1H NMR spectra of *trans*-$[PdCl(C_4H_4N_2\text{-}C^2)(PMe_2Ph)_2]ClO_4$ show that the heterocyclic moiety undergoes restricted rotation around the Pd–C^2 bond and that the 2-pyrazyl group is protonated predominantly at the N^1 atom. These results and the ^{13}C NMR data for the PEt_3 derivatives are interpreted on the basis of a significant $d_\pi \rightarrow \pi^\star$ back-bonding contribution to the palladium–carbon bond of the protonated ligands.

Introduction

We previously described the protonation and methylation of some 2-pyridyl-palladium(II) and -platinum(II) compounds by strong mineral acids and dimethylsulfate, respectively [1]. The electrophilic attack occurs only at the nitrogen atom of the σ-bonded heterocyclic group, without cleavage of the metal–carbon bond. The multinuclear NMR spectra of the resulting products suggest a relevant contribution of the carbene-like structure **A** to the electronic configuration of this new type of ligand:

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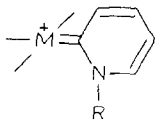
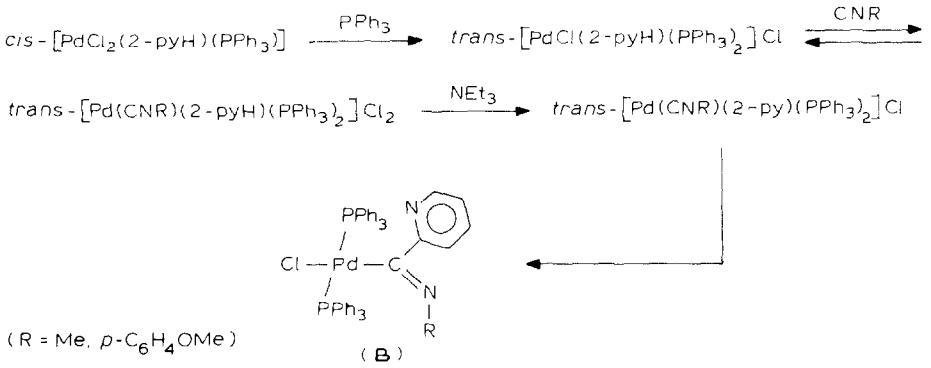


(R = H, Me)

(A)

The complex *cis*-$[PdCl_2(2\text{-pyH})(PPh_3)]$ (2-pyH = *N*-protonated 2-pyridyl) also proved to be a convenient starting material for the preparation of derivatives **B** containing an imino(2-pyridyl)methyl group, according to the following reaction sequence [2]:



(R = Me, *p*-C_6H_4OMe)

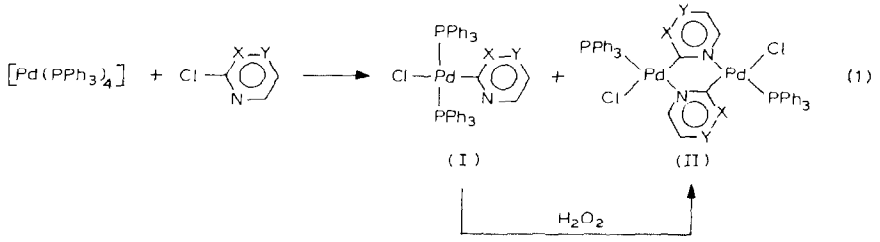
(B)

As an extension of our studies on *C*-palladated nitrogen ligands, we report here the preparation of 2-pyrimidyl- and 2-pyrazyl-palladium(II) complexes and their protonation. The new compounds have been characterized mainly by multinuclear NMR spectroscopy in order to elucidate the nature of the palladium-carbon bond and to ascertain the site of proton attack.

Results and discussion

Preparation and protonation reactions

The oxidative addition of 2-chloropyrimidine or 2-chloropyrazine to $[Pd(PPh_3)_4]$ yields a mixture of products I and II (eq. 1 and Fig. 1), in which the binuclear complex II predominates (molar ratio I/II ~ 1/4):



(I) (II) (1)

(X = N; Y = CH: 2-pyrimidyl (2-pym) complexes Ia, IIa ;
X = CH; Y = N: 2-pyrazyl (2-pyz) complexes Ib, IIb)

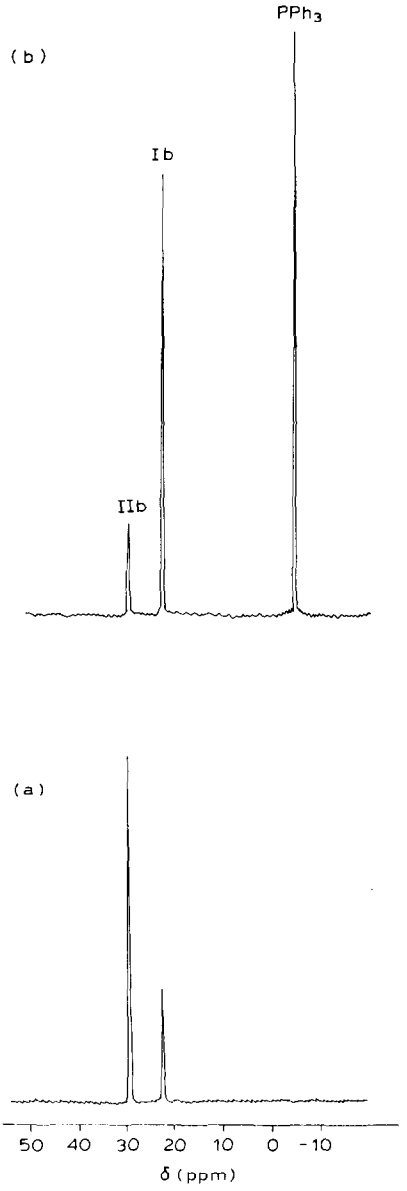


Fig. 1. ^{31}P NMR spectrum in CD_2Cl_2 of the mixture of products Ib and IIb obtained from the oxidative addition of 2-chloropyrazine to $[Pd(PPh_3)_4]$ (a); after addition of an excess of PPh_3 (b).

The mononuclear compound I is quantitatively converted into II upon treatment of the mixture with H_2O_2. This behaviour can be related to the existence of equilibrium 2, which shifts completely to the right when the free phosphine is oxidized by H_2O_2, whereas it moves in favour of I when an excess of PPh_3 is added (Fig. 1).

$$2\ I \rightleftarrows II + 2\ PPh_3 \qquad (2)$$

TABLE 1

ANALYTICAL AND PHYSICAL DATA

Compound	Analyses(Found (calcd.)(%))				Molar Conductivity [a] (ohm^{-1} cm^2 mol^{-1})	IR (cm^{-1})				
	C	H	N	Cl		ν(N–H)	ν(Cl–O)	δ(Cl–O)	ν(Pd–P)	ν(Pd–Cl)
$[PdCl(\mu\text{-}2\text{-pym})(PPh_3)]_2$	54.9	3.7	5.8	7.5						328m;
(IIa)	(54.68)	(3.75)	(5.80)	(7.34)						314m
$[PdCl(\mu\text{-}2\text{-pyz})(PPh_3)]_2$	54.3	3.8	5.7	7.4						334m
(IIb)	(54.68)	(3.75)	(5.80)	(7.34)						311m
$[PdCl_2(2\text{-pymH})(PPh_3)]$	50.6	3.6	5.4	13.8	24.3 [b]	3180ms;3145w				312ms;
(IIIa)	(50.84)	(3.68)	(5.39)	(13.64)						292ms
$[PdCl_2(2\text{-pyzH})(PPh_3)]1/3CH_2Cl_2$	48.7	3.6	5.1	17.4	23.1 [b]	3155ms;3125ms				314ms;
(IIIb)	(48.95)	(3.62)	(5.11)	(17.25)						282ms
trans-$[PdCl(2\text{-pymH})(PPh_3)_2]ClO_4$	56.8	4.0	3.3	8.5	90.3	3190w;3160w	1135s;1110s	627s;		323m
(IVa)	(56.79)	(4.05)	(3.31)	(8.38)			1050s	619s		
trans-$[PdCl(2\text{-pyzH})(PPh_3)_2]ClO_4$	56.4	4.1	3.3	8.4	108.0	3190sh;3175w;	1120sh;1095vs;	625s;		325m
(IVb)	(56.79)	(4.05)	(3.31)	(8.38)		3140w	1050s	620sh		
trans-$[PdCl(2\text{-pymH})(PMe_2Ph)_2]ClO_4$	40.3	4.4	4.6	12.0	92.7	3210sh;	1130sh;1110vs;	630s;	424m	318m;
(Va)	(40.19)	(4.38)	(4.69)	(11.86)		3200m,br;3160w	1050s	620s		300mw
trans-$[PdCl(2\text{-pyzH})(PMe_2Ph)_2]ClO_4$	39.9	4.4	4.6	11.7	94.1	3205m,br;	1025sh;1112vs;	626s;	427m	319m
(Vb)	(40.19)	(4.38)	(4.69)	(11.86)		3180mw;3145mw	1060s	620sh		
trans-$[PdCl(2\text{-pymH})(PEt_3)_2]ClO_4$	34.3	6.2	5.0	12.8	94.5	3250sh;	1110vs;1050s	625s;	416w [c]	325m;
(VIa)	(34.46)	(6.14)	(5.02)	(12.71)		3200m,br;3160m		620s		315w
trans-$[PdCl(2\text{-pyzH})(PEt_3)_2]ClO_4$	34.6	6.1	5.0	12.6	97.2	3195m;3175m;	1130sh;1110vs;	627s [c]	418w [c]	328m;
(VIb)	(34.46)	(6.14)	(5.02)	(12.71)		3135m	1060s	620sh		315w

[a] For 10^{-3} *M* MeOH solution at 20°C. [b] For 10^{-3} *M* DMSO solution at 25°C. [c] Tentative assignment.

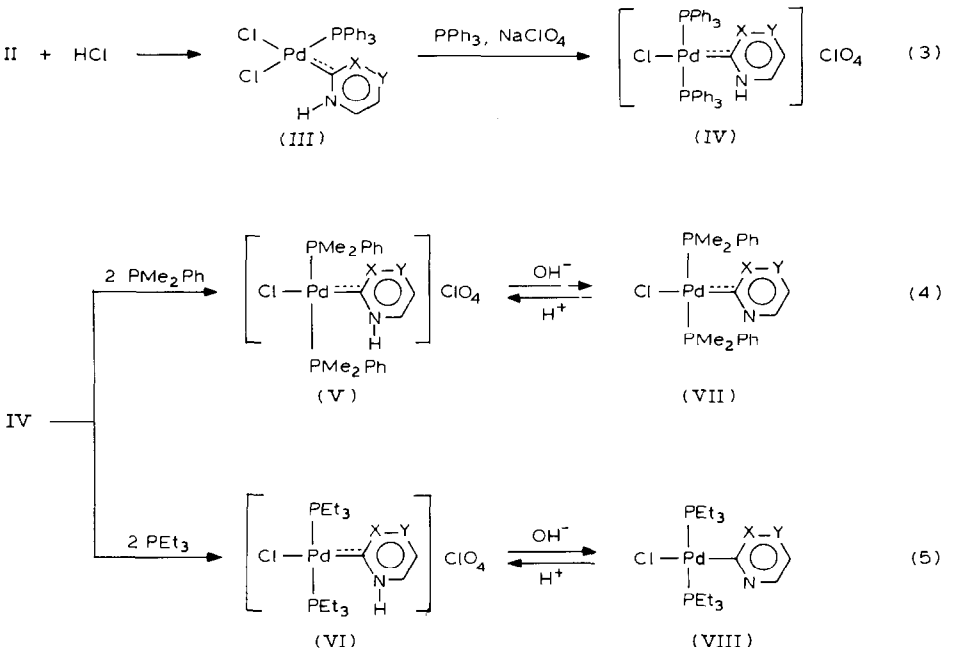
The complexes I cannot be isolated as pure samples from reaction 2 even in the presence of a large excess of triphenylphosphine. They are more conveniently prepared by a different route based on deprotonation of derivatives of type IV, as will be described in a forthcoming paper [3].

The dimeric nature of II is confirmed by molecular weight measurements (see Experimental). Their spectral data (Tables 1 and 2) suggest a non-planar structure with bridging C^2,N^1 heterocyclic ligands and with a *trans*-N–Pd–PPh_3 arrangement, analogous to that reported for the 2-pyridyl complexes $[PdX(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)]_2$ (X = Cl, Br) [4,5]. The observed Pd–Cl stretching frequencies (328 and 314 cm^{-1} for IIa; 334 and 311 cm^{-1} for IIb) and ^{31}P NMR signals (a singlet at 28.4 and 29.9 ppm in CD_2Cl_2 for IIa and IIb, respectively) are quite close to the corresponding values for $[PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)]_2$ (ν(Pd–Cl) 325 and 311 cm^{-1}; $\delta(^{31}P)$ singlet at 29.7 ppm in CD_2Cl_2).

In particular, the multiplicity of the H^6 proton resonance in both IIa and IIb can be rationalized by taking into account an additional coupling with the ^{31}P nucleus of PPh_3 *trans* to the N^1-bonded heterocycle. An approximate first-order analysis, depicted in Fig. 2, gives $^4J(P\text{–}H^6)$ values of 3.0 Hz for IIa and of 3.2 Hz for IIb, which are comparable with those observed for the methyl proton signals of complexes containing *trans*-(Me)N–Pd–PPh_3 geometries (2–3 Hz) [6].

The complexes II react readily with a methanolic solution of HCl to yield the *cis*-N-protonated derivatives III (Scheme 1), characterized by two ν(Pd–Cl) bands in the range 334–311 cm^{-1} and by N–H stretching frequencies in the range 3180–3125 cm^{-1}.

(*continued on p. 266*)



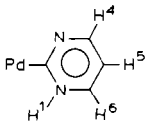
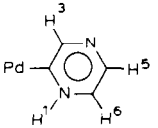
SCHEME 1. X = N; Y = CH: 2-pyrimidyl (2-pym) and *N*-protonated 2-pyrimidyl (2-pymH) complexes IIIa–VIIIa; X = CH; Y = N: 2-pyrazyl (2-pyz) and *N*-protonated 2-pyrazyl (2-pyzH) complexes IIIb–VIIIb.

TABLE 2

^{1}H AND ^{31}P NMR DATA [a]

Compound	Heterocyclic ring protons [b]					Phosphine protons					Solvent
	H^1	H^3	H^4	H^5	H^6	P-C_6H_5	P-CH_3	P-CH_2	P-CH_2-CH_3	$\delta(^{31}P)$	
IIa			m [c]	6.49 T $J(H^4-H^5)$ 5.5	8.46 D_T $J(H^5-H^6)$ 5.5 $J(H^4-H^6)$ 2.5 $J(P-H^6)$ 3.0	8.0–7.0 M				28.4 S	CD_2Cl_2
IIb		m [c]		m [c]	8.34 D_T $J(H^5-H^6)$ 3.2 $J(H^3-H^6)$ 1.4 $J(P-H^6)$ 3.2	8.0–7.0 M				29.9 S	CD_2Cl_2
IIIa	n.o.		8.43 D $J(H^4-H^5)$ 5.5	7.18 T	8.43 D $J(H^5-H^6)$ 5.5	7.9–7.3 M				24.1 S	DMSO-d_6
IIIb	n.o.	8.91 D $J(H^3-H^5)$ 1.3		8.27 D	8.10 D_D $J(H^5-H^6)$ 3.2	7.8–7.2 M				25.8 S	DMSO-d_6
IVa	n.o.		7.95 D $J(H^4-H^5)$ 5.3	6.63 T	7.95 D $J(H^5-H^6)$ 5.3	7.6–6.9 M				20.9 S	$CDCl_3$
IVb	n.o.	8.85 D $J(H^3-H^5)$ 1.1		7.91 D $J(H^5-H^6)$ 3.5	m [c]	7.8–7.1 M				22.3 S	$CDCl_3$
Va	n.o.		8.4–8.0 br	6.67 T $J(H^4-H^5) =$ $J(H^5-H^6) = 5.3$	8.0–7.6 br	7.4–7.0 M	1.85 T $J(P-H)$ 7.9 [d]			−3.9 S	$CDCl_3$
	n.o. [e]		8.18 D [e] $J(H^4-H^5)$ 5.5	6.74 T [e]	8.18 D [e] $J(H^5-H^6)$ 5.5						$CDCl_3$
	13.1 br [f]		8.40 D_D [f] $J(H^4-H^5) \sim 5.5$ $J(H^4-H^6) \sim 1.5$	6.76 T [f]	7.76 D_T [f] $J(H^1-H^6) \sim 5.5$ $J(H^5-H^6) \sim 5.5$	7.5–7.0 M [f]	1.76 [f,g] 1.72 [f,g]				CD_2Cl_2

VIIa [h]			8.05 D $J(H^4-H^5)$ 4.9	6.43 T	8.05 D $J(H^5-H^6)$ 4.9	7.6–7.0 M	1.55 T $J(P-H)$ 6.8 [d]			−7.5 S	$CDCl_3$
Vb	n.o.	8.70 D $J(H^3-H^6)$ 1.4		8.02 D	7.62 D_D $J(H^5-H^6)$ 3.4	7.4–7.1 M	1.93 [g] 1.89 [g]				CD_2Cl_2
	13.5 br [f]	8.66 S,br [f] $J(H^3-H^6) < 0.7$		7.98 D [f]	7.45 D_D [f] $J(H^5-H^6)$ 3.1 $J(H^1-H^6)$ 5.3		1.82 T [f] 1.77 T [f] $J(P-H) \sim 7$			−2.1 S [f]	CD_2Cl_2
VIIb [h]		8.02 D $J(H^3-H^6)$ 1.5		7.75 D	8.06 D_D $J(H^5-H^6)$ 2.9	7.5–7.0 M	1.63 T $J(P-H)$ 7.0 [d]			−6.7 S	$CDCl_3$
VIa	n.o.		8.95 D $J(H^4-H^5)$ 5.0	7.41 T	8.95 D $J(H^5-H^6)$ 5.0			1.9–1.3 M	1.09 Q	17.9 S	$CDCl_3$
	13.7 br [f]		9.02 D_D [f] $J(H^4-H^5)$ 5.0 $J(H^4-H^6)$ 2.1	7.44 T [f] $J(H^5-H^6) \sim 5.3$	8.75 D_T [f] $J(H^1-H^6) \sim 5.5$						CD_2Cl_2
VIIIa [h]			8.60 D $J(H^4-H^5)$ 5.0	7.00 T	8.60 D $J(H^5-H^6)$ 5.0			1.8–1.3 M	1.08 Q	15.5 S	$CDCl_3$
VIb	n.o.	9.29 D $J(H^3-H^6)$ 1.1		8.66 D	8.77 D_D $J(H^5-H^6)$ 3.5			2.1–1.5 M	1.14 Q	19.6 S	$CDCl_3$

[a] ^1H chemical shifts (δ) in ppm from TMS at 30°C; ^{31}P chemical shifts (δ) in ppm frcm external 85% H_3PO_4 (down-field shifts taken as positive); coupling constants in Hz; S, singlet; D, doublet; T, triplet, Q, quintet; D_D, doublet of doublets; D_T, doublet of triplets; M, multiplet; br, broad; n.o., not observed; satisfactory integration values have been obtained. [b] Heterocyclic protons labelling:  and  [c] Masked by the intense phenyl proton resonances.

[d] $J(P-H) = |^2J(P-H) + {}^4J(P'-H)|$. [e] In the presence of trace amount of HCl. [f] Spectrum recorded at −60°C. [g] Poorly resolved overlapping triplets. [h] Obtained from treatment of the corresponding N-protonated derivative with aqueous KOH.

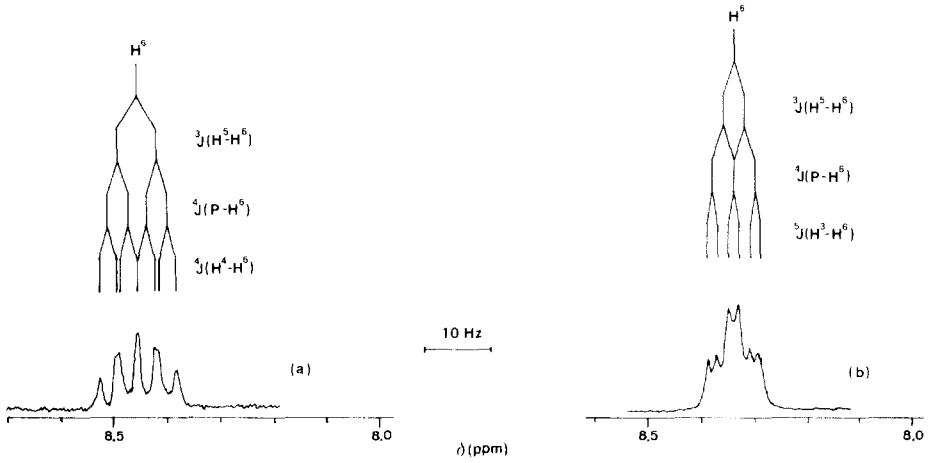


Fig. 2. Signal of the H^6 proton of the complex IIa (a), and of the complex IIb (b), in CD_2Cl_2.

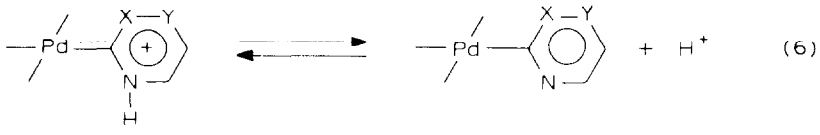
As in the case of $[PdCl(\mu\text{-}2\text{-py})(PPh_3)]_2$ [1], the reaction of II with HCl involves breaking of the Pd–N bond and monoprotonation of the heterocyclic ligand (even with an excess of HCl), without cleavage of the $Pd–C^2$ σ bond.

The compound IIIb crystallizes with 1/3 of a CH_2Cl_2 molecule, as shown by elemental analysis and by GLC measurements of a saturated solution in dimethylsulfoxide. Both products III are not sufficiently soluble in chlorinated solvents for molecular weight determinations. In CH_2Cl_2 suspension, however, they react smoothly with PPh_3 yielding the cationic complexes IV, isolated as perchlorate salts, from which the PMe_2Ph and PEt_3 analogues V and VI are easily obtained by ligand substituion reactions. The 2-pymH and 2-pyzH groups must be rather strongly bound to the palladium center since they are retained in all the reaction products IV–VI of Scheme I. Further evidence for the formulation of V and VI comes from the easy deprotonation to the corresponding neutral derivatives VII and VIII, characterized in solution by multinuclear NMR spectroscopy (Tables 2 and 3).

The cationic complexes IV–VI are uni-univalent electrolytes in MeOH solution and have a *trans*-P–Pd–P geometry, as shown by the presence of only one singlet in the ^{31}P spectrum of each compound and also by the presence of only one ν(Pd–P) vibration in the range 427–424 cm^{-1} for the PMe_2Ph derivatives V. The splitting into two or three bands of the typical ν(N–H), ν(Cl–O) and δ(Cl–O), and the presence in some cases (complexes Va, VIa, VIb) of a second weaker ν(Pd–Cl) absorption at lower frequency indicate that the 2-pymH and 2-pyzH compounds are largely associated in the solid state through hydrogen bonding beween the N–H group and the perchlorate anion and/or the chloride ligand.

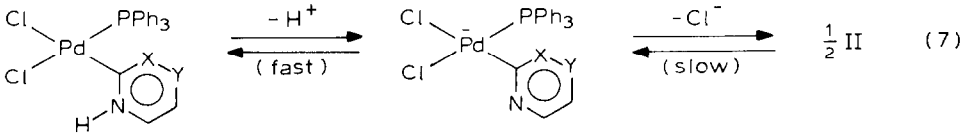
^1H NMR spectra of the protonated complexes

The ^1H NMR spectra (Table 2) can be interpreted on the basis of proton dissociation in solution (eq. 6):



(6)

At room temperature the proton exchange is fast, and brings about the disappearance of both the H^1 signal and the $^3J(H^1-H^6)$ coupling for the H^6 proton. For complexes III in DMSO-d_6, the fast reversible process 6 is followed by a second, slow reversible process involving the formation of a small but detectable amount of the parent dimer II:



(7)

For a saturated solution of IIIb at 30°C, a molar ratio IIIb/IIb of ca. 20/1 was estimated from integration of the corresponding ^{31}P signals. Addition of a slight excess of HCl shifted the equilibria 7 to the left with complete disappearance of the characteristic ^1H and ^{31}P signals of II.

A comparison with the ^1H NMR spectrum of the *N*-protonated 2-pyridyl complex *cis*-[$PdCl_2$(2-pyH)(PPh_3)], which was recorded under comparable experimental conditions [1], shows that the 2-pymH and 2-pyzH analogues behave as stronger acids, in line with the pK_a values of pyridinium (5.25), pyrimidinium (1.31) and pyridazinium (0.65) cations in aqueous solution [7].

This is further supported by the increase in molar conductivity values of the *cis* neutral complexes in dimethylsulfoxide at 25°C on going from *cis*-[$PdCl_2$(2-pyH)(PPh_3)], 6.3 ohm^{-1} cm^2 mol^{-1}, to *cis*-[$PdCl_2$(2-pyzH)(PPh_3)], 23.1, and to *cis*-[$PdCl_2$(2-pymH)(PPh_3)], 24.3.

The heterocyclic ring protons of the 2-pym derivatives VIIa and VIIIa give rise to first-order AX_2 spectra. For the *N*-protonated 2-pymH species, time-averaged AX_2 spectra are also observed at 30°C due to the fast exchange of the proton between the N^1 and N^3 atoms in the equilibrium 6. Exceptionally, for complex Va, *trans*-[PdCl(2-pymH)(PMe_2Ph)$_2$]ClO_4, this exchange is relatively slow, and the protons H^4 and H^6 appear as two broad unresolved resonances in the ranges 8.4–8.0 and 8.0–7.6 ppm, respectively. Addition of trace amount of HCl to the $CDCl_3$ solution increases the exchange rate (probably through formation of low-concentration N^1,N^3-diprotonated species) and causes the coalescence of the H^4 and H^6 signals into a sharp doublet at 8.18 ppm. When a CD_2Cl_2 solution of Va is cooled to −60°C the exchange rate decreases markedly and the equilibrium 6 shifts almost completely to the left, so that the N–H resonance is now clearly detected at 13.1 ppm. In these conditions, the H^4, H^5 and H^6 protons appear as an AMX system, with an additional coupling of H^6 with the N–H proton. The low-temperature spectrum of VIa, *trans*-[PdCl(2-pymH)(PEt_3)$_2$]ClO_4, in CD_2Cl_2 is quite similar, except for a down-field shift of 0.6–1 ppm for the 2-pymH signals. Also in this case, the N–H proton resonates at a rather low field, 13.7 ppm, and H^6 appears as a doublet of triplets because of the similarity of the values of $^3J(H^5-H^6)$ and $^3J(H^1-H^6)$ (spectrum (c) of Fig. 3).

The ring protons of the 2-pyz and 2-pyzH derivatives give rise to ABX spectra, which can reasonably be analyzed by first-order approximation because of the large $\Delta\nu/J$ ratio of the AB system (H^5 and H^6 protons). The assignment of H^3, H^5 and H^6 resonances is based on the relative values of coupling constants, in accordance

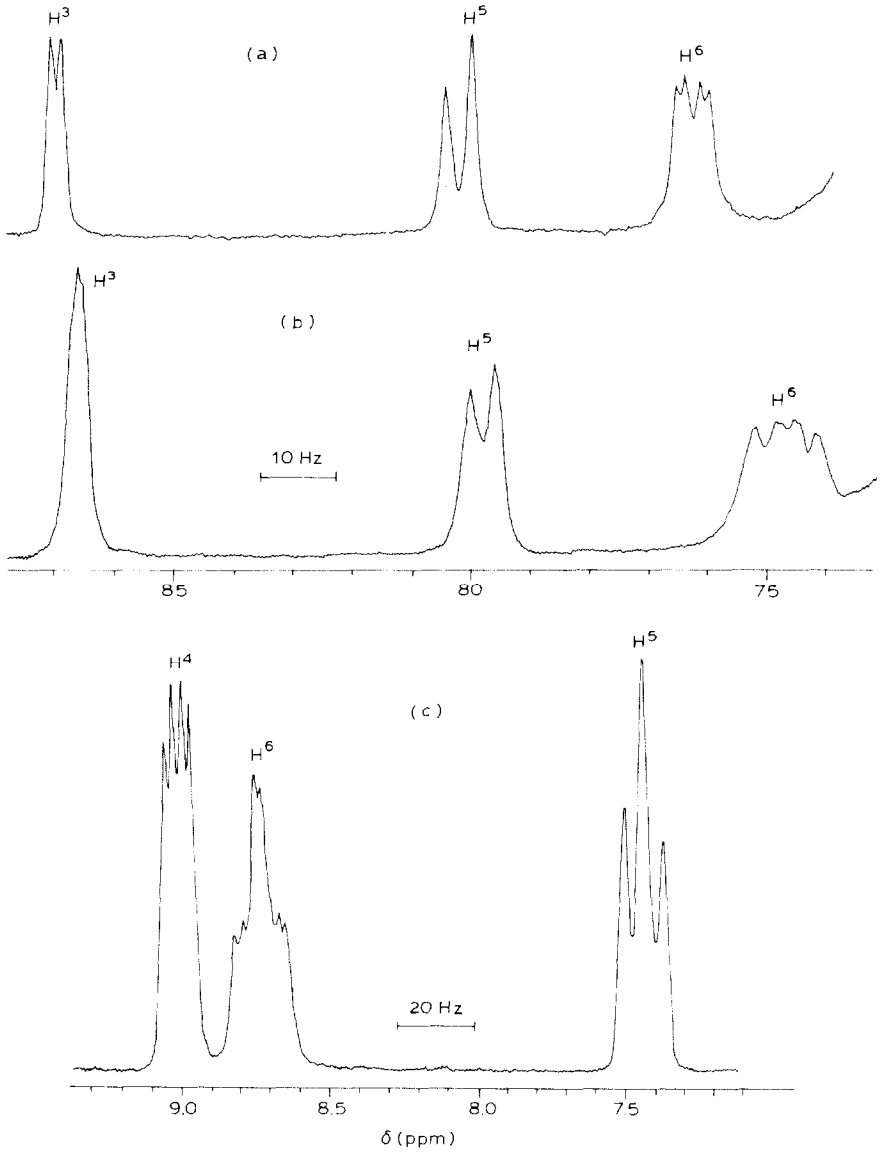


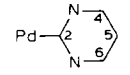
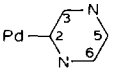
Fig. 3. ^{1}H NMR spectrum in the range 8.7–7.4 ppm of the complex Vb in CD_2Cl_2 at 30°C (a) and at −60°C (b); ^{1}H NMR spectrum in the range 9.3–7.1 ppm of complex VIa in CD_2Cl_2 at −60°C (c).

with literature data on 2-substituted pyrazines and N-protonated or methylated pyrazinium cations [8–10]. Since in the 2-palladated species $^4J(H^3–H^5)$ is very close to zero, and is never observed within the resolution limit of the instrument, $\delta(H^6)$ is easily assigned to the resonance with a doublet of doublets pattern (see Table 2). The protonation of the 2-pyz group may occur at either the N^1 or the N^4 nitrogen atom. The variable temperature spectra of Vb, *trans*-$[PdCl(2\text{-}pyzH)(PMe_2Ph)_2]ClO_4$, in CD_2Cl_2 show that equilibrium 6 shifts in favour of the N^1-protonated species on cooling. The H^6 signal at 7.62 ppm broadens progressively, and at −60°C the

TABLE 3

^{13}C NMR SPECTRAL DATA FOR PEt_3 DERIVATIVES [a]

Compound	Heterocyclic ring carbons					Phosphine carbons	
	C^2	C^3	C^4	C^5	C^6	P-CH_2	P-CH_2-CH_3
VIIIa [b]	189.8		154.2	115.1	154.2	14.4 J(P-C) 25.6 [c]	7.6
VIa	194.3 ^2J(P-C) 8.2		160.8 [d]	116.1	147.5 [d]	14.5 J(P-C) 27.8 [c]	7.7
VIIIb [b]	177.2	152.3 ^3J(P-C) 12.3		137.8	145.7	14.3 J(P-C) 25.8 [c]	7.8
VIb	181.3 ^2J(P-C) 17.2	159.5 ^3J(P-C) 4.8		142.0	139.6	14.9 J(P-C) 27.4 [c]	7.9

[a] Chemical shifts (δ) in ppm from TMS, in CD_2Cl_2 at 30°C; coupling constants in Hz; ring carbon labelling:  ,  [b] Obtained from treatment of the corresponding N-protonated derivative with aqueous KOH. [c] $J(P-C) = |^1J(P-C) + {}^3J(P'-C)|$. [d] The two signals coalesce into a broad singlet at 154.2 ppm upon addition of a minute amount of HCl.

$^3J(H^1-H^6)$ coupling is clearly observed (spectrum (b) of Fig. 3), along with the N–H resonance at 13.5 ppm.

At 30°C some N^4-protonated groups may be present, but the N^1–H species is still predominant, as can be inferred from the small effect of temperature on the H^3, H^5, H^6 chemical shifts and from the enhanced basicity of the N^1 nitrogen atom in Pd–C^2 bonded heterocycles. The 2-pyridyl complex *trans*-[PdBr(C_5H_4N-C^2)-$(PEt_3)_2$] is actually a stronger base (pK_a 8.04) than its 3-pyridyl analogue *trans*-[PdBr(C_5H_4N-C^3)$(PEt_3)_2$] (pK_a 5.47) [5].

As can be seen in Table 2, the protonation of 2-pym and 2-pyz groups of VIIa and VIIb, respectively, brings about a down-field shift for the pyrimidyl H^4, H^5 protons and for the pyrazyl H^3, H^5 protons, and an up-field shift for the H^6 proton of both ligands. Furthermore, the equivalence of the two ^{31}P phosphine nuclei and the occurrence of two P–Me triplets (1/1 integration ratio) for the 2-pymH complex Va (at −60°C) and for the 2-pyzH complex Vb (in the temperature range −60 to 30°C) indicate a molecular structure in which the asymmetric N^1-protonated ligands are perpendicular to the palladium coordination plane, with restricted rotation about the metal–carbon bond. In contrast the 2-pyz group appears to be freely rotating in VIIb, since its NMR spectra are characterized by a $\delta(^{31}P)$ singlet at −6.7 ppm and by only one δ(H) 1/2/1 P–Me triplet at 1.63 ppm.

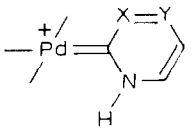
^{13}C NMR spectra

The $^{13}C\{^1H\}$ NMR spectra of PEt_3 derivatives are listed in Table 3. The assignment of the heterocycle ring carbons is based on coupling constant and chemical shift considerations, in comparison with the literature data for 2-substituted pyrimidines [11] and pyrazines [12], for monoprotonated or monomethylated nitrogen heteroaromatic compounds [13], and for the 2-pyridyl complexes *trans*-[MX(2-py)$(PEt_3)_2$] and *trans*-[MX (2-pyH)$(PEt_3)_2$]ClO_4 (M = Pd, Pt; X = Cl, Br) [1,5]. The lower field resonance is attributed to the palladium bonded C^2 carbon. For complexes VI, this is supported by the 1/2/1 triplet pattern of the signal, which

is due to coupling with the equivalent ^{31}P nuclei of the *trans* PEt_3 ligands. Because of its reduced intensity, no ^{31}P coupling is observed for the deprotonated derivatives VIII. In accordance with the good donor properties of the *trans*-$PdBr(PEt_3)_2$ group, which induces a higher electron density on the *para* (C^5) carbon of the 2-pyridyl ligand [5], the higher field resonance of VIIIa (115.1 ppm) and of VIIIb (137.8 ppm) is assigned to the C^5 atom of 2-pym and 2-pyz ligands, respectively. In 2-substituted pyrimidines and pyrazines, the C^5 carbon is increasingly shielded with increasing electron-donating abilities of the substituent [11,12]. On the other hand, the signal at 145.7 ppm of VIIIb can reasonably be assigned to the 2-pyrazyl C^6 carbon, as it is the least affected by the substituent properties [12] (cf. the pyrazine ^{13}C resonance at 145.04 ppm [12b]). In contrast to its ^1H NMR spectrum at 30°C and to the ^{13}C NMR spectra of monoprotonated pyrimidinium cations [13], the ^{13}C NMR spectrum of the 2-pymH complex VIa in CD_2Cl_2 is not time-averaged by the proton exchange between the equivalent N^1 and N^3 nitrogen atoms in the equilibrium 6. The C^4 and C^6 resonances are in fact detected as two well-separated singlets at 160.8 and 147.5 ppm, respectively, and coalesce to a broad signal at 154.2 ppm only on addition of a minute amount of HCl. By taking into account the frequency separation between $\delta(C^4)$ and $\delta(C^6)$ (266 Hz) and that between $\delta(H^4)$ and $\delta(H^6)$ under conditions of slow exchange (21.5 Hz, at −60°C), the life-time (τ) for the N-protonated 2-pymH group in VIa at 30°C can be estimated approximately in the range: $6 \times 10^{-4} < \tau < 7 \times 10^{-3}$ sec. The effects of protonation on the ^{13}C chemical shifts of the 2-pyz ligand in VIIIb are quite similar to those observed for the 2-pyridyl ligand in *trans*-[MX (2-py)$(PEt_3)_2$] [1], suggesting that the 2-pyz group is essentially still N^1-protonated at 30°C, in agreement with the ^1H NMR data.

Another interesting feature of the ^{13}C NMR spectra is the deshielding of the palladium bound C^2 carbon upon protonation of both 2-pym and 2-pyz moieties, which parallels the down-field shift of $\delta(C^2)$ in *trans*-[MX (2-pyH)$(PEt_3)_2$]ClO_4 [1], but is in contrast to the shielding of the α carbons (C^2 and C^6) of monoprotonated or monomethylated nitrogen heteroaromatics [13].

By using the same arguments as for N-protonated 2-pyridyl complexes [1], the C^2 deshielding can be explained by an increased Pd–C^2 bond order, or , in terms of valence bond theory, by a significant contribution of the carbene-like limiting structure **C** to the electronic configuration of the protonated ligands:



(**C**)

Consistently, the restricted rotation of 2-pymH and 2-pyzH groups in the PMe_2Ph derivatives V is better rationalized in terms of an electronic effect than by an unusual increase in steric bulk of the 2-pym and 2-pyz ligands upon protonation.

Experimental

The complex $[Pd(PPh_3)_4]$ was prepared by a published method [14]. All other chemicals were reagent grade and used without further purification. Infrared spectra were recorded with a Perkin–Elmer 983 instrument, using Nujol mulls and CsI plates in the range 4000–200 cm^{-1}. The ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra

were recorded with a Varian FT80A spectrometer operating at 79.542, 32.203 and 20.000 MHz, respectively, at 30°C. The molecular weights were determined in 1,2-dichloroethane at 37°C with a Knauer osmometer. Conductivity measurements were carried out with a Philips PR 9500 bridge.

All reactions were carried out at room temperature, unless otherwise stated. When required, an inert atmosphere (N_2) was used. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator.

Preparation of [PdCl(μ-2-pym)(PPh_3)]$_2$ (IIa) and [PdCl(μ-2-pyz)(PPh_3)]$_2$ (IIb)

A suspension of [Pd(PPh_3)$_4$] (4.62 g, 4 mmol) in benzene (ca. 200 ml) was treated with 2-chloropyrimidine or 2-chloropyrazine (0.69 g, 6 mmol) under N_2. The mixture was heated to reflux for 6–8 h. The solid [Pd(PPh_3)$_4$] quickly dissolved and a yellow product began to precipitate within 1 h. Concentration to small volume and dilution with Et_2O gave a mixture of Ia and IIa (1.85 g) or Ib and IIb (2.36 g) in a molar ratio I/II of ca. 1/4, as shown by ^{31}P NMR spectroscopy in CD_2Cl_2 ($\delta(^{31}P)$ as a singlet at 23.5 and 22.7 ppm for Ia and Ib, respectively). The mixture was suspended in CH_2Cl_2 (ca. 250 ml), an excess of H_2O_2 (3 ml of a 30% aqueous solution) was added and the mixture was stirred for 3–4 h. The resulting yellow solution was dried (Na_2SO_4), filtered, and concentrated to small volume. Addition of Et_2O gave the crude product II as a yellow precipitate, which was redissolved in CH_2Cl_2 (ca. 200 ml) and treated with charcoal. After filtration, MeOH (ca. 50 ml) was added to the clear solution and CH_2Cl_2 was evaporated off until a precipitate appeared. Precipitation was completed by dropwise addition of Et_2O. (Yields, based on the initial amount of [Pd(PPh_3)$_4$]: IIa, 1.78 g, 92.1%; IIb, 1.66 g, 85.9%. Mol. weight found, 980 for IIa, 1020 for IIb; calcd. 966.4).

Preparation of cis-[$PdCl_2$(2-pymH)(PPh_3)] (IIIa) and cis-[$PdCl_2$(2-pyzH)(PPh_3)] · $\frac{1}{3}CH_2Cl_2$ (IIIb)

A solution of II (0.97 g, 1 mmol) in CH_2Cl_2 (ca. 150 ml) was treated with HCl (6.3 ml of a 0.35 *M* methanolic solution, molar ratio Pd/HCl 1/1.1). Some pale-yellow product III began to precipitate after 10–15 min. The mixture was set aside overnight, the solvent was then partially evaporated, and the precipitation was completed by adding Et_2O. (Yields, based on the theoretical amount: IIIa, 0.98 g, 93.9%; IIIb, 1.03 g, 93.6%)

Preparation of trans-[PdCl(2-pymH)(PPh_3)$_2$]ClO_4 (IVa) and trans-[PdCl(2-pyzH)(PPh_3)$_2$]ClO_4 (IVb)

A suspension of III (2 mmol) suspended in CH_2Cl_2 (100 ml) was treated with PPh_3 (0.525 g, 2 mmol) with stirring. When dissolution was complete (ca. 30 min), a solution of $NaClO_4 \cdot H_2O$ (0.56 g, 4 mmol) in MeOH (5 ml) was added. After 10 min stirring the mixture was evaporated to dryness and the solid residue was extracted with CH_2Cl_2 (80 ml) and charcoal. After filtration of the extract and concentration, the white product was precipitated by dropwise addition of Et_2O (Yield: IVa, 1.63 g, 96.3%; IVb, 1.62 g, 95.7%).

Preparation of trans-[PdCl(2-pymH)(L)$_2$]ClO_4 (L = PMe_2Ph, Va; PEt_3, VIa) and trans-[PdCl(2-pyzH)(L)$_2$]ClO_4 (L = PMe_2Ph, Vb; PEt_3, VIb)

(a) A solution of IVa (0.85 g, 1 mmol) in CH_2Cl_2 (100 ml) was treated with

PMe_2Ph (0.28 g, 2 mmol) under N_2. After 1 h stirring the solution was concentrated to small volume and the white product Va was precipitated by dilution with Et_2O. It was purified by reprecipitation from the same solvents (0.4 g, 66.6%).

(b) A suspension of IVa (2.11 g, 2.5 mmol) in a solution of PEt_3 (0.65 g, 5.5 mmol) in Et_2O (250 ml) under N_2 was stirred overnight. The white product VIa was filtered off and purified by two successive precipitations from CH_2Cl_2/Et_2O (0.88 g, 63.3%).

(c) A suspension of IVb (0.85 g, 1 mmol) in a solution of PMe_2Ph (0.28 g, 2 mmol) in Et_2O (ca. 80 ml) under N_2 was stirred overnight. The white product Vb was purified as described above for VIa (0.50 g, 83.2%).

(d) A suspension of IVb (0.85 g, 1 mmol) in a solution of PEt_3 (0.25 g, 2.1 mmol) in Et_2O (ca. 80 ml) under N_2 was stirred overnight. The white product VIb was purified as described above for VIa (0.47 g, 83.9%).

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