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PROTONATION AND METHYLATION REACTIONS OF 2-PYRIDYL-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES

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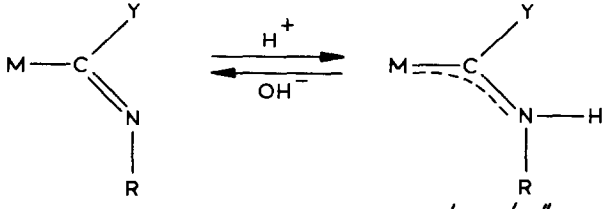
Summary

The reactions of strong acids HX and $HClO_4$ with the 2-pyridyl complexes $[PdX(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)]_2$ (X = Cl, Br), *trans*-$[PdCl(C_5H_4N\text{-}C^2)(PEt_3)_2]$ and $[PdCl(C_5H_4N\text{-}C^2)(dppe)]$ yield the *N*-protonated derivatives *cis*-$[PdX_2(C_5H_5N\text{-}C^2)(PPh_3)]$, *trans*-$[PdCl(C_5H_5N\text{-}C^2)(PEt_3)_2]ClO_4$ and $[PdCl(C_5H_5N\text{-}C^2)(dppe)]ClO_4$, respectively. The terminal 2-pyridyl group of *trans*-$[PdCl(C_5H_4N\text{-}C^2)(PEt_3)_2]$ and $[PdCl(C_5H_4N\text{-}C^2)(dppe)]$ also reacts with $Me_2SO_4/NaClO_4$ to give *trans*-$[PdCl(C_5H_4(1\text{-}Me)N\text{-}C^2)(PEt_3)_2]ClO_4$ and $[PdCl(C_5H_4(1\text{-}Me)N\text{-}C^2)(dppe)]ClO_4$. Analogous *N*-protonation or *N*-methylation reactions occur with *trans*-$[PtBr(C_5H_4N\text{-}C^2)(L)_2]$ (L = PEt_3, PPh_3). The complexes *trans*-$[MX(C_5H_5N\text{-}C^2)(PMe_2Ph)_2]ClO_4$ (M = Pd, X = Cl and Br; M = Pt, X = Br) exhibit restricted rotation of the protonated 2-pyridyl group around the M–C bond. This and other chemical results and spectral data, such as the ^{13}C NMR data of the PEt_3 derivatives, are interpreted in terms of a significant contribution of a carbene-like limiting structure to the electronic configuration of this new type of ligand.

Introduction

The metal–carbon σ-bonded imino functions have an enhanced basicity and can be easily protonated to the corresponding conjugated acids, which have been formulated as aminocarbene ligands [1]:



(Y = H, alkyl or aryl group, OR′, NR′R″)

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The terminal or bridging 2-pyridyl group $C_5H_4N-C^2$ (denoted throughout this work by a 2-py) in transition metal complexes, such as $[PdBr(\mu\text{-}2\text{-py})(PPh_3)]_2$, [2], *trans*-$[PdBr(2\text{-py})(PEt_3)_2]$ [3] and *trans*-$[PtBr(2\text{-py})(PPh_3)_2]$ [4], may be regarded as a special type of σ-bonded imino ligand, in which the imino carbon and nitrogen atoms are involved in a six-membered aromatic ring. This view is supported by the markedly stronger basicity of *trans*-$[PdBr(2\text{-py})(PEt_3)_2]$ than of free pyridine [3] and also by the course of migratory insertion reactions of one or two isocyanide molecules into the palladium–2-pyridyl bond [4], which parallels that of analogous reactions involving the palladium–1-iminoalkyl bond [5].

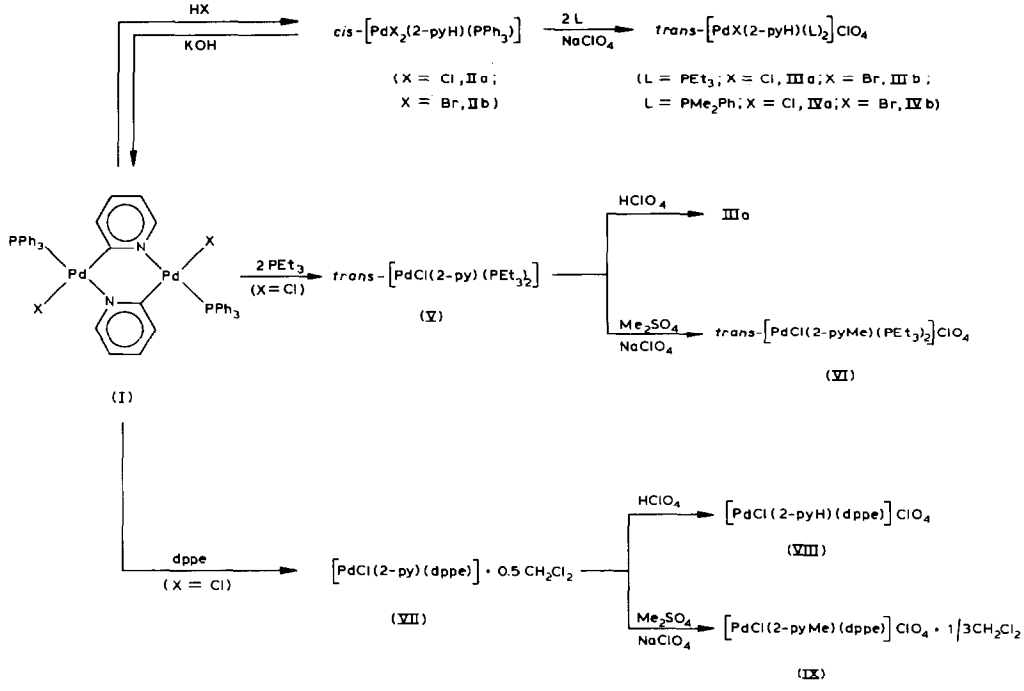
Because of our interest in the chemistry of complexes containing the M–C=N– unit, we have carried out some protonation and methylation reactions of palladium(II)- and platinum(II)-2-pyridyl compounds, and investigated the nature of the resulting products mainly by ^1H, ^{31}P and ^{13}C NMR spectroscopy.

Results and discussion

Protonation and methylation reactions

The reactions studied are depicted in Scheme 1 and Scheme 2.

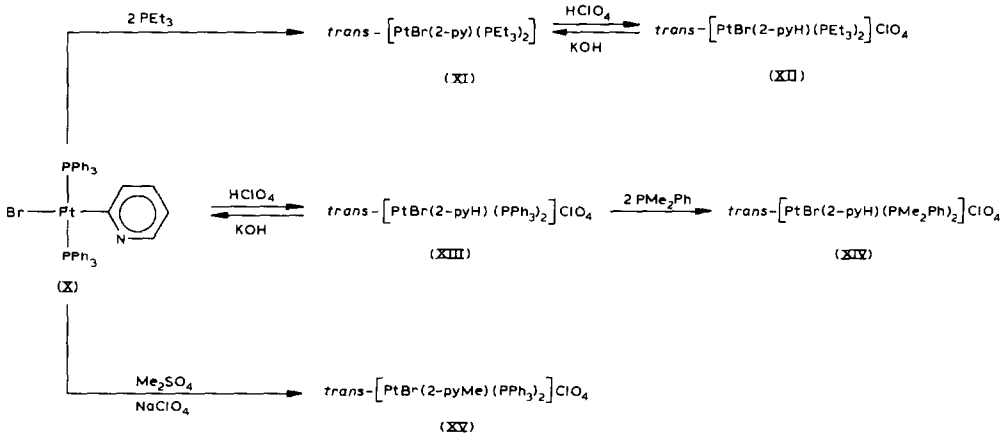
SCHEME 1



(2-py = 2-pyridyl group, $C_5H_4N-C^2$; 2-pyH and 2-pyMe = 1-protonated, $C_5H_5N-C^2$, and 1-methylated, $C_5H_4(1\text{-Me})N-C^2$ ligands, respectively; dppe = 1,2-bis(diphenylphosphino)ethane)

The PEt_3, PMe_2Ph and dppe derivatives were obtained by ligand substitution reactions from the parent PPh_3 compounds containig either the 2-py or the protonated 2-pyH ligand. The dppe complexes VII and IX crystallize with 1/2 and 1/3 of

SCHEME 2



a CH_2Cl_2 molecule, respectively, as shown by elemental analysis and ^1H NMR spectra (the CH_2Cl_2 signal occurs as a singlet at 5.26 ppm for VII in $CDCl_3$). The complexes V and XI were not isolated as solids, but were characterized in solution by multinuclear NMR spectroscopy (see further).

A marked difference in reaction rates is observed, depending on whether the 2-pyridyl group is acting as a C^2, *N*-bridging (complexes I) or as a C^2-terminal ligand (complexes V, VII, X and XI). The latter compounds are readily protonated at room temperature by methanolic $HClO_4$, whereas the reaction of the binuclear complexes I with HX is slow under comparable conditions. No reaction occurs between I and Me_2SO_4 even under forcing conditions (large excess of Me_2SO_4 and prolonged reaction times in refluxing 1,2-dichloroethane). In contrast to I [4], the compounds II do not undergo any migratory insertion of isocyanides (CNC_6H_{11}, CNC_6H_4OMe-*p*) into the metal–carbon bond.

As shown by chemical and spectral evidence, the electrophilic attack involves only the 2-pyridyl nitrogen atom, without cleavage of the M–C σ-bond. The presence of a rather acidic N–H group in the protonated products is indicated by the ease of hydrogen-deuterium exchange upon treatment with D_2O and by the reactions with KOH, in which the starting 2-pyridyl complexes are regenerated. The solid state IR spectra of complex IIIa is characterized by three ν(N–H) bands at 3208, 3180 and 3128 cm^{-1}, which shift to 2370, 2308 and 2240 cm^{-1} in the *N*-deuterated analogue, prepared by recrystallization of IIIa from a CH_2Cl_2/MeOD mixture. In the ^1H NMR spectra, the δ(N–H) signal appears as a broad unresolved absorption at rather low field, 14.4–10.1 ppm, and disappears immediately upon addition of D_2O. For the methylated derivatives, the δ(Me) resonance of the 2-pyMe group is observed as a singlet at 4.49 and 3.94 ppm for VI and IX, respectively, and as a singlet with ^{195}Pt satellites at 3.93 ppm for XV (^4J(Pt–H) 6.0 Hz). These low-field chemical shifts are better interpreted on the basis of a C_5H_4(1-Me)N–C^2 ligand (with a methyl group linked to a nitrogen atom bearing a partial positive charge) rather than on the basis of an *N*-coordinated 2-methylpyridine (which would result from electrophilic cleavage of the metal–carbon bond). This ligand in [PdX(η^3-crotyl)(2-methylpyridine)] (X = Cl, Br) and in *trans*-[NiR(2-methylpyridine)(PMe_2Ph)$_2$]ClO_4 (R = mesityl) exhibits δ(Me) resonances at markedly higher field (2.3–3.0 ppm) [6,7]. For compari-

son, we prepared the cationic complex *trans*-[PtBr(2-methylpyridine)(PPh_3)$_2$]BF_4 (see Experimental) and found that its spectral features are quite different from those of the structural isomer XV: ν(Pt–Br) 214 cm^{-1}; δ(Me) 2.95 ppm (^4J(Pt–H) 7.3 Hz); $\delta(^{31}P)$ 7.0 ppm (^1J(Pt–P) 3745.9 Hz).

All the cationic complexes are uni-univalent electrolytes in MeOH solution (Table 1) and have a *trans* P–M–P geometry, as shown by the NMR spectral data and by the occurrence of one M–P stretching vibration at 417–414 cm^{-1} (PEt_3 derivatives) and at 431–425 cm^{-1} (PMe_2Ph derivatives).

They are further characterized by the typical ν(Cl–O) and δ(Cl–O) vibrations of the perchlorate anion at ca. 1100 and 625 cm^{-1}, respectively, which are generally split into two or three bands because of symmetry reduction resulting from solid state effects and/or hydrogen bonding in the case of 2-pyH derivatives. Substantial hydrogen bonding with the perchlorate anion (or with the halide ligands in II) may also account for the presence of three ν(N–H) bands in all the 2-pyH complexes, in the range 3260–3110 cm^{-1}. Similar ν(N–H) splittings had been observed in cationic and neutral aminocarbene complexes of platinum and palladium, such as *trans*-[PtCl{CH(NHR)}(PEt_3)$_2$]ClO_4 [8], *trans*-[PdCl{C(NHPh)Ph}(PPh_3)$_2$]ClO_4 and *cis*-[$PdCl_2$(C(NHPh)Ph}(PPh_3)] [9]. The assignment of a *cis* configuration to IIa is based on the observation of two ν(Pd–Cl) vibrations at 304 and 276 cm^{-1}. In *cis*-[$PdCl_2$(C(NHPh)Ph}(PPh_3)] the corresponding bands were found at 306 and 267 cm^{-1} [9]. By analogy, a *cis* structure is also assigned to the bromo analogue IIb, even though only one ν(Pd–Br) band is observed at 190 cm^{-1}. This value seems to be too low for an asymmetric stretching vibration of a *trans* Br–Pd–Br arrangement, which occurs as an intense band in the range 255–265 cm^{-1} for $[PdBr_3(L)]^-$ and 261–279 cm^{-1} for *trans*-[$PdBr_2(L)_2$] (L = PMe_3, $AsMe_3$, PEt_3, $AsEt_3$) [10]. The two IR active ν(Pd–Br) bands of IIb are probably coincident, both tertiary phosphine and 2-pyH ligands having comparable *trans*-influences, as can be inferred from the similarity of ν(Pd–Br) values in the complexes *cis*-[$PdBr_2(PMe_3)_2$] (181 and 208 cm^{-1}), [$PdBr(PMe_3)_3$]BF_4 (203 cm^{-1}) [10] and *trans*-[PdBr(2-pyH)$(L)_2$]ClO_4 (L = PEt_3, 191; PMe_2Ph, 183 cm^{-1}).

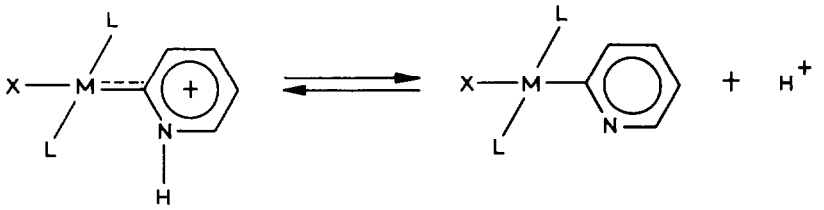
The ν(Pt–Br) absorption of *trans*-[PtBr(2-py)(PPh_3)$_2$] at 180 cm^{-1} increases of ca. 20 cm^{-1} in the protonated and methylated derivatives XIII and XV, while a smaller high-frequency shift of ν(Pd–Cl) (ca. 10 cm^{-1}) is also observed on going from complex VII to VIII and IX, in which the chloride ligand is *cis* to the 2-py, 2-pyH and 2-pyMe groups, respectively. These effects can be related to a decreased *trans*-influence of the *C*-bonded organic moiety and also to an increased positive charge on the central metal upon protonation or methylation. In addition to absorptions essentially due to Pd–Cl stretching modes (near 300 cm^{-1}), the far IR spectra of chloro complexes with *trans* Cl–Pd–2-pyH or Cl–Pd–2-pyMe geometries show another band in the range 256–240 cm^{-1}, which shifts to 237–224 cm^{-1}, with reduced intensity, in the bromo analogues. Such halogen dependence may be rationalized by assigning this band to a skeletal vibration, probably ν(Pd–2-pyH) or ν(Pd–2-pyMe), partially coupled with ν(Pd–Cl).

^1H and ^{31}P NMR spectra

The ^1H and ^{31}P NMR spectra of 2-py, 2-pyH and 2-pyMe complexes are listed in Table 2.

As mentioned above, the $\delta(H^1)$ signal generally occurs as a broad unresolved

band because of a fast exchange in solution:



The position of this equilibrium depends on the solvent, the temperature and the nature of the particular compound. In $CDCl_3$ and CD_2Cl_2 it is shifted more to the right than in DMSO-d_6, but it moves to the left on cooling. The dissociation increases in the order M = Pd > Pt and X = Br > Cl, and appears to be little affected by L. For complex IIIb in $CDCl_3$ and complex IVb in CD_2Cl_2, both H^1 signal and $^3J(H^1-H^6)$ coupling for the H^6 proton are absent under normal experimental conditions. However, they can be clearly observed when IVb is dissolved in DMSO-d_6 and when the $CDCl_3$ solution of IIIb is either cooled to −60°C or treated with $HClO_4$ at 30°C.

The pyridyl-ring protons of 2-py, 2-pyMe and 2-pyD complexes (the latter being obtained in solution by adding D_2O to the 2-pyH analogues) exhibit spectra of ABCD type, similar to those of 2-substituted pyridines [11], as can be seen in Fig. 1 for complex V.

A detailed analysis of such a four-spin system is beyond the scope of this work. However, on the basis of literature data [3,11] and on deuteration and spin-decoupling experiments, it is possible to assign, at least tentatively, the pyridyl-ring proton resonances for PEt_3 derivatives, and also for the other complexes when the signals are not masked by the P–Ph proton absorptions. Thus, the lower-field multiplet (8.7–7.9 ppm) is assigned to the H^6 proton, since in the 2-pyH complexes it shows a coupling ($^3J(H^1-H^6) \sim 6$ Hz) with the H^1 proton, which disappears upon deuteration or in the corresponding 2-pyMe compounds. Following the assignment reported for 2-substituted pyridines [11], the higher-field multiplet is attributed to the H^5 proton. This is supported also by spin-decoupling tests carried out on the 2-pyMe complex VI. By irradiating at 8.7 ppm (H^6 resonance), the multiplet centered at 7.4 ppm changes considerably (it becomes a four-lines signal), whereas the absorptions in the range 7.9–7.5 ppm (H^3 and H^4 protons) are only little affected. Under first-order approximation, the following coupling constants can be obtained: $^3J(H^5-H^6)$ 6.2; $^3J(H^4-H^5)$ 6.5; $^4J(H^3-H^6) \sim 1$; $^4J(H^3-H^5)$ 2.5 Hz. From the resonance pattern of the H^6 proton in the spectra of the other compounds of Table 2, $^3J(H^5-H^6)$ coupling constants of similar magnitude (5–6 Hz) are also measured. In general, the H^3 and H^4 protons give rise to two overlapping multiplets in a chemical shift range intermediate between $\delta(H^6)$ and $\delta(H^5)$ signals.

As can be seen in Table 2, protonation or methylation of terminal 2-py ligand brings about a down-field shift (0.2–0.5 ppm) for all the pyridyl-ring protons. An increasing deshielding is also observed for the complexes *trans*-$[MX(2\text{-pyH})(L)_2]ClO_4$ when L is changed in the order $PEt_3 > PMe_2Ph > PPh_3$, other things being equal. This trend is clearly related to the number of phenyl groups attached to the phosphorus atom of L and may be accounted for by the increasing shielding effect of phenyl ring currents with decreasing *n* in square-planar compounds of the type

(Continued on p. 402)

TABLE 1

ANALYTICAL, PHYSICAL DATA, AND CHARACTERISTIC IR BANDS

Compound		Melting point (°C) [a]	Analyses (Found (calcd.) (%))				Molar conductivity (ohm^{-1} cm^2 mol^{-1}) [b]	IR (cm^{-1})			
			C	H	N	X		ν(N–H)	ν(M–X)	ν(M–P)	Other bands
cis-[$PdCl_2$(2-pyH)(PPh_3)]	(IIa)	220 (dec.)	53.5 (53.26)	3.8 (3.89)	2.6 (2.70)	13.8 (13.67)		3180sh; 3162m; 3105m	304m; 276m		245m
cis-[$PdBr_2$(2-pyH)(PPh_3)]	(IIb)	243	45.5 (45.46)	3.2 (3.32)	2.2 (2.31)	26.5 (26.30)		3180sh; 3155m; 3110m	190m		224mw
trans-[PdCl(2-pyH)(PMe_2Ph)$_2$]ClO_4	(IVa)	197	42.4 (42.27)	4.6 (4.56)	2.3 (2.35)	11.8 (11.88)	102.9	3260sh; 3225m, br; 3144m	314m	427m	249m
trans-[PdBr(2-pyH)(PMe_2Ph)$_2$]ClO_4	(IVb)	198	39.4 (39.34)	4.2 (4.24)	2.2 (2.18)	3.1 [c] (3.12)	92.6	3225m, br; 3190sh 3140m	183m	425m	237w
trans-[PdCl(2-pyH)(PEt_3)$_2$]ClO_4	(IIIa)	187	36.6 (36.67)	6.4 (6.34)	2.4 (2.52)	12.6 (12.74)	105.2	3208m, 3180sh, 3128m	315m	415m	256ms
trans-[PdBr(2-pyH)(PEt_3)$_2$]ClO_4	(IIIb)	186	33.7 (33.96)	5.7 (5.87)	2.3 (2.33)	3.4 [c] (3.33)	102.1	3210m; 3185m; 3130m	191m	414m	235w

trans-[PdCl(2-pyMe)(PEt_3)$_2$]ClO_4	(IV)	220	37.8 (37.88)	6.4 (6.53)	2.4 (2.45)	12.4 (12.42)	106.3		309m	417m	240m
[PdCl(2-py)(dppe)]·0.5CH_2Cl_2	(VII)	163–166	57.0 (57.25)	4.4 (4.42)	2.0 (2.12)	10.4 (10.73)			295m		
[PdCl(2-pyH)(dppe)]ClO_4	(VIII)	221	51.4 (51.80)	3.9 (4.07)	1.8 (1.95)	10.0 (9.86)	97.9	3230m, br; 3180sh 3130mw	304m		
[PdCl(2-pyMe)(dppe)]$ClO_4 \cdot \frac{1}{3}CH_2Cl_2$	(IX)	170	50.9 (51.02)	4.1 (4.19)	1.8 (1.84)	12.5 (12.42)	93.9		305m		
trans-[PtBr(2-py)(PPh_3)$_2$]	(X)	216	55.9 (56.11)	3.8 (3.90)	1.5 (1.60)	9.0 (9.11)			180m		
trans-[PtBr(2-pyH)(PPh_3)$_2$]ClO_4	(XIII)	258	49.9 (50.34)	3.7 (3.61)	1.3 (1.43)	2.08 [c] (2.04)	115.1	3215m; 3200sh; 3135m	201m		250w
trans-[PtBr(2-pyMe)(PPh_3)$_2$]ClO_4	(XV)	273	50.9 (50.84)	3.8 (3.76)	1.3 (1.41)	2.0 [c] (2.02)	103.8		200m		255w
trans-[PtBr(2-pyH)(PMe_2Ph)$_2$]ClO_4	(XIV)	245	34.8 (34.56)	3.8 (3.73)	1.8 (1.92)	2.68 [c] (2.74)	113.2	3260sh; 3220m, br 3145m	193m	431m	247w
trans-[PtBr(2-pyH)(PEt_3)$_2$]ClO_4	(XII)	218	29.7 (29.60)	5.1 (5.11)	2.0 (2.03)	2.9 [c] (2.9)	107.7	3205m; 3185sh; 3130m	198m	415m	248mw

[a] Uncorrected values. [b] For 10^{-3} *M* MeOH solution at 20°C. [c] Total halogen content in meq g^{-1}.

TABLE 2

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

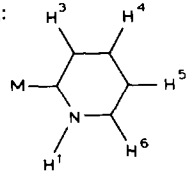
Compound		Pyridyl ring protons [b]			
		H^1 or N–CH_3	$H^3 + H^4$	H^5	H^6
cis-[$PdCl_2$(2-pyH)(PPh_3)]	(IIa)	10.1 br [c]	m [d]	7.0m	8.0m $^3J(H^1-H^6)$ = 6.0 $^3J(H^5-H^6)$ ~ 5.5
cis-[$PdBr_2$(2-pyH)(PPh_3)]	(IIb)	14.3 br [c]	m [d]	6.9m	7.9m $^3J(H^1-H^6)$ = 6.0 $^3J(H^5-H^6)$ ~ 5.5
trans-[PdCl(2-pyH)(PMe_2Ph)$_2$]ClO_4	(IVa)	13.1 br [c]	m [d]	6.9m	8.0m $^3J(H^1-H^6)$ = 6.0 $^3J(H^5-H^6)$ ~ 6
trans-[PdBr(2-pyH)(PMe_2Ph)$_2$]ClO_4	(IVb)	12.3 br [c]	m [d]	7.1m	8.2m,br $^3J(H^1-H^6)$ ~ 6 $^3J(H^5-H^6)$ ~ 6
trans-[PdCl(2-py)(PEt_3)$_2$] [g]	(V)		7.4–7.0m	6.7m	8.4m $^3J(H^5-H^6)$ ~ 5
trans-[PdCl(2-pyH)(PEt_3)$_2$]ClO_4	(IIIa)	13.6 br [c]	7.9–7.5m	7.2m	8.6m $^3J(H^1-H^6)$ ~ 6 $^3J(H^5-H^6)$ ~ 6
trans-[PdBr(2-pyH)(PEt_3)$_2$]ClO_4 [h]	(IIIb)	13.4 br [c] (13.2) [i]	7.9–7.5m (8.0–7.6) [i]	7.3m (7.3) [i]	8.6m $^3J(H^1-H^6)$ = 6.0 $^3J(H^5-H^6)$ ~ 5.5 (8.6) [i]
trans-[PdCl(2-pyMe)(PEt_3)$_2$]ClO_4	(VI)	4.49s	7.9–7.5m	7.4m	8.7m $^3J(H^5-H^6)$ = 6.2
[PdCl(2-py)(dppe)]·0.5CH_2Cl_2	(VII)		7.1–6.8m	6.6m	m [d]
[PdCl(2-pyH)(dppe)]ClO_4	(VIII)	14.4br [c]	m [d]	m [d]	8.3m,br
[PdCl(2-pyMe)(dppe)]$ClO_4 \cdot \frac{1}{3}CH_2Cl_2$	(IX)	3.94s	m [d]	m [d]	m [d]
trans-[PtBr(2-py)(PPh_3)$_2$]	(X)		6.7–5.9m [k]		m [d]
trans-[PtBr(2-pyH)(PPh_3)$_2$]ClO_4	(XIII)	12.5br [c]	m [d]	6.6m	m [d]

Phosphine protons					
P–C_6H_5	P–CH_3	P–CH_2	P–CH_2–CH_3	δ(P)	Solvent
7.8–7.2m				n.r.[e]	DMSO-d_6
7.8–7.2m				n.r.[e]	DMSO-d_6
7.6–7.1m	1.83t J(P–H) = 7.7[f] 1.69t J(P–H) = 7.5[f]			−4.2s	CD_2Cl_2
7.7–7.2m	1.69t J(P–H) = 7.6[f] 1.53t J(P–H) = 7.2[f]			n.r.[e]	DMSO-d_6
		1.8–1.3m	1.08q	12.4s	$CDCl_3$
		1.8–1.3m	1.04q	17.7s	$CDCl_3$
		1.8–1.4m	1.04q	16.2s	$CDCl_3$
		1.7–1.2m	0.97q	18.0s	$CDCl_3$
8.3–7.2m		2.9–1.8m		47.4d 29.7d ^2J(P–P) = 31.8	CD_2Cl_2
8.2–7.2m		m[j]		58.5d; 45.0d ^2J(P–P) = 20.0	DMSO-d_6
8.3–7.0M		3.1–1.8m		57.0d; 46.4d ^2J(P–P) = 19.4	CD_2Cl_2
7.8–7.2m				22.9t ^1J(Pt–P) = 3196.7	CD_2Cl_2
7.9–7.0m				19.1t[f] ^1J(Pt–P) = 2651.3	CD_2Cl_2

TABLE 2 (continued)

Compound		Pyridyl ring protons [b]			
		H^1 or N-CH_3	$H^3 + H^4$	H^5	H^6
trans-[PtBr(2-pyMe)$(PPh_3)_2$]ClO_4	(XV)	3.93t ^4J(Pt–H) = 6.0	m [d]	6.7m	m [d]
trans-[PtBr(2-pyH)$(PMe_2Ph)_2$]ClO_4	(XIV)	13.1 br [c]	m [d]	6.8m	7.9m,br $^3J(H^1-H^6) \sim 6$ $^3J(H^5-H^6) \sim 6$
trans-[PtBr(2-py)$(PEt_3)_2$] [g]	(XI)		7.5–7.0m	6.8m	8.3m $^3J(H^5-H^6) \sim 5$
trans-[PtBr(2-pyH)$(PEt_3)_2$]ClO_4	(XII)	13.2br [c]	7.9–7.5m	7.2m	8.6m,br $^3J(H^1-H^6) \sim 6$ $^3J(H^5-H^6) \sim 6$

[a] ^{1}H chemical shifts (δ) in ppm from TMS at 30°C; ^{31}P chemical shifts (δ) from external 85% H_3PO_4 (downfield shifts taken as positive); coupling constants in Hz; s = singlet, d = doublet, t = triplet, tt triplet of triplets, q = quintet, m = multiplet, br = broad; satisfactory integration values have been obtained. [b] Pyridyl protons labelling:



trans-[MXY$(PR_nPh_{3-n})_2$] (R = alkyl group; $n = 0$–3), in the proximity of the plane passing through the X–M–Y atoms and perpendicular to the metal-coordination plane [12]. The 2-pyH group in *trans*-[MX(2-pyH)$(PMe_2Ph)_2$]ClO_4 in fact lies in a plane of this type, as can be inferred from ^{1}H and ^{31}P NMR data. The ^{31}P NMR spectra of IV and XIV are characterized by singlet ^{31}P resonances (with ^{195}Pt satellites in the case of XIV), which are indicative of mutually *trans* PMe_2Ph ligands. Furthermore, the ^{1}H NMR spectra exhibit 1/2/1 triplet patterns for δ(P–Me), typical of virtually coupled *trans*-PMe_nPh_{3-n} ($n = 1$–3) moieties. The equivalence of the two ^{31}P phosphine nuclei and the occurrence of two distinct P–Me triplets (1/1 integration ratio) for each complex indicate a molecular structure in which the asymmetric 2-pyH ligand is oriented perpendicularly to the coordination plane with hindered rotation about the metal–carbon bond. In this geometry, the two methyl groups on the same phosphine have different magnetic environments because there is no plane of symmetry through the $MX(C^2)P_2$ atoms. Analogous configurations have been reported for *trans*-[NiX(R)$(PMe_2Ph)_2$] (X = halide, C_6Cl_5; R = *o*- or *m*-tolyl) [13] or *trans*-[NiR′(L)$(PMe_2Ph)_2$]$^+$ (R′ = mesityl; L = 2- and 3-methylpyri-

Phosphine protons					
P–C_6H_5	P–CH_3	P–CH_2	P–CH_2–CH_3	δ(P)	Solvent
7.8–7.1m				17.6t ^1J(Pt–P) = 2632.1	CD_2Cl_2
7.7–7.1m	1.95tt J(P–H) = 8.0 [f] ^3J(Pt–H) = 28.0 1.83tt J(P–H) = 7.8 [f] ^3J(Pt–H) = 30.4			−7.7t ^1J(Pt–P) = 2427.3	CD_2Cl_2
		1.9–1.2m	0.93q	12.6t ^1J(Pt–P) = 2825.6	$CDCl_3$
		1.9–1.3m	0.97q	13.3t ^1J(Pt–P) = 2386.2	$CDCl_3$

the ppm range is given for H^3 and H^4 protons since they appear as two overlapping multiplets; the chemical shifts of H^5 and H^6 proton refer to the center of the corresponding multiplets. [c] Broad unresolved signal. [d] Masked by the intense phenyl proton resonances. [e] Not recorded. [f] J(P–H) = $|^2J$(P–H)+^4J(P′–H)|. [g] Obtained upon treatment of the corresponding 2-pyH derivative with aqueous KOH. [h] Spectrum recorded in the presence of added $HClO_4$. [i] In $CDCl_3$ solution at −60°C. [j] Masked by the H_2O and DMSO resonances. [k] Overlapping multiplets. [l] In $CDCl_3$ solution.

dine) [7], where the planar asymmetric ligands R or L are perpendicular to the nickel coordination plane, with restricted rotation around the Ni–R or Ni–L bond due to steric interaction of the *o*- and *m*-methyl groups with the *trans* PMe_2Ph ligands.

When a CD_2Cl_2 solution of complex XIV is treated with aqueous KOH, quantitative deprotonation takes place and the resulting 2-pyridyl derivative, *trans*-[PtBr(2-py)$(PMe_2Ph)_2$], shows δ(P–Me) as only one 1/2/1 triplet at 1.54 ppm (see Fig. 2) and $\delta(^{31}P)$ as a singlet at −7.2 ppm, both signals being flanked by ^{195}Pt satellites (^3J(Pt–Me) 32.6 and ^1J(Pt–P) 2889.2 Hz).

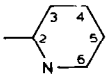
These NMR data strongly suggest that the 2-py ligand is freely rotating in the deprotonated product, so as to produce two average planes of symmetry (one in the platinum coordination plane and the second perpendicular to it through the Br–Pt–C atoms). At ambient temperature, free rotation around the M–C(sp^2) bond occurs also for other cyclic asymmetric ligands in complexes of the type *trans*-[$M(C_6Cl_5)R(PMe_2Ph)_2$] (M = Ni; R = 2-furyl or 2-thienyl [13b]; M = Ni, Pd, Pt; R = cyclic α-alkoxyvinyl or alkyl(alkoxy)carbene [14]).

Models based on structural data for *trans*-[PdBr(2-py)$(PEt_3)_2$] [3] and on Pauling

TABLE 3

^{13}C (^{1}H) NMR SPECTRAL DATA FOR PEt_3 DERIVATIVES [a]

Compound	Pyridyl-ring carbons					N–CH_3	Phosphine carbons	
	C^2	C^3	C^4	C^5	C^6		P–CH_2	P–CH_2–CH_3
trans-[PdBr(2-py)(PEt_3)$_2$] [b]	179.7 ^2J(P–C) = 6.0	133.3 ^1J(C–H) = 163.2	132.5 ^1J(C–H) = 161.8	117.5 ^1J(C–H) = 163.2	149.1 ^1J(C–H) = 176.5		14.9 ^1J(C–H) = 129.4	8.1 ^1J(C–H) = 129.4
trans-[PdBr(2-pyH)(PEt_3)$_2$]ClO_4 (IIIb)	184.9 ^2J(P–C) = 7.5	137.3 ^3J(P–C) ~ 3	139.4	120.7	142.9		15.1 J(P–C) [c] = 28.3	7.9
trans-[PdCl(2-pyH)(PEt_3)$_2$]ClO_4 (IIIa)	183.6 ^2J(P–C) = 8.0	137.3 ^3J(P–C) ~ 3	139.4	120.5	142.8		14.5 J(P–C) [c] = 27.6	7.8
trans-[PdCl(2-pyMe)(PEt_3)$_2$]ClO_4 (VI)	186.6 ^2J(P–C) = 7.5	137.5 ^1J(C–H) = 168.4	137.5 ^1J(C–H) = 168.4	122.1 ^1J(C–H) = 171.2	146.3 ^1J(C–H) = 188.0	52.9 ^1J(C–H) = 142.0	14.3 J(P–C) [c] = 28.2 ^1J(C–H) = 131.2	7.9 ^1J(C–H) = 131.2
trans-[PtBr(2-py)(PEt_3)$_2$] [d] (XI)	163.7 ^2J(P–C) = 7.2	134.0 ^2J(Pt–C) = 110.0 ^3J(P–C) = 3.5	132.7 ^3J(Pt–C) = 62.0	116.9 ^4J(Pt–C) = 12.0	149.1 ^3J(Pt–C) = 97.5		14.2 J(P–C) [c] = 33.8 ^2J(Pt–C) = 36.0	7.6 ^3J(Pt–C) = 25.7
trans-[PtBr(2-pyH)(PEt_3)$_2$]ClO_4 (XII)	168.1 ^2J(P–C) = 8.4	137.9 ^2J(Pt–C) = 68.8	140.2 ^3J(Pt–C) = 55.2	120.0 ^4J(Pt–C) = 10.0	142.0 ^3J(Pt–C) = 62.0		14.3 J(P–C) [c] = 34.4 ^2J(Pt–C) = 31.0	7.5 ^3J(Pt–C) = 23.6

[a] Chemical shifts (δ) in ppm from TMS, in $CDCl_3$ at 30°C; coupling constants in Hz; pyridyl-ring carbon labelling:  [b] From Ref. 20. [c] J(P–C) = $|^1J$(P–C) + ^3J(P′–C)|. [d] Obtained upon treatment of the corresponding 2-pyH derivative with aqueous KOH.

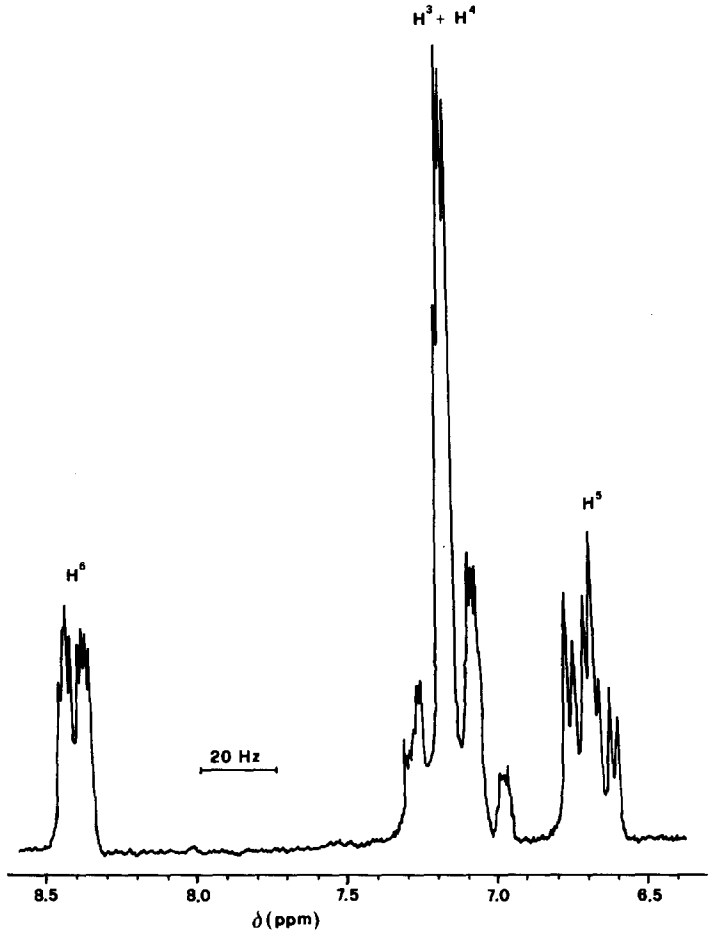
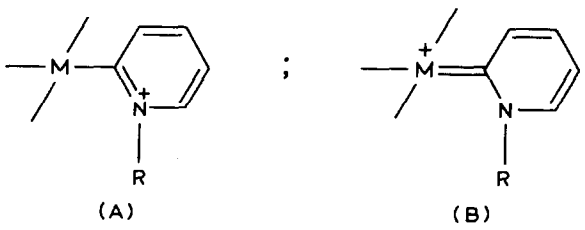


Fig. 1. ^{1}H NMR spectrum of *trans*-[PdCl(2-py)$(PEt_3)_2$] (V) in $CDCl_3$, in the pyridyl-proton range.

covalent radii [15] show that the 2-py and 2-pyH ligands have comparable steric requirements (unless large changes in bond distances and angles occur upon protonation) and that rotation about the M–C bond involves only some H ··· H interaction between pyridyl-ring protons (H^1 and H^6) and P–Me or *ortho* P–Ph protons of PMe_2Ph. Consequently, restricted rotation of 2-pyH in IV and XIV seems to be due more to electronic than to steric factors. In terms of valence bond theory, the 1-protonated and 1-methylated 2-pyridyl ligands may be represented, among the others, by the limiting structure A (corresponding to a 1-R-2-pyridylium group) and B (corresponding to a 1-R-2-pyridylidene group):



A 2-pyridylidene moiety has previously been investigated on purely theoretical grounds as far as the energy levels and charge density distribution are concerned [16].

A significant contribution of the carbene-like structure B brings about (i) a partial double bond character in the M–C bond (π back-donation of metal *d* electrons of appropriate symmetry), which would account for the observed hindered rotation of the protonated ligand and the inertness of the M–C bond towards electrophilic attack and migratory insertion of isocyanides, and (ii) a lower electron charge density on the metal center, which would account for the higher frequency shift of

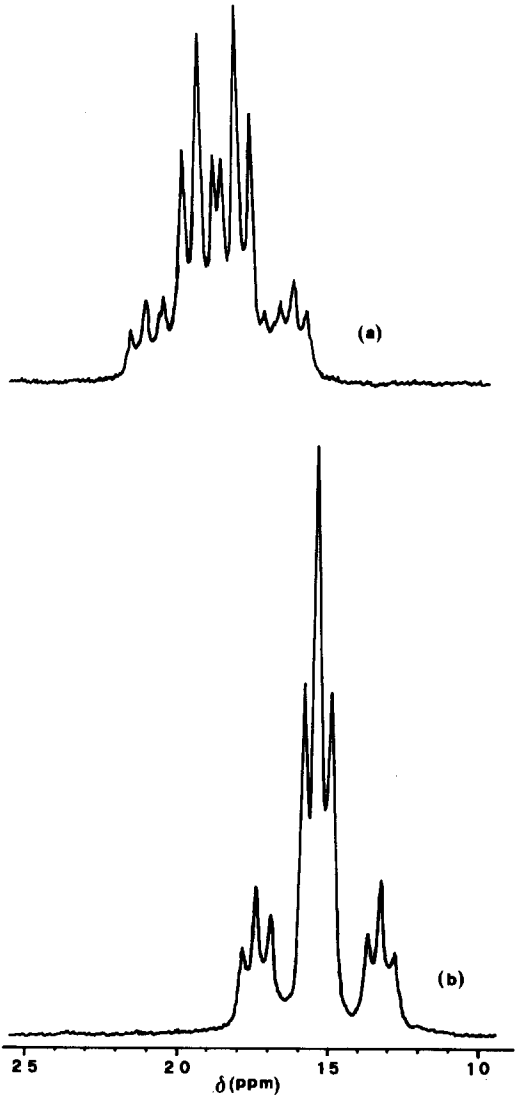


Fig. 2. The δ(P–Me) resonance patterns of (a) *trans*-[PtBr(2-pyH)$(PMe_2Ph)_2$]ClO_4 (XIV) and (b) *trans*-[PtBr(2-py)$(PMe_2Ph)_2$] in CD_2Cl_2 at 30°C.

ν(Pd–Cl) on going from the dppe complex VII to the protonated or methylated derivatives VIII or IX. The marked decrease (565–440 Hz) in ^1J(Pt–P) values upon protonation or methylation of *trans*-[PtBr(2-py)$(L)_2$] ($L = PPh_3$, PMe_2Ph, PEt_3) may be related to a decreased σ-donor/π-acceptor ratio of 2-pyR relative to the parent 2-py ligand. In the series of complexes *cis*-[$PtCl_2(PBu^n_3)(L)$], the ^1J(Pt–P) coupling constant relative to the ^{31}P nucleus of PBu^n_3 was found to depend on the *cis* ligand L in the order: $L = PBu^n_3$, $PEt_3 > PMe_2Ph > PPh_3 > P(OMe)_3 > P(OPh)_3$ [17]. Although steric factors may also be important, this is the order of decreasing σ-donor/π-acceptor ratio of L, as suggested by IR data for *cis*-[$PdCl_2(CNC_6H_4Me$-*p*$)(L)$] [18]. It is of interest that the ^2J(P–P) coupling constant of dppe complexes also decreases, from 31.8 Hz for VII to 20.0 and 19.4 Hz for VIII and IX, respectively.

As for the bis(dimethylphenylphosphine) complexes, a *trans* configuration is assigned to the bis(triethylphosphine) and bis(triphenylphosphine) analogues on the basis of ^{31}P resonance patterns. In each case a singlet is observed, with symmetrical ^{195}Pt satellites for platinum derivatives. This is further confirmed by the appearance of characteristic virtually coupled quintets for the methyl ^1H NMR signals of the coordinated PEt_3 ligands.

^{13}C NMR spectra

The $^{13}C\{^1H\}$ NMR spectra of PEt_3 derivatives are listed in Table 3.

The assignment of pyridyl-ring carbons is based on chemical shift and coupling constant considerations, as well as on previous ^{13}C data for pyridinium, 1-Me-pyridinium salts [19] and for *trans*-[$PdBr(2\text{-py})(PEt_3)_2$] [20]. The higher field resonance is attributed to the C^5 carbon, as it shows the smallest Pt–C coupling in complexes XI and XII. On the other hand, the lower field resonance is assigned to the quaternary C^2 carbon, as no C^2–H coupling is observed in the proton-coupled spectrum of VI. This signal appears as a 1/2/1 triplet due to coupling with the equivalent ^{31}P nuclei of the *trans* PEt_3 ligands. Because of its reduced intensity, no ^{195}Pt satellites are observed for XI and XII. The signal in the range 149.1–142.0 ppm is very close to the chemical shifts of α-carbons in pyridine and pyridinium cation, and is therefore assigned to the C^6 carbon. The assignment of C^3 and C^4 carbons follows from the different values of J(Pt–C) and J(P–C), on the assumption that coupling constants generally decrease with increasing number of bonds between the coupled nuclei. However, this assignment may possibly be reversed, since in M–Ph derivatives (M = Sn, Pt) the ^3J(M–C) for the *meta* carbons is larger than ^2J(M–C) for the *ortho* carbons [21]. The chemical shift of the N–Me carbon in the 2-pyMe complex VI (52.9 ppm) is in a good agreement with δ(N–Me) values in 4-substituted 1-methylpyridinium cations [19].

In the pyridinium salts, the β carbons (C^3, C^5) and the γ carbon (C^4) are shifted downfield by 3.1 and 9.8 ppm, respectively, relative to free pyridine, whereas for the α carbons (C^2, C^6) an upfield shift of 7.2 ppm is observed [19]. The deshielding of β and γ carbons arise from charge polarization effects (decreased electron density), whereas the shielding of the α carbons is explained by a decrease in N–C_α bond order [22] and a concomitant increase in the average excitation energy ΔE [23], which more than compensate for the decrease in charge density on the α carbons.

As can be seen in Table 3, the protonation of the 2-py group brings about downfield shifts for C^3, C^4 and C^5 carbons and an upfield shift for the C^6 carbon,

which are of comparable magnitude to those observed in the protonation of pyridine and can be interpreted in the same way. In contrast, the metal bound C^2 carbon is now deshielded. This effect can be explained by taking into account the contribution of the carbene-like structure B to the electronic configuration of the 2-pyH ligand, since an increased M–C^2 bond order would result in a lower value of ΔE and a larger value of the two-center paramagnetic shielding term (Q_{AB}) in the Pople expression for the paramagnetic screening constant [24]. Similar arguments have been advanced to account for the low-field chemical shift of the carbene–carbon resonances in transition metal-carbene complexes [25]. The marked decrease in J(Pt–C) values for the pyridyl-ring carbons in the protonated derivative XII is probably related to an increased π-character of the Pt–2-pyH bond, as previously suggested for platinum-carbene compounds derived from protonation of iminomethyl ligands [8].

The ^{13}C parameters of the PEt_3 ligands are similar to those reported for related systems [26]. The resonance patterns (a 1/2/1 triplet for P–CH_2– and a singlet for P–CH_2–CH_3, with symmetrical ^{195}Pt satellites in XI and XII) lend further support to the *trans* configuration of these complexes, as already proposed on the basis of ^1H and ^{31}P NMR data.

Experimental

The complexes I, [PdX(μ-2-py)(PPh_3)]$_2$ (X = Cl, Br) [20], and [Pt(PPh_3)$_4$] [27] were prepared by published methods. All other chemicals were reagent grade, and used without further purification. Infrared spectra were recorded with Perkin–Elmer 597 and 580-B instruments, using Nujol mulls and CsI plates in the range 4000–250 cm^{-1} and polythene plates in the range 600–170 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 $CDCl_3$ solutions for ^{13}C NMR spectra contained ca. 4×10^{-2} *M* [Cr(acac)$_3$] in order to reduce the relaxation times for all the ^{13}C nuclei.

All the 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. "Methanolic perchloric acid" refers to a solution made up by diluting 6 ml of 60–62% aqueous perchloric acid to 250 ml with MeOH; titration showed it to be 0.22 *M* in acid.

Preparation of cis-[PdX$_2$(2-pyH)(PPh$_3$)] (X = Cl, IIa; X = Br, IIb)

The complex I (1 mmol) dissolved in CH_2Cl_2 (50 ml) was treated with a methanol solution of HX (molar ratio Pd/HX 1/3) and the mixture was set aside overnight. The microcrystalline pale-yellow product II, which began to precipitate after 4–5 h, was filtered off and the solution was concentrated to small volume. Addition of diethyl ether gave a second crop of protonated derivative II. (Yield, based on the theoretical amount: 83% IIa; 95% IIb).

Preparation of trans-[PdX(2-pyH)(L)$_2$]ClO$_4$ (L = PEt$_3$; X = Cl, IIIa; X = Br, IIIb; L = PMe$_2$Ph; X = Cl, IVa; X = Br, IVb)

These compounds were prepared by the following procedure:

(a) The complex II, *cis*-[PdX$_2$(2-pyH)(PPh_3)] (1 mmol), suspended in CH_2Cl_2 (50

ml) was treated with two equivalents of the phosphine L under dinitrogen. The resulting clear solution was stirred for 30 min, then an excess of $NaClO_4 \cdot H_2O$ (0.42 g, 3 mmol) dissolved in MeOH (10 ml) was added. After stirring for 10 min, the mixture was evaporated to dryness and the solid residue was extracted with CH_2Cl_2 (50 ml) and charcoal. After filtration of the extract, MeOH (10 ml) was added, and the more volatile CH_2Cl_2 was slowly evaporated off until some precipitate appeared, and precipitation was completed by dropwise addition of diethyl ether. The white complexes III and IV can be recrystallized in a similar way from the same mixture of solvents (Yield: 75% IIIa; 80% IIIb; 67% IVa; 78% IVb).

When the complex IIIa was recrystallized from a dry CH_2Cl_2/MeOD mixture (3/2 v/v) and dry diethyl ether was used to complete the precipitation, the *N*-deuterated analogue was obtained. This compound must be filtered under dry N_2 and dried in vacuo, in order to avoid partial D-H exchange with the moisture of the air.

(b) The complex IIIa was also obtained by protonation of the intermediate V, *trans*-[PdCl(2-py)$(PEt_3)_2$]. The binuclear complex [PdCl(μ-2-py)$(PPh_3)]_2$ (0.964 g, 1 mmol) was suspended in dry diethyl ether (80 ml) and added with PEt_3 (0.473 g, 4 mmol), under N_2. The mixture was stirred overnight then treated with charcoal and filtered. The solution was evaporated to dryness to leave an oily residue. This was dissolved in MeOH (50 ml) and an MeOH solution of $HClO_4$ was added (molar ratio Pd/$HClO_4$ = 1/3). After concentration to small volume, the product IIIa was precipitated and recrystallized as described above (Yield 0.64 g, 57.5%).

Preparation of trans-[PdCl(2-pyMe)$(PEt_3)_2$]ClO_4 (VI)

The complex *trans*-[PdCl(2-py)$PEt_3)_2$], obtained as an oily residue from the reaction of [PdCl(μ-2-py)$(PPh_3)]_2$ (0.482 g, 0.5 mmol) with PEt_3 (0.236 g, 2 mmol) as described above, was dissolved in benzene (40 ml) and added with an excess of Me_2SO_4 (1.26 g, 10 mmol). The mixture was heated at 60°C for 2 h and set aside overnight at room temperature. Concentration to small volume and dilution with diethyl ether gave a white precipitate, which was redissolved in CH_2Cl_2 (50 ml) and treated with a solution of $NaClO_4 \cdot H_2O$ (0.42 g, 3 mmol) in 10 ml of MeOH. The white product VI was isolated and purified as in the case of the protonated derivatives III and IV (Yield 0.38 g, 66.6%).

In a second preparation, the starting compound *trans*-[PdCl(2-py)$(PEt_3)_2$] was prepared from deprotonation of IIIa (0.557 g, 1 mmol), dissolved in CH_2Cl_2 (50 ml), with alcoholic KOH (molar ratio Pd/KOH = 1/1). The reaction mixture was taken to dryness and the oily residue was treated with benzene and charcoal. Filtration gave a clear solution, which was used for the reaction with Me_2SO_4 (Yield 0.35 g, 63%).

Preparation of [PdCl(2-py)(dppe)] –0.5CH_2Cl_2 (VII), [PdCl(2-pyH)(dppe)]ClO_4 (VIII) and [PdCl(2-pyMe)(dppe)]ClO_4 –1/3CH_2Cl_2 (IX)

(a) The complex [PdCl(μ-2-py)$(PPh_3)]_2$ (1.45 g, 1.5 mmol) was dissolved in CH_2Cl_2 (80 ml) and treated with dppe (1.20 g, 3 mmol). After stirring for 30 min, the solution was concentrated to small volume and the product VII was precipitated by addition of diethyl ether. It was purified by double reprecipitation from the same solvents (Yield 1.65 g, 83.2%). This compound decomposes slowly at room temperature, even under N_2, and its colour changes from off-white to yellow-orange.

(b) Methanolic $HClO_4$ was added to a solution of VII (0.66 g, 1 mmol) in 50 ml of CH_2Cl_2 (molar ratio $Pd/HClO_4 = 1/3$). The product was worked up as in the case of protonation of V, to yield the white product VIII (0.61 g, 85%).

(c) A solution of VII (0.66 g, 1 mmol) in 50 ml of CH_2Cl_2 was treated with Me_2SO_4 (1.26 g, 10 mmol). After heating to reflux for 2 h and standing overnight at room temperature, the mixture was worked up as for the methylation of V, to give the white product IX (0.60 g, 78.8%).

Reaction of cis-[$PdCl_2$(2-pyH)(PPh_3)] (IIa) with KOH

Alcoholic KOH (8.5 ml of a 0.09 *N* solution) was added dropwise to a stirred suspension of IIa (0.40 g, 0.77 mmol) in CH_2Cl_2 (50 ml). After 15 min, the solvents were evaporated to dryness, and the solid residue was treated with CH_2Cl_2 and charcoal. The mixture was filtered and the clear solution was concentrated to small volume. Upon addition of diethyl ether, the binuclear complex [PdCl(μ-2-py)(PPh_3)]$_2$ (0.30 g, 80.7%) was obtained as a yellow microcrystalline precipitate.

Preparation of trans-[PtBr(2-py)(PPh_3)$_2$] (X), trans-[PtBr(2-pyH)(PPh_3)$_2$]ClO_4 (XIII) and trans-[PtBr(2-pyMe)(PPh_3)$_2$]ClO_4 (XV)

(a) A suspension of [$Pt(PPh_3)_4$] (6 g, 4.82 mmol) in benzene (100 ml), containing 2-bromopyridine (1.52 g, 9.64 mmol), was heated at 90°C for 7 h under N_2. After standing overnight at room temperature the mixture was treated with charcoal, filtered, and the clear solution was concentrated to small volume. Addition of Et_2O/n-hexane (3/1 v/v) gave a pale-yellow precipitate, which was redissolved in a C_6H_6/CH_2Cl_2 mixture (1/1 v/v). After treatment of the solution with charcoal, filtration and concentration, the analytically pure product X (3.5 g, 82.7%) was precipitated by dilution with Et_2O/n-hexane (3/1 v/v).

(b) The reaction of X (1 g, 1.14 mmol) with methanolic $HClO_4$ was carried out in the same way as for the protonation of VII, yielding the white complex XIII (1 g, 89.7%).

(c) The reaction of X (0.88 g, 1 mmol) with Me_2SO_4 was carried out as described above for the methylation of VII (Yield of product XV 0.75 g, 75.6%).

Preparation of trans-[PtBr(2-pyH)(PEt_3)$_2$]ClO_4 (XII)

The complex X (1.755 g, 2 mmol) was suspended in dry Et_2O (80 ml) and added with PEt_3 (0.473 g, 4 mmol) under N_2. The mixture was stirred overnight and worked up as in the preparation of IIIa, to give the white product XII (0.76 g, 55%) by protonation of the initially formed *trans*-[PtBr(2-py)(PEt_3)$_2$] with $HClO_4$.

Preparation of trans-[PtBr(2-pyH)(PMe_2Ph)$_2$]ClO_4 (XIV)

The protonated complex XIII (0.98 g, 1 mmol) suspended in dry Et_2O (80 ml) was treated with PMe_2Ph (0.276 g, 2 mmol) and stirred for 24 h under N_2. The white insoluble product was filtered off, washed several times with Et_2O and dissolved in a CH_2Cl_2/MeOH mixture (5/1 v/v). The solution was slowly concentrated until a little precipitation of XIV occurred, and precipitation was completed by dropwise addition of Et_2O (Yield 0.45 g, 62%).

Reaction of trans-[PtBr(2-pyH)(PPh_3)$_2$]ClO_4 (XIII) with KOH

This reaction was carried out in the same way as for deprotonation of *cis-*

$[PdCl_2(2\text{-pyH})(PPh_3)]$. Treatment of XIII (0.49 g, 0.5 mmol) with alcoholic KOH (molar ratio Pt/KOH 1/1) regenerated the complex X (0.33 g, 75%).

Preparation of trans-[PtBr(2-methylpyridine)(PPh_3)$_2$]BF_4

A stirred suspension of $[PtBr_2(PPh_3)_2]$ (0.44 g, 0.5 mmol) in acetone (50 ml) was treated with $AgBF_4$ (0.098 g, 0.5 mmol). After 30 min, the insoluble AgBr was filtered off, and 2-methylpyridine (0.10 g, 1.07 mmol) was added to the clear solution. The solvent was evaporated to small volume and the product was precipitated by dilution with Et_2O. It was purified by reprecipitation from a CH_2Cl_2/Et_2O mixture (0.39 g, 79.6%). This compound was characterized by elemental analysis (Found: C, 51.5; H, 3.9; N, 1.5. $C_{42}H_{37}BBrF_4NP_2Pt$ calcd.: C, 51.50; H, 3.81; N, 1.43%), conductivity measurements (Λ_M 87.0 ohm^{-1} cm^2 mol^{-1} for a MeOH solution 10^{-3} *M* at 20°C), and by IR, ^1H and ^{31}P NMR spectra (ν(B–F) 1050 cm^{-1}).

References

1 (a) P.M. Treichel, Advan. Organomet. Chem., 11 (1973) 21; (b) D.J. Cardin, B. Cetinkaya, M.J. Doyle and M.F. Lappert, Chem. Soc. Rev., 2 (1973) 99.
2 K. Nakatsu, K. Kinoshita, H. Kanda, K. Isobe, Y. Nakamura and S. Kawaguchi, Chem. Lett., (1980) 913.
3 K. Isobe, E. Kai, Y. Nakamura, K. Nishimoto, T. Miwa, S. Kawaguchi, K. Kinoshita and K. Nakatsu, J. Amer. Chem. Soc., 102 (1980) 2475.
4 A. Mantovani and B. Crociani, J. Organomet. Chem., 236 (1982) C37.
5 (a) B. Crociani, M. Nicolini and R.L. Richards, J. Organomet. Chem., 104 (1976) 259; (b) B. Crociani and R.L. Richards, ibid., 154 (1978) 65.
6 J.W. Faller and M.J. Mattina, Inorg. Chem., 11 (1972) 1296.
7 M. Wada, K. Oguro and Y. Kawasaki, J. Organomet. Chem., 178 (1979) 261.
8 D.F. Christian, H.C. Clark and R.F. Stepaniak, J. Organomet. Chem., 112 (1976) 227.
9 B. Crociani, M. Nicolini and T. Boschi, J. Organomet. Chem., 33 (1971) C81.
10 D.A. Duddell, P.L. Goggin, R.J. Goodfellow, M.G. Norton and J.G. Smith, J. Chem. Soc. (A), (1970) 545.
11 V.J. Kowalewski and D.G. Kowalewski, J. Chem. Phys., 37 (1962) 2603.
12 B. Crociani, G. Bandoli and D.A. Clemente, J. Organomet. Chem., 184 (1980) 269.
13 (a) J.R. Moss and B.L. Shaw, J. Chem. Soc. (A), (1966) 1793; (b) M. Wada, K. Kusabe and K. Oguro, Inorg. Chem., 16 (1977) 446.
14 (a) K. Oguro, M. Wada and R. Okawara, J. Organomet. Chem., 159 (1978) 417; (b) M. Wada and Y. Koyama, ibid., 209 (1981) 115; (c) M. Wada, K. Sameshima, K. Nishiwaki and Y. Kawasaki, J. Chem. Soc., Dalton Trans., (1982) 793.
15 L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 224.
16 R. Gleiter and R. Hoffmann, J. Amer. Chem. Soc., 90 (1968) 5457.
17 F.H. Allen and S.N. Sze, J. Chem. Soc. (A), (1971) 2054.
18 P. Uguagliati, B. Crociani, U. Belluco and L. Calligaro, J. Organomet. Chem., 112 (1978) 111.
19 J.E. Figard, J.V. Paukstelis, E.F. Byrne and J.D. Petersen, J. Amer. Chem. Soc., 99 (1977) 8417.
20 K. Isobe and S. Kawaguchi, Heterocycles, 16 (1981) 1603.
21 M.H. Chisholm and S. Godleski, Progr. Inorg. Chem., 20 (1976) 299.
22 R.J. Pugmire and D.M. Grant, J. Amer. Chem. Soc., 90 (1968) 697.
23 A.J. Jones, D.M. Grant, J.G. Russell and G. Fraenkel, J. Phys. Chem., 73 (1969) 1624.
24 J.A. Pople, Mol. Phys., 7 (1964) 301.
25 J.A. Connor, E.M. Jones, E.W. Randall and E. Rosenberg, J. Chem. Soc. Dalton Trans., (1972) 2419.
26 B. Crociani and R.L. Richards, J. Organomet. Chem., 144 (1978) 85.
27 R. Ugo, F. Cariati and G. LaMonica, Inorg. Synt., 11 (1968) 105.