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Preparation and reactions of 2-pyridylplatinum(II) complexes $[PtCl(C_5H_4N\text{-}C^2)(L)_2]$ (L = tertiary phosphine). Compounds with a markedly nucleophilic pyridine nitrogen atom

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Abstract

The 2-pyridyl complex *trans*-$[PtCl(C_5H_4N\text{-}C^2)(PPh_3)_2]$ (I) can be prepared in high yield by oxidative addition of 2-chloropyridine to $[Pt(PPh_3)_4]$. The reaction of I with 1,2-bis(diphenylphosphino)ethane yields the *cis* derivative $[PtCl(C_5H_4N\text{-}C^2)(dppe)]$ (II). In polar solvents, the latter rearranges to the binuclear cationic complex $[Pt(\mu\text{-}C_5H_4N\text{-}C^2,N)(dppe)]_2Cl_2$. The reaction of I with $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (1/0.5 molar ratio) gives the products $[PtCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)]_2$ (IV) and $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$. ^{31}P NMR monitoring of the reaction suggests that PPh_3 transfer occurs in a binuclear platinum/palladium intermediate with a bridging 2-pyridyl ligand, and leads initially to a chloride-bridged species $[Pt(\mu\text{-}Cl)(C_5H_4N\text{-}C^2)(PPh_3)]_2$, which then rearranges to the more stable compound IV. Complexes I and II are readily *N*-protonated by HCl or $HClO_4$ to give the cationic derivatives $[PtCl(C_5H_5N\text{-}C^2)(PPh_3)_2]^+$ and $[PtCl(C_5H_5N\text{-}C^2)(dppe)]^+$. In dichloromethane or 1,2-dichloroethane, the terminal 2-pyridyl group of I and II is slowly *N*-alkylated by the solvent to give $[PtCl\{(1\text{-}R)C_5H_4N\text{-}C^2\}(PPh_3)_2]Cl$ and $[PtCl\{(1\text{-}R)C_5H_4N\text{-}C^2\}(dppe)]Cl$ ($R = CH_2Cl$ or CH_2CH_2Cl).

Introduction

In the recent years the chemistry of 2-pyridyl complexes of nickel(II) and palladium(II) has been studied in detail, with special attention being given to reactions with electrophiles (involving the pyridyl nitrogen atom), isocyanides, or carbon monoxide (involving migratory insertion into the metal–carbon bond) [1–3].

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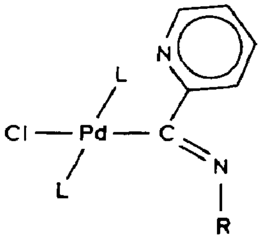
It was shown that the 2-pyridyl group in *trans*-[PdBr(C_5H_4N-C^2)(PEt_3)$_2$] is more basic than free pyridine [4]. This accounts for the easy *N*-protonation and *N*-methylation of the compounds [MX(C_5H_4N-C^2)(L)$_2$] (M = Ni, Pd; X = Cl, Br; L = tertiary phosphine) by strong mineral acids and dimethyl-sulfate, respectively [1], and for the tendency to give binuclear complexes [MX(μ-C_5H_4N-C^2,*N*)(PPh_3)]$_2$ (M = Ni, Pd), in which the 2-pyridyl group acts as a bridging ligand [2c,5,6]. On the other hand, the migratory insertion of isocyanides (CNR) into the Pd–C^2 bond of *trans*-[PdCl(C_5H_4N-C^2)(L)$_2$] [2] yields compounds containing an imino(2-pyridyl)methyl group, the coordination chemistry of which is currently under investigation [7]:



A similar insertion was found to occur in the reactions of the complexes *trans*-[PdCl(C_5H_4N-C^2)(PPh_3)$_2$] [2c] and *trans*-[PdCl{(6-Cl)C_5H_3N-C^2}(PPh_3)$_2$] [3] with carbon monoxide.

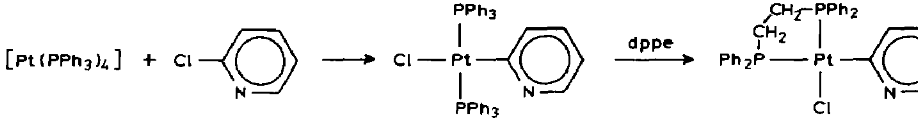
The 2-pyridyl complexes of platinum(II) have been less studied. To our knowledge, only a few derivatives, namely *trans*-[PtBr(C_5H_4N-C^2)(PPh_3)$_2$] and *trans*-[PtCl{(6-Cl)C_5H_3N-C^2}(PPh_3)$_2$], have been prepared and subjected to ligand substitution reactions and protonation or methylation at the pyridyl nitrogen [1b,3b,8].

As an extension of our research in this field, we report here the synthesis and some reactions of the complexes *trans*-[PtCl(C_5H_4N-C^2)(PPh_3)$_2$] and [PtCl(C_5H_4N-C^2)(dppe)] (dppe = 1,2-bis(diphenylphosphino)ethane), in which the pyridyl nitrogen has a markedly nucleophilic character, as to be alkylated even by chlorinated solvents, such as dichloromethane and 1,2-dichloroethane.

Results and discussion

Preparation of complexes I and II with a terminal 2-pyridyl ligand

The complex *trans*-[PtCl(C_5H_4N-C^2)(PPh_3)$_2$] (I) is obtained in high yield by oxidative addition of 2-chloropyridine to [Pt(PPh_3)$_4$] at 100–110 °C in toluene (eq. 1). At lower temperatures the reaction is very slow, whereas at higher temperatures



(I) (II) (1)

some of the binuclear complex IV is also formed (see further). The complex [PtCl(C_5H_4N-C^2)(dppe)] (II) is readily obtained from I by ligand substitution in a diethyl ether suspension. The compounds I and II and their derivatives have been characterized by elemental analyses, molecular weight and conductivity measurements, IR spectroscopy with the solid and, ^1H and ^{31}P NMR spectroscopy (Table 1).

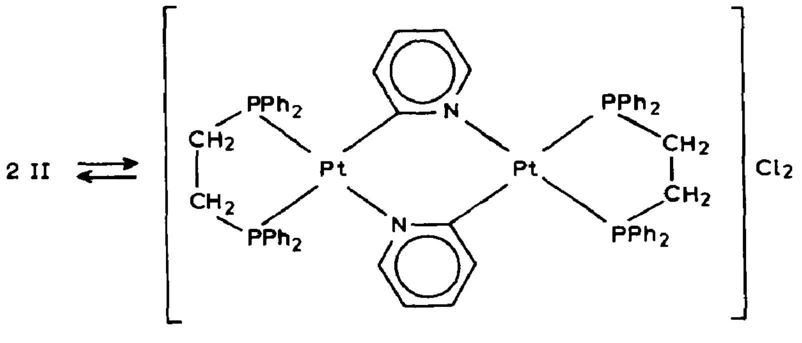
The experimental molecular weight of I in 1,2-dichloroethane (750) is significantly lower than the calculated value of 833.2 owing to partial *N*-alkylation by the solvent (see further). The IR spectrum of I shows a single ν(Pt–Cl) band at 275 cm^{-1}, at lower frequency than that for II (302 cm^{-1}), in which the chloride ligand is *trans* to a phosphorus atom of the chelating phosphine. This suggests a *trans* configuration for I, in which the Pt–Cl bond is weakened by a ligand of strong *trans* influence, such as the C^2-bonded 2-pyridyl group (cf. the ν(Pt–Cl) value of 285 cm^{-1} for *trans*-[PtCl{(6-Cl)C_5H_3N-C^2}$(PPh_3)_2$] [8], and the ν(Pd–Cl) value of 289 cm^{-1} for *trans*-[PdCl(C_5H_4N-C^2)$(PPh_3)_2$] [2c]). The ^{31}P NMR spectra of I in CD_2Cl_2 and C_6D_6 are indicative of a *trans* geometry in solution, as they show a single resonance flanked by ^{195}Pt satellites with a ^1J(Pt–P) coupling constant of ca. 3250 Hz.

The ^{31}P NMR spectrum of II in CD_2Cl_2 shows a central AB system for the two non-equivalent phosphorus nuclei. On the basis of *trans* influence arguments [9], the resonance at 36.7 ppm with a ^1J(Pt–P) of 1590 Hz is assigned to the phosphorus *trans* to the 2-pyridyl group, whereas the resonance at 35.2 ppm with a ^1J(Pt–P) of 4247 Hz is assigned to phosphorus *trans* to the chloride ligand. Comparable ^{31}P NMR spectral parameters have been reported for a series of arylplatinum(II) complexes, [PtCl(R)(dppe)] [10].

The ^1H NMR spectral data for I and II and their derivatives are not reported in Table 1 since they are mainly of little relevance. In most cases, the 2-pyridyl protons appear as overlapping multiplets in the range 6–7 ppm, and some are also masked by the intense phenyl proton signals of the phosphine ligands in the range 7–8 ppm.

Formation of binuclear complexes with C^2, N-bridging 2-pyridyl ligands

At ambient temperature, complex II undergoes the reversible reaction 2 at rates which depend on the solvent polarity (eq. 2). In 1,2-dichloroethane, IIIa is formed more slowly than in dichloromethane, and in both solvents, there is also a parallel alkylation at the pyridyl nitrogen. (see below). However, upon addition of a highly polar solvent, such as methanol, the equilibrium 2 is shifted quickly and almost quantitatively to the right, so that the binuclear cationic complex IIIa can be isolated (with two H_2O molecules of crystallization) or converted into the corresponding perchlorate salt IIIb.



(2)

(III a)

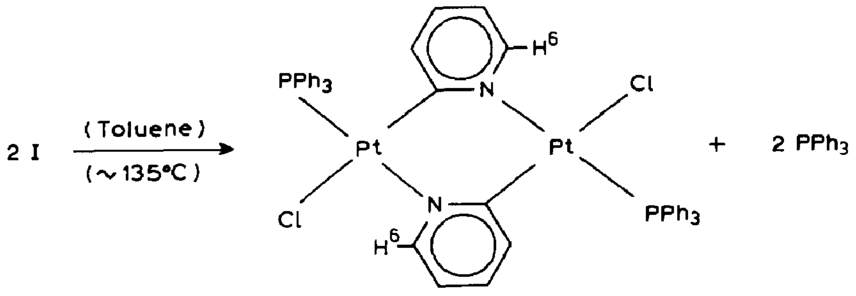
Table 1

Analytical and physical data. Characteristic IR absorptions, and ^{31}P NMR resonances

Compound	Analyses (Found (calc.)(%))				Molar conductivity [a] (ohm^{-1} cm^2 mol^{-1})	IR (cm^{-1}) [b]		^{31}P NMR [c]	
	C	H	N	Cl		ν(Pt–Cl)	Other bands		
trans-[PtCl(C_5H_4N-C^2)(PPh_3)$_2$] (I)	59.0 (59.10)	4.1 (4.11)	1.7 (1.68)	4.3 (4.25)		275ms		23.7s ^1J(Pt–P) 3249	22.7s [d] ^1J(Pt–P) 3253
[PtCl(C_5H_4N-C^2)(dppe)] (II)	52.7 (52.66)	4.0 (3.99)	2.0 (1.98)	5.1 (5.01)		302ms		36.7d (*trans* to C) ^1J(Pt–P) 1590	35.2d (*trans* to Cl) ^1J(Pt–P) 4247; ^2J(P–P) 3.9
[Pt(μ-C_5H_4N-C^2,*N*)(dppe)]$_2$$Cl_2$·2$H_2O$ (IIIa)	51.0 (51.35)	4.1 (4.17)	2.0 (1.93)	5.0 (4.89)	173.6		3380m(br) [ν(O–H)] 1625m [δ(O–H)]	41.1m (*trans* to C) ^1J(Pt–P) 1855 ^4J(Pt–P) 21	28.1m (*trans* to N) ^1J(Pt–P) 3324
[Pt(μ-C_5H_4N-C^2,*N*)(dppe)]$_2$(ClO_4)$_2$ (IIIb)	48.1 (48.29)	3.6 (3.66)	1.8 (1.82)	4.6 (4.60)	181.0 46.2 [e]		1095vs [ν(Cl–O)] 624s [δ(Cl–O)]	41.2m (*trans* to C) ^1J(Pt–P) 1850 ^4J(Pt–P) 19	27.8 m (*trans* to N) ^1J(Pt–P) 3328
[PtCl(μ-C_5H_4N-C^2,*N*)(PPh_3)]$_2$ (IV)	48.5 (48.38)	3.4 (3.35)	2.4 (2.45)	6.3 (6.21)		308m 282ms		9.8s (*trans* to N) ^1J(Pt–P) 3875	
trans-[PtCl(C_5H_5N-C^2)(PPh_3)$_2$]Cl (Va)	56.3 (56.62)	4.0 (4.06)	1.6 (1.61)	8.2 (8.15)	97.9	307m	2700m(br) [ν(N–H)]	20.8s ^1J(Pt–P) 2767	
trans-[PtCl(C_5H_5N-C^2)(PPh_3)$_2$]ClO_4 (Vb)	52.8 (52.74)	3.8 (3.78)	1.5 (1.50)	7.7 (7.59)	100.8	313ms	3230m(br), 3150m [ν(N–H)] 1115s, 1100s, 1055s [ν(Cl–O)] 625s, 616s [δ(Cl–O)]	20.9s ^1J(Pt–P) 2690	

[PtCl(C_5H_5N-C^2)(dppe)]Cl (VIa)					90.8	303ms	2700m(br) [ν(N–H)]	39.6d (*trans* to Cl) ^1J(Pt–P) 3712	38.8d (*trans* to C) ^1J(Pt–P) 2020, ^2J(P–P) 6.0
[PtCl(C_5H_5N-C^2)(dppe)]ClO_4 (VIb)	46.1 (46.11)	3.6 (3.62)	1.7 (1.73)	8.6 (8.78)	99.4	303ms	3230m(br), 3200(sh), 3140mw [ν(N–H)] 1120(sh), 1100vs, 1065s [ν(Cl–O)] 623s, 615(sh) [δ(Cl–O)]	40.0s [f] ^1J(Pt–P) 3662	 ^1J(Pt–P) 2005, ^2J(P–P) 5.8
trans-[PtCl{(1-CH_2Cl)C_5H_4N-C^2}- $(PPh_3)_2$]ClO_4 (VIIb)	51.1 (51.36)	3.7 (3.69)	1.4 (1.43)	11.0 (10.83)	93.2	312ms	1095vs [ν(Cl–O)] 624s [δ(Cl–O)]	19.6s ^1J(Pt–P) 2602	
trans-[PtCl{(1-CH_2CH_2Cl)C_5H_4N-C^2}- $(PPh_3)_2$]ClO_4 (VIIIb)	51.6 (51.84)	3.8 (3.84)	1.4 (1.41)	10.7 (10.68)	89.6	309ms	1098vs [ν(Cl–O)] 623s [δ(Cl–O)]	19.7s ^1J(Pt–P) 2637	
[PtCl{(1-CH_2Cl)C_5H_4N-C^2}- (dppe)]ClO_4 (IXb)	45.2 (44.90)	3.6 3.53)	1.5 (1.64)	12.3 (12.42)	93.0	310(sh), 296ms	1100vs [ν(Cl–O)] 623s, [δ(Cl–O)]	39.9d (*trans* to C) ^1J(Pt–P) 2104	38.7d (*trans* to Cl) ^1J(Pt–P) 3549, ^2J(P–P) 6.8
[PtCl{(1-CH_2CH_2Cl)C_5H_4N-C^2}- (dppe)]ClO_4 (Xb)	45.8 (45.56)	3.7 (3.71)	1.5 (1.61)	12.2 (12.22)	90.8	316ms	1105vs [ν(Cl–O)] 623s [δ(Cl–O)]	40.3d (*trans* to C) ^1J(Pt–P) 2072	38.2d (*trans* to Cl) ^1J(Pt–P) 3539; ^2J(P–P) 6.5

[a] For 10^{-3} *M* solutions in MeOH at 20 °C. [b] As Nujol mulls. [c] In CD_2Cl_2 solution at 30 °C; chemical shifts (δ) from external 85% H_3PO_4 (downfield shifts taken as positive); coupling constants in Hz; s, singlet; d, doublet; m, multiplet. [d] In C_6D_6 solution. [e] In CH_2Cl_2 solution. [f] In $(CD_3)_2SO$ solution.



(IV)

(3)

The molar conductivity values of IIIa and IIIb are in the expected range for bi-uni, univalent electrolytes in methanol [11]. Furthermore, in the ^{31}P NMR spectra, the phosphorus nuclei bound to platinum isotopes with a nuclear magnetic moment I=O give rise to an AA′BB′ spin system consisting of two symmetrical multiplets of closely spaced lines (which are poorly resolved in the case of IIIb). The multiplet at ca. 41 ppm is flanked by two sets of ^{195}Pt satellites with $^{1}J(Pt-P)$ values of 1850–1855 Hz and $^{4}J(Pt-P)$ values of 19–21 Hz, whereas only one set is observed for the multiplet at ca. 28 ppm ($^{1}J(Pt-P)$ 3324–3328 Hz). In view of the large difference in the $^{1}J(Pt-P)$ couplings, the lower field signal is assigned to phosphorus *trans* to the C^2-bonded 2-pyridyl group and the higher field one to phosphorus *trans* to the *N*-bonded bridging ligand.

Complex I has no tendency to react with displacement of chloride ligands as complex II does. However, when a toluene solution of I is heated under reflux, the binuclear compound IV is formed (eq. 3). This reaction is very slow and irreversible. After 9 h, the integrated ^{31}P NMR spectrum of the mixture indicates a I/IV molar ratio of ca. 1.5/1. On the other hand, treatment of IV with a large excess of PPh_3, in 1,2-dichloroethane does not yield any trace of I even upon prolonged refluxing.

Complex IV is more conveniently prepared from reaction 4, which takes ca. 5 h to reach completion in dichloromethane at room temperature.

$$I + \tfrac{1}{2}\left[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)\right]_2 \rightarrow \tfrac{1}{2}IV + \left[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)\right] \qquad (4)$$

The binuclear nature of IV is confirmed by molecular weight measurements (see Experimental). The spectral data suggest a non-planar structure with bridging C^2,N-2-pyridyl ligands and with a *trans*-$NPtPPh_3$ arrangement, analogous to that reported for $[PdBr(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)]_2$ [5]. In the ^{1}H NMR spectrum, the N-coordination of the heterocyclic ligand is implied by the coupling of the H^6-pyridyl proton (resonating as a multiplet at 8.35 ppm) with the ^{31}P nucleus of the *trans*-PPh_3 ligand ($^{4}J(P-H^6)$ 3.5 Hz) and with the ^{195}Pt isotope ($^{3}J(Pt-H^6)$ 36.5 Hz). The ^{31}P NMR data are also consistent with the proposed formulation, the large $^{1}J(Pt-P)$ value of 3875 Hz and the absence of $^{4}J(Pt-P)$ coupling giving further support to a *trans*-$NPtPPh_3$ geometry (cf. the ^{31}P NMR spectrum of IIIa and IIIb).

An alternative chloride-bridged structure $[Pt(\mu\text{-}Cl)(C_5H_4N\text{-}C^2)(PPh_3)]_2$ is not in accord with most of the observed spectral features (e.g., a comparison with the $\nu(Pt-Cl)$ values of I and II shows that the $\nu(Pt-Cl)$ bands of IV at 308 and 282

cm^{-1} are at too high frequencies to arise from bridging chlorides *trans* to ligands of strong *trans* influence, such as PPh_3 and 2-pyridyl group), and is ruled out also by the absence of reaction with either an excess of PPh_3 or HCl. In contrast, the chloride-bridges of the arylplatinum complexes $[Pt(\mu\text{-}Cl)(R)(L)]_2$ (L = tertiary phosphine) are readily split by a variety of neutral ligands, including PPh_3 [12,13], and the terminal 2-pyridyl group of I and II is readily *N*-protonated by strong mineral acids, as is described later.

Mechanism of reaction 4

In contrast to the very fast reaction of *trans*-$[PdCl(C_5H_4N\text{-}C^2)(PPh_3)_2]$ with $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (1/0.5 molar ratio) [2c], reaction 4 is sufficiently slow to be monitored by ^{31}P NMR spectroscopy. At ambient temperature, however, the spectra give little information about the nature of the possible intermediates. A better understanding of the course of the reaction is obtained from the variable temperature spectra reported in Fig. 1.

The spectrum (a), recorded after 10 min from mixing of the reactants, shows that even at the lowest temperatures used (−50 °C) some PPh_3 transfer from platinum to palladium occurs, with formation of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ (**B**) (singlet at 22.8 ppm) and of a platinum product **C** characterized by a singlet at 13.8 ppm with

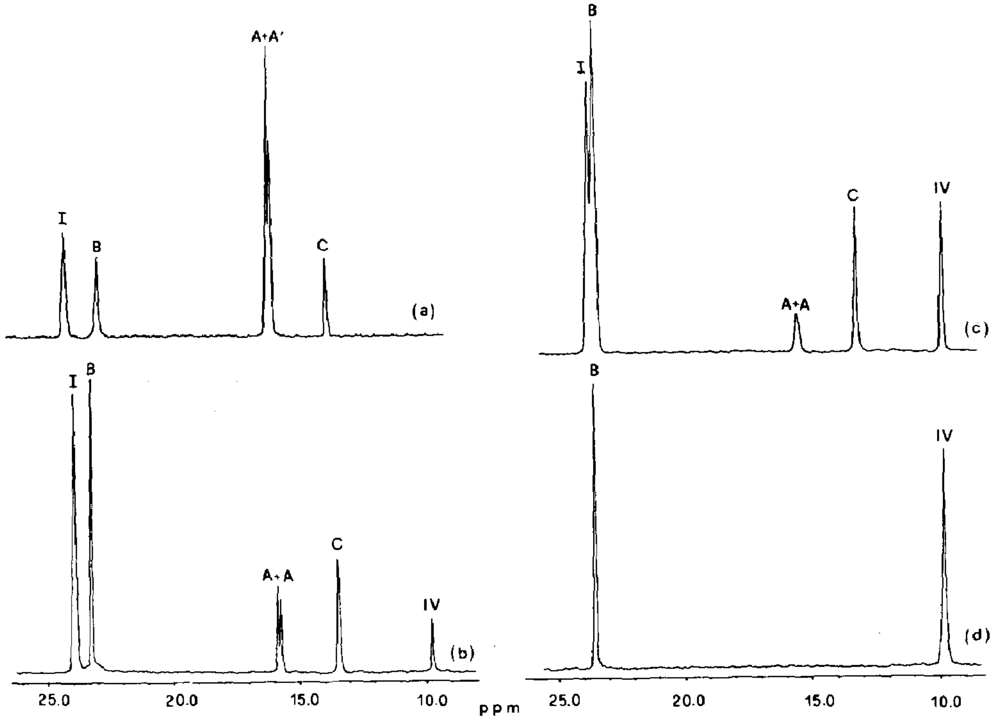
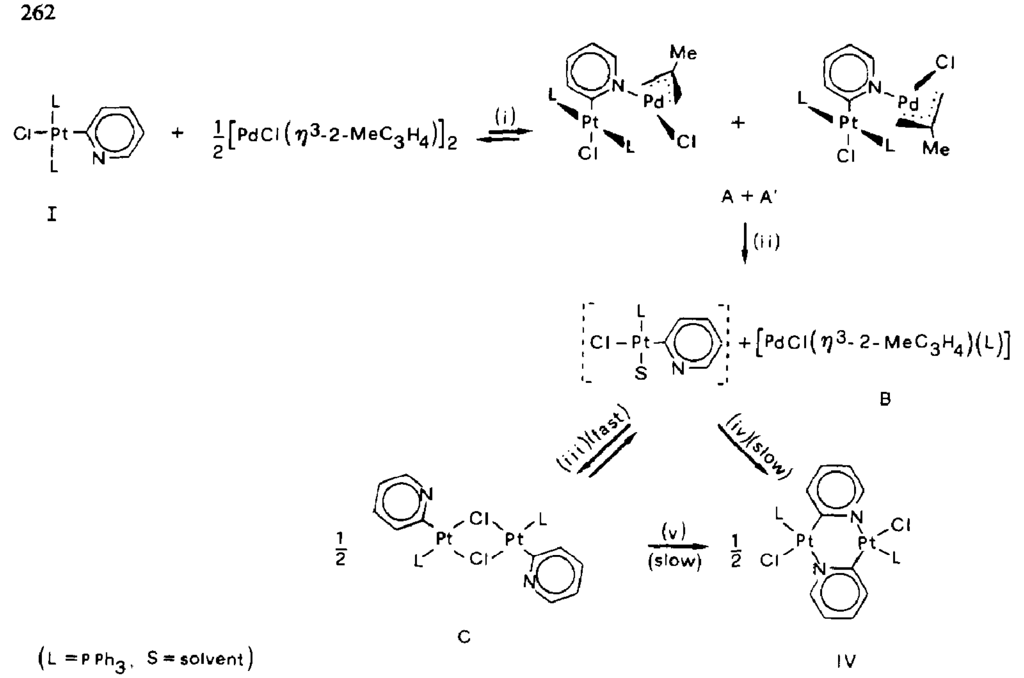


Fig. 1. Variable temperature ^{31}P NMR spectra of the reaction mixture *trans*-$[PtCl(C_5H_4N\text{-}C^2)(PPh_3)_2]/[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (1/0.5 molar ratio) in CD_2Cl_2, with initial concentration of 8.3×10^{-2} *M* for the platinum complex: (a) spectrum at −50 °C, recorded after 10 min from dissolution of the reactants; (b) at −10 °C; (c) at 30 °C; (d) final spectrum, recorded after 5 h at ambient temperature. The signal of each platinum species is flanked by two symmetrically spaced ^{195}Pt satellites which fall outside the reported range of 9–26 ppm (see text).



Scheme 1

a large ^1J(Pt–P) value of 5053 Hz. Platinum-phosphorus coupling constants of comparable magnitude have been observed only for the chloride-bridged complexes $[Pt(\mu\text{-}Cl)(R)(L)]_2$ (R = aryl or acyl group; L = tertiary phosphine) [12–15], and therefore the resonance at 13.8 ppm is assigned to a compound of the type $[Pt(\mu\text{-}Cl)(C_5H_4N\text{-}C^2)(PPh_3)]_2$. Furthermore, spectrum (a) indicates the presence of some unchanged complex I and of two intermediates **A** and **A′** with rather close ^{31}P chemical shifts and ^1J(Pt–P) couplings (16.2 ppm, 3130 Hz, and 16.0 ppm, 3117 Hz, respectively). At −10 °C (spectrum b), the concentration of **A** and **A′** decreases considerably with concomitant increase in concentration of I and of the products **B** and **C**. A small quantity of the binuclear complex IV is also formed, as shown by the singlet at 9.8 ppm with a ^1J(Pt–P) value of 3875 Hz. When the temperature is raised to 30 °C (spectrum c), the relative amount of IV increases, while the signals of **A** and **A′** merge into a weaker and broader band at 15.5 ppm. With time, the resonances of I, **A** and **A′**, and **C** progressively disappear, and eventually (after ca. 5 h at room temperature) spectrum (c) is recorded, in which only signals from products **B** and IV are present.

The observed spectral changes can be accounted for in terms of the mechanism proposed in Scheme 1.

In keeping with the well-known ability of 2-substituted pyridines to split the chloride-bridges of the allylic dimers $[PdCl(\eta^3\text{-all})]_2$ [16], the initial equilibrium step (i) leads to a binuclear intermediate, which may exist in two diastereoisomeric forms **A** and **A′** (each with a distinct $\delta(^{31}P)$ signal) if rotation about the Pd–N bond is restricted. The formation of such species is supported by the high-field shift of the ^{31}P resonance and by the lowering of the ^1J(Pt–P) coupling of the starting complex I upon complexation through the 2-pyridyl nitrogen (cf. the similar spectral changes caused by *N*-protonation or *N*-alkylation of I, see Table 1). The intermediates **A** and

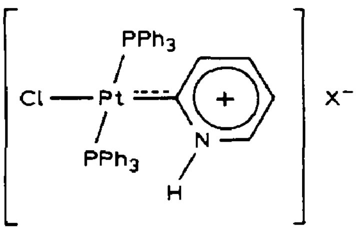
A′ are predominant in the system at −50 °C, but tend to dissociate into the starting reactants as the temperature is raised, probably because of steric repulsion arising from the bulk of the *trans* PPh_3PtPPh_3 unit (which, on the other hand, may be responsible for the hindered rotation around the Pd–N bond). The observation of a weak and broad band for A and A′ at 30 °C may be accounted for by the presence of only one diastereoisomer or by a fast interconversion of A and A′ associative with an increased rate of the reactions in equilibrium (i) on the NMR time scale.

In these intermediates, the two metal centers are brought into such a close proximity that PPh_3 transfer from platinum to palladium can also occur (step ii) to yield the product B and a labile transient species (either a 14-electron T-shaped species or a solvent adduct), which quickly dimerizes to the kinetically favoured complex C (step iii). The thermodynamically more stable compound IV is formed at a lower rate either by a slow dimerization (iv) of the transient in equilibrium with C [15] or by a slow rearrangement (v) of C, presumably through an intermolecular splitting of the chloride-bridges by the terminal 2-pyridyl ligands of C itself.

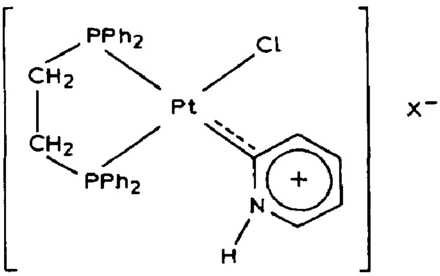
Protonation of complexes I and II

The terminal 2-pyridyl group of I and II is readily *N*-protonated by HCl or $HClO_4$ to yield the cationic derivatives V and VI. The molar conductivities in methanol are in the expected range for uni-univalent electrolytes [11]. In dichloromethane, however, the molar conductivities are rather low (e.g., 7.5 ohm^{-1} cm^2 mol^{-1} for a 10^{-3} *M* solution of Vb). From the splitting of the ν(N–H), ν(Cl–O), and δ(Cl–O) vibrations into two or three bands in the IR spectra of the perchlorate salts Vb and VIb, and from the detection of ν(N–H) as a broad band at 2700 cm^{-1} for the chloride salts Va and VIa (Table 1), it appears that complexes V and VI are mainly associated through hydrogen bonding between the N–H group and the anion X^-. Consistently, in the ^1H NMR spectra, the N–H resonance is observed as a broad band at rather low field: 12.5 ppm for Vb in CD_2Cl_2, and 14.5 ppm for VIb in $(CD_3)_2SO$.

In line with previous results on protonation of *trans*-$[PtBr(C_5H_4N\text{-}C^2)(PPh_3)_2]$ [1b], the *trans* influence of the *N*-protonated 2-pyridyl moiety is significantly reduced compared with that of the terminal 2-pyridyl ligand. Thus, a high-frequency shift of ca. 35 cm^{-1} of the ν(Pt–Cl) band is seen on going from I to V, while the ^1J(Pt–P) coupling constant for the phosphorus atom *trans* to the 2-pyridyl group in II is increased by ca. 420 Hz on going to the corresponding protonated derivatives VI.



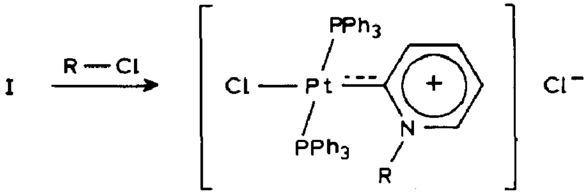
(Va : X^- = Cl^- ;
Vb : X^- = ClO_4^-)



(VIa : X^- = Cl^- ;
VIb : X^- = ClO_4^-)

Alkylation of complexes I and II by chlorinated solvents

In dichloromethane or 1,2-dichloroethane solution, compound I undergoes slow *N*-alkylation by the solvent, as shown in eq. 5. Conductivity measurements and ^{31}P NMR spectra of the mixtures at various times indicate that reaction 5 takes ca. 2 days for completion in both solvents at 30 °C.



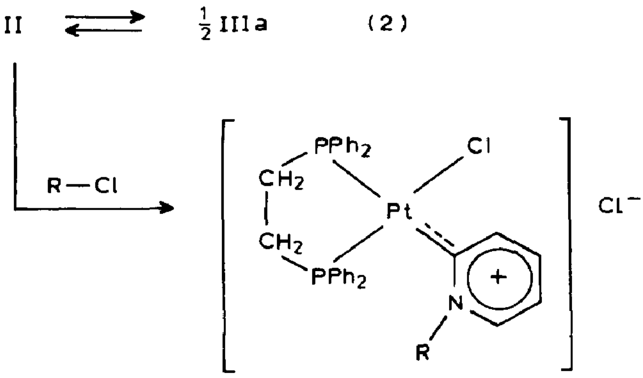
(5)

(VIIa : R = CH_2Cl ;
VIIIa : R = CH_2CH_2Cl)

A similar reaction is found to occur for complex II (eq. 6). In this case, however, a parallel and reversible formation of the binuclear complex IIIa also takes place. ^{31}P NMR monitoring of the reaction at 30 °C shows that in 1,2-dichloroethane the alkylated product Xa is initially formed faster than IIIa. After 3 h, the typical resonances of IIIa start to decrease and eventually disappear during ca. 24 h. After this time, only complex Xa is detected in solution.

In dichloromethane, both products IIIa and IXa are initially formed at comparable rates. In this case also, the binuclear complex IIIa is later converted into IXa, but at lower rate than in 1,2-dichloroethane, suggesting that the reverse reaction of equilibrium 2 is slower in dichloromethane. Thus after 24 h in dichloromethane a substantial amount of IIIa (ca. 20%) is still present, and a longer time (4 days) is required for quantitative formation of IXa.

The *N*-alkylated products are more conveniently isolated and characterized as the corresponding perchlorate derivatives VIIb–Xb, which behave as uni-univalent electrolytes in methanol (see Table 1). Complexes VIIB and VIIIb exhibit ν(Pt–Cl) values and ^{31}P NMR parameters rather close to those of the *N*-protonated compounds V. However, the presence of the *N*-bonded CH_2Cl grouping in VIIb is clearly demonstrated by the ^{1}H NMR spectrum in CD_2Cl_2 in which the methylene



(2)

(6)

(IXa : R = CH_2Cl ;
Xa : R = CH_2CH_2Cl)

protons resonate as a singlet at 6.04 ppm with closely spaced ^{195}Pt satellites ($^4J(Pt-H)$ 4.9 Hz). For VIIIb, the CH_2CH_2Cl protons appear approximately as an A_2X_2 spectrum with $\delta(CH_2Cl)$ as a triplet at 3.63 ppm ($^3J(H-H)$ 6.6 Hz), and $\delta(NCH_2)$ as a triplet at 4.61 ppm, the latter signal showing also a $^4J(Pt-H)$ coupling of 7.0 Hz.

In the ^1H NMR spectrum of IXb, the $\delta(CH_2Cl)$ signal is observed as an AB spin system centred at 6.08 ppm, the two non-equivalent protons having slightly different ^{195}Pt couplings ($^4J(Pt-H_A)$ 2.5 Hz and $^2J(Pt-H_B)$ 4.0 Hz). For Xb, the protons of the CH_2CH_2Cl moiety give rise to a complicate ABCD spectrum in the range 5.0–3.5 ppm.

Reactions 5 and 6 are unprecedented for complexes with terminal 2-pyridyl ligands, and are indicative of a remarkably high nucleophilic character of the 2-pyridyl nitrogen in the compounds I and II.

Experimental

The complexes $[Pt(PPh_3)_4]$ and $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ were prepared by published methods [17,18]. 1,2-Dichloroethane was distilled from anhydrous K_2CO_3. All other chemicals were reagent grade and used without further purification. Infrared spectra were recorded with a Perkin–Elmer 1430 instrument, using Nujol mulls and CsI windows in the range 4000–200 cm^{-1}. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectra were recorded with a Varian FT 80A spectrometer. Molecular weights were determined with a Knauer osmometer at 37 ° C in 1,2-dichloroethane. The conductivity measurements were carried out with a CDM 83 conductivity meter. The solvents were evaporated to small volume or to dryness at reduced pressure in a rotary evaporator. Methanolic $HClO_4$ or HCl refer to solutions made up by diluting 12 ml of 70% aqueous perchloric acid or 15 ml of 37% aqueous hydrochloric acid to 500 ml with MeOH. The resulting concentrations (0.28 *M* for $HClO_4$ or 0.36 *M* for HCl) were determined by titration.

Preparation of trans-$[PtCl(C_5H_4N\text{-}C^2)(PPh_3)_2]$ (I)

A suspension of $[Pt(PPh_3)_4]$ (6.22 g, 5 mmol) in 200 ml of toluene containing 2-chloropyridine (1.72 g, 15 mmol) was heated at 100–110 ° C for 6 h under N_2. After being kept overnight at room temperature, the mixture was concentrated to small volume and diluted with Et_2O, to yield the crude product I (3.54 g) contaminated by a small amount of *cis*-$[PtCl_2(PPh_3)_2]$ ($\nu(Pt-Cl)$ 318 and 292 cm^{-1}; $\delta(^{31}P)$ as a singlet at 13.9 ppm with a $^1J(Pt-P)$ value of 3678 Hz in CD_2Cl_2). The solid was extracted with benzene (ca. 150 ml) so as to leave the insoluble compound *cis*-$[PtCl_2(PPh_3)_2]$. After addition of charcoal and filtration, the solution was evaporated to small volume and diluted with Et_2O to precipitate the off-white microcrystalline complex I (3.37 g, 80.9% yield, based on the theoretical amount).

Preparation of $[PtCl(C_5H_4N\text{-}C^2)(dppe)]$

The ligand dppe (0.44 g, 1.1 mmol) was added to a stirred suspension of complex I (0.83 g, 1 mmol) in Et_2O (100 ml). After 24 h, the mixture was filtered and the insoluble product II was washed several times with Et_2O. The compound (0.69 g, 97.6%) was sufficiently pure to be used for reactions. For elemental analysis, the white solid (0.60 g) was redissolved in 50 ml of CH_2Cl_2/C_6H_6 mixture (3/2 v/v) and treated with charcoal. After filtration, the more volatile CH_2Cl_2 solvent was quickly evaporated at reduced pressure to induce some precipitation of II, and this was completed by dilution with Et_2O.

Preparation of $[Pt(\mu\text{-}C_5H_4N\text{-}C^2,N)(dppe)]_2X_2$ *($X^- = Cl^-$, IIIa; $X^- = ClO_4^-$, IIIb)*

(a) A solution of II (1.41 g, 2 mmol) in CH_2Cl_2 (ca. 80 ml) was diluted with MeOH (ca. 50 ml). Concentration to small volume and dilution with Et_2O gave the product IIIa, containing two H_2O molecules of crystallization, as a white precipitate (1.33 g, 91.7%).

(b) A solution of IIIa (0.72 g, 0.5 mmol) in CH_2Cl_2 (50 ml) was treated with $NaClO_4 \cdot H_2O$ (0.35 g, 2.5 mmol) dissolved in 10 ml of MeOH. The solvents were evaporated to dryness, and the solid residue was extracted with CH_2Cl_2 (50 ml) in the presence of charcoal. After filtration, the solution was diluted with MeOH (30 ml). Concentration to small volume and addition of Et_2O yielded IIIb as a white microcrystalline solid (0.69 g, 89.5%).

Preparation of $[PtCl(\mu\text{-}C_5H_4\text{-}C^2,N)(PPh_3)]_2$ *(IV)*

Complex I (0.83 g, 1 mmol) was added to a stirred solution of $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ (0.20 g, 0.5 mmol) in 15 ml of CH_2Cl_2. As shown by IR and ^{31}P NMR spectra at various times, the reaction was complete in ca. 5 h at room temperature. Stirring was continued for another hour, then C_6H_6 (60 ml) was added. Removal of CH_2Cl_2 at reduced pressure caused almost quantitative precipitation of IV. The off-white solid was filtered off, washed with C_6H_6, and purified by reprecipitation from a concentrated CH_2Cl_2 solution with Et_2O (0.51 g, 89.3%). Molecular weight, found 1150, calcd. 1141.8.

The mother liquor from the first precipitation of IV was concentrated to small volume and diluted with light petroleum ether to yield a pale-yellow solid (0.31 g), which was identified as $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_3)]$ by IR (ν(Pd–Cl) 275 cm^{-1}), ^1H and ^{31}P NMR spectroscopy.

Attempted bridge-splitting reactions of IV with PPh_3 *or HCl*

(a) A solution of IV (0.28 g, 0.25 mmol) in 1,2-dichloroethane (30 ml) was refluxed for several hours in the presence of an excess of PPh_3 (0.52 g, 2 mmol). The ^{31}P NMR spectra at various times showed no evidence for formation of complex I.

(b) A solution of IV (0.28 g, 0.25 mmol) in CH_2Cl_2 (30 ml) was treated with 7 ml of methanolic HCl 0.36 *M* (Pt/HCl molar ratio ~ 1/5). After 24 h stirring the unchanged complex IV was recovered almost quantitatively by diluting the concentrated solution with Et_2O.

Protonation of complexes I and II with HCl or $HClO_4$

Methanolic HCl 0.36 *M* (8.3 ml) or $HClO_4$ 0.28 *M* (10.7 ml) was added to a solution of the 2-pyridyl complex I or II (1 mmol) in 70 ml of CH_2Cl_2 (molar ratio Pt/HX 1/3). The protonated product was precipitated by adding Et_2O to the concentrated solution. The white solid was redissolved in CH_2Cl_2, treated with charcoal and filtered. After addition of MeOH (30 ml) to the filtrate the solution was concentrated to induce partial precipitation of complex V or VI. The precipitation was completed by dilution with Et_2O (yields 84–95%).

Alkylation of complexes I and II by chlorinated solvents

(a) Complex I (0.42 g, 0.5 mmol) was dissolved in 10 ml of CH_2Cl_2 or 1,2-dichloroethane, and the solution was thermostatted at 30 °C for 60 h. During this time, the progress of the reaction was monitored by ^{31}P NMR spectra. A solution of $NaClO_4 \cdot H_2O$ (0.21 g, 1.5 mmol), in 10 ml of MeOH was added, and immediate precipitation of NaCl was observed. The solvents were evaporated off, and the solid residue was extracted with CH_2Cl_2 (50 ml) in the presence of charcoal. After filtration, the solution was worked up as described above for the protonated products to yield the *N*-alkylated derivative VIIb (0.38 g, 77.4%) or VIIIb (0.41 g, 82.3%).

(b) A solution of II (0.35 g, 0.5 mmol) in 10 ml of CH_2Cl_2 or 1,2-dichloroethane was thermostatted at 30 °C. The ^{31}P NMR spectra, recorded at various times showed that reaction with 1,2-dichloroethane was complete in ca. 1 day, and that with CH_2Cl_2 in ca. 4 days. In both cases, however, the solution was kept at 30 °C for another day before addition of $NaClO_4 \cdot H_2O$ (0.21 g, 1.5 mmol) dissolved in 10 ml of MeOH. The mixture was worked up as described above for alkylation of I to yield product IXb (0.30 g, 70.1%) or Xb (0.34 g, 78.1%).

Acknowledgements

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