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Structural studies on 2-pyridyl complexes of the platinum triad metals. The crystal and molecular structure of the 2-pyridylium derivative *trans*-$[PdCl(C_5H_5N\text{-}C^2)(PMe_2Ph)_2]ClO_4$

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Abstract

In solution, the complex *trans*-$[PdCl(C_5H_4N\text{-}C^2)(PMe_2Ph)_2]$ (1) is in equilibrium with a small amount of the binuclear species $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PMe_2Ph)\}_2]$ (2), which can be isolated upon recrystallization. The compound 1 is easily N-protonated by $HClO_4$ to the 2-pyridylium product *trans*-$[PdCl(C_5H_5N\text{-}C^2)(PMe_2Ph)_2]ClO_4$ (3), which crystallizes in the orthorhombic space group $P2_12_12_1$, with cell parameters $a=15.761(3)$, $b=14.369(2)$, $c=11.132(2)$ Å and $Z=4$. The X-ray crystal structure analysis of 3, using 3744 observed reflections in the refinement and resulting in a final R value of 0.0298, shows that the coordination around palladium is essentially square-planar with Pd–C = 1.970(5), Pd–Cl = 2.368(2), Pd–P(1) = 2.317(1) and Pd–P(2) = 2.318(1) Å. The planar pyridine ring is perpendicular to the coordination plane, and the N–H group is involved in hydrogen bonding with an oxygen of the perchlorate anion, at a contact distance of 2.08(6) Å. Extensive hydrogen bonding occurs also in dichloromethane solution and accounts for the hindered rotation of the 2-pyridylium ligand around the Pd–C^2 bond.

Introduction

In previous investigations we found that in the cationic complexes *trans*-$[MX(C_5H_5N\text{-}C^2)(PMe_2Ph)_2]ClO_4$ (M = Ni, Pd, Pt; X = Cl, Br; $C_5H_5N\text{-}C^2$ = 2-pyridylium) and *trans*-$[PdCl(C_4H_4N_2\text{-}C^2)(PMe_2Ph)_2]ClO_4$ ($C_4H_4N_2\text{-}C^2$ = 2-pyrazylium) the N^1-protonated heterocyclic moieties exhibit restricted rotation around the M–C^2 bond, whereas in the neutral compounds *trans*-$[PtBr(C_5H_4N\text{-}C^2)(PMe_2Ph)_2]$ and *trans*-$[PdCl(C_4H_3N_2\text{-}C^2)(PMe_2Ph)_2]$ the 2-pyridyl and 2-pyrazyl groups are freely rotating around the M–C^2 bond [1-3]. On the basis of ^1H and ^{13}C NMR data, this feature was interpreted in terms of a significant $d_\pi \rightarrow \pi^*$ backbonding contribution to the metal–carbon bond of the protonated ligands. On the other hand, however, steric factors arising from extensive association in solution through hydrogen bonding between the N^1–H group and the perchlorate anion might also be important.

In order to get a better insight into the bonding properties and steric requirements of such ligands, we have now synthesized the 2-pyridyl complex *trans*-$[PdCl(C_5H_4N\text{-}C^2)(PMe_2Ph)_2]$ (1) and its derivatives $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PMe_2Ph)\}_2]$ (2), *trans*-$[PdCl(C_5H_5N\text{-}C^2)(PMe_2Ph)_2]ClO_4$ (3), and have carried out an X-ray structural analysis of the N^1-protonated compound 3.

Experimental

The complex *trans*-$[PdCl(C_5H_4N\text{-}C^2)(PMe_2Ph)_2]$ (1) was isolated from the reaction of $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PPh_3)\}_2]$ (1 mmol) with PMe_2Ph (molar ratio Pd/PMe_2Ph 1/2) in Et_2O/n-pentane (1/4 vol./vol., 50 ml) under nitrogen. The mixture was stirred for 24 h to give the product as a pale yellow powder

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(0.51 g, 51.4%). *Anal.* Calc. for $C_{21}H_{26}NP_2ClPd$: C, 50.83; H, 5.28; N, 2.82; Cl, 7.14. Found: C, 50.2; H, 5.2; N, 2.8; Cl, 7.2%. IR: ν(Pd–Cl) 285 cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta(H^6)$ as a multiplet at 8.30 ppm; δ(P–Me) as a broad singlet at 1.40 ppm, due to fast exchange with a small amount of free phosphine (see further). ^{31}P NMR (CD_2Cl_2): $\delta(^{31}P)$ as a singlet at −8.1 ppm (from 85% H_3PO_4 as external standard).

Recrystallization of complex **1** from hot benzene/n-hexane or diethyl ether/n-pentane gave yellow microcrystals of a new compound, identified as the binuclear species **2** with bridging 2-pyridyl ligands, $[\{PdCl(\mu\text{-}C_5H_4N\text{-}C^2,N)(PMe_2Ph)\}_2]$. *Anal.* Calc. for $C_{13}H_{15}NPClPd$: C, 43.60; H, 4.22; N, 3.91; Cl, 9.90. Found: C, 43.4; H, 4.2; N, 3.9; Cl, 9.8%. IR: ν(Pd–Cl) 320(sh), 310 cm^{-1}: ^1H NMR (CD_2Cl_2): $\delta(H^6)$ as a multiplet at 8.27 ppm; δ(P–Me) as two doublets at 1.98 and 1.65 ppm, with ^2J(P–H) of 11.2 and 10.8 Hz, respectively. ^{31}P NMR (CD_2Cl_2): $\delta(^{31}P)$ as a singlet at 2.5 ppm. The complex *trans*-$[PdCl(C_5H_5N\text{-}C^2)(PMe_2Ph)_2]ClO_4$ (**3**) was obtained from the reaction of *cis*-$[PdCl_2(C_5H_5N\text{-}C^2)(PPh_3)]$ with two equivalents of PMe_2Ph and successive treatment with an excess of $NaClO_4$, or from direct protonation of **1** with $HClO_4$ as described in ref. 1. The product was recrystallized from hot methanol in the form of white transparent prisms.

TABLE 1. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Pd–P(1)	2.317(1)	Pd–P(2)	2.318(1)
Pd–Cl(1)	2.368(2)	Pd–C(1)	1.970(5)
P(1)–C(6)	1.816(5)	P(1)–C(7)	1.804(6)
P(1)–C(8)	1.824(3)	P(2)–C(14)	1.810(5)
P(2)–C(15)	1.805(5)	P(2)–C(16)	1.815(4)
Cl(2)–O(1)	1.379(6)	Cl(2)–O(2)	1.410(5)
Cl(2)–O(3)	1.409(6)	Cl(2)–O(4)	1.417(5)
C(1)–N(1)	1.362(7)	C(1)–C(5)	1.366(7)
N(1)–C(2)	1.344(8)	C(2)–C(3)	1.342(13)
C(3)–C(4)	1.378(11)	C(4)–C(5)	1.379(9)
Cl(1)–Pd–C(1)	178.6(1)	P(2)–Pd–C(1)	89.7(2)
P(2)–Pd–Cl(1)	89.4(1)	P(1)–Pd–C(1)	90.5(1)
P(1)–Pd–Cl(1)	90.3(1)	P(1)–Pd–P(2)	177.6(1)
Pd–P(1)–C(8)	108.2(1)	Pd–P(1)–C(7)	113.8(2)
Pd–P(1)–C(6)	119.2(2)	C(7)–P(1)–C(8)	106.2(2)
C(6)–P(1)–C(8)	105.4(2)	C(6)–P(1)–C(7)	103.0(3)
Pd–P(2)–C(16)	118.3(1)	Pd–P(2)–C(15)	111.7(2)
Pd–P(2)–C(14)	111.6(2)	C(15)–P(2)–C(16)	103.9(2)
C(14)–P(2)–C(16)	105.8(2)	C(14)–P(2)–C(15)	104.3(3)
O(3)–Cl(2)–O(4)	106.6(3)	O(2)–Cl(2)–O(4)	109.9(3)
O(2)–Cl(2)–O(3)	111.7(4)	O(1)–Cl(2)–O(4)	108.8(4)
O(1)–Cl(2)–O(3)	109.0(4)	O(1)–Cl(2)–O(2)	110.6(4)
Pd–C(1)–C(5)	124.8(4)	Pd–C(1)–N(1)	119.2(4)
N(1)–C(1)–C(5)	116.0(5)	C(1)–N(1)–C(2)	124.0(5)
N(1)–C(2)–C(3)	119.9(6)	C(2)–C(3)–C(4)	119.0(8)
C(3)–C(4)–C(5)	119.9(7)	C(1)–C(5)–C(4)	121.2(5)

Crystal data for $C_{21}H_{27}NP_2O_4Cl_2Pd$ are: $M = 596.7$, orthorhombic space group $P2_12_12_1$; $a = 15.761(3)$, $b = 14.369(2)$, $c = 11.132(2)$ Å; $V = 2521.1(8)$ Å^3, $D_{calc} = 1.57$ g cm^{-3}, for $Z = 4$; μ(Mo Kα) = 9.97 cm^{-1}. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The final difference Fourier maps revealed the positions of most hydrogen atoms. However, they were introduced on the idealized positions (d(C–H) = 0.95 Å and unique $U = 0.08$ Å^2). The structure converged $R = 0.0298$, $R_w = 0.0296$, 272 parameters, largest shift/e.s.d. for final cycle 0.05, residual electron density 0.3 e Å^{-3}. Selected distances and bond angles are listed in Table 1.

Computer programs used were SHELX-76 [4] for structure solution and refinement, and ORTEP [5] for drawings.

Results and discussion

The crystal structure of complex **3** contains discrete cation/anion units. An ORTEP view of the asymmetric units is shown in Fig. 1, with the atom labelling scheme. In the cation, the chloride is linked to palladium in *trans* position to the σ bonded 2-pyridylium group, the other two sites of the square-

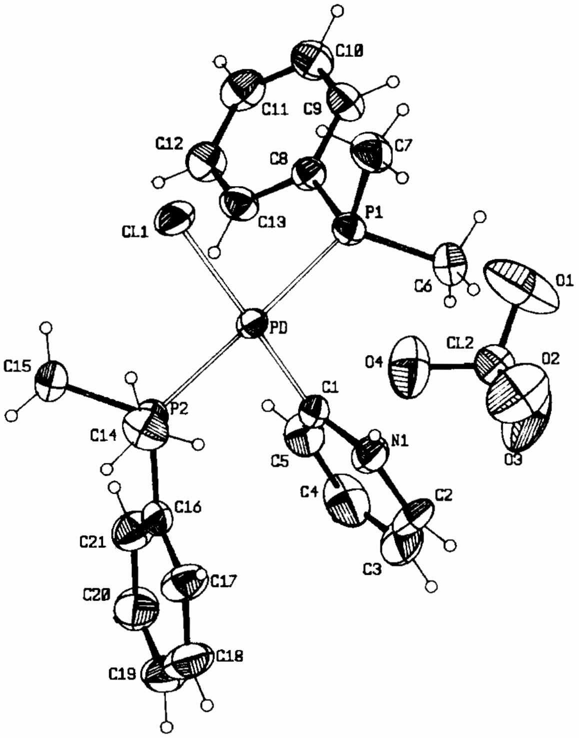

Fig. 1. Perspective view of complex **3**. The thermal elipsoids are at 40% probability.

planar arrangement being occupied by the phosphorus atoms of dimethylphenylphosphine ligands. The coordination plane around the central metal is rather regular with angular values in the range 89.4–90.5(1)°. The deviations from the least-squares plane of the coordinated atoms are Cl(1) 0.004(2), C(1) 0.043(5), P(1) −0.003(1), P(2) −0.003(1) Å, with Pd 0.0451(6) Å out of the plane. The planar pyridine ring is orthogonal to the coordination plane, with a dihedral angle of 90.0(1)°. The N(1)–H hydrogen is involved in a short contact distance of 2.08(6) Å with the O(4) oxygen of the perchlorate anion (N(1)–H 0.96(6) Å, N(1)–H·····O(4) angle 162(4)°). Such hydrogen bonding explains the absence of statistic disorder in the perchlorate group, and the splitting of ν(Cl–O) (1110 and 1075 $\mathrm{cm^{-1}}$) and δ(Cl–O) (627 and 615 $\mathrm{cm^{-1}}$) bands in the solid state IR spectrum. Consistently, three absorptions are observed at 3260(sh), 3225 and 3144 $\mathrm{cm^{-1}}$, attributable to stretching vibrations of the N–H····O grouping [1].

The N(1)–H and C(5)–H hydrogens are oriented towards palladium at distances of 2.82(5) and 3.07(1) Å, respectively, which are in any case too large for any significant interaction. Furthermore, no relevant steric interactions with the phosphine substituents are found when the 2-pyridylium group (without the hydrogen bonded perchlorate anion) is rotated around the Pd–C(1) bond axis.

The Pd–Cl(1) bond length of 2.368(1) Å compares well with the value of 2.3807(9) Å for the corresponding bond (with chloride *trans* to the 2-pyridylium ligand) in *cis*-$[\mathrm{PdCl_2(C_5H_5N}\text{-}C^2)(\mathrm{PR'_2Ph})]\cdot\mathrm{C_6H_6}$ (R′ = 2-pyridyl) [6]. The Pd–P bond distances (2.317(1) and 2.318(1) Å) are in agreement with those observed in complexes having a *trans* P–Pd–P geometry [7]. The Pd–C(1) bond length of 1.970(5) Å is close to the value of 1.980(3) Å for the same bond in *cis*-$[\mathrm{PdCl_2(C_5H_5N}\text{-}C^2)(\mathrm{PR'_2Ph})]\cdot\mathrm{C_6H_6}$ [6], and appears to be only slightly shortened if compared to the Pd-2-pyridyl bond (1.993(6) Å) in *trans*-$[\mathrm{PdBr(C_5H_4N}\text{-}C^2)(\mathrm{PEt_3})_2]$ [8]. Unfortunately, no comparison can be made with the Pd–C bond length in the parent compound **1**, since the latter product cannot be isolated in a crystalline form suitable for X-ray analysis. Any attempted recrystallization (see 'Experimental') leads to formation of the binuclear species **2**.

$$\underset{\mathbf{1}}{2[\mathrm{PdCl(C_5H_4N}\text{-}C^2)(\mathrm{PMe_2Ph})_2]} \rightleftharpoons$$

$$\underset{\mathbf{2}}{[\{\mathrm{PdCl}(\mu\text{-}\mathrm{C_5H_4N}\text{-}C^2,N)(\mathrm{PMe_2Ph})\}_2]} + 2\mathrm{PMe_2Ph}$$

The establishment of the above equilibrium in $\mathrm{CD_2Cl_2}$ solutions of **1** is confirmed by the ^{1}H and ^{31}P NMR spectra, which exhibit the typical signals of both complexes (with a large predominance of **1**).

In conclusion, the N-protonation of the 2-pyridyl group in **1** does not cause any relevant shortening in the Pd–C bond and/or any marked increase in the steric requirements of the ligand. Thus, the observed hindered rotation of the 2-pyridylium moiety of complex **3** in $\mathrm{CD_2Cl_2}$ solution [1] is better rationalized on the basis of extensive cation/anion association through a rather strong hydrogen bond between the N–H group and the $\mathrm{ClO_4^-}$ anion. This is supported by the low value of molar conductivity (1.4 $\Omega^{-1}\ \mathrm{cm^2\ mol^{-1}}$) for a 10^{-2} mol $\mathrm{dm^{-3}}$ $\mathrm{CH_2Cl_2}$ solution of **3** (i.e. at a concentration comparable with that used for ^{1}H NMR spectra), and by the detection of two ν(Cl–O) bands at 1110 and 1057 $\mathrm{cm^{-1}}$, two δ(Cl–O) bands at 627 and 615 $\mathrm{cm^{-1}}$, and three ν(N–H····O) absorptions at 3220, 3200(sh) and 3140 $\mathrm{cm^{-1}}$, in the IR spectrum of the same solution.

Supplementary material

Tables of fractional atomic coordinates, thermal parameters, interatomic bond distances and angles, and structures factors are available on request from author F.B.

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