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# <sup>31</sup>P NMR and DFT studies on square-planar bis(diphenylphosphinoethyl)phenylphosphine (triphos) complexes of Pt(II) with pyridines and anilines

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#### Abstract

Cationic complexes of the type [Pt(L)(triphos)](ClO<sub>4</sub>)<sub>2</sub>, where L is a 4-substituted pyridine {L = 4-R-py = 4-cyanopyridine (4-CN-py), isonicotinic acid (4-COOH-py), methylisonicotinate (4-COOMe-py), 4-acetylpyridine (4-MeCO-py), pyridine (4-H-py), 4-methylpyridine (4-Me-py), 4-aminopyridine (4-NH<sub>2</sub>-py)} or a 4-substituted aniline {L = 4-R-an = 4-nitroaniline (4-NO<sub>2</sub>-an), 4-cyanoaniline (4-CN-an), 4-chloroaniline (4-Cl-an), aniline (4-H-an), 4-methylaniline (4-Me-an), 4-methoxyaniline (4-MeO-an)}, have been prepared from *cis/trans*-PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>. The *cis* and *trans* <sup>1</sup>J<sub>Pt-P</sub> coupling constants measured in CD<sub>3</sub>NO<sub>2</sub> were found to be dependent upon the pK<sub>a</sub> of L. For the series of the *para*-substituted pyridines 4-R-py the linear correlations <sup>1</sup>J<sub>Pt-P1</sub> = 2918 – 16.9 pK<sub>a</sub> and <sup>1</sup>J<sub>Pt-P2</sub> = 2371 + 5.8 pK<sub>a</sub> (P<sub>1</sub> = phosphorus nucleus *trans* to N, P<sub>2</sub> = phosphorus nuclei *cis* to N) were found. The complexes with L = *para*-substituted anilines 4-R-an show a different behaviour. The results are discussed on the basis of DFT calculations. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Platinum; Triphos; DFT; Heteronuclear NMR; Pyridines; Anilines

### 1. Introduction

The ability of a transition-metal ion to transmit electronic effects among ligands has been studied for a long time in connection with both ground-state and kinetic properties of co-ordination compounds. Since the initial development of heteronuclear NMR spectroscopy, a great number of papers correlating the NMR data and the properties of co-ordination and organometallic complexes has appeared in the literature. Mainly because of the favourable presence of both platinum and phosphorus NMR-active isotopes, most of these studies has been concerned with platinum-phosphine complexes [1] and, since the <sup>1</sup>J<sub>Pt-P</sub> coupling constant is an easily determinable data, correlations between this coupling constant and some properties of the co-ordinate ligands have often been made.

The ligand triphos  $\{\text{triphos} = \text{bis}(\text{diphenylphosphino-})$ ethyl)phenylphosphine} is really interesting for heteronuclear NMR studies, because once co-ordinated to platinum it allows to evaluate at the same time both the *trans* and the cis  ${}^{1}J_{Pt-P}$  coupling constants. Here, the preparation of a series of cationic complexes of the type  $[Pt(L)(triphos)](ClO_4)_2$  is reported, where the ligands L are nitrogen-donors, namely 4-substituted pyridines  $\{4-R-py = 4-cyanopyridine (4-CN-py), isonicotinic acid$ (4-COOH-py), methylisonicotinate (4-COOMe-py), 4-acetylpyridine (4-MeCO-py), pyridine (4-H-py), 4-methylpyridine (4-Me-py), 4-aminopyridine  $(4-NH_2-py)$ and 4-substituted anilines  $\{4-R-an = 4-nitroaniline (4-NO_2-an),$ 4-cyanoaniline (4-CN-an), 4-chloroaniline (4-Cl-an), aniline (4-H-an), 4-methylaniline (4-Me-an), 4-methoxyaniline (4-MeO-an)}. The results of a  ${}^{31}P$  NMR study about the influence of the donor capability of L, as measured by its  $pK_a$ , on the *trans* and *cis*  ${}^{\bar{1}}J_{Pt-P}$  coupling constants, are discussed. DFT calculations were also performed to better give insight into the observed variations of  ${}^{1}J_{Pt-P}$  with

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 $pK_a$  caused by the changes of the electronic and steric properties of the co-ordinated ligands L.

## 2. Experimental

All reagents were Aldrich or Fluka products in the highest available purity and were used without any further treatment. Solvents were dried using standard techniques.

## 2.1. Physical measurements

Infrared spectra (4000–400 cm<sup>-1</sup>, KBr disks) were recorded on a Perkin–Elmer Spectrum One spectrophotometer. NMR spectra (<sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H} with inverse-gated decoupling) were obtained either on AC 200 or AVANCE 300 Bruker spectrometers in CD<sub>3</sub>NO<sub>2</sub> at temperatures comprised between 298 and 243 K. <sup>1</sup>H NMR spectra are referred to internal tetramethylsilane, while <sup>31</sup>P NMR chemical shifts are reported with respect to 85% H<sub>3</sub>PO<sub>4</sub>. SwaN-MR and MestRe-C software packages were used to treat the NMR data [2]. The conductivity of  $1 \times 10^{-3}$  mol dm<sup>-3</sup> solutions of the new complexes in DMF at 25° was measured with a Radiometer CDM 83 instrument. Elemental analyses (C, H, N) were performed by the microanalytical laboratory at the Department of Pharmaceutical Sciences, University of Padua.

#### 2.2. Computational details

Computational geometry optimisation of the complexes was performed using the restricted DFT B3PW91 method with the CEP-121G basis set (CEP-31G on the Pt atom). Geometry convergence was accelerated using the GDIIS algorithm and a first refinement of the structures was obtained using the restricted semi-empirical PM3 method. Geometry optimisation of the free nitrogen-donor ligands was obtained with restricted DFT B3LYP/6-311+G\*\* calculations [3]. All calculations were carried out with computers equipped with Intel Pentium 4 Northwood processors operating at 2.6 GHz frequency or IBM G4 operating at 1.25 GHz. Software used were GAUSSIAN-98 and SPARTAN-02 [4].

## 2.3. Preparation of the complexes

The  $[PtCl(triphos)]^+$  species has already been reported as the chloride salt [5], but we preferred to isolate it as the perchlorate salt following the procedure described below [6]. separated out of the solution was filtered off, washed with methanol and diethylether and dried under vacuum (yield >90%).

2.4.  $[Pt(4-R-py)(triphos)](ClO_4)_2(1^R)$ { $R = CN, COOH, COOMe, MeCO, H, Me, NH_2$ }  $[Pt(4-R-an)(triphos)](ClO_4)_2(2^R)$ { $R = NO_2, CN, Cl, H, Me, MeO$ }

The complexes  $[Pt(4-R-py)(triphos)](ClO_4)_2$  (1<sup>R</sup>) and  $[Pt(4-R-an)(triphos)](ClO_4)_2$  (2<sup>R</sup>) have been prepared by adding the stoichiometric amount of solid AgClO<sub>4</sub> to a solution of  $[PtCl(triphos)](ClO_4)$  in nitromethane. In a typical preparation, 0.021 g (0.1 mmol) of AgClO<sub>4</sub> were added to a 5 mL solution of  $[PtCl(triphos)](ClO_4)$  (0.086 g, 0.1 mmol) in CH<sub>3</sub>NO<sub>2</sub>. After 12 h under stirring the AgCl formed was filtered off and a slight excess (1.5:1) of the appropriate pyridine or aniline was added. The resulting solution was heated to about 50 °C for 2 h and then filtered if necessary. By slow addition of diethylether the product which separated out was filtered, washed twice with diethylether and dried under vacuum (yield >70% in all cases).<sup>1</sup>

Anal. Calc. for C<sub>40</sub>H<sub>37</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>8</sub>P<sub>3</sub>Pt (1<sup>CN</sup>): C, 46.52; H, 3.61; N, 2.71. Found: C, 46.61; H, 3.62; N, 2.73%. Anal. Calc. for  $C_{40}H_{38}Cl_2NO_{10}P_3Pt$  (1<sup>COOH</sup>): C, 45.68; H, 3.64; N, 1.33. Found: C, 45.59; H, 3.65; N, 1.32%. Anal. Calc. for  $C_{41}H_{40}Cl_2NO_{10}P_3Pt$  (1<sup>COOMe</sup>): C, 46.21; H, 3.78; N, 1.31. Found: C, 46.09; H, 3.80; N, 1.29%. Anal. Calc. for  $C_{41}H_{40}Cl_2NO_9P_3Pt$  (1<sup>MeCO</sup>): C, 46.91; H, 3.84; N, 1.33. Found: C, 46.81; H, 3.82; N, 1.34%. Anal. Calc. for  $C_{39}H_{38}Cl_2NO_8P_3Pt$  (1<sup>H</sup>): C, 46.49; H, 3.80; N, 1.39. Found: C, 46.36; H, 3.78; N, 1.40%. Anal. Calc. for  $C_{40}H_{40}Cl_2NO_8P_3Pt$  (1<sup>Me</sup>): C, 47.02; H, 3.95; N, 1.37. Found: C, 47.14; H, 3.97; N, 1.39%. Anal. Calc. for  $C_{39}H_{39}Cl_2N_2O_8P_3Pt \ (1^{NH_2}): \ C, \ 45.80; \ H, \ 3.84; \ N, \ 2.74.$ Found: C, 45.93; H, 3.85; N, 2.72%. Anal. Calc. for  $C_{40}H_{39}Cl_2N_2O_{10}P_3Pt$  (2<sup>NO<sub>2</sub></sup>): C, 45.04; H, 3.69; N, 2.63. Found: C, 45.11; H, 3.70; N, 2.65%. Anal. Calc. for  $C_{41}H_{39}Cl_2N_2O_8P_3Pt$  (2<sup>CN</sup>): C, 47.05; H, 3.76; N, 2.68. Found: C, 47.13; H, 3.74; N, 2.70%. Anal. Calc. for  $C_{40}H_{39}Cl_3NO_8P_3Pt$  (2<sup>C1</sup>): C, 45.49; H, 3.72; N, 1.33. Found: C, 45.60; H, 3.70; N, 1.34%. Anal. Calc. for  $C_{40}H_{40}Cl_2NO_8P_3Pt$  (2<sup>H</sup>): C, 47.02; H, 3.95; N, 1.37. Found: C, 46.90; H, 3.93; N, 1.36%. Anal. Calc. for  $C_{41}H_{42}Cl_2NO_8P_3Pt$  (2<sup>Me</sup>): C, 47.55; H, 4.09; N, 1.35. Found: C, 47.49; H, 4.11; N, 1.36%. Anal. Calc. for C<sub>41</sub>H<sub>42</sub>Cl<sub>2</sub>NO<sub>9</sub>P<sub>3</sub>Pt (2<sup>OMe</sup>): C, 46.82; H, 4.03; N, 1.33. Found: C, 46.90; H, 4.01; N, 1.34.

All the  $1^{R}$  and  $2^{R}$  complexes show the signals due to the triphos and the pyridine or the aniline ligands in the <sup>1</sup>H NMR and IR spectra. Some characteristic IR and <sup>1</sup>H NMR data are reported below:

To a warm (ca. 50 °C) solution of *cis/trans*-PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub> [7] (0.390 g, 1.0 mmol) in methanol (25 mL) a stoichiometric amount of solid triphos (0.534 g, 1.0 mmol) was added in successive small portions. After 10 min the reaction mixture was allowed to cool to room temperature and a solution of an excess of LiClO<sub>4</sub> (0.202 g, 1.5 mmol) in methanol (10 mL) was slowly added. The white solid complex [PtCl(triphos)](ClO<sub>4</sub>) which

<sup>&</sup>lt;sup>1</sup> Safety note: perchlorate salts of metal complexes with organic ligands are potentially explosive; however, all the prepared compounds, in the experimental conditions described, appeared to be stable both in solution and in the solid state.

IR (cm<sup>-1</sup>):  $\mathbf{1}^{\text{CN}}$  2237 w ( $v_{\text{CN}}$ );  $\mathbf{1}^{\text{COOH}}$  1733 s ( $v_{\text{CO}}$ );  $\mathbf{1}^{\text{COOMe}}$  1730 s ( $v_{\text{CO}}$ );  $\mathbf{1}^{\text{MeCO}}$  1694 s ( $v_{\text{CO}}$ );  $\mathbf{1}^{\text{NH}_2}$  3466 m, 3363 m ( $v_{\text{NH}}$ );  $\mathbf{2}^{\text{CN}}$  2251 s, 2210 sh ( $v_{\text{CN}}$ ).

1 1004 s ( $v_{CO}$ ), 1 1004 s ( $v_{CO}$ ). <sup>1</sup>H NMR (ppm, 298 K): 1<sup>COOMe</sup> 3.93 (s, 3H, CH<sub>3</sub>); 1<sup>MeCO</sup> 2.56 (s, 3H, CH<sub>3</sub>); 1<sup>Me</sup> 2.36 (s, 3H, CH<sub>3</sub>); 1<sup>NH<sub>2</sub></sup> (s, br, 2H, NH<sub>2</sub>); 2<sup>Me</sup> 2.19 (s, 3H, CH<sub>3</sub>); 2<sup>OMe</sup> 3.93 (s, 3H, CH<sub>3</sub>).

<sup>31</sup>P NMR chemical shifts and  ${}^{1}J_{Pt-P}$  coupling constants are collected in Table 1. All the  $\Lambda_{\rm M}$  values measured are comprised between 140 and 150  $\Omega^{-1}$  mol<sup>-1</sup> cm<sup>2</sup>, as expected for 2:1 electrolytes in DMF [8].

#### 3. Results and discussion

## 3.1. Preparation of the complexes

The synthetic routes used for the preparation of the complexes  $[PtCl(triphos)](ClO_4),$ [Pt(4-R-py)-(triphos) (ClO<sub>4</sub>)<sub>2</sub> (1<sup>R</sup>) and [Pt(4-R-an)(triphos)] (ClO<sub>4</sub>)<sub>2</sub>  $(2^{R})$  are outlined in Scheme 1 and the details are given in Section 2, so here only few comments are made. Although the isolation of the chloro-complex  $[PtCl(triphos)]^+$  as chloride salt has already been reported [5], we have used an alternative method starting from the isomeric mixture of PtCl<sub>2</sub>(SMe<sub>2</sub>)<sub>2</sub>, which we found very convenient for the synthesis of a wide variety of Pt(II) chloro-complexes with polydentate ligands [6]. Treatment of [PtCl(triphos)](ClO<sub>4</sub>) with silver perchlorate followed by the addition of the appropriate nitrogen-donor ligand afforded the desired  $1^{R}$ or  $2^{R}$  complex in pure form and in good yield. All the characterization data (IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR, conductivity, elemental analyses) are in good agreement with the purposed formulations. Spectroscopic data of the 1<sup>H</sup> derivative have been also compared with those of the already known [Pt(pyridine)(triphos)](CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> complex [9].

The pyridines and anilines, all *para*-substituted, were chosen to cover a wide range of basicity  $(1.90 \le pK_a \text{ pyridines} \le 9.11, 1.00 \le pK_a \text{ anilines} \le 5.34)$ . Moreover, the relationship between the basicity and the nucleophilic behaviour of some of the nitrogen-donor ligands consid-

ered has been already investigated and discussed in kinetic studies [10]. It is also known [11] that there is a linear relationship between the  $pK_a$  values and the proton affinity, PA (i.e., the enthalpy of a proton breaking-off in the gaseous phase) for the series of the considered pyridines and anilines, so the medium contribution to the  $pK_a$  determination is almost constant for both the types of nitrogen-donor ligands.

# 3.2. NMR and DFT studies

The <sup>31</sup>P {<sup>1</sup>H} NMR spectra of all the  $\mathbf{1}^{R}$  and  $\mathbf{2}^{R}$  complexes consist of two sharp peaks, each with <sup>195</sup>Pt satellites. The  $J_{P1-P2}$  phosphorus–phosphorus couplings are unobservable for all the prepared complexes, but this is expected for square-planar triphos derivatives with all the phosphorus atoms co-ordinated to the same metal centre [9,12]. The <sup>31</sup>P NMR data of the  $\mathbf{1}^{R}$  and  $\mathbf{2}^{R}$  derivatives are reported in Table 1, together with the p $K_{a}$  values [13] of the *para*-substituted pyridines and anilines.

There in no apparent regularity in the variation of the <sup>31</sup>P chemical shifts, while there are interesting trends for the coupling constants. For the *para*-substituted pyridines, a variation of  $pK_a$  in the range 1.90–9.11 leads to a linear variation of  ${}^{1}J_{Pt-P1}$  (P<sub>1</sub> = phosphorus nucleus *trans* to N) from 2895 to 2768 Hz. The linear relationship  ${}^{1}J_{Pt-P1} = 2918 \pm 4 - 16.9 \pm 0.9 pK_a$  is followed, as shown in Fig. 1A. There is also a linear rise (42 Hz within the considered  $pK_a$  range) of the  ${}^{1}J_{Pt-P2}$  couplings (P<sub>2</sub> = phosphorus nuclei *cis* to N) while the  $pK_a$  value increases (see Fig. 1B); the equation is  ${}^{1}J_{Pt-P2} = 2371 \pm 1 + 5.8 \pm 0.2 pK_a$ . It is to be noted that the derivatives of 4-COOH-py and 4-COOMe-py, both having the same  $pK_a$  (3.26), give exactly the same *trans* and *cis*  ${}^{1}J_{Pt-P2}$  coupling constants.

The linear relationship between  ${}^{1}J_{\text{Pt-P1}}$  and  ${}^{1}J_{\text{Pt-P2}}$  coupling constants is given by the equation  ${}^{1}J_{\text{Pt-P1}} = 9700 \pm 300 - 2.9 \pm 0.1 {}^{1}J_{\text{Pt-P2}}$ . The variation of donor capability of the pyridines affects mostly the *trans*  ${}^{1}J_{\text{Pt-P}}$  coupling constant, also considering that there are two *cis* phosphorus atoms and only one *trans* phosphorus atom.

Table 1 <sup>31</sup>P {<sup>1</sup>H} NMR data for complexes 1–2 and  $pK_a$  values of the 4-substituted pyridines and anilines

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Complex		<sup>31</sup> P { <sup>1</sup> H} NMR $\delta$ (J/Hz)	pK <sub>a</sub>					
1 <sup>CN</sup>	$\left[ Pt(4-CN-py)(triphos) \right]^{2+}$	82.5 (s, ${}^{1}J_{Pt-P1} = 2895$ , P <sub>1</sub> ); 49.3 (s, ${}^{1}J_{Pt-P2} = 2382$ , P <sub>2</sub> )	1.90					
1 <sup>COOH</sup>	[Pt(4-COOH-py)(triphos)] <sup>2+</sup>	82.7 (s, ${}^{1}J_{Pt-P1} = 2861$ , P <sub>1</sub> ); 48.8 (s, ${}^{1}J_{Pt-P2} = 2390$ , P <sub>2</sub> )	3.26					
1 <sup>COOMe</sup>	[Pt(4-COOMe-py)(triphos)] <sup>2+</sup>	82.8 (s, ${}^{1}J_{Pt-P1} = 2861$ , P <sub>1</sub> ); 48.8 (s, ${}^{1}J_{Pt-P2} = 2390$ , P <sub>2</sub> )	3.26					
1 <sup>MeCO</sup>	[Pt(4-MeCO-py)(triphos)] <sup>2+</sup>	82.6 (s, ${}^{1}J_{Pt-P1} = 2855$ , P <sub>1</sub> ); 48.8 (s, ${}^{1}J_{Pt-P2} = 2392$ , P <sub>2</sub> )	3.51					
1 <sup>H</sup>	$[Pt(4-H-py)(triphos)]^{2+}$	82.4 (s, ${}^{1}J_{Pt-P1} = 2827$ , P <sub>1</sub> ); 48.6 (s, ${}^{1}J_{Pt-P2} = 2404$ , P <sub>2</sub> )	5.17					
1 <sup>Me</sup>	$[Pt(4-Me-py)(triphos)]^{2+}$	82.8 (s, ${}^{1}J_{Pt-P1} = 2815$ , P <sub>1</sub> ); 47.9 (s, ${}^{1}J_{Pt-P2} = 2406$ , P <sub>2</sub> )	6.03					
1 <sup>NH2</sup>	$[Pt(4-NH_2-py)(triphos)]^{2+}$	83.0 (s, ${}^{1}J_{Pt-P1} = 2768$ , P <sub>1</sub> ); 46.7 (s, ${}^{1}J_{Pt-P2} = 2424$ , P <sub>2</sub> )	9.11					
$2^{NO_2}$	$[Pt(4-NO_2-an)(triphos)]^{2+}$	85.0 (s, ${}^{1}J_{Pt-P1} = 3292$ , P <sub>1</sub> ); 48.4 (s, ${}^{1}J_{Pt-P2} = 2364$ , P <sub>2</sub> )	1.00					
2 <sup>CN</sup>	$[Pt(4-CN-an)(triphos)]^{2+}$	85.0 (s, ${}^{1}J_{Pt-P1} = 3255$ , P <sub>1</sub> ); 48.4 (s, ${}^{1}J_{Pt-P2} = 2520$ , P <sub>2</sub> )	1.74					
2 <sup>Cl</sup>	$[Pt(4-Cl-an)(triphos)]^{2+}$	85.0 (s, ${}^{1}J_{Pt-P1} = 2949$ , P <sub>1</sub> ); 48.1 (s, ${}^{1}J_{Pt-P2} = 2461$ , P <sub>2</sub> )	3.98					
2 <sup>H</sup>	$\left[ Pt(4-H-an)(triphos) \right]^{2+}$	80.8 (s, ${}^{1}J_{Pt-P1} = 2806$ , P <sub>1</sub> ); 48.2 (s, ${}^{1}J_{Pt-P2} = 2447$ , P <sub>2</sub> )	4.60					
2 <sup>Me</sup>	$[Pt(4-Me-an)(triphos)]^{2+}$	84.8 (s, ${}^{1}J_{Pt-P1} = 2918$ , P <sub>1</sub> ); 47.8 (s, ${}^{1}J_{Pt-P2} = 2469$ , P <sub>2</sub> )	5.08					
2 <sup>MeO</sup>	$[Pt(4-MeO-an)(triphos)]^{2+}$	$80.4$ (s. ${}^{1}J_{Pt}$ $_{P1} = 2780$ , $P_1$ ); $47.9$ (s. ${}^{1}J_{Pt}$ $_{P2} = 2457$ , $P_2$ )	5.34					



Scheme 1. Synthesis of  $[PtCl(triphos)]^+$ ,  $[Pt(4-R-py)(triphos)]^{2+}$  (1<sup>R</sup>) and  $[Pt(4-R-an)(triphos)]^{2+}$  (2<sup>R</sup>) complexes.



Fig. 1. Plot of  ${}^{1}J_{Pt-P1}$  against  $pK_{a}$  (A) and of  ${}^{1}J_{Pt-P2}$  against  $pK_{a}$  (B) for  $\mathbf{1}^{R}$  complexes.

The use of 4-substituted pyridines allows to exclude steric effects due to the different R groups, so that the linear relationships between the  $pK_a$  and the  ${}^1J_{Pt-P}$  values can be attributed only to electronic effects. It is generally assumed [1] that the magnitude of the  ${}^1J_{Pt-P}$  coupling constant is dominated by the Fermi contact term, expressed by the following relation:

$${}^{1}J_{Pt-P} \propto \frac{\gamma_{Pt}\gamma_{P}\alpha_{Pt}^{2}\alpha_{P}^{2}|\psi_{Pt(6s)}(0)|^{2}|\psi_{P(3s)}(0)|^{2}}{\Delta E}.$$
 (1)

In the relation,  $\gamma_{Pt}$  and  $\gamma_P$  are the gyromagnetic ratios for the <sup>195</sup>Pt and <sup>31</sup>P isotopes,  $\alpha_{Pt}^2$  and  $\alpha_P^2$  represent the s-characters of the localized hybrid orbitals in a valence bond description,  $|\psi_{Pt(6s)}(0)|^2$  and  $|\psi_{P(3s)}(0)|^2$  are the electron densities of the s orbitals at nucleus,  $\Delta E$  is an average singlet– triplet excitation energy. It is also assumed that the most important term for the variation of the magnitude of  ${}^{1}J_{\text{Pt-P}}$  is  $\alpha_{\text{Pt}}^{2}$  so, following relation (1), the decrease of the *trans*  ${}^{1}J_{\text{Pt-P1}}$  coupling constant with the increase of the pK<sub>a</sub> represents primarily the change in 6s character of the hybrid orbital of platinum used in the bond with P<sub>1</sub>. The increase of donor capability of the co-ordinated pyridine increase the Pt 6s character of the Pt–N bond at the expense of the *trans* Pt–P bond. The  ${}^{1}J_{\text{Pt-P2}}$  trend suggests that the weakening of the Pt–P<sub>1</sub> bond strengthens the bonds between the metal centre and the other two phosphorus atoms in the *cis* positions.

Mather et al. have reported a correlation of the  ${}^{1}J_{Pt-P}$  coupling constants with the Pt–P bond lengths in some trialkyl phosphine complexes of Pt(II) and Pt(IV) [14] and subsequent studies for Pt(0) complexes [15] have shown similar results, in which the shorter Pt–P distances are associated with larger values of  ${}^{1}J_{Pt-P}$ . We tried to correlate the  ${}^{1}J_{Pt-P}$  coupling constants of the  $\mathbf{1}^{R}$  complexes with the

bond lengths by optimising with DFT calculations the geometries of the derivatives of the pyridines with the greatest  $pK_a$  difference, the  $[Pt(4-CN-py)(triphos)]^{2+}$  ( $1^{CN}$ ) and  $[Pt(4-NH_2-py)(triphos)]^{2+}$  ( $1^{NH_2}$ ) cations. The difference in nucleophilicity between the two considered pyridines is well expressed by both the calculated dipolar moment  $\mu$  (whose vector is oriented from the R group towards the pyridine-N atom) and the Mulliken charge on the pyridine-N atoms for the free species (see Table 2). Also the electrostatic potential surfaces on the pyridine-N atoms shown in Fig. 2 allow to understand the different nucleophilicity of the two pyridines.

The calculated  $r_{Pt-P1}$ ,  $r_{Pt-P2}$  and  $r_{Pt-N}$  bond lengths for the 1<sup>CN</sup> and 1<sup>NH<sub>2</sub></sup> complexes are reported in Table 2; unfortunately, the differences between the corresponding bond lengths of the two derivatives are too small to be really significant, probably because of the relatively small difference of the <sup>1</sup>J<sub>Pt-P</sub> couplings of the two complexes.

Also in the case of the complexes with the *para*-substituted anilines  $2^{R}$  a relationship between the  $pK_{a}$  values of the anilines and the  ${}^{1}J_{Pt-P1}$  coupling constants of the  $2^{R}$  derivatives is observed (see Fig. 3), but this correlation is less linear in comparison with the one of the  $1^{R}$  derivatives. Moreover, for the  $2^{R}$  complexes there is an irregular trend of the  ${}^{1}J_{Pt-P2}$  values against  $pK_{a}$ .

A possible explanation for the different behaviour of the  $2^{R}$  derivatives compared to  $1^{R}$  complexes is that steric effects due to the change of the 4-R group of the anilines cannot be completely excluded, as done in the case of the 4-substituted pyridines. In fact, by rotating the P<sub>2</sub>-Pt-N-H dihedral angle in the optimised models of the  $[Pt(4-R-an)(triphos)]^{2+}$  cations, a steric interaction between the R group and the phenyl rings bonded to the  $P_2$  atoms can be observed. If the steric hindrance between the phenyl rings bonded to the P<sub>2</sub> atoms and the aniline blocked the rotation around the Pt-N bond, two different rotamers at an energy minimum would be possible, with the phenyl ring bonded to the P<sub>1</sub> atom and the aryl group of the aniline in Z (sin rotamer) or E (anti rotamer) position, as shown in Fig. 4. The calculated energy difference between the two rotamers is quite small, about 5 kcal/mol.

As, on the contrary, the NMR spectra of the  $2^{R}$  derivatives show the signals of only one species in a temperature range between 298 and 243 K, there should be free rotation around the Pt–N bond. This means that the geometry in solution of the  $2^{R}$  derivatives in not affected only by the nucleophilicity of the aniline ligand, as observed for the  $1^{R}$  complexes, but also by the different bulk of the 4-R group. The sum of the electronic and the steric effects on the geometry of the [Pt(4-R-an)(triphos)]<sup>2+</sup> cations

Fig. 2. Potential electrostatic surfaces on the pyridine-N atom for the 4-CN-py and 4-NH<sub>2</sub>-py ligands.



Fig. 3. Plot of  ${}^{1}J_{Pt-P1}$  against p $K_{a}$  for  $2^{R}$  complexes.



Fig. 4. Rotamers of the  $[Pt(4-R-an)(triphos)]^{2+}$  cations.

Table 2

Calculated  $r_{Pt-P}$  and  $r_{Pt-N}$  bond lengths for complexes  $\mathbf{1}^{CN}$  and  $\mathbf{1}^{NH_2}$ , dipolar moment and Mulliken charge on the pyridine-N atom for the free ligands

Complex		$r_{\mathrm{Pt-P1}}(\mathrm{A})$	$r_{\rm Pt-P2}$ (A)	$r_{\mathrm{Pt-N}}\left(\mathrm{A}\right)$	Pyridine	$\mu$ (Debye)	N charge
1 <sup>CN</sup>	$[Pt(4-CN-py)(triphos)]^{2+}$	2.3258	2.4083	2.1070	4-CN-ру	2.00	$-0.060 \\ -0.112$
1 <sup>NH<sub>2</sub></sup>	$[Pt(4-NH_2-py)(triphos)]^{2+}$	2.3270	2.4055	2.1023	4-NH <sub>2</sub> -ру	4.08	

explains the less linear correlation between the  $pK_a$  and the  ${}^{1}J_{Pt-P1}$  values of these derivatives and the irregular trend of the  ${}^{1}J_{Pt-P2}$  values.

#### 4. Conclusions

In conclusion, the <sup>31</sup>P NMR spectroscopy of derivatives of the Pt(II)–triphos fragment allowed us to observe small changes of the electronic and steric properties of the coordinated ligands by measuring the  ${}^{1}J_{Pt-P}$  coupling constants. Further investigations will be carried out in order to ascertain whether this approach could be an effective way for investigating and comparing other series of molecules with co-ordinating ability.

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