#### Inorganica Chimica Acta 363 (2010) 3498-3505

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



## Quantification of *cis* and *trans* influences in $[PtX(PPh_3)_3]^+$ complexes. A <sup>31</sup>P NMR study

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## ARTICLE INFO

Article history: Received 4 June 2010 Accepted 1 July 2010 Available online 7 July 2010

Keywords: cis influence trans influence cis influence weight trans influence weight Platinum phosphine complexes

#### ABSTRACT

In [PtX(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> complexes (X = F, Cl, Br, I, AcO, NO<sub>3</sub>, NO<sub>2</sub>, H, Me) the mutual *cis* and *trans* influences of the PPh<sub>3</sub> groups can be considered constants in the first place, therefore the one bond Pt–P coupling constants of P<sub>(cis)</sub> and P<sub>(trans)</sub> reflect the *cis* and *trans* influences of X. The compounds [PtBr(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**2**), [PtI(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**3**), [Pt(AcO)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**4**), [Pt(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**5**), and the two isomers [Pt(NO<sub>2</sub>-*O*)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**6a**) and [Pt(NO<sub>2</sub>-*N*)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**6b**) have been newly synthesised and the crystal structures of **2** and **4**·CH<sub>2</sub>Cl<sub>2</sub>·0.25C<sub>3</sub>H<sub>6</sub>O have been determined. From the <sup>1</sup>*J*<sub>PtP</sub> values of all compounds we have deduced the series: I > Br > Cl > NO<sub>3</sub> > ONO > F > AcO > NO<sub>2</sub> > H > Me (*cis* influence) and Me > H > NO<sub>2</sub> > AcO > I > ONO > Br > Cl > F > NO<sub>3</sub> (*trans* influence). These sequences are like those obtained for the (neutral) *cis*- and *trans*-[PtClX(PPh<sub>3</sub>)<sub>2</sub>] derivatives, showing that there is no dependence on the charge of the complexes. On the contrary, the weights of both influences, relative to those of X = Cl, were found to depend on the charge and nature of the complex.

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## 1. Introduction

*cis* and *trans* influences of a ligand X can be defined as the ability of that ligand to weaken the bond between a metal and a ligand L, respectively, *cis* or *trans* to X [1–6]. The comprehension of these influences is therefore important for understanding and rationalising some properties of square planar and octahedral transition metal complexes. These include stability, occurrence of geometrical isomers, bond strengths, as well as ligand reactivity (through the link with the *cis* and *trans* effects) [1–5]. Because of such importance, these influences have been the subject of many investigations from their early recognition [6] to the present days [2,3,7–10]. Interestingly, the scope of these influences has recently been expanded, since they were found to play a role also in main group [11] and lanthanide chemistry [12].

These studies were mostly based on either X-ray crystallography or spectroscopic (IR and NMR) investigations, although both techniques suffer some limitations. Thus X-ray derived M–L bond lengths may be affected by crystal packing and conformational effects and only few M–L bond stretches can be unambiguously assigned (M–H, certain M–Cl and few others); CO stretching frequencies have also been used [13]. NMR investigations are usually based on the values of one bond coupling constants, which can

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be considered an estimate of the M–L bond strength [1,13–19], but this technique can be used only when both M and the donor atom of L are NMR active (<sup>195</sup>Pt–<sup>31</sup>P, <sup>103</sup>Rh–<sup>31</sup>P, etc.). <sup>2</sup>*J*<sub>MC</sub> and <sup>3</sup>*J*<sub>MH</sub> have also been employed [1,20].

We have recently been studying *cis* and *trans* influences in Pt(II) bis(triphenylphosphine) complexes. In a first paper [21] we have used the one bond Pt–P coupling constants to evaluate the order of *cis* influence of some anionic ligands X and Y in a series of *trans*-[PtXY(PPh<sub>3</sub>)<sub>2</sub>] complexes (type **A**, see Scheme 1). In these compounds the mutual *trans* influence of the two phosphine groups can be considered constant throughout the series, consequently  ${}^{1}J_{PtP}$  of the various derivatives give an insight of the *cis* influence of X and Y.

A second paper [14] dealt with the *cis*-[PtXY(PPh<sub>3</sub>)<sub>2</sub>] isomers (type **B** of Scheme 1). Here each P atom experiences the *cis* influence of a PPh<sub>3</sub> group, the *trans* influence of X and the *cis* influence of Y (or the other way round). Assuming that the mutual *cis* influence of the two phosphine groups is constant, the  ${}^{1}J_{PtP}$  values of each P nucleus depends on the *cis* and *trans* influences of X and Y. We have been able to discriminate the two influences, showing that the former, although of lower importance, is by no means irrelevant and must be taken into account when rationalising  ${}^{1}J_{PtP}$ as well as Pt–P bond distances. We could also justify the sequences of both influences in terms of Pt–P bonding and charge on Pt [14].

We were also interested in quantifying the influences, i.e. to ascertain "how much" a given X (or Y) ligand influences the Pt–P bonds *cis* or *trans* to such ligand, in other words the *cis* or *trans* 





weight of X (or Y). Since there is no possibility of obtaining the absolute values of such ability, we used the *cis* and *trans* influences of Cl as references, putting its abilities to zero. The difference between  ${}^{1}J_{PtP}$  of the Cl derivative with that of a compound with a given X, gives an estimate of such ability, i.e. how much X influences the Pt–P bonds (either *cis* or *trans*) with respect of Cl [14,10–22].

Since these two investigations dealt with neutral compounds, we wondered whether charged species would affect the *cis* and *trans* sequences and/or their weights. Therefore we extended our study to a series of cationic complexes of formula  $[PtX(PPh_3)_3](BF_4)$  (type **C**, Scheme 1: X = Cl, **1**; Br, **2**; I, **3**; AcO, **4**; NO<sub>3</sub>, **5**; NO<sub>2</sub>-O, **6a**; NO<sub>2</sub>-N, **6b**; F, **7**; H, **8** and Me, **9**). Besides the interest in the comparison with the neutral compounds, the ligand X is *trans* to a phosphine (P1 in Scheme 1) and *cis* to two other phosphine groups (P2 and P3, Scheme 1) therefore we can observe both influences of X within the same complex. This can be done if we assume, in the first place, that the mutual *cis* and *trans* influences of the three PPh<sub>3</sub> groups are constant.

#### 2. Experimental

## 2.1. General

All chemicals were reagent grade. Solvents were used as received. Elemental analyses were performed at the Microanalytical Laboratory at the Università degli Studi di Milano. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker Advance DRX 300 at 300 and 121 MHz, respectively;  $\delta_{\rm H}$  values are in ppm *versus* external Me<sub>4</sub>Si,  $\delta_{\rm P}$  values are in ppm *versus* external H<sub>3</sub>PO<sub>4</sub>, <sup>1</sup>J<sub>PtP</sub> coupling constants (Hz) have been found reproducible to ±3 Hz. Infrared spectra were recorded from KBr disks with a JASCO FT-IR 410 spectrophotometer having 2 cm<sup>-1</sup> resolution.

*cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [14,23], [Pt<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub> [24], [PtCl(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**1**) [25,26], *cis*-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [14], *cis*-[PtCl(AcO)(PPh<sub>3</sub>)<sub>2</sub>] [14] and *trans*-[PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [14,21] were synthesised as described in the literature. All reactions involving silver salts were performed in the dark.

## 2.2. Preparation of complexes

## 2.2.1. Synthesis of [Pt<sub>2</sub>(µ-Br)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>](BF<sub>4</sub>)<sub>2</sub>

This reaction was performed under a nitrogen atmosphere using the Schlenk technique. A solution of AgBF<sub>4</sub> (42.8 mg, 0.23 mmol) in acetone (3 mL) was added to a solution of *cis*-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (200.1 mg, 0.23 mmol) in dichloromethane (15 mL) and the mixture was stirred at room temperature for 2 h and filtered. The solution was concentrated by evaporation under reduced pressure, and treated with diisopropyl ether (40 mL) yielding a white solid (112.7 mg, 55% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 16.1 (s, <sup>1</sup>*J*<sub>PtP</sub> = 3747 Hz). IR: *v*(BF<sub>4</sub>) 1054 cm<sup>-1</sup> *Anal.* Calc. for C<sub>72</sub>H<sub>60</sub>B<sub>2</sub>Br<sub>2</sub>F<sub>8</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 48.78; H, 3.41. Found: C, 49.27; H 3.73%.

## 2.2.2. Synthesis of $[PtBr(PPh_3)_3](BF_4)$ (2)

PPh<sub>3</sub> (18.9 mg, 0.072 mmol) was added to a solution of  $[Pt_2(\mu-Br)_2(PPh_3)_4](BF_4)_2$  (63.9 mg, 0.036 mmol) in nitromethane (2 mL) and the mixture was stirred at room temperature for 30 min. Diisopropyl ether (40 mL) was added yielding a white solid (69.2 mg, 84% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 12.5 (t, <sup>2</sup>J<sub>PP</sub> = 18.0 Hz, <sup>1</sup>J<sub>PtP</sub> = 3624 Hz, 1P, P<sub>(trans</sub>), 19.4 (d, <sup>2</sup>J<sub>PP</sub> = 18.0 Hz, <sup>1</sup>J<sub>PtP</sub> = 2468 Hz, 2P, P<sub>(cis</sub>)). IR: v(BF<sub>4</sub>) 1053 cm<sup>-1</sup>. Anal. Calc. for C<sub>56</sub>H<sub>45</sub>BBrF<sub>4</sub>P<sub>3</sub>Pt: C, 56.46; H, 3.95. Found: C, 56.18; H 4.15%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diisopropyl ether into a dichloromethane solution.

#### 2.2.3. Synthesis of $[PtI(PPh_3)_3](BF_4)$ (3) [27]

The reaction was performed under a nitrogen atmosphere with the use of the Schlenk technique. A solution of  $AgBF_4$  (15.5 mg, 0.079 mmol) in acetone (5 mL) was added to a solution of trans- $[PtI_2(PPh_3)_2]$  (76.6 mg, 0.079 mmol) in dichloromethane (10 mL); the mixture was stirred at room temperature for 1 h, and then filtered. The solvent was removed under reduced pressure and the residue was dissolved in nitromethane and then PPh<sub>3</sub> (53.2 mg, 0.20 mmol) was added. The mixture was stirred at room temperature for 2 h, concentrated and treated with diethyl ether, yielding a yellow solid. (52.2 mg, 55% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 8.1$  (t,  ${}^{2}J_{PP} = 17.6$  Hz,  ${}^{1}J_{PtP} = 3480$  Hz, 1P, P<sub>(trans)</sub>), 12.4 (d,  ${}^{2}J_{PP}$  = 17.6 Hz,  ${}^{1}J_{PtP}$  = 2459 Hz, 2P, P<sub>(cis)</sub>).  ${}^{31}P$  NMR (121 MHz,  $d_6$ -acetone, 25 °C):  $\delta$  = 8.3 (t, <sup>2</sup> $J_{PP}$  = 17.6 Hz, <sup>1</sup> $J_{PtP}$  = 3511 Hz, 1P,  $P_{(trans)}$ ), 12.5 (d, <sup>2</sup> $J_{PP}$  = 17.6 Hz, <sup>1</sup> $J_{PtP}$  = 2474 Hz, 2P,  $P_{(cis)}$ ). IR:  $v(BF_4)$ 1055 cm<sup>-1</sup>. Anal. Calc. for C<sub>54</sub>H<sub>45</sub>BF<sub>4</sub>IP<sub>3</sub>Pt: C, 54.25; H, 3.79. Found: C, 53.83; H 4.23%.

## 2.2.4. Synthesis of [Pt(AcO)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (4)

The reaction was performed under a nitrogen atmosphere with the use of the Schlenk technique. A solution of AgBF<sub>4</sub> (12.1 mg, 0.062 mmol) in acetone (2 mL) was added to a solution of *cis*-[PtCl(AcO)(PPh<sub>3</sub>)<sub>2</sub>] (51.2 mg, 0.062 mmol) in dichloromethane (5 mL) and the mixture was stirred at room temperature for 1 h, then it was filtered. PPh<sub>3</sub> (26.0 mg, 0.099 mmol) was added and the solution was left under stirring for 1 h, and then treated with diisopropyl ether (40 mL) yielding a white solid (44.0 mg, 63% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.28 (s, 3H, CH<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 3.5 (t, <sup>2</sup>J<sub>PP</sub> = 19.8 Hz, <sup>1</sup>J<sub>PtP</sub> = 3478 Hz, 1P, P<sub>(trans</sub>)), 22.7 (d, <sup>2</sup>J<sub>PP</sub> = 19.8 Hz, <sup>1</sup>J<sub>PtP</sub> = 2676 Hz, 2P, P<sub>(cis)</sub>). IR: *v*(C=O) 1634, 1368, 1308, *v*(BF<sub>4</sub>), 1056 cm<sup>-1</sup>. *Anal.* Calc. for C<sub>56</sub>H<sub>48</sub>BF<sub>4</sub>O<sub>2</sub>P<sub>3</sub>Pt: C, 59.64; H, 4.29. Found: C, 59.71; H, 4.64%. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diisopropyl ether into a dichloromethane solution.

## 2.2.5. Synthesis of [Pt(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (5) [26]

AgNO<sub>3</sub> (8.4 mg, 0.049 mmol) was added to a solution of  $[PtCl(PPh_3)_3](BF_4)$  (1) (31.1 mg, 0.028 mmol) in dichloromethane (10 mL) and the mixture was refluxed for 2.5 h, hot filtered, the

filtrate was concentrated under reduced pressure and treated with diisopropyl ether (40 mL) yielding a white solid (18.1 mg, 57% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 2.7 (t, <sup>2</sup>*J*<sub>PP</sub> = 19.2 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 3761 Hz, 1P, P<sub>(trans)</sub>), 22.2 (d, <sup>2</sup>*J*<sub>PP</sub> = 19.2 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 2609 Hz, 2P, P<sub>(cis)</sub>). IR: *v*(NO<sub>3</sub>) 1516, 1265 *v*(BF<sub>4</sub>) 1057 cm<sup>-1</sup>. *Anal.* Calc. for C<sub>54</sub>H<sub>45</sub>BF<sub>4</sub>NO<sub>3</sub>P<sub>3</sub>Pt·4H<sub>2</sub>O: C, 53.92; H, 4.40; N, 1.16. Found: C, 53.93; H, 4.27; N, 1.19%.

# 2.2.6. Synthesis of $[Pt(NO_2)(PPh_3)_3](BF_4)$ (**6a**) and $[Pt(ONO)(PPh_3)_3](BF_4)$ (**6b**)

The reaction was performed under a nitrogen atmosphere with the use of the Schlenk technique. AgNO<sub>2</sub> (13.7 mg, 0.089 mmol) was added to a solution of [PtCl(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**1**) (83.1 mg, 0.075 mmol) in dichloromethane (20 mL) and the mixture was refluxed for 7 h. The filtered solution was concentrated under reduced pressure and treated with diisopropyl ether (40 mL) yielding a white solid (45.7 mg, 55% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = -1.4$  (t, <sup>2</sup>*J*<sub>PP</sub> = 21.4 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 2838 Hz, 1P, P<sub>(trans)</sub>), 15.0 (d, <sup>2</sup>*J*<sub>PP</sub> = 21.4 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 2692 Hz, 2P, P<sub>(cis)</sub>): [Pt(NO<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub>] (BF<sub>4</sub>) (**6a**);  $\delta = 3.5$  (t, <sup>2</sup>*J*<sub>PP</sub> = 18.4 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 3520 Hz, 1P, P<sub>(trans)</sub>), 21.5 (d, <sup>2</sup>*J*<sub>PP</sub> = 18.4 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 2633 Hz, 2P, P<sub>(cis)</sub>): [Pt(ONO) (PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**6b**). <sup>31</sup>P NMR (121 MHz, acetone-*d*<sub>6</sub>, 25 °C):  $\delta = -1.4$  (t, <sup>2</sup>*J*<sub>PP</sub> = 22.3 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 2817 Hz, 1P, P<sub>(trans)</sub>), 14.9 (d, 2*J*<sub>PP</sub> = 22.3 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 19.0 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 3478 Hz, 1P, P<sub>(trans)</sub>), 21.4 (d, <sup>2</sup>*J*<sub>PP</sub> = 19.0 Hz, <sup>1</sup>*J*<sub>PtP</sub> = 2649 Hz, 2P, P<sub>(cis)</sub>): [Pt(ONO)(PPh<sub>3</sub>)<sub>3</sub>](BF<sub>4</sub>) (**6b**). IR: *v*(NO) 1322, 1286, 1177, 886, 850, *v*(BF<sub>4</sub>) 1056 cm<sup>-1</sup>. Anal. Calc. for C<sub>54</sub>H<sub>45</sub>BF<sub>4</sub>NO<sub>2</sub>P<sub>3</sub>Pt: C, 58.18; H, 4.07; N, 1.26. Found: C, 58.43; H, 4.13; N, 1.14%.

#### 2.2.7. Synthesis of [PtBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]

KBr (1000.2 mg, 8.40 mmol) was added to a solution of  $K_2$ [PtCl<sub>4</sub>] (155.7 mg, 0.38 mmol) in water (5 mL) and the solution was left at room temperature for 15 min. Acetonitrile (2 mL) was added and the mixture was refluxed for 2.5 h, then cooled. The yellow solid was filtered, washed with water and dried in vacuo (76.1 mg, 46% yield). IR:  $v(C \equiv N)$  2337 cm<sup>-1</sup>. *Anal.* Calc. for C<sub>4</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub>Pt·KBr: C, 8.64; H, 1.08; N, 5.03. Found: C, 8.66; H, 1.01; N, 4.65%.

#### 2.2.8. Synthesis of trans-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]

PPh<sub>3</sub> (50.8 mg, 0.19 mmol) was added to a solution of [PtBr<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (54.9 mg, 0.099 mmol) in nitromethane (5 mL) and the mixture was stirred at 50 °C for 30 min. The yellow solid was filtered, washed with diisopropyl ether and dried in vacuo (85.7 mg 99% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 19.3 (s, <sup>1</sup>*J*<sub>PtP</sub> = 2561 Hz, 2P)<sup>1</sup>. *Anal.* Calc. for C<sub>36</sub>H<sub>30</sub>Br<sub>2</sub>P<sub>2</sub>Pt: C, 49.17; H, 3.44. Found: C, 48.95; H 3.25%.

## 2.2.9. Synthesis of [PtBrCl(CH<sub>3</sub>CN)<sub>2</sub>]

KBr (180.9 mg, 1.52 mmol) was added to a solution of K<sub>2</sub>[PtCl<sub>4</sub>] (157.7 mg, 0.38 mmol) in water (5 mL) and the mixture was stirred at room temperature for 15 min. Acetonitrile (2 mL) was added, the mixture was refluxed for 2.5 h, cooled and the yellow solid was filtered, washed with water and dried in vacuo (52.8 mg, 35% yield). IR:  $\nu$ (C=N) 2338 cm<sup>-1</sup>. *Anal.* Calc. for C<sub>4</sub>H<sub>6</sub>BrClN<sub>2</sub>Pt·1.5H<sub>2</sub>O: C, 11.46; H, 2.16; N, 6.68. Found: C, 11.46; H, 1.72; N, 6.38%.

## 2.2.10. Synthesis of trans-[PtBrCl(PPh<sub>3</sub>)<sub>2</sub>]

 $PPh_3~(47.9~mg,~0.18~mmol)$  was added to a solution of  $[PtBrCl(CH_3CN)_2]~(39.2~mg,~0.093~mmol)$  in nitromethane (10~mL)

and the mixture was stirred at 50 °C for 30 min. The yellow solid was filtered, washed with diisopropyl ether and dried in vacuo (46.7 mg, 60% yield). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 20.3 (s, <sup>1</sup>*J*<sub>PtP</sub> = 2596 Hz, 2P). *Anal.* Calc. for C<sub>36</sub>H<sub>30</sub>BrClP<sub>2</sub>Pt: C, 51.78; H, 3.62. Found: C, 51.67; H, 3.65%.

#### 2.3. X-ray data collections and structure determinations

Crystal data are summarised in Table 1. The diffraction experiments were carried out on a Bruker APEX II CCD area-detector diffractometer, at 296 K for **2**, and at 150 K for **4** CH<sub>2</sub>Cl<sub>2</sub> 0.25C<sub>3</sub>H<sub>6</sub>O, using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) with a graphite crystal monochromator in the incident beam. No crystal decay was observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT [28], and an empirical absorption correction was applied (SADABS) [29] to the collected reflections. The calculations were performed using the Personal Structure Determination Package [30] and the physical constants tabulated therein [31]. The structures were solved by direct methods (SHELXS) [32] and refined by full-matrix least-squares, using all reflections and minimising the function  $\Sigma w (F_o^2 - kF_c^2)^2$  (refinement on  $F^2$ ). In the asymmetric unit of compound  $4 \cdot CH_2 Cl_2 \cdot 0.25C_3 H_6 O$ there are two disordered half molecules of CH<sub>2</sub>Cl<sub>2</sub>, whose atoms have occupancy factors of 0.50 each, and one disordered half molecule of C<sub>3</sub>H<sub>6</sub>O, whose atoms have also occupancy factors of 0.50 each (see Section 3). All the non-hydrogen atoms of these disordered molecules, having occupancy factors of 0.50, have been refined with isotropic thermal factors, and their hydrogen atoms have been ignored. All the other non-hydrogen atoms of both compounds have been refined with anisotropic thermal parameters, and all their hydrogen atoms have been placed in ideal positions (C-H = 0.970 Å), with the thermal parameter U being 1.10 times that of the atom to which they are attached, and not refined. For the non-centrosymmetric compound 2, both the inverted structure models were fully refined: final  $R_2$  and  $R_{2w}$  indices were 0.076 and 0.103 for the correct one, and 0.081 and 0.111 for the other. In the final Fourier maps the maximum residuals were  $3.44(1.32) e Å^{-3}$  at 0.25 Å from Pt, and 2.54(46) e Å<sup>-3</sup> at 0.38 Å from Pt1, for **2** and 4-CH<sub>2</sub>Cl<sub>2</sub>·0.25C<sub>3</sub>H<sub>6</sub>O, respectively. Minimum peaks (holes), in the same order, were −2.84(1.32), and −1.47(46) e Å<sup>-3</sup>.

## 3. Results and discussion

#### 3.1. Synthesis and characterisation

The synthetic paths to compounds **C** are outlined in Scheme 2. All complexes were all isolated as their BF<sub>4</sub> salts. Compound 2 was obtained through a reaction sequence similar to that reported for 1 [24–26]: reaction of cis-[PtBr<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] with AgBF<sub>4</sub> gives the dinuclear  $[Pt_2(\mu-Br)_2(PPh_3)_4]^{2+}$ , which, upon treatment with PPh<sub>3</sub>, yields 2. Compounds 3 and 4 were prepared by similar methods starting from trans-[PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] and cis-[Pt(AcO)Cl(PPh<sub>3</sub>)<sub>2</sub>], respectively, without isolating the dinuclear intermediates. The  $NO_3$  (5) and NO<sub>2</sub> (**6a** and **6b**) complexes were obtained by metathesis reactions, treating **1** with the appropriate silver salt. The reaction with AgNO<sub>2</sub> (performed under strict anaerobic conditions since nitrite is easily oxidised under these conditions [14]) gave a solid which analysed correctly for [Pt(NO<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>), whose IR spectrum showed bands suggestive of the presence of the nitro and nitrito linkage isomers [33] (see Section 2). The <sup>31</sup>P NMR spectrum of this material showed two sets of <sup>31</sup>P triplets and doublets, in approximately 1:1 ratio. One set is assigned to  $[Pt(NO_2-N)(PPh_3)_3]^+$  on the grounds of the similarity of the chemical shifts and Pt-P coupling constants (see Table 2) with those of trans-[PtCl(NO<sub>2</sub>-*N*)(PPh<sub>3</sub>)<sub>2</sub>] ( $\delta$ , 16.6 ppm; <sup>1</sup>*J*<sub>PtP</sub>, 2760 Hz) and, particularly, with

<sup>&</sup>lt;sup>1</sup> Excess of PPh<sub>3</sub> must be avoided, since it catalyses isomerisation to the *cis* isomer. <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 14.3 (s, <sup>1</sup>J<sub>PtP</sub> = 3614 Hz, 2P). This behaviour is opposite to that of [PtI<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] which, in the presence of excess of PPh<sub>3</sub> is converted quantitatively to the *trans* isomer [14].

Table 1	
Crystallographic	data.

Compound	2	<b>4</b> ⋅CH <sub>2</sub> Cl <sub>2</sub> ⋅0.25C <sub>3</sub> H <sub>6</sub> O
Formula	$C_{54}H_{45}BBrF_4P_3Pt$	$C_{231}H_{203}B_4Cl_8F_{16}O_9P_{12}Pt_4$
Μ	1148.69	4906.8
Colour	colourless	pale yellow
Crystal system	orthorhombic	triclinic
Space group	Pna21	ΡĪ
a (Å)	20.1334(10)	12.8129(7)
b (Å)	18.1811(9)	21.0111(11)
c (Å)	13.0873(6)	21.7134(11)
α (°)	90	70.270(1)
β (°)	90	86.620(1)
γ (°)	90	75.770(1)
U (Å <sup>3</sup> )	4790.6(4)	5331.7(5)
Ζ	4	1
F(000)	2272	2453
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.593	1.528
T (K)	296	150
$\lambda$ (Mo K $\alpha$ )	0.71073	0.71073
Crystal dimensions (mm)	$0.17 \times 0.23 \times 0.35$	$0.09 \times 0.38 \times 0.46$
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	39.34	29.03
Minimum and maximum transmission factors	0.763-1.000	0.691-1.000
Scan mode	ω	ω
Frame width (°)	0.50	0.50
Time per frame (s)	20	20
Number of frames	3300	3300
Detector-sample distance (cm)	5.00	5.00
θ-range (°)	3.00-30.00	3.00-29.00
Reciprocal space explored	full sphere	full sphere
Number of reflections (total; independent)	163 445, 15 227	181 579, 33 227
R <sub>int</sub>	0.0322	0.0413
Final $R_2$ and $R_{2w}$ indices <sup>a</sup> ( $F^2$ , all reflections)	0.076, 0.103	0.060, 0.095
Conventional $R_1$ index $[I > 2\sigma(I)]$	0.042	0.034
Reflections with $l > 2\sigma(l)$	8229	22 448
Number of variables	576	1274
Goodness-of-fit (GOF) <sup>b</sup>	0.985	0.968

<sup>a</sup>  $R_2 = [\Sigma(|F_0^2 - kF_c^2|)/\Sigma F_0^2], R_{2W} = [\Sigma w(F_0^2 - kF_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}.$ <sup>b</sup>  $[\Sigma w(F_0^2 - kF_c^2)^2/(N_0 - N_v)]^{1/2}$ , where  $w = 4F_0^2/\sigma(F_0^2)^2, \sigma(F_0^2) = [\sigma^2(F_0^2) + (pF_0^2)^2]^{1/2}$ ,  $N_o$  is the number of observations,  $N_v$  the number of variables of  $N_v$ . ables, and p = 0.02 for **2**, and = 0.04 for **4** CH<sub>2</sub>Cl<sub>2</sub>  $= 0.25C_3H_6O_2$ 

those of cis-[Pt(NO<sub>2</sub>-N)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] ( $\delta$ , -1.3 ppm; <sup>1</sup>J<sub>PtP</sub>, 3148 Hz) [14,21]. The other set of resonances is assigned to the NO<sub>2</sub>-O isomer: both the chemical shifts and the Pt-P coupling constants are very similar to those of [Pt(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>3</sub>]<sup>+</sup> and of [Pt(A- $(CO)(PPh_3)_3^{\dagger}$  (Table 2), i.e. to compounds with a PtO(anionic)P<sub>3</sub> coordination set. We were unable to isolate the two isomers because of the very similar physico-chemical properties. In the case of **2** and **4** we could obtain crystals suitable for X-ray diffraction studies (see Section 2).

## 3.2. Description of the crystal and molecular structures of 2 and of $4 \cdot CH_2Cl_2 \cdot 0.25C_3H_6O$

The structure of **2** consists of the packing of  $[PtBr(PPh_3)_3]^+$  cations and  $BF_4^-$  anions in the molar ratio 1:1 in the orthorhombic non-centrosymmetric space group Pna21. An ORTEP view of the cation is shown in Fig. 1. The metal atom displays a square-planar geometry with a slight tetrahedral distortion, maximum displacements from the least-square plane being +0.049(2) and -0.061(3)Å for atoms Br and P3, respectively. Selected bond lengths and angles are reported in Table 3, together with the corresponding values of 4·CH<sub>2</sub>Cl<sub>2</sub>·0.25C<sub>3</sub>H<sub>6</sub>O (see below) and some data adapted from the literature of [PtCl(PPh<sub>3</sub>)<sub>3</sub>](ClO<sub>4</sub>)·2CH<sub>2</sub>Cl<sub>2</sub> (1·2CH<sub>2</sub>Cl<sub>2</sub>) [36], for comparison.

The structure of 4·CH<sub>2</sub>Cl<sub>2</sub>·0.25C<sub>3</sub>H<sub>6</sub>O consists of the packing of  $[Pt(AcO)(PPh_3)_3]^+$  cations,  $BF_4^-$  anions, dichloromethane solvent molecules, and acetone solvent molecules, in the molar ratio 1:1:1:0.25, in the triclinic space group P1. The asymmetric unit of **4**·CH<sub>2</sub>Cl<sub>2</sub>·0.25C<sub>3</sub>H<sub>6</sub>O contains two crystallographic independent cations, two crystallographic independent anions, one ordered molecule of  $CH_2Cl_2$  (occupancy factors = 1.00), two, intersected and disordered, half molecules of  $CH_2Cl_2$  (occupancy factors = 0.50 for each atom), and one half molecule of acetone (occupancy factors = 0.50 for each atom), disordered and lying near a crystallographic inversion centre. For ease of comparison, we have labelled the inner core atoms of one of the two independent cations as Pt1, P1, P2, P3, O1, C1, O2, and C2 (cation 1 in Table 2), and the corresponding atoms of the other cation (cation 2 in Table 2) Pt1<sup>°</sup>, P1<sup>°</sup>, P2<sup>°</sup>, P3<sup>°</sup>, O1<sup>°</sup>, C1<sup>°</sup>, O2<sup>°</sup>, and C2<sup>°</sup>. An ORTEP view of the asterisked cation is shown in Fig. 2. Selected bond parameters for both cations are listed in Table 3. The conformations of the ligands of the two independent cations are identical, as far as the phosphine moieties are concerned, including the phenyl carbon atoms (the conformations of the corresponding ligands in the cation of 2 are not identical, but actually very similar, as can be seen comparing Figs. 1 and 2). On the contrary, the conformations of the two acetato ligands are different. Atom Pt1 displays a square-planar coordination with a square-pyramidal distortion, maximum displacements from the least-squares plane being +0.028(3) and -0.042(1) Å for atoms O1 and Pt1, respectively. From the point of view of planarity, the asterisked cation is different. Thus, atom Pt1<sup>adopts</sup> a square-planar coordination with a slight tetrahedral distortion, maximum displacements from the least-squares planes being +0.031(1) and -0.026(1) Å for atoms P3<sup>\*</sup> and P1<sup>\*</sup>, respectively. The two acetato ligands are strictly planar. The dihedral angles between the metal atom best planes and the planes of their acetato ligands are 117.5(1) and 73.9(1)°, for cation 1 and the asterisked cation, respectively.



Scheme 2.

Table 2 $^{31}P$  NMR data for  $[PtX(PPh_3)_3]^+$  (type C) complexes.<sup>a</sup>

	P2 and P3 ( <i>cis</i> to X)		P1 (trans to X)	
Х	δ	$^{1}J_{\text{PtP}}$	δ	${}^{1}J_{PtP}$
I ( <b>3</b> )	12.4	2459	8.3	3480
Br ( <b>2</b> )	19.4	2468	12.5	3624
Cl (1)	23.4	2487	12.8	3647
$ONO_{2}(5)$	22.2	2609	2.7	3761
ONO (6b)	21.5	2633	3.5	3520
F (7) [34]	26.5	2640	3.0	3701
AcO (4)	22.7	2676	3.5	3478
NO <sub>2</sub> (6a)	15.0	2692	-1.5	2838
H (8) [35]	22.5	2821	23.1	2219
Me (9) [35]	28.4	2931	20.2	1919

<sup>a</sup>  $\delta$  values in ppm versus aqueous H<sub>3</sub>PO<sub>4</sub>, <sup>1</sup>J<sub>PtP</sub> values in Hz.

In all the three cations, the steric hindrance of the three phosphine groups forces the two  $P_{(cis)}$ -Pt- $P_{(trans)}$  angles to be greater than 90°.

## 3.3. NMR studies

#### 3.3.1. NMR Spectra

The <sup>31</sup>P NMR spectra of type **C** complexes are reported in Table 2, where the compounds have been arranged in the order of decreasing *cis* influence (see below). The spectra consist of a doublet and a triplet, at higher fields, due to  $P_{(cis)}$  and  $P_{(trans)}$ , respectively. <sup>2</sup>*J*<sub>PP</sub> values are in the 18–21 Hz range. There does not seem to be a simple relationship between  $\delta_P$  and the nature of X, except for the halides derivatives, whose  $\delta_{Pcis}$  is shifted to lower fields with increasing electronegativity.

#### 3.3.2. cis and trans influences series

Remembering the definition of influence and that higher  ${}^{1}J_{PtP}$  values correspond to stronger Pt–P bonds, the coupling constants reported in Table 2 give the sequences:

 $I > Br > CI > NO_3 > ONO > F > AcO > NO_2 > H > Me (cis influence)$ Me > H > NO<sub>2</sub> > AcO > I > ONO > Br > Cl > F > NO<sub>3</sub> (trans influence)



**Fig. 1.** ORTEP view of cation  $[PtBr(PPh_3)_3]^+$  in compound  $[PtBr(PPh_3)_3](BF_4)$  (**2**). Ellipsoids are drawn at the 30% probability level. The BF<sub>4</sub><sup>-</sup> anion and the hydrogen atoms have been omitted for clarity.

The former sequence is like that obtained in the case of type **A** and **B** complexes [14,21] and similar to what is usually reported in the literature [16,18,19], showing that this order is independent on the charge of the complex. The *trans* sequence differs from that obtained for type **B** complexes only for the position of I, which was found lower than Cl, but was probably affected by some uncertainty [14]. With this exception, also the *trans* influence sequence can be considered independent on the charge of the complex.

#### Table 3

Selected bond lengths (Å) and angles (°) for 1-2CH<sub>2</sub>Cl<sub>2</sub><sup>a</sup>, 2 and 4-CH<sub>2</sub>Cl<sub>2</sub>-0.25C<sub>3</sub>H<sub>6</sub>O, with Estimated Standard Deviations (Esd's) on the last figure in parentheses.

	$1 \cdot 2CH_2Cl_2 (X = Cl)^a$	<b>2</b> (X = Br)	$4 \cdot CH_2 Cl_2 \cdot 0.25C_3 H_6 O (X = AcO)$	
			Cation 1	Cation 2
Pt-P1	2.266(2)	2.295(1)	2.265(1)	2.264(1)
Pt-P2	2.359(2)	2.347(1)	2.355(1)	2.342(1)
Pt-P3	2.368(2)	2.363(1)	2.370(1)	2.373(1)
Pt-Cl/Br/O1	2.360(2)	2.440(1)	2.068(2)	2.070(2)
P1-Pt-P2	98.91(8)	96.34(5)	98.41(3)	95.05(3)
P1-Pt-P3	95.87(8)	94.44(5)	94.45(3)	95.93(3)
P1-Pt-Cl/Br/O1	169.58(10)	176.00(4)	172.99(8)	175.73(7)
P2-Pt-Cl/Br/O1	83.77(9)	87.62(4)	87.51(7)	88.89(7)
P3-Pt-Cl/Br/O1	83.43(9)	81.65(4)	79.52(7)	80.18(7)
P2-Pt-P3	162.27(8)	168.37(6)	166.95(3)	168.95(3)

<sup>a</sup> adapted from ref. [36].



**Fig. 2.** ORTEP view of the asterisked cation  $[Pt(AcO)(PPh_3)_3]^+$  in compound  $4 \cdot CH_2Cl_2 \cdot 0.25C_3H_6O$  (see text). Ellipsoids are drawn at the 30% probability level. The other independent cation, the two BF<sub>4</sub><sup>-</sup> anions, the solvent molecules, and the hydrogen atoms have been omitted for clarity.

The *trans* sequence of the halides is in accordance with the suggestion that there is an inverse correlation between the *trans* influence of a ligand and its electronegativity [37,38].

The two sequences are only roughly opposite: the order I > Br > CI holds for both sequences [2,16,18] and their position is higher than those of F and NO<sub>3</sub> in both sequences. The fact that there seems to be little relationship between the two series confirms that the two phenomena are originated by different mechanisms.

In fact the *trans* influence is believed to be due to the competition of two ligands, *trans* to each other, for the same hybrid orbital of the metal centre [1,2,10,38,39], i.e. to the competition between two *trans* ligands for the opportunity to donate electron density to Pt [2]. Thus the higher *trans* influence is displayed by ligands with a relevant covalent character of their Pt–X bond.

On the other hand the *cis* influence is related to the ability of the influencing ligand to lower the positive charge on the metal [21], a mechanism confirmed also by our <sup>31</sup>P NMR and DFT investigations [14,21]. Thus the strongest *cis* influence is displayed by I, Br and Cl

which, being both  $\sigma$  and  $\pi$  donors to Pt(II) [40], decrease efficaciously the positive charge on the metal [22,41].

## 3.3.3. Weights of the cis and trans influences

Having established that the sequences are not charge-dependent, we wondered whether their abilities are affected by the charge of the complexes.

To do so we adopted the same approach used in the preceding papers. If we subtract  ${}^{1}J_{(cis)}$  (or  ${}^{1}J_{(trans)}$ ) of each compound from the corresponding values of the Cl derivative, we obtain the weight (in Hz) of the influences of each X ligand *relative* to weight of Cl, which is set to 0 and used as the reference. Since we subtract the *J* value of a given compound from that of the Cl derivative, a negative value means a lower influence of that ligand with respect to that of Cl.

The weights of the *cis* influence of the various X in type **C** complexes are collected in column A of Table 4. These weights decrease from I to Me, following the cis influence sequence. The absolute values are all lower than those found in the preceding studies for neutral complexes trans-[PtClX(PPh<sub>3</sub>)<sub>2</sub>] (type A) and cis- $[PtClX)PPh_3_2$  (type **B**) (Table 4, columns *D* and *E*, respectively) [14.21], meaning a decreased relevance of the *cis* influence in cationic complexes **C**. We think that this is a consequence of the positive charge of the complex. In fact the *cis* influence is related to the ability of a ligand of lowering the positive charge on Pt [21]. In Pt(II) complexes Pt-P back donation can be considered marginally relevant [42] and it is likely to be negligible in cationic complexes, thus the Pt(II)-P bond can be described, mainly, as donation from the lone pair of P to Pt, which becomes weaker as the positive charge on Pt decreases [21]. Such decrease is of lower importance in cationic than in neutral complexes, since in the former Pt carries a residual and substantial positive charge.

Column B of Table 4 reports the weights of the trans influence of the various X, relative to that of Cl, in compounds C. With the exception of Me, these figures are higher, than those obtained in the case of (neutral) *cis*-[PtClX(PPh<sub>3</sub>)<sub>2</sub>] [14], reported in column *F*, showing that the charge plays a role also in this case. Such an increase of weight induced by the positive charge is in accordance with the view that the trans influence is due to the competition of two trans ligands for the same metal hybrid orbital: a positive charge on the metal centre enhances  $X \rightarrow Pt$  donation, weakening donation of the ligand trans to X. The low trans ability of NO<sub>3</sub> may have this origin: its interaction with Pt(II) has a rather high ionic character [14], making the Pt orbitals available for a strong interaction in the trans position. As for the low trans weight of F, besides its high electronegativity (see above [37,38]), one could envisage that its bond with Pt involves a 2s-6s interaction, originating a rather weak Pt-F bond (compound 7 is little stable [34]), allowing a strong interaction in the *trans* position.

Comparison of columns *A*, *B*, *D*, *E* and *F* show that the values of the weights depend on the nature of the complex, i.e. on the metal

## Table 4

Weights of the *cis* and *trans* influences.<sup>a</sup>

Х	Α	В	С	D	Е	F
Ι	28	167	-1021	75	253	-10
Br	19	23	-1156	34	55	8
Cl	0	0	-1160	0	0	0
$ONO_2$	-122	-114	-1152	-130	-169	-185
ONO	-146	127	-887	-	-	-
F	-153	-54	-1061	-	-	-
AcO	-189	169	-802	-223	-283	113
$NO_2$	-205	809	-146	-243	-276	799
Н	-344	1428	602	-389	-	-
Me	-444	1728	1012	-517	-827	1946

<sup>a</sup> *A*, weight of the *cis* influence of X referred to that of Cl in type **C** complexes; *B*, *trans* weight of X referred to that of Cl in type **C** complexes; *C*,  ${}^{1}_{PtP(cis)} - {}^{1}_{JetP(trans)}$  of type **C** complexes; *D*, *cis* weight calculated in the case of *trans*-[PtClX(PPh<sub>3</sub>)<sub>2</sub>] (type **A**) derivatives [21], signs are inverted to be in accordance with those used in the present paper, the Br derivative was not included in that paper and has been newly synthesised, see Section 2; *E*, *cis* weight calculated for *cis*-[PtClX(PPh<sub>3</sub>)<sub>2</sub>] (type **B**) [14]; *F*, *trans* weight calculated for the same compounds **B** [14].

environment (trans-PtXYP<sub>2</sub>, cis-PtXYP<sub>2</sub>, or PtXP<sub>3</sub>). Interestingly, however, the various weights display a clear analogy in the three compounds. All the NO<sub>3</sub> weights are negative, for AcO, NO<sub>2</sub>-N, H and Me the *cis* weights are negative and the *trans* weights positive; the Br weights are all positive. The exception to this trend is given by I. Its *trans* weight is rather high and positive in compounds **C**. but negative in type **B** cis-[PtClI(PPh<sub>3</sub>)<sub>2</sub>]. This is somewhat puzzling. It is tempting to attribute this behaviour to the softness of I, which may destabilise the Pt-P bond in trans through antisymbiosis [43-46] (an inverse relationship between trans influence and ligand hardness has been proposed [10]). This does not occur in **B**, because in this compound P2 (*trans* to I, Scheme 1, X = CI, Y = I) is *cis* to the highly *cis* influencing Cl, thus the actual influencing ability of a ligand depends on the metal environment (i.e. its coordination set). However we must remember that both the position and the weight of I in **B** may be affected by some uncertainty, as stated above.

#### 3.3.4. Relative importance of the cis and trans influences

The *cis* influence has usually been reported to be of lower importance [1,18,47], although there are examples where the contrary has been observed. For instance, in type **B** compounds the *cis* influences of the halides are higher than their *trans* influences [14] and van Eldik reported that in certain Pt(II) complexes the kinetic *cis* effect is more dominant than the *trans* effect [22].

In compounds **C**, there is a span of about 500 and 1500 Hz for  ${}^{1}J_{PtP(cis)}$  and  ${}^{1}J_{PtP(trans)}$ , respectively (see Table 3), showing that the trans influence is about three times more effective. The greater importance of the trans influence is also revealed by the values of column B of Table 4 (trans weights), which are higher than those of column A (*cis* weights). Moreover the differences  ${}^{1}J_{cis} - {}^{1}J_{trans}$ (column C, Table 4), are negative and *increase* (i.e. the Pt-P bonds cis to X become stronger) in the order halides to Me (the same order of decreasing cis influence) becoming positive for H and Me. Thus in type **C** complexes the *trans* influences is more relevant for X from I to NO<sub>2</sub>, but less important for H an Me. The fact that in type **B** compounds the *cis* influence of the halides is higher than their trans influence, is likely to be due to the presence of a cis-PtXY moiety, where both influences of X and Y operate in a concerted way. In other words the importance of both influences depend on the coordination set.

## 4. Conclusions

A main aim of this work was the study of the role of the charge of the complex on the *cis* and *trans* influences of some anionic ligands. It turns out that the sequences of both influences are unaffected by the charge, since they are the same as those obtained for the neutral *cis*- and *trans*-[PtXY(PPh<sub>3</sub>)<sub>2</sub>] complexes. On the contrary, we found a charge-dependence of the weights of either influence. The *trans* weights are higher than those obtained for the neutral complexes, whereas the *cis* weights are lower. These latter findings are a clear evidence of the role of the charge, as explained above.

An interesting point concerns the relative importance of the two influences. We have previously found that in type **B** complexes the *cis* influence of the halides is higher than their *trans* influence [14] but in the case of compounds **C**, the data of column *C* of Table 4 suggest that the *cis* influence is about one third less relevant than the *trans* influence throughout the series. This different behaviour can be due to both the different charge and the different coordination environments of Pt in **B** and **C**. In particular in (neutral) compounds **B** there is a *cis*-PtXYP<sub>2</sub> coordination set, and the *cis* and *trans* influences of both X and Y operate simultaneously in a concerted way.

Finally throughout this and the preceding papers we have used the working hypothesis that the mutual *cis* and *trans* influences of the phosphines are constant within each type of compound, and our results seem to be consistent with such hypothesis. An evaluation of the weights of these influences remains, however, is still an open question.

The results here presented pose a number of new problems, like understanding how the mutual influences of the ligands operate. Moreover, although the *cis* and *trans* sequences are in line with those usually accepted and reported on textbooks, we wonder how their weights are affected by different co-ligands (for instance amines instead of phosphines) or in complexes of different metal ions. These problems require further studies, which will be undertaken in the near future.

#### Acknowledgements

This work has been supported by the Italian Ministero della Pubblica Istruzione. We thank Alberto Ferrandi for some experimental work.

#### Appendix A. Supplementary data

CCDC 771161 and 771162 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.07.002.

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