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Note

Trans influence of triphenylstibine. Crystal and molecular structures of *cis*-[$PtCl_2(SbPh_3)_2$] and *trans*-[$PtI_2(SbPh_3)_2$]

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Abstract

Crystals of *cis*-[$PtCl_2(SbPh_3)_2$] (**1**) are monoclinic, space group $P2_1/a$ with $a = 20.5708(12)$, $b = 10.1942(4)$, $c = 33.3984(15)$ Å, $\beta = 94.394(4)°$ and $Z = 8$. Substitution of chloride for iodide yields *trans*-[$PtI_2(SbPh_3)_2$] (**2**), the crystals of which are monoclinic, space group $P2_1/c$ with $a = 18.108(4)$, $b = 10.102(2)$, $c = 19.115(5)$ Å, $\beta = 95.241(16)°$ and $Z = 4$. The average Pt–Cl distance in **1** is 2.338(12) Å, implying a *trans* influence of triphenyl stibine comparable with that of triphenyl phosphine, as opposed to what has been reported earlier. IR and Raman data for **1** and **2** are reported and discussed.

Keywords: Crystal structures; Stibine complexes; Platinum complexes; *trans* Influence

1. Introduction

Platinum(II) coordination compounds with stibine ligands have been much less investigated than those with ligands of the lighter pnictogens [1,2]. In our current studies [3–5] of ground state *trans* influence and kinetic *trans* effect of different p-block elements in platinum(II) chemistry we have examined the triphenyl stibine ligand in this respect. Earlier investigations by means of IR and NMR spectroscopy have indicated that stibines have a weaker *trans* influence than phosphines and arsines [6,7]. However, only one crystal structure of a platinum triphenylstibine complex has been reported [5] and there are so far no data on Pt-Cl distances *trans* to such ligands. The absence of crystal structures has also given rise to some confusion concerning the *cis–trans* isomers of diiodobisstibineplatinum(II) complexes [8]. To our knowledge there are only two investigations dealing with the *trans* effect of stibine ligands, and they report the R_3Sb ligands to have a slightly higher *trans* effect than phosphines [5,9]. We here report crystal and molecular structures and IR and Raman data for *cis*-[$PtCl_2(SbPh_3)_2$] and *trans*-[$PtI_2(SbPh_3)_2$].

2. Experimental

2.1. Chemicals and preparations

All solvents were of A.R. quality (Labscan) and used as received. *cis*-[$PtCl_2(SbPh_3)_2$] (**1**) and *cis*-[$PtCl_2(AsPh_3)_2$] (**3**) were prepared according to the literature [8,10]. Recrystallisation of **1** from CH_2Cl_2 gave yellow crystals suitable for X-ray crystallography. *trans*-[$PtI_2(SbPh_3)_2$] (**2**) was prepared from **1** (0.116 g, 0.12 mmol) by stirring together with NaI (0.062 g, 0.41 mmol, Merck pa) in acetone at room temperature for 5 h. The solvent was evaporated and CH_2Cl_2 was added. After filtration the CH_2Cl_2 was allowed to evaporate to give red crystals suitable for X-ray crystallography. ^1H NMR (CD_2Cl_2): δ 7.43 (br, 3H), 7.69 (br, 2H).

2.2. Spectroscopic measurements

IR spectra were recorded from polyethylene pellets on a Bio-Rad FTS 6000 FT-IR spectrometer. Raman spectra were recorded on a Bio-Rad FT-Raman spectrometer. NMR spectra were recorded on a Varian Unity 300 spectrometer.

2.3. Structure determinations

Intensity data were collected at room temperature on an Enraf Nonius CAD-4 diffractometer with graphite-mono-

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chromated Mo Kα radiation ($\lambda = 0.71069$ Å) using the ω–2θ scan technique. Three standard reflections were measured at regular intervals and correction for decay was made. In the case of **1** decay was substantial owing to loss of solvent. Unit cell dimensions were obtained from 17 to 25 reflections with $10° < \theta < 21°$. The heavy atoms were found with automatic Patterson methods. Difference Fourier methods revealed the remaining atoms and the structures were refined by full-matrix least-squares calculations using the TEXSAN crystallographic software package of Molecular Structure Corporation [11]. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$. I and $\sigma(I)$ were corrected for Lorentz, polarisation and absorption effects. The structure of **2** contains residuals with $\Delta\rho > 1$, all within 1 Å from a heavy atom (Pt, I or Sb). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the phenyl rings were placed at calculated positions and were included in the structure factor calculations. Crystal data and detailed experimental information are given in Table 1.

Table 1
Crystal data and details of data collection and refinement

Compound	1	2
Chemical formula	$C_{36}H_{30}Cl_2PtSb_2$	$C_{36}H_{30}I_2PtSb_2$
Mw	972.1	1155.0
Space group	$P2_1/a$	$P2_1/c$
a (Å)	20.5708(12)	18.108(4)
b (Å)	10.1942(4)	10.102(2)
c (Å)	33.3984(15)	19.115(5)
β (°)	94.394(4)	95.241(16)
V (Å^3)	6983.3(1.1)	3482.2(1.1)
Z	8	4
D_{calc} (g cm^{-3})	1.85	2.20
μ (cm^{-1})	57.62	73.26
Crystal size (mm)	0.20 × 0.10 × 0.20	0.30 × 0.30 × 0.15
Data collection		
No. measured reflections	15442	11389
No. unique reflections	15017	11095
θ-interval	2.0–26.3	2.3–30.4
h	−25 → 0	−25 → 25
k	−12 → 0	0 → 14
l	−41 → 41	−27 → 0
Intensity variation in standard reflections (%)	−36.9	−4.8
Absorption correction	ψ-scan	ψ-scan
Range of transmission factors	0.51–1	0.49–1
Refinement		
No. reflections used in refinement	6576	4907
Reflections excluded	$I < 2.5\sigma(I)$	$I < 3\sigma(I)$
No. parameters	766	370
R [a]	0.044	0.056
R_w [b]	0.043	0.064
S	1.17	1.64

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma|F_o|^2]^{1/2}$ with $w = 1/\sigma^2(F)$.

3. Results and discussion

3.1. Crystal structures

Molecular structures of **1** and **2** are shown in Figs. 1 and 2, respectively. For **1**, only one of the crystallographically independent complexes is shown (no. 1). Both crystal structures consist of discrete molecules packed by van der Waals forces. The coordination geometries are distorted square-planar with angles ranging between 84.0 and 96.3° in **1** and between 87.8 and 93.0° in **2**. The largest deviation from a least-squares plane through PtX_2Sb_2 is 0.14 Å in **1** (complex 1) and 0.016 Å in **2**. Key distances are given in Table 2. **1** crystallises with four molecules of CH_2Cl_2 in the unit cell as seen from the stereo picture in Fig. 3. Final fractional atomic coordinates of the non-hydrogen atoms are given in Tables 3 and 4.

3.2. IR and Raman data

IR and Raman data of the three complexes are given in Table 5. The peak assignments were straightforward except in a few cases. The Raman spectra of **2** display three or more bands in the region 100–200 cm^{-1} and the assignment was based on the observed intensities (the ν(Pt–I) being the most intense) and an earlier assignment of the corresponding vibration in $[NBu_4][PtI_3(PF_3)]$ (146 cm^{-1}) [12]. In the IR spectrum of **3** the bands at 339 and 349 cm^{-1} have previously been assigned to ν(Pt–Cl) [13], but on the basis of intensity and the fact that those bands are absent in the Raman spectrum we instead propose that the bands at 300 and

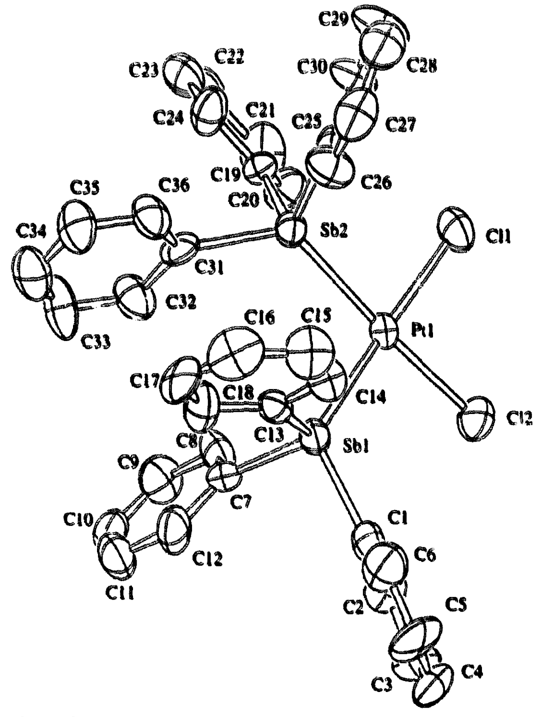

Fig. 1. Ortep drawing with atomic numbering of one of the asymmetric units of *cis*-$[PtCl_2(SbPh_3)_2]$ (**1**). The ellipsoids denote 50% probability.

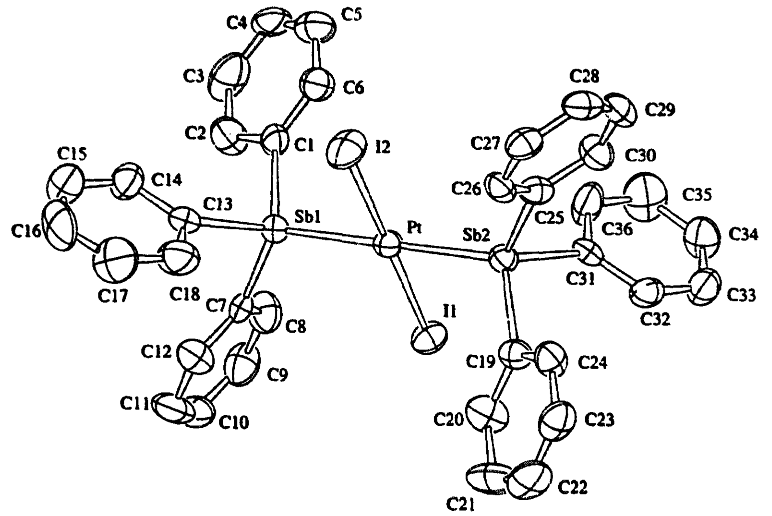

Fig. 2. Ortep drawing with atomic numbering of *trans*-[$PtI_2(SbPh_3)_2$] (**2**). The ellipsoids denote 50% probability.

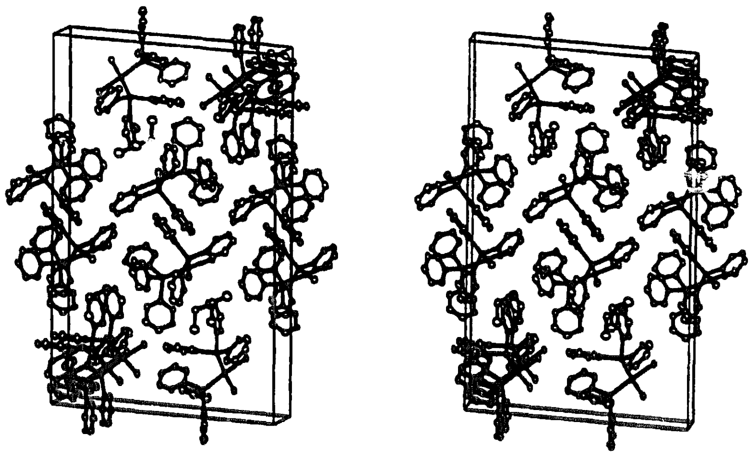

Fig. 3. Stereo view of the unit cell in *cis*-[$PtCl_2(SbPh_3)_2$] (**1**). The ellipsoids denote 20% probability.

Table 2
Crystallographic distances (Å)

	1 (X = Cl)	**2** (X = I)
Pt1–X1	2.354(3)	2.607(1)
Pt1–X2	2.326(4)	2.597(1)
Pt1–Sb1	2.491(1)	2.550(1)
Pt1–Sb2	2.510(1)	2.554(1)
Pt2–Cl3	2.333(3)	
Pt2–Cl4	2.337(4)	
Pt2–Sb3	2.512(1)	
Pt2–Sb4	2.497(1)	

E.s.d.s in the least significant figure are given in parentheses.

321 cm^{-1} be assigned to ν(Pt–Cl). IR data for **1** have been reported earlier and our findings do not differ from those [8]. Our data also show that **1** keeps its *cis* configuration in CH_2Cl_2 solution, since the asymmetric ν(Pt–Cl) band is clearly visible in the solution Raman spectra. Earlier investigations of **2** are not in agreement with our present findings. McAuliffe et al. [8] report the compound to be *cis* in the solid state and *trans* in solution and so do Chatt et al. [14] for the corresponding triethyl compound. Dickinson et al. [15] only report a *cis* complex. However, the crystal structure together with the IR and Raman data presented here unequivocally show that **2** is *trans* both in the solid state and in CH_2Cl_2 solution. In Refs. [8,14] the fact that yellow [$PtI_2(SbPh_3)_2$] turns red upon melting or dissolution was taken as evidence of a *cis* to *trans* isomerisation. However, we have found that the colour of the solid **2** is largely dependent on the crystal size; when the red crystals formed from the dichloromethane solution are ground in a mortula the colour changes from bright red to orange–yellow without any change in the Raman spectrum.

3.3. *trans* Influence sequence

To measure the *trans* influence, X-ray, IR and NMR data have been extensively used [6]. The most convincing evidence for the order of *trans* influence of pnictogen donors in platinum(II) chemistry originates from an NMR study of ^1J(Pt–P) coupling constants [7], indicating that the *trans* influence sequence is P > As > Sb. The same order has been found using ν(Pt–Cl) vibration frequencies *trans* to R_3L ligands (assuming the reduced masses of the Pt fragments to

Table 3
Fractional atomic coordinates and B_{eq} for **1**

Atom	x/a	y/b	z/c	B_{eq}
Pt(1)	0.24014(2)	0.02551(5)	0.11270(2)	2.63(2)
Pt(2)	0.06995(2)	0.01168(5)	0.38506(2)	2.55(2)
Sb(1)	0.14383(4)	0.03750(9)	0.06288(3)	2.88(4)
Sb(2)	0.18885(4)	−0.1227(1)	0.16136(3)	2.99(4)
Sb(3)	−0.04319(4)	0.04823(9)	0.35313(3)	2.90(4)
Sb(4)	0.05165(4)	−0.22149(8)	0.40411(3)	2.73(4)
Cl(1)	0.3341(1)	0.0040(4)	0.1571(1)	4.7(2)
Cl(2)	0.2934(2)	0.1697(4)	0.0723(1)	4.8(2)
Cl(3)	0.1754(1)	−0.0008(4)	0.4160(1)	4.5(2)
Cl(4)	0.0860(2)	0.2304(3)	0.3673(1)	4.5(2)
Cl(5)	0.7071(3)	0.0045(7)	0.3069(2)	11.0(4)
Cl(6)	0.6325(3)	0.0484(7)	0.2333(2)	10.9(4)
C(1)	0.1543(6)	0.116(1)	0.0049(5)	3.6(7)
C(2)	0.1640(7)	0.252(2)	0.0009(5)	4.3(8)
C(3)	0.1661(8)	0.308(2)	−0.0370(6)	6(1)
C(4)	0.1615(8)	0.229(2)	−0.0701(6)	6(1)
C(5)	0.151(1)	0.095(2)	−0.0667(5)	7(1)
C(6)	0.1492(7)	0.040(2)	−0.0288(5)	6(1)
C(7)	0.0699(6)	0.164(1)	0.0812(5)	3.7(7)
C(8)	0.0828(6)	0.247(2)	0.1137(5)	4.5(8)
C(9)	0.0371(8)	0.333(1)	0.1253(5)	4.7(8)
C(10)	−0.0230(7)	0.336(2)	0.1031(5)	4.8(9)
C(11)	−0.0365(7)	0.259(2)	0.0711(5)	6(1)
C(12)	0.0102(7)	0.174(2)	0.0595(5)	4.8(8)
C(13)	0.1028(6)	−0.150(1)	0.0498(4)	3.2(6)
C(14)	0.1452(7)	−0.245(2)	0.0377(5)	4.2(8)
C(15)	0.1273(8)	−0.374(2)	0.0307(5)	6(1)
C(16)	0.064(1)	−0.408(2)	0.0365(5)	6(1)
C(17)	0.0202(7)	−0.316(2)	0.0489(6)	6(1)
C(18)	0.0404(7)	−0.185(2)	0.0555(5)	4.9(9)
C(19)	0.1968(6)	−0.045(1)	0.2202(4)	3.1(7)
C(20)	0.2220(7)	0.077(2)	0.2275(5)	4.7(8)
C(21)	0.2245(8)	0.133(2)	0.2652(6)	6(1)
C(22)	0.1982(7)	0.063(2)	0.2959(5)	6(1)
C(23)	0.1720(7)	−0.056(2)	0.2887(6)	6(1)
C(24)	0.1719(6)	−0.111(2)	0.2510(5)	4.8(8)
C(25)	0.2313(6)	−0.313(1)	0.1652(4)	3.6(7)
C(26)	0.2141(7)	−0.403(2)	0.1342(5)	5.1(9)
C(27)	0.2425(8)	−0.525(2)	0.1366(6)	6(1)
C(28)	0.2867(9)	−0.558(2)	0.1671(7)	6(1)
C(29)	0.3021(8)	−0.469(2)	0.1974(6)	7(1)
C(30)	0.2751(7)	−0.347(2)	0.1967(5)	4.7(8)
C(31)	0.0879(6)	−0.168(1)	0.1602(4)	3.6(7)
C(32)	0.0441(7)	−0.064(1)	0.1599(5)	4.8(8)
C(33)	−0.0222(7)	−0.087(2)	0.1624(6)	7(1)
C(34)	−0.0456(7)	−0.213(2)	0.1628(5)	5(1)
C(35)	−0.0023(7)	−0.314(2)	0.1621(5)	5.1(9)
C(36)	0.0640(6)	−0.289(1)	0.1597(5)	4.3(8)
C(37)	−0.0448(6)	0.122(1)	0.2935(4)	3.6(7)
C(38)	0.0106(6)	0.125(2)	0.2733(5)	4.7(8)
C(39)	0.0106(9)	0.183(2)	0.2356(5)	6(1)
C(40)	−0.044(1)	0.236(2)	0.2186(5)	6(1)
C(41)	−0.0998(9)	0.236(2)	0.2369(5)	5(1)
C(42)	−0.1009(6)	0.178(1)	0.2761(5)	4.5(8)
C(43)	−0.0920(7)	0.187(1)	0.3864(5)	3.9(7)
C(44)	−0.0633(6)	0.244(1)	0.4202(5)	3.9(7)
C(45)	−0.0966(7)	0.331(1)	0.4422(5)	4.2(8)
C(46)	−0.1578(8)	0.369(2)	0.4297(5)	4.7(8)
C(47)	−0.1878(6)	0.316(2)	0.3957(5)	4.7(8)
C(48)	−0.1569(7)	0.220(2)	0.3735(5)	4.5(8)
C(49)	−0.1166(6)	−0.098(1)	0.3490(4)	3.3(7)
C(50)	−0.1476(7)	−0.128(1)	0.3836(5)	4.4(8)
C(51)	−0.1917(7)	−0.232(2)	0.3839(5)	5.3(9)
C(52)	−0.2029(8)	−0.306(2)	0.3503(6)	6(1)
C(53)	−0.1734(8)	−0.277(1)	0.3158(5)	4.6(8)
C(54)	−0.1301(6)	−0.174(1)	0.3160(4)	3.7(7)
C(55)	0.1299(6)	0.340(1)	0.4275(4)	3.3(7)
C(56)	0.1704(7)	0.302(1)	0.4610(5)	4.1(8)
C(57)	0.2211(7)	−0.381(2)	0.4752(5)	4.7(8)
C(58)	0.2335(7)	−0.497(2)	0.4577(6)	5(1)
C(59)	0.1941(8)	−0.537(2)	0.4248(6)	6(1)
C(60)	0.1419(7)	−0.457(1)	0.4108(4)	4.1(7)
C(61)	0.0133(6)	−0.332(1)	0.3535(4)	3.1(6)
C(62)	0.0264(6)	−0.278(1)	0.3166(5)	4.1(8)
C(63)	0.0022(8)	−0.340(2)	0.2817(5)	5(1)
C(64)	−0.033(1)	−0.454(2)	0.2828(6)	7(1)
C(65)	−0.0453(9)	−0.504(2)	0.3196(7)	7(1)
C(66)	−0.0230(7)	−0.443(1)	0.3538(5)	4.8(8)
C(67)	−0.0143(6)	0.233(1)	0.4500(4)	3.2(7)
C(68)	−0.0333(7)	−0.350(1)	0.4653(5)	4.8(8)
C(69)	−0.0762(8)	−0.355(2)	0.4963(5)	5.3(9)
C(70)	−0.0982(7)	−0.240(2)	0.5105(5)	4.5(8)
C(71)	−0.0792(7)	−0.124(1)	0.4962(5)	4.2(8)
C(72)	−0.0364(7)	−0.117(1)	0.4655(5)	4.2(8)
C(73)	0.6355(8)	0.068(2)	0.2853(5)	6(1)

be approximately equal). In the case where R = Ph the situation is not totally clear, but a comparison of IR data from different sources [6,16] agrees with the above picture as do our vibrational data for **1** and **3** together with those reported for *cis*-[$PtCl_2(PPh_3)_2$] (**4**) [16], see Table 5. It is obvious that the ν(Pt–Cl) frequencies for *cis*-[$PtCl_2L_2$] (**1**, **3** and **4**) show a slight trend with the nature of the *trans* group, but this variation is too small to allow any definite conclusions about the *trans* influence order.

Crystallographic data are much more scarce. The only crystal structure of a platinum stibine complex, [$PtI_3(SbPh_3)$]$^-$, reported so far reveals a Pt–I distance of 2.637(2) Å *trans* to the stibine as compared with 2.662(3) Å *trans* to triphenylphosphine in an analogous complex indicating a *trans* influence of P > Sb [5]. The present study seems to be the first crystallographic investigation of the *trans* influence of stibine ligands on Pt–Cl distances in platinum(II) chemistry and it shows that the average Pt–Cl distance in **1** of 2.338(12) Å is somewhat shorter than the corresponding average distance of 2.345(16) Å in *cis*-[$PtCl_2(PPh_3)_2$] [17]. However, the difference is too small to be significant and could very well be due to other effects such as crystal packing. In this context it would also be interesting to compare with a Pt–Cl distance *trans* to triphenylarsine, but there is no report in the literature of any crystal structure of **3** and neither have we been able to grow crystals of this compound suitable for X-ray diffraction. The crystal structure of a similar compound, dichloro-[diphenyl(*o*-vinylphenyl)arsine] platinum(II), reveals a Pt–Cl distance of 2.318(4) Å *trans* to the arsine (which probably has electronic properties not too different from Ph_3As) [18]. In view of the reported Pt–I distances and

Table 4
Fractional atomic coordinates and B_{eq} for **2**

Atom	x/a	y/b	z/c	B_{eq}
Pt	0.241952(28)	0.125571(51)	−0.223053(27)	2.53(2)
I(1)	0.292861(53)	−0.060304(91)	−0.300159(49)	3.38(4)
I(2)	0.191221(65)	0.31427(11)	−0.148581(62)	5.02(5)
Sb(1)	0.137621(47)	0.175897(85)	−0.318116(47)	2.61(4)
Sb(2)	0.349347(47)	0.075389(85)	−0.130805(46)	2.59(4)
C(1)	0.15962(71)	0.3449(13)	−0.37880(77)	3.2(6)
C(2)	0.12263(87)	0.3616(16)	−0.44689(81)	4.3(7)
C(3)	0.1366(11)	0.4728(20)	−0.48442(98)	6(1)
C(4)	0.18473(97)	0.5682(15)	−0.4539(12)	5(1)
C(5)	0.21975(94)	0.5494(15)	−0.39059(92)	4.3(8)
C(6)	0.20788(80)	0.4412(14)	−0.35288(82)	3.7(7)
C(7)	0.10683(68)	0.0324(12)	−0.39665(74)	2.8(6)
C(8)	0.14514(84)	0.0185(17)	−0.45595(85)	4.3(8)
C(9)	0.12430(93)	−0.0757(18)	−0.50484(87)	4.7(8)
C(10)	0.06501(96)	−0.1576(15)	−0.49611(95)	4.6(8)
C(11)	0.02850(97)	−0.1461(15)	−0.43638(95)	4.7(8)
C(12)	0.04883(82)	−0.0522(14)	−0.38785(71)	3.5(6)
C(13)	0.03101(75)	0.2107(13)	−0.28612(80)	3.3(6)
C(14)	−0.01989(85)	0.2956(15)	−0.32349(83)	4.0(7)
C(15)	−0.0915(10)	0.3015(19)	−0.3067(11)	6(1)
C(16)	−0.11379(92)	0.2246(23)	−0.2520(12)	6(1)
C(17)	−0.0638(11)	0.1475(20)	−0.2139(13)	7(1)
C(18)	0.00805(96)	0.1399(16)	−0.2307(10)	4.9(9)
C(19)	0.34230(74)	−0.1088(13)	−0.07982(72)	3.0(6)
C(20)	0.31047(93)	−0.2175(16)	−0.11447(78)	4.4(8)
C(21)	0.3035(12)	−0.3401(16)	−0.0802(12)	6(1)
C(22)	0.3294(10)	−0.3497(17)	−0.0106(11)	5(1)
C(23)	0.35957(88)	−0.2438(17)	0.02482(86)	4.4(8)
C(24)	0.36653(79)	−0.1250(15)	−0.00887(77)	3.7(7)
C(25)	0.37524(79)	0.1996(13)	−0.04052(70)	3.0(6)
C(26)	0.32485(73)	0.2128(13)	0.00863(77)	3.2(6)
C(27)	0.34413(85)	0.2912(14)	0.06700(74)	3.5(7)
C(28)	0.41221(93)	0.3519(13)	0.07599(78)	3.8(7)
C(29)	0.46251(81)	0.3361(15)	0.02715(90)	4.1(7)
C(30)	0.44445(79)	0.2604(15)	−0.03213(78)	3.7(7)
C(31)	0.45303(68)	0.0707(12)	−0.17156(65)	2.5(5)
C(32)	0.50863(80)	−0.0170(13)	−0.14965(73)	3.3(6)
C(33)	0.57733(82)	−0.0166(15)	−0.17483(84)	4.0(7)
C(34)	0.59125(87)	0.0767(17)	−0.22631(86)	4.5(8)
C(35)	0.5376(11)	0.1655(20)	−0.2495(10)	6(1)
C(36)	0.46831(85)	0.1635(17)	−0.22123(98)	5.0(8)

Table 5
Vibrational data for *cis*-[$PtCl_2L_2$] (**1**, **3** and **4**) and *trans*-[$PtI_2(SbPh_3)_2$] (**2**) (cm^{-1})

Complex (L)	**4** (PPh_3) ν(Pt–Cl)	**3** ($AsPh_3$) ν(Pt–Cl)	**1** ($SbPh_3$) ν(Pt–Cl)	**2** ν(Pt–I)
IR (solid)	316 [a], 297 [b]	321 [a], 300 [b]	324 [a], 302 [b]	180 [a]
Raman (solid)	316 [a], 294 [b]	319 [a], 299 [b]	323 [a], 302 [b]	151 [b]
Raman (CH_2Cl_2)			325 [a,c]	153 [b]

[a] Asymmetric.
[b] Symmetric.
[c] Symmetric band obscured by the CH_2Cl_2 band at 285 cm^{-1}.

disregarding any *cis* effects the data so far give us a crystallographically determined *trans* influence order of P > Sb > As, disagreeing with that determined from vibrational spectroscopy and NMR. The present data, placing P and Sb ahead of As, are on the limit of what can be considered significant and needless to say further crystal structure data are necessary to settle this matter, preferably for a series of complexes in which only the *trans* group is varied. It can finally be noted that Ph_3Sb, as expected, has a higher *trans* influence than chloride as seen from the Pt–Sb distances.

4. Supplementary material

All atomic coordinates, thermal parameters, bond lengths, angles and least-squares planes have been deposited as supplementary material and are available from the authors on request.

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