cis Influence in trans-Pt(PPh₃)₂ complexes†‡

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The *cis* influence of a series of anionic ligands X and Y has been evaluated through the magnitude of the Pt–P coupling constants for compounds of formula *trans*-[PtXY(PPh₃)₂]. The order of decreasing *cis* influence was found to be $I > Cl > SePh ~ SPh ~ SEt > NO_3 > AcO ~ NO_2 > H > Me > Ph > mtc (mtc =$ *N*,*N*-dimethylmonothiocarbamato-*S*); moreover, the*cis*influences of the various ligands was found to be additive. The X-ray structures of three representative compounds (*t*-4: X = Cl, Y = NO₃;*t*-5: X = Cl, Y = AcO and*t*-12: X = Y = NO₂) have also been determined.

Introduction

In the course of our work on Pt(II) phosphine complexes,¹ we obtained *cis*- and *trans*-[Pt(mtc)₂(PPh₃)₂] (mtc, *N*,*N*-dimethylmonothiocarbamato-*S*, Me₂NC(O)*S*⁻). Whilst the platinum phosphorus coupling constants of *cis*-[PtXY(PPh₃)₂)] complexes are normally larger than those displayed by the *trans* isomer, we found, unexpectedly, that the *trans* isomer of [Pt(mtc)₂(PPh₃)₂] showed a Pt–P coupling constant larger than that of the *cis* derivative (3676 and 3277 Hz, respectively).^{1a}

One bond coupling constants are dominated by the Fermi contact interaction of nuclei with s electrons² and are usually taken as an estimate of bond strength, provided such bonds involves hybrid orbitals with some s character. Such strength depends, inter alia, on the nature of the other ligands. Consequently, the increased strength of the Pt-P bonds, observed in trans-[Pt(mtc)₂(PPh₃)₂], must arise from the influence of the mtc ligands cis to the phosphine groups, in other words from a low cis influence of the mtc ligands. The cis influence can in fact be defined as the ability of a ligand A to weaken a bond between a metal and a ligand B, cis to A. The cis influence is a ground state phenomenon and it is distinguished from the *cis* effect, which is the ability of a ligand A to accelerate the substitution rate of a ligand B, cis to A. The cis and the trans effects are important tools in designing synthetic pathways, whereas the cis and trans influences are important to rationalise bond strengths in complexes, and therefore the knowledge of a cis influence series is of the outmost importance.

We then reasoned that in complexes of the type *trans*- $[PtXY(PPh_3)_2]$ the mutual *trans* influence of the two PPh₃ groups remains constant throughout, consequently any variation of the properties of the Pt–P bonds in these complexes must arise from the *cis* influence of X and Y. We therefore considered these complexes suitable for an evaluation of such influence and report herein the ³¹P NMR data of a number of complexes of formula

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‡ Dedicated to Prof. Renato Ugo on the occasion of his 70th birthday

Table 1 Numbering of cis- and trans-[PtXY(PPh₃)₂] compounds

х	Y	cis	trans	
Cl	Cl	<i>c</i> -1	t- 1	
Ι	Ι	c- 2	t- 2	
Cl	Ι	c- 3	t- 3	
Cl	NO ₃	c- 4	t- 4	
Cl	AcO	c -5	t- 5	
AcO	AcO	c -6	t- 6	
Ι	AcO	c-7	t-7	
NO ₃	AcO	c- 8	t- 8	
NO ₃	NO_3	c -9	t -9	
Cl	NO ₂	<i>c</i> -10	t-10	
Ι	NO ₂	<i>c</i> -11	t-11	
NO ₂	NO_2	<i>c</i> -12	t-12	

trans-[PtXY(PPh₃)₂], where X and Y are anionic ligands (Table 1). The choice of exploring only neutral complexes was made in order to avoid any possible influence of the charge. We also report the X-ray structures of three compounds, namely *t*-4 (X = Cl, Y = NO₃), *t*-5·CHCl₃ (X = Cl and Y = AcO) and *t*-12·2CHCl₃ (X = Y = NO₂). The spectra of some *cis*-[PtX₂(PPh₃)₂] complexes (*i.e.* those with X = Y) are also reported and briefly discussed.

Results and discussion

Synthesis and characterisation

There are a number of published procedures for the preparation of trans-[PtCl₂(PPh₃)₂] (*t*-1),³ but we have found that a reliable, simple and selective synthesis is a slight modification of that suggested by Kukushkin,⁴ *i.e.* reaction of trans-[PtCl₂(CH₃CN)₂]⁵ and PPh₃,⁶ in a 1 : 1.9 ratio (excess of phosphine must be avoided as it catalyses *trans* to *cis* isomerisation^{3f,7}) in nitromethane, in which *t*-1 is sparingly soluble. This procedure resulted in yields up to 80%. The compound *trans*-[PtI₂(PPh₃)₂] (*t*-2) has been prepared by reaction of PPh₃ with either K₂[PtI₄] in water–acetone,⁸ or *cis/trans*-[PtI₂(PhCN)₂] in benzene;⁹ the former method gave *t*-2-*c*-2 in a 4 : 1 ratio, whereas the latter reaction gave almost pure *t*-2. Reaction of *t*-1 with KI also gives *t*-2, but in very poor yields.

Stepwise substitutions of the chloride or iodide ligands have been performed by treatment of t-1 or t-2 with the appropriate silver salt. In the case of the acetato complexes, we could prepare only *trans*-[PtCl(AcO)(PPh₃)₂] (t-5), treating *trans*-[PtCl₂(PPh₃)₂]

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with one mole equivalent of AgAcO, since a second mole of AgAcO produced isomerisation to cis-[Pt(AcO)₂(PPh₃)₂] (*c*-6). The *trans* diacetato isomer, *t*-6, has been synthesised by Basato *et al.* from platinum acetate.¹⁰

Some compounds of the iodo-Y series, prepared from *t*-2, could not be isolated. The Cl–I compound (*t*-3) was characterised in the mixture obtained by reaction of *t*-1 with KI by ESI mass spectroscopy, which showed a cluster of peaks at m/z 904.0111 (calcd for $[M + Na]^+$, 904.0100). ³¹P NMR spectroscopy of the residue of this reaction showed peaks (all with ¹⁹⁵Pt satellites) due to *t*-1, *c*-1, two doublets, very likely due to *cis*-[PtClI(PPh₃)₂] (*c*-3), and a resonance at δ 18.8 ppm, which was therefore assigned to *t*-3. The I–AcO derivative was not obtained: reaction of *t*-2 with AgAcO gave rise to *c*-6.

Rather interestingly, the reaction of $trans-[PtI_2(PPh_3)_2]$ with AgNO₃ gave, unexpectedly, $[PtI(NO_2)(PPh_3)_2]$ (*t*-11) and Ph₃PO. Such a redox reaction is likely to be triggered by *t*-2, since in a blank experiment (Et₄N)NO₃ does not oxidise PPh₃ under the same conditions.

The *trans* structure of the mixed X–Y complexes was confirmed by the presence of only one ³¹P resonance, since for *cis*-[PtXY(PPh₃)₂] two doublets would be expected due to the two non equivalent P atoms. The geometry of *trans*-[Pt(NO₃)₂(PPh₃)₂] (*t*-9) was deduced by the fact that its ³¹P NMR spectrum is different from that of the *cis* isomer.¹ Compounds *t*-4, *t*-5 and *t*-12 (and *t*-8) were characterised by X-ray diffraction studies (see below). Moreover, it has been reported that a medium intensity band at 550 ± 5 cm⁻¹ in the IR spectrum, which has been assigned to a PC₃ overtone,¹¹ is typical of the *cis* configuration of Pt(PPh₃)₂ derivatives,¹¹ its absence being indicative of the *trans* geometry. This feature was found to be in accordance with the NMR or structural evidence. The nitro linkage isomerism of NO₂, observed in the crystal structure of *t*-12, is suggested also for *t*-10 and *t*-11 by their infrared spectra.^{12,13}

X-Ray structures of t-4, t-5·CHCl₃ and t-12·2CHCl₃

The structure of t-4 consists of the packing of *trans*-[PtCl(NO₃)(PPh₃)₂] molecules with no unusual van der Waals contacts. An ORTEP¹⁴ view of the molecule is shown in Fig. 1, and selected bond lengths and angles are listed in Table 2. The

Fig. 1 ORTEP view of *trans*-[PtCl(NO₃)(PPh₃)₂] (*t*-4) (hydrogen atoms not shown for clarity). Ellipsoids are drawn at the 30% probability level.

Table 2 Selected bond lengths (Å) and angles (°) for *t*-4, *t*-5·CHCl₃ and *t*-12·2CHCl₃

	t- 4	t-5·CHCl ₃	t-12·2CHCl ₃
Pt-Cl	2.297(1)	2.314(1)	
Pt–P1	2.311(1)	2.302(1)	2.337(1)
Pt–P2	2.313(1)	2.310(1)	_
Pt–O1	2.044(2)	2.030(2)	
Pt–N	_ ``	_	2.002(3)
Cl-Pt-P1	89.5(1)	88.8(1)	_ ``
Cl-Pt-P2	88.6(1)	91.5(1)	
Cl-Pt-O1	175.1(1)	178.5(1)	
P1–Pt–P2	178.0(1)	179.2(1)	
P1–Pt–O1	89.8(1)	90.1(1)	
P2-Pt-O1	92.1(1)	89.6(1)	
P-Pt-P'	_ ``	_ ``	180
P-Pt-N	_	_	89.4(1)
P-Pt-N'			90.6(1)
N–Pt–N′	_	_	180

platinum atom displays a square-planar coordination with a slight tetrahedral distortion, maximum distances from the best plane being +0.063(1) and -0.045(1) Å for atoms O1 and P1, respectively. The nitrate ligand is strictly planar, and is almost perpendicular to the metal best plane (dihedral angle $84.1(1)^\circ$).

The structure of t-5-CHCl₃ consists of the packing of *trans*-[PtCl(CH₃COO)(PPh₃)₂] and CHCl₃ molecules in the molar ratio 1 : 1 with no unusual van der Waals contacts. The complex is shown in Fig. 2 and selected bond lengths and angles are reported in Table 2. The platinum atom displays a square-planar coordination with a very slight square-pyramidal distortion, maximum distances from the best plane being +0.014(1) and -0.006(1) Å for atoms Pt and O1, respectively. Also, the strictly planar, acetato ligand is almost perpendicular to the metal best plane (dihedral angle 88.6(1)°).



Fig. 2 ORTEP view of *trans*-[PtCl(AcO)(PPh₃)₂] (t-5) (hydrogen atoms and CHCl₃ molecule not shown for clarity). Ellipsoids are drawn at the 30% probability level.

The structure of *t*-12·2CHCl₃ consists of the packing of *trans*-[Pt(NO₂)₂(PPh₃)₂] and CHCl₃ molecules in the molar ratio 1 : 2 with no unusual van der Waals contacts. An ORTEP view of *t*-12 is shown in Fig. 3 and selected bond lengths and angles are reported in Table 2. The platinum atom lies on a crystallographic inversion centre and therefore adopts a strictly (square)-planar coordination. The NO₂ group is *N*-coordinated and forms a dihedral angle of 75.9(1)° with the metal coordination plane.

 Table 3
 Pt—P bond lengths of some trans-[PtXY(PPh₃)₂] complexes

Х	Y	Complex	$d_{ ext{Pt-P}}/ ext{\AA}$	Reference
NO ₂	NO ₂	t-12	2.337(1)	а
Cl	CF ₃		2.328(2)	15
AcO	AcO	t- 6	2.320	10
Ι	Ι	t-2	2.318(2)	16
Cl	Cl	t-1	2.3163(11)	17
mtc	mtc		2.316(6)	1
Cl	NO ₃	t- 4	2.312	a
Cl	AcO	t-5	2.306	а
SePh	SePh		2.300	18
Cl	Me		2.296	19

" This work. " Mean value.



Fig. 3 ORTEP view of trans-[Pt(NO₂)₂(PPh₃)₂] (t-12) (hydrogen atoms and CHCl₃ molecules not shown for clarity). Ellipsoids are drawn at the 30% probability level.

The Pt–P bond distances of *t*-4 and *t*-5 are similar and fall into the range usually found for similar compounds (see Table 3 for some examples). There is a slight decrease of these bond lengths on passing from *t*-1 (2.3163(11) Å),¹⁷ to *t*-4 (mean value 2.312 Å) and *t*-5 (mean value 2.306 Å). The Pt–P bond is rather long in *t*-12, although not exceptional; for example bonds of this length are also found in *trans*-[Pt(NO₂)₂{(*p*-MeC₆H₄)₃P}₂].²⁰ The Pt–Cl bond in *t*-4 (*trans* to NO₃) is shorter than that in *t*-5 (*trans* to AcO) (see Table 2). The Pt–O(acetato) distance is similar to those of *trans*-[Pt(AcO)₂(PPh₃)₂] (mean value 2.038 Å).¹⁰ The Pt–N bonds in *t*-12 (2.002(3) Å), are shorter than those of the above cited *p*-tolilphosphine complex (Pt–N, 2.030(5) Å),²⁰ while the N–O bonds (N–O1 = 1.236(3), N–O2 = 1.240(3) Å) are longer (1.213 Å).²⁰

We have also obtained crystals of *t*-**8**, but found a disorder in the NO₃ and AcO positions, not enabling an acceptable refinement. The compound crystallises in the monoclinic space group $P2_1/n$, with a = 9.494(1), b = 19.484(2), c = 9.845(1) Å, $\beta = 110.54(1)^\circ$, V = 1705.2(5) Å³, Z = 2. The platinum atom lies on a crystallographic inversion centre and the nitrato and acetato groups are therefore disordered. We checked for a solution in noncentrosymmetric space group *Pn*, but with no results. However, although disordered, this structure confirms the characterisation of *t*-**8** as *trans*-[Pt(AcO)(NO₃)(PPh₃)₂].

Table 4 ³¹P NMR parameters of *trans*-[PtXY(PPh₃)₂] complexes^a

Х	Y	δ /ppm	$J_{\rm PtP}/{ m Hz}$	Reference
Cl	Ι	18.8	2555	b
	Cl	20.7	2630	b
	SPh	24.2 (in $C_6 D_6$)	2745	21
	NO ₃	16.6	2760	b
	AcO	18.3	2853	Ь
	NO ₂	16.4	2873	Ь
	Н	28.9	3019	b
	Me	29.6	3147	22
	Ph	25.4 (in CH ₂ Cl ₂)	3157	23
Order o	f decreasing	cis influence: $I > Cl > Sl$	$Ph > NO_3 >$	
AcO >	$NO_2 > H > I$	Me > Pn	2402	h
1		12./	2492	b b
		18.8	2000	24
	F	13.6	2/4/	24
0 1	NO ₂	13.0	2795	b
Order o	f decreasing a	cis influence: $I > CI > F$	$> NO_2$	4
AcO	CI	18.3	2853	<i>b</i>
	NO ₃	13.8	2990	<i>b</i>
	AcO	14.6	3080	10
Confirn	ns $Cl > NO_3$	> AcO		
H	Ι	28.3	2928	25
	SCN	29.9	2934	25
	NCS	26.7	3002	25
	Cl	28.9	3019	Ь
	N_3	29.9	3046	25
	CF_3	29.6 (in CH ₂ Cl ₂)	3118	26
	Ph	31.1 (in CH ₂ Cl ₂)	3120	27
Order o	f decreasing a	cis influence: I > SCN >	$\cdot NCS > Cl >$	
$N_3 > C$	$F_3 \sim Ph$			
Ph	Н	31.1 (in CH ₂ Cl ₂)	3120	27
	Me	29.7 (in CD_2Cl_2)	3223	28
	F	23.7 (in CD_2Cl_2)	3269	28
Order o Me)	f decreasing a	cis influence: $H > Me >$	F (confirms H	>

^{*a*} CDCl₃ solutions, unless otherwise stated, ppm from H₃PO₄. ^{*b*} This work, or measured in our laboratory.

³¹P NMR spectra

In order to establish a series of *cis* influence, we have recorded the ³¹P NMR spectra and measured the ¹ J_{PtP} values of various series of *trans*-[PtXY(PPh₃)₂] complexes, in which one ligand, X, is kept constant and Y is varied. These parameters are reported in Table 4, together with some data obtained from the literature. The orders of decreasing *cis* influence of each series, as deduced from the ¹ J_{PtP} values, are also included in the Table.

Table 5 reports the data of compounds *trans*-[PtX₂(PPh₃)₂], *i.e.* those with X = Y.

 Table 5
 ³¹P NMR parameters of trans-[PtX₂(PPh₃)₂] complexes^a

X	δ /ppm	$^{1}J_{\mathrm{PtP}}/\mathrm{Hz}$	Reference
I	12.7	2496	^b .9
Cl	20.7	2630	b
SePh	22.4 (in $C_6 D_6$)	2831	29
SPh	22.4 (in $C_6 D_6$)	2860	29
SEt	24.1 (in $C_6 D_6$)	2867	29
NO ₃	12.6	2900	b
NO ₂	15.9	3060	b
AcO	14.6	3080	10
mtc	14.9	3676	1

 $^{\it a}$ CDCl_3 solutions, unless otherwise stated, ppm from H_3PO_4. $^{\it b}$ This work, or measured in our laboratory.

<i>t</i> -1 as reference compound ($X = Cl$)		<i>t</i> - 2 as reference compound $(X = I)$		<i>t</i> -9 as reference compound ($X = NO_3$)				
Y	$\Delta J/\mathrm{Hz}$	$2\Delta J/\mathrm{Hz}^{b}$	Y	$\Delta J/{ m Hz}$	$2\Delta J/\mathrm{Hz}^{b}$	Y	$\Delta J/\mathrm{Hz}$	$2\Delta J/\mathrm{Hz}^{b}$
I	-67 ^c	-134	Ι	0	0	Ι	_	-408
Cl	0	0	Cl	67	134	Cl	-140	-270
SePh	115^{c}	230	F	255		NO ₃	0	0
SPh	115	230	NO_2	303 ^c	558	AcO	90	0
NO ₃	130	270						
AcO	223	450						
NO_2	243	410						
Н	389	_						
Me	517	1034 ^d						
Ph	527	1054 ^e						
mtc	590 ^c	1180						

Table 6 Differences of the coupling constants, ΔJ , for some ligands using t-1, t-2 and t-9 as references^a

^{*a*} Calculated from Tables 3 and 4. ^{*b*} These values refer to the *trans*-[PtX₂(PPh₃)₂] series (Table 5), unless otherwise stated. ^{*c*} Calculated from the X₂ derivative. ^{*d*} Calculated from the Cl–Me derivative. ^{*e*} Calculated from the Cl–Ph derivative.

Considering all the series of Tables 4 and 5, we obtain the order of decreasing *cis* influence: $I > Cl > SePh \sim SPh \sim SEt > NO_3 > AcO \sim NO_2 > H > Me > Ph > mtc.$

This series is similar to those reported in the literature.^{26,30} Note: (i) the high *cis* influence of I and Cl; (ii) the weak *cis* influence of thiocarbamato (mtc), compared to the higher influence of the other group 16 ligands and (iii) the weak *cis* influence of H, Ph and Me.

In the above series, the ligands F, SCN, NCS, N₃ and CF₃ have not been included because of the lack of cross comparisons. However, considering the H–Y series, one can note the rather high *cis* influence of the halogenides and pseudohalogenides (SCN being slightly higher than its linkage isomer) compared to CF₃ and Ph.

We can also estimate the contribution to *cis* influence of the various ligands calculating the difference, ΔJ , of the coupling constants of a given derivative from that of a reference compound. These values, calculated using three different reference compounds, *i.e.* t-1, t-2, and t-9, are reported in Table 6. Note that also these ΔJ values confirm the trend of *cis* influence reported above.

Additivity of *cis* influence has been noted previously,^{21,26,31} and this property is confirmed by our data. See, for instance, the three sequences Cl₂, Cl-NO₃, (NO₃)₂ ($\Delta J \sim 130$ Hz); Cl₂, Cl-AcO, (AcO)₂ ($\Delta J \sim 225$ Hz) and Cl₂, Cl–SPh, SPh₂ ($\Delta J \sim 120$ Hz). It is noteworthy that, using additivity as a rule, we can predict the coupling constant of a given compound. For instance ${}^{1}J_{PtP}$ of t-8 (X = NO₃, Y = AcO) can be obtained from the value of the dichloro complex (t-1), adding 130 Hz (the difference of the values between t-1 and t-4) and 225 Hz (ΔJ between the Cl₂ and Cl-AcO derivatives). The result (2985 Hz) is in good agreement with the experimental value (2990 Hz). In the above calculation, we have taken the dichloro derivative as a reference compound, but one can start from any compound, for instance from the dinitrato derivative t-9, J_{PtP} of the Cl–AcO compound (t-5) can be calculated from the values of Table 5, as follows: 2900 - 140 + 90 = 2850 Hz, experimental 2853 Hz.

Comments on Pt-P bond lengths

Some Pt–P bond lengths in complexes of the type *trans*- $[PtXY(PPh_3)_2]$ have been collected in Table 3. Taking shortening

of these bond lengths as an indication of decreasing *cis* influence, from the values of the X = Y complexes, we obtain the following order of decreasing *cis* influence: $NO_2 > AcO > I > Cl > mtc$ or, from the series of the Cl–X derivatives: $CF_3 > NO_3 > Cl > AcO > Me$.

These orders are different from those obtained from ${}^{1}J_{PtP}$ values. Indeed, a relationship between coupling constants and bond lengths has been questioned³² (see however, ref. 33 and 34), and in the present case it seems to hold only for the sequence *t*-1, *t*-4, *t*-5. However, bond distances reflect factors such as ionic, or covalent radii, steric hindrance, crystal packing, whereas one-bond Pt–P coupling constants are mainly sensitive to the effects of X and Y on the Pt(6 s) orbital³⁰ and, consequently, on bonding interactions, *i.e.* on the amount of P→Pt donation.

Thus, the *cis* influence series obtained from the ${}^{1}J_{PP}$ values is mainly due to electronic (bonding) factors, whereas the series deduced from the X-ray data are influenced by both steric and electronic effects, which are difficult to discriminate. An instance of relationship between bond distances and electronic parameters of *cis* ligands has been reported by Kukushkin and Konovalon.³⁵

cis-[PtX₂(PPh₃)] derivatives

Having established a series of the *cis* influence of some X and Y ligands, one wonders what is the order of the *trans* influence of these ligands. In Table 7, we have collected the ³¹P NMR data of some *cis*-[PtX₂(PPh₃)₂] complexes, and the ¹ J_{PP} values increase in

Table 7 ³¹P NMR parameters of *cis*-[PtX₂(PPh₃)₂] complexes^a

X	δ /ppm	$^{1}J_{\mathrm{PtP}}/\mathrm{Hz}$	References
NO ₃	3.6	4010	Ь
AcO	5.76	3861	10
Cl	14.9	3672	b
Ι	11.89	3454	9
mtc	15.7	3277	1
SePh	19.1	2968	36
SPh	19.7 (in $C_6 D_6$)	2960	21
Me	27.7 (in CD ₂ Cl ₂)	1900	37

^{*a*} CDCl₃ solutions, unless otherwise stated, ppm from H₃PO₄. ^{*b*} This work, or measured in our laboratory.

the order: Me < SePh ~ SPh < mtc < I < Cl < AcO < NO₃, which gives a sequence similar to that usually accepted for *trans* influence.³⁸ It is neither opposite nor parallel to the above described series of *cis* influence, and mtc displays a behaviour similar to that of the other group 16 donor ligands, as expected. However, it is important to note that in *cis*-[PtX₂(PPh₃)₂] both *trans* and *cis* influences are simultaneously operative, at least in principle, even if the latter are normally believed to be less relevant,^{32,38} and are difficult to discriminate. More work should be done to elucidate this point.

Conclusions

One-bond coupling constants have often been used to investigate trans and cis influences in Pt and Rh compounds.39,40 In fact, such constants can be assumed as an estimate of the strength of a bond, provided such bond possesses some s character. Coupling constants can be considered a transfer of information of the spin state between two nuclei, mediated by the s electrons of a given bond(s). In Pt(II), back donation can be considered of little relevance, at least in the first place,⁴¹ consequently for the compounds studied in this paper, we can assume that Pt-P bonds are formed mainly by donation from an sp³ orbital of P to an hybrid Pt orbital with some 6 s character. Under this approximation, Pt-P bonds become weaker as the central platinum atom becomes less positively charged; in fact the larger cis influence is displayed by ligands such as halides and pseudohalides, in particular by Cl or I, which being both σ and π donors to Pt(II),⁴² lower the positive charge on Pt. Also of note is the finding that strong donors display also a strong (kinetic) cis effect, because they lower the positive charge on Pt, reducing its electrophilicity.43 Thus, the very low cis influence of mtc can be tentatively ascribed to a low negative charge of the sulfur donor atom, adjacent to the electron withdrawing C=O group.

trans-[PtXY(PPh₃)₂] complexes have proved to be a good model for studying *cis* influence, by consideration of the ${}^{1}J_{PP}$ values, because the mutual *trans* influence of the phosphine groups is constant. We have thus obtained a series of *cis* influence, which can be rationalised in terms of change of the positive charge on Pt.

Although, in principle, cis-[PtX₂(PPh₃)₂] complexes should be useful for studying *trans* influence, such a study is more tricky, because in these complexes cis influence is also operative and is difficult to discriminate. We are planning to undertake this study in this direction.

Experimental

Elemental analyses were performed at the Microanalytical Laboratory, the University of Milano. ³¹P {¹H} NMR spectra (Tables 4, 5 and 7) were recorded on a Bruker Advance DRX 300 at 121 MHz; δ values (ppm) are *vs.* external H₃PO₄ (see Tables 4 and 5 for values). ESI Mass spectra were recorded with a LCQ Advantage Thermofluxional instrument, or a ICR-FTMS APEX II with a 4.7 T magnet, Bruker Daltonics from CH₂Cl₂-methanol 1 : 1 solutions. Isotope cluster abundance was checked by computer simulation.

Chemicals were reagent grade and used as received. *cis/trans*-[PtCl₂(CH₃CN)₂],⁵ *trans*-[PtCl₂(CH₃CN)₂],⁵ [PtI₂(PhCN)₂],⁹ and *cis*-[PtCl₂(PPt)₃)₂]⁴⁴ were synthesised as described in the literature.

All reactions involving silver salts were performed in the dark.

trans-[PtCl₂(PPh₃)₂] (t-1)

t-1 was synthesised using a slight modification of the method described by Kukushkin.⁴ PPh₃ (650.0 mg, 2.50 mmol) was slowly added to a heated (50 °C) suspension of *trans*-[PtCl₂(CH₃CN)₂] (475.0 mg, 1.35 mmol) in nitromethane (10 mL). The mixture was left at 50 °C for 30 min. *t*-1 was isolated as a yellow solid, washed three times with hot nitromethane and dried at the air (720.0 mg, 73%). Found: C 54.70, H 3.77. Calcd for C₃₆H₃₀Cl₂P₂Pt (790.57): C 54.69, H 3.83. *m/z* (ESI) 719 ([Pt(PPh₃)₂]⁺, 100%), 754 ([PtCl(PPh₃)₂]⁺, 30%).

trans-[PtI₂(PPh₃)₂] (t-2)

PPh₃ (137.3 mg, 0.52 mmol) was added to a suspension of *cis/trans*-[PtI₂(PhCN)₂] (180.0 mg, 0.28 mmol) in benzene (20 mL). The slurry was refluxed for 4 h, cooled to 10 °C and the orange product was obtained by addition of diisopropyl ether (223.0 mg, 88%). Found: C 44.25, H 3.26. Calcd for $C_{36}H_{30}I_2P_2Pt$ (973.46): C 44.42, H 3.11. *m/z* (ESI) 719 ([M – 2I]⁺, 35%), 846 ([M – I]⁺, 100), 994 ([M + Na]⁺, 20).

Alternative preparation. Solid KI (837.0 mg, 5.04 mmol) was added to a stirred solution of K_2PtCl_4 (500.0 mg, 1.20 mmol) in water (10 mL). After 15 min, a solution of PPh₃ (639.1 mg, 2.40 mmol) in acetone (10 mL) was added and the mixture was stirred at room temperature for 2 h, when the orange solid was filtered, washed with acetone and dried *in vacuo* (1090.0 mg, 93%). ³¹P NMR showed that this residue consisted of a 4 : 1 mixture of *t*-2–*c*-2.

Attempted synthesis of trans-[PtClI(PPh₃)₂] (t-3)

Potassium iodide (12.0 mg, 0.07 mmol) was added to a CHCl₃ solution (20 mL) of *t*-**1** (552.7 mg, 0.07 mmol), followed by a crystal of 18-crown-6. The slurry was refluxed for 8 h, filtered and the solution was evaporated to dryness *in vacuo*. ³¹P NMR of the yellow residue showed the presence of *t*-**1**, *c*-**1** and *t*-**2**, two doublets (J_{PP} 12 Hz) at δ 11.5 ppm (J_{PP} 3685 Hz) and 13.7 (J_{PP} 3408 Hz), assigned to *c*-**3** and a singlet with Pt satellites at δ 18.8 ppm (J_{PP} 2556 Hz), assigned to *t*-**3**. This compound was approximately 30% of the mixture. Attempts to isolate it were unsuccessful. Similar results were obtained using LiI as a source of iodide, or by reaction of *t*-**2** with KCl in the presence of 18-crown-6.

trans-[PtCl(NO₃)(PPh₃)₂] (t-4)

t-1 (113.5 mg, 0.14 mmol) and AgNO₃ (24.6 mg, 0.14 mmol) were suspended in CHCl₃ (15 mL) and heated at 50 °C for 6 h. The hot mixture was filtered and the filtrate was evaporated to dryness yielding *t*-4 as a yellow solid (100.1 mg, 85%). Found: C 50.48, H 3.54, N 1.68. Calcd for $C_{36}H_{30}NClO_3P_2Pt\cdot1/3CHCl_3$ (856.91): C 50.92, H 3.57, N 1.63. v_{max} (KBr)/cm⁻¹ 1483 and 1270 (NO₃). *m/z* (ESI) 840 ([M + Na]⁺, 40%). Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diisopropyl ether into a CHCl₃ solution.

trans-[PtCl(AcO)(PPh₃)₂] (t-5)

t-1 (110.0 mg, 0.14 mmol) and AgAcO (23.6 mg, 0.14 mmol) were suspended in CHCl₃ (10 mL) and heated at 50 $^{\circ}$ C for 6 h. The

hot mixture was filtered and the filtrate was evaporated to dryness yielding *t*-**5** as a pale yellow solid (70.0 mg, 61%). Found: C 50.21, H 3.79. Calcd for $C_{38}H_{33}O_2ClP_2Pt\cdotCHCl_3$ (933.54): C 50.18, H 3.67. $v_{max}(KBr)/cm^{-1}$ 1604, 1362 and 1316 (CO). *m/z* (ESI) 754 ([M - AcO]⁺, 100%), 778 ([M - Cl]⁺, 10), 814 ([M + 1]⁺, 5), 836 (M + Na]⁺, 70). Crystals suitable for X-ray diffraction were grown by slow diffusion of diisopropyl ether into a CHCl₃ solution.

Attempted preparation of trans-[Pt(AcO)₂(PPh₃)₂] (t-6)

Reaction of either *t*-1 or *t*-2 with two molar equivalents of AgAcO gave invariably *cis*-[Pt(AcO)₂(PPh₃)₂], identified by its ³¹P NMR spectrum, ¹⁰ plus minor amounts of other unidentified compounds.

Attempted preparation of trans-[PtI(AcO)(PPh₃)₂] (t-7)

The reaction of equimolar amounts of t-**2** and AgAcO in CHCl₃ at 60 °C led invariably to *cis*-[Pt(AcO)₂(PPh₃)₂], *c*-**7**, and some unreacted starting material identified through their ³¹P NMR signals.

trans-[Pt(AcO)(NO₃)(PPh₃)₂] (t-8)

t-4 (100.0 mg, 0.12 mmol) and AgAcO (21.1 mg, 0.12 mmol) were suspended in CHCl₃ (15 mL) and heated at 50 °C for 7 h. The hot mixture was filtered and the filtrate was evaporated to dryness yielding *t*-**5** as a yellow solid (83.2 mg, 82%). Found: C 53.84, H 4.05, N 1.76. Calcd for C₃₈H₃₃NO₅P₂Pt (840.71): C 54.29, H 3.96, N 1.67. v_{max} (KBr)/cm⁻¹ 1647 (AcO), 1483 and 1265 (NO₃). *m/z* (ESI) 841 ([M + 1]⁺, 50%). Crystals suitable for X-ray diffraction studies were obtained by slow diffusion of diisopropyl ether into a CHCl₃ solution.

cis/trans-[Pt(NO₃)₂(PPh₃)₂] (c/t-9)

t-4 (130.0 mg, 0.16 mmol), AgNO₃ (100.2 mg, 0.59 mmol) and 18-crown-6 (10 mg, 0.04 mmol) were suspended in CHCl₃ (10 mL) and heated under reflux for 2 d. The hot mixture was filtered, evaporated to dryness yielding a pale yellow solid, which was washed with diisopropyl ether (80.5 mg, 60%). The ³¹P NMR spectrum of this residue showed only two resonances at δ 3.6 ppm (J_{PtP} 4010 Hz), due to *c*-9,¹ and 12.6 ppm (J_{PtP} 2900 Hz). Elemental analysis and ESI mass spectra of this residue were consistent with the stoichiometry [Pt(NO₃)₂(PPh₃)₂], consequently the signal at 12.6 ppm was assigned to *t*-9. Found: C 41.80, H 2.78, N 2.94. Calcd for C₃₆H₃₀N₂O₆P₂Pt·2CHCl₃ (1082.43): C 42.17, H 2.98, N 2.59. v_{max} (KBr)/cm⁻¹ 1481 and 1259 (NO₃). *m*/*z* (ESI) 866 ([M + Na]⁺, 60%).

trans-[PtCl(NO₂)(PPh₃)₂] (t-10)

t-1 (99.0 mg, 0.13 mmol) and AgNO₂ (19.4 mg, 0.13 mmol) were suspended in CHCl₃ (10 mL) and heated at 60 °C for 6 h. The mixture was hot filtered and the filtrate was evaporated to dryness yielding *t*-10 as a yellow solid (43.2 mg, 44%). Found: C 51.83, H 3.70, N 1.54. Calcd for C₃₆H₃₀NClO₂P₂Pt·1/4CHCl₃ (830.95): C 52.24, H 3.67, N 1.68. v_{max} (KBr)/cm⁻¹: 1408 and 1331 (NO₂). *m/z* (ESI) 802 ([M + H]⁺, 30%), 824 ([M + Na]⁺, 70%).

trans-[PtI(NO₂)(PPh₃)₂] (t-11)

Solid AgNO₂ (9.2 mg, 0.06 mmol) was added to a solution of *t*-**2** (60.0 mg, 0.06 mmol) in CHCl₃ (10 mL) and the mixture was refluxed for 6 h. The hot mixture was filtered and the filtrate was evaporated to dryness yielding *t*-**11** as a yellow solid (23.1 mg, 43%). Found: C 45.86, H 3.24, N 1.20. Calcd for $C_{36}H_{30}NIO_2P_2Pt\cdot1/2CHCl_3$ (952.25): C 46.04, H 3.23, N 1.47. $v_{max}(KBr)/cm^{-1}$: 1408 and 1323 (NO₂). *m/z* (ESI) 719 ([M – NO₂ – I]⁺, 100%), 765 ([M –I]⁺, 10%), 845 ([M – NO₂]⁺, 95%), 915 ([M + Na]⁺, 20%).

trans-[Pt(NO₂)₂(PPh₃)₂] (t-12)

From t-4. *t*-**4** (80.0 mg, 0.10 mmol) and AgNO₂ (100 mg, 0.64 mmol) were suspended in CHCl₃ (10 mL) and heated under reflux for 2 d. The hot mixture was filtered, taken to dryness yielding pale yellow *t*-**12** (10.0 mg, 12%). Found: C40.64, H 3.58, N 2.47. Calcd for C₃₆H₃₀N₂O₄P₂Pt·2CHCl₃·4H₂O (1050.41): C 40.66, H 3.59, N 2.49. v_{max} (KBr)/cm⁻¹: 1415 and 1335 (NO₂). *m/z* (ESI) 765 ([M – NO₂]⁺, 60%).

From t-1. t-1 (156.0 mg, 0.20 mmol) and $AgNO_2$ (75.9 mg, 0.50 mmol) were suspended in CHCl₃ and heated under reflux for 10 h. The hot mixture was filtered, taken to dryness yielding t-12 as a white solid (39.7 mg, 25%). Crystals for X-ray diffraction studies were grown by diffusion of diisopropyl ether into a chloroform solution.

Attempted preparation of *trans*-[PtI(NO₃)(PPh₃)₂], reduction of nitrate to nitrite

trans-[PtI₂(PPh₃)₂] (102.0 mg, 0.10 mmol) and AgNO₃ (17.3 mg, 0.10 mmol) were refluxed in CHCl₃ (20 mL) for 2 h. The filtered solution was evaporated to dryness *in vacuo* leaving a yellow solid whose ³¹P NMR showed the presence of *t*-**11** (δ 13.0 ppm, J_{PtP} = 2795 Hz) and Ph₃PO (δ 29.8 ppm).

X-Ray data collection and structure determination[†]

Crystal data are summarised in Table 8. The diffraction experiments were carried out on a Bruker SMART CCD area-detector diffractometer, at 223 K for t-4, and at 150 K for t-5. CHCl₃ and t-12.2CHCl₃, using MoK α 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,45 and an empirical absorption correction was applied (SADABS)⁴⁶ to the collected reflections. The calculations were performed using the Personal Structure Determination Package⁴⁷ and the physical constants tabulated therein.48 The structures were solved by direct methods (SHELXS)49 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). All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms of the CH₃ moiety in t-5 CHCl₃ were found in the final Fourier maps and not refined. All the other hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter U1.10 times that of the carbon atom to which they are attached, and not refined. In spite of the low-temperature data collection, in t-4 there are three carbon atoms with high thermal parameters. In the

Table 8	Crystallographic data for compounds trans-[PtCl(NO ₃)(PPh ₃) ₂] (t-4),	trans-[PtCl(AcO)(PPh ₃) ₂]·CHCl ₃ (t-5·CHCl ₃) and trans-[Pt(NO ₂)(PPh ₃) ₂]
(<i>t</i> -12·2Cl	HCl ₃)	

	<i>t-</i> 4	t-4·CHCl ₃	$t-12 \cdot 2 \text{CHCl}_3$
Formula	$C_{36}H_{30}CINO_3P_2Pt$	$C_{39}H_{34}Cl_4O_2P_2Pt$	$C_{38}H_{32}Cl_6N_2O_4P_2P_1$
$M_{\rm r}/{ m g}~{ m mol}^{-1}$	817.14	933.55	1050.45
Colour	Pale yellow	Colourless	Colourless
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\overline{1}$
a/Å	11.901(1)	12.484(1)	7.9386(7)
b/Å	23.988(2)	11.084(1)	11.158(1)
c/Å	12 213(1)	27.857(2)	12 025(1)
$\alpha/^{\circ}$	90	90	91.880(1)
$\beta/^{\circ}$	111 77(1)	101.86(1)	102,303(1)
$\gamma/^{\circ}$	90	90	104.799(1)
$U/Å^3$	3237 9(4)	3772 2(4)	1001 8(2)
Z	4	4	1
F(000)	1608	1840	516
$D_{\rm s}/{\rm g}~{\rm cm}^{-3}$	1.676	1.644	1.741
T/K	223	150	150
Crystal dimensions/mm	$0.28 \times 0.32 \times 0.49$	$0.21 \times 0.23 \times 0.40$	$0.10 \times 0.15 \times 0.45$
$\mu (MoK\alpha)/cm^{-1}$	45.94	41.60	40.61
Min. and max. transmission factors	0.619-1.000	0.692-1.000	0.706-1.000
Scan mode	ω	ω	ω
Frame width/°	0.30	0.50	0.50
Time per frame/sec.	10	10	30
No. of frames	3660	1500	2160
Detector-sample distance/cm	6.00	6.00	6.00
θ-range	3–28	3–28	3–27
Reciprocal space explored	Full sphere	Full sphere	Full sphere
No. of reflections (total, independent)	61 238, 8584	47 543, 9733	17 082, 4658
$R_{ m int}$	0.0292	0.0206	0.0437
Final R_2 and w R_2 indices ^{<i>a</i>} (F^2 , all reflections)	0.028, 0.051	0.026, 0.047	0.049, 0.053
Conventional R_{I} index $[I > 2\sigma(I)]$	0.020	0.018	0.030
Reflections with $I > 2\sigma(I)$	7338	8486	4409
No. of variables	397	433	241
Goodness of fit ^b	1.003	0.968	0.974

 ${}^{a} R_{2} = [\Sigma(|F_{o}^{2} - kF_{c}^{2}|/\Sigma F_{o}^{2}], wR_{2} = [\Sigma w/(F_{o}^{2} - kF_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}. {}^{b} [\Sigma w(F_{o}^{2} - kF_{c}^{2})^{2}/(N_{o} - N_{v})]^{1/2}, where w = 4F_{o}^{2}/\sigma(F_{o}^{2})^{2}, \sigma(F_{o}^{2}) = [\sigma^{2}(F_{o}^{2}) + (pF_{o}^{2})^{2}]^{1/2}. N_{o} \text{ is the number of observations, } N_{v} \text{ the number of variables, and } p = 0.03 \text{ for } t\text{-}\mathbf{4} \text{ and } t\text{-}\mathbf{5} \cdot \text{CHCl}_{3}, \text{ and } p = 0.02 \text{ for } t\text{-}\mathbf{12} \cdot 2\text{CHCl}_{3}.$

final Fourier maps the maximum residuals were 1.98(13) e Å⁻³ at 0.75 Å from Pt, 0.64(8) e Å⁻³ at 0.90 Å from Cl4, and 1.49(22) e Å⁻³ at 0.61 Å from Cl2 for *t*-4, *t*-5·CHCl₃, and *t*-12·2CHCl₃, respectively.

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