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cis- AND trans-INFLUENCE OF LIGANDS IN PLATINUM(II) COMPLEXES. THE CRYSTAL AND MOLECULAR STRUCTURE OF cis-$[PtCl_2(PEt_3)(CO)]$

LJUBICA MANOJLOVIĆ-MUIR, KENNETH W. MUIR and TIHOMIR SOLOMUN
Department of Chemistry, University of Glasgow,
Glasgow G12 8QQ (Great Britain)

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Summary

In the complexes cis-$[PtCl_2(PEt_3)L]$, where L = Cl^-, $C(NPhCH_2)_2$, C(OEt)NHPh, CNPh, CO, PEt_3, $P(OPh)_3$ or PF_3, ligands L exert cis-influence on the Pt-P bond lengths (ca. 0.06Å), which is almost as large as their trans-influence on the Pt-Cl(trans to L) bond lengths (ca. 0.07Å). The two effects are independent of each other and lead to different cis- and trans-influence series of L. The trend in Pt-Cl(cis to L) distances, displaying a variation of about 0.03Å, reflects the change in the length, and presumably strength, of the Pt-P bonds.

The X-ray analysis of cis-$[PtCl_2(PEt_3)(CO)]$ was based on diffractometric intensities of 1820 independent reflections. The crystal structure was solved by the heavy atom method and refined by full-matrix least-squares to R = 0.037. The crystals are orthorhombic, space group $Pca2_1$, a = 12.777, b = 8.587, c = 11.424Å, Z = 4. They are built of discrete monomeric molecules with cis-square planar geometry. Selected bond lengths are: Pt-C 1.855(14), Pt-P 2.265(3), Pt-Cl(trans to C) 2.296(4) and Pt-Cl(trans to P) 2.368(3)Å.

Introduction

In square planar transition metal complexes the effects of ligands on the strength of cis-metal-ligand bonds are of interest, not only intrinsically, but also because they are germane to the much studied phenomenon of trans-influence. The existance of cis-influence in platinum(II) complexes has been inferred from spectroscopic results [1].

We, however, first noted in 1974 that the bond lengths in cis-$[PtCl_2(PPh_3)(CO)]$, compared with those in other cis-$[PtCl_2(PR_3)L]$ complexes (PR_3 = PMe_3, PEt_3 or PEt_2Ph and L = PMe_3, carbenoid or isocyanide), indicate that the carbonyl group weakens the Pt-P and strengthens the Pt-Cl bonds cis to itself; this was in conformity with trends displayed by ^1J(Pt-P) coupling constants and ν(Pt-Cl) stretching frequencies in analagous complexes [2]. While we considered it likely that these observations reflect a cis-influence of the carbonyl group, we pointed out that since the complexes compared contain different PR_3 ligands the effects of the phosphine substituents may also be involved [2-4]. Variations in the Pt-P bond lengths in the complexes cis-$[PtCl_2(PR_3)L]$ have also been noticed by Russell et al. [5].

To investigate variations in the lengths of platinum-ligand bonds cis and trans to L, originating from change in the nature of L only, we have chosen to examine a series of triethylphosphine complexes cis-$[PtCl_2(PEt_3)L]$. Crystallographic studies of such complexes with L = Cl^-, $C(OEt)NHPh$, $C(NPhCH_2)_2$, CNPh, PEt_3, PF_3 or $P(OPh)_3$ have already been carried out in this laboratory and elsewhere [6-12], and we report here the results of an accurate X- ray analysis of the compound with L = CO. The crystal structure of this compound was first determined by E.M. Badley, using photographic diffraction data, but the results obtained are of low accuracy [9].

Experimental

Crystals of cis-[$PtCl_2(PEt_3)(CO)$] are air-stable transparent needles elongated along $\underset{\sim}{a}$.

Crystal data

$C_7H_{15}Cl_2OPPt$, M.W. = 412.2. Orthorhombic, space group $Pca2_1$, a = 12.777, b = 8.587, c = 11.424Å, U = 1253.4Å^3, Z = 4, D_c = 2.184gcm^{-3}, $F(000)$ = 768. Mo-K_α radiation, λ = 0.71069Å, μ(Mo-K_α) = 118.3 cm^{-1}.

Measurements

A crystal of approximate dimensions 0.50 x 0.21 x 0.24 mm was selected for the analysis and its principal faces, belonging to the forms {100}, {010} and {001}, were indentified by optical goniometry and X-ray measurements.

The crystal symmetry and preliminary unit cell dimensions were determined from oscillation and Weissenberg photographs. Systematically absent reflections are consistent with space groups $Pca2_1$ (No. 29) and $Pcam$, the latter being an unconventional setting of the space group $Pbcm$ (No. 57). The non-centrosymmetric space group $Pca2_1$ was later proved correct by a successful structure analysis. The preliminary unit cell dimensions were adjusted by a least-squares treatment of the setting angles for 22 reflections, centred on a Hilger and Watts' Y290 four-circle diffractometer controlled by a PDP8 computer.

The intensities of reflections were measured on the Y290 diffractometer, using molybdenum radiation, a graphite monochromator and a pulse-height analyser. The θ-2θ scan technique was employed. Each reflection was scanned through a θ range of 0.6°, with a scan step of 0.02° and a counting time of 2s per step. The local background was counted for 15s at each end of the scan range. The intensities of two strong reflections, periodically remeasured throughout the experiment, varied by less than ± 5% of their mean values.

The integrated intensities, $\underline{I}$, and their standard deviations, $\sigma(\underline{I})$, were obtained using relationships described earlier ($\underline{q} = 0.04$) [13]. They were corrected for Lorentz, polarisation, counting-loss and absorption effects. The transmission factors on $\underline{F}^2$, calculated by Gaussian integration, varied between 0.07 and 0.16.

The intensities of all $\underline{hkl}$ reflections with $\theta(\text{Mo-}\underline{K}_\alpha) \leq 35°$ were measured. Of these, only 1820 (ca. 66%), for which $\underline{I} \geqslant 3\sigma(\underline{I})$, were used in the subsequent calculations.

Structure analysis

The position of the platinum atom, at $\underline{z} = 1/4$, was found from a Patterson function. With $\underline{Z} = 4$, the space group Pcam would then require all molecules to lie in mirror planes normal to $\underset{\sim}{c}$. This proved incompatible with the difference synthesis phased by the platinum atom, and the space group $\underline{Pca2_1}$ was therefore adopted in the subsequent analysis. Interpretation of this synthesis was complicated by pseudo-symmetry, giving rise to four possible arrangements for atoms co-ordinated to platinum. Each of these arrangements was refined and the one which gave an acceptable set of platinum-ligand bond lengths and angles, and also the lowest value of $\underline{R}$, was used in further calculations. The positions of the remaining non-hydrogen atoms were determined from subsequent difference syntheses.

The structure was refined by a least-squares minimisation of the function $\Sigma\{(|\underline{F}_o|-|\underline{F}_c|)/\sigma(\underline{F}_o)\}^2$. The atomic scattering factors were taken from ref. 14, and the anomalous scattering of platinum, chlorine and phosphorus atoms was accounted for [14]. Hydrogen atoms were not located. Refinement of the positional and anisotropic vibrational parameters of all non-hydrogen atoms converged at $\underline{R} = 0.037$ and $\underline{R}_w = 0.047$.

The correctness of the indexing of reflections was then verified, by refining the structure with $\underline{h\overline{kl}}$ reflections re-indexed as $\underline{h\bar{k}l}$. This refinement converged at $\underline{R} = 0.039$ and $\underline{R}_w = 0.049$, both significantly greater than the values obtained with the original indexing.

In the last cycle of refinement all parameters shifted by $\leq 0.05\sigma$. The standard deviation of an observation of unit weight was 1.71. The mean values of $(|\underline{F}_o| - |\underline{F}_c|)^2/\sigma^2(\underline{F}_o)$ showed no systematic trends when analysed as a function of

TABLE 1

FRACTIONAL ATOMIC COORDINATES

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$
Pt	0.04379(3)	-0.03769(3)	1/4
Cl(1)	0.1001(3)	0.2962(3)	0.2146(3)
Cl(2)	0.1884(3)	-0.0513(4)	0.1511(4)
P	-0.0024(2)	-0.2141(3)	0.2789(3)
O	-0.1411(8)	0.1743(13)	0.3710(14)
C(1)	-0.0731(11)	0.1187(14)	0.3245(14)
C(2)	0.1003(9)	-0.3213(15)	0.3563(12)
C(3)	0.1231(13)	-0.2580(19)	0.4789(15)
C(4)	-0.1270(11)	-0.2363(15)	0.3580(13)
C(5)	-0.1503(13)	-0.4099(17)	0.3829(15)
C(6)	-0.0189(10)	-0.3149(13)	0.1414(11)
C(7)	-0.1042(12)	-0.2477(17)	0.0656(15)

TABLE 2

THERMAL PARAMETERS OF ATOMS[a]

Atom	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
Pt	45.1(2)	33.5(1)	45.2(2)	1.5(1)	-0.4(3)	-4.1(3)
Cl(1)	77(2)	38(1)	75(2)	-8(1)	-6(2)	3(1)
Cl(2)	64(2)	58(2)	92(3)	0(2)	32(2)	-10(2)
P	45(1)	34(1)	45(1)	-1(1)	-1(1)	-5(1)
O	67(7)	68(6)	147(12)	25(6)	25(8)	-18(8)
C(1)	57(7)	37(5)	83(9)	-6(5)	4(7)	-2(6)
C(2)	45(6)	48(6)	63(7)	5(5)	-6(5)	1(5)
C(3)	73(9)	79(9)	69(9)	12(8)	-13(7)	-3(8)
C(4)	57(7)	53(7)	58(7)	-5(6)	8(6)	-4(6)
C(5)	87(10)	51(6)	80(10)	-15(7)	6(9)	2(7)
C(6)	61(7)	41(5)	50(6)	-1(5)	0(5)	-13(5)
C(7)	62(8)	69(9)	69(9)	6(7)	-17(7)	-6(8)

[a] Each atom was assigned an anisotropic temperature factor of the form $\exp(-2 \times 10^{-3}\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} \underline{h}_i\underline{h}_j\underline{a}_i^*\underline{a}_j^*\underline{U}_{ij})$.

$|\underline{F}_o|$ or $\sin\theta$.* The extreme function values in the final difference synthesis (1.5 and -1.6 $e\text{Å}^{-3}$), were associated with the position of the platinum atom. The final positional and vibrational parameters of atoms are presented in Tables 1 and 2, and a view of the molecular structure is shown in Figure 1.

The computer programs used are listed in ref. 12.

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[*] A list of the final values at $|\underline{F}_o|$ and $|\underline{F}_c|$ can be obtained from the authors on request.

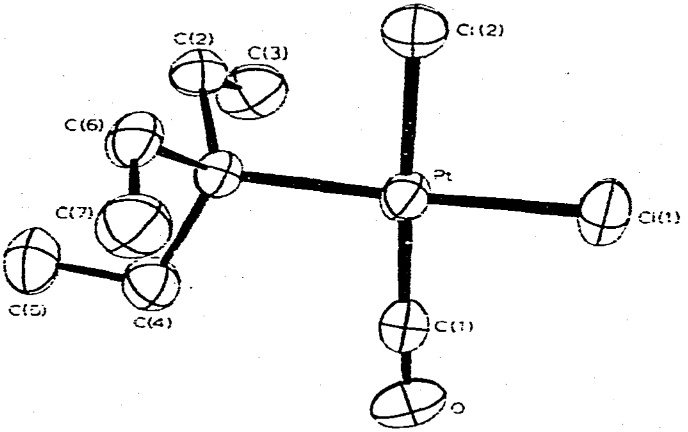

Figure 1. A perspective view of the molecule, with thermal ellipsoids displaying 50% probability. Hydrogen atoms are omitted.

Results and discussion

Crystal and molecular structure of *cis*-[$PtCl_2(PEt_3)(CO)$]

The crystal structure is built of discrete monomeric molecules. The shortest distances between atoms in different molecules are close to the sums of the appropriate van der Waals radii.

The molecules display a *cis*-square planar coordination around the platinum atom and almost ideal C_s symmetry.

The orientation of the phosphine ligand, evident from the Cl(2)-Pt-P-C torsion angles (Table 3), is such as to bring the ethyl group involving the atoms C(4) and C(5) into the coordination plane of platinum. The arrangement of the other two ethyl groups is such as to make the planes through the atoms P, C(2) and C(3) and P, C(6) and C(7) nearly coincident (dihedral angle 3°), and both normal to the plane defined by the atoms P, C(4) and C(5) (dihedral angles 93 and 90°). The conformations about the P-C bonds are staggered, as shown by the Pt-P-C-C torsion angles (Table 3). From an inspection of models it appears that such a conformation of the PEt_3 ligand and its orientation, with respect to the coordination plane of the metal atom, are favourable for the minimisation of steric repulsions in a square planar molecule. It is therefore not surprising that similar PEt_3 conformations and orientations have been observed in several other *cis*-$[PtCl_2(PEt_3)L]$ molecules [12]. The bond lengths and angles in the triethylphosphine ligand are normal (Table 3), the Pt-P-C and C-P-C angles showing the expected deviations from the ideal tetrahedral value [15].

The non-bonding intramolecular contacts and the angular distortions in the coordination plane of platinum indicate that the molecule is subject to some steric strain. Thus the C(1)...C(4), Cl(2)...C(2) and Cl(2)...C(6) distances are 3.15, 3.48 and 3.49Å, respectively, and the P-Pt-C(1) and P-Pt-Cl(2) angles deviate from 90° by 4.7 and -2.1° (Table 3). The individual displacements of the Pt, P, Cl(1) and Cl(2) atoms from their least-squares plane* do not exceed 0.002Å; the displacements of the C(1), O, C(4) and C(5) atoms from the same plane are less than 0.06Å.

The Pt-Cl(1) and Pt-Cl(2) distances, 2.368(3) and 2.296(4)Å respectively, show that the triethylphosphine ligand exerts a substantially larger *trans*-influence than the carbonyl group, while the Pt-P distance [2.265(3)Å] reflects the *cis*-influence of the carbonyl group (see below). The Pt-C distance [1.855(14)Å] is the same as that [1.858(7)Å] in the analagous compound *cis*-$[PtCl_2(PPh_3)(CO)]$, and indicates that

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* Defined by the equation $-0.518\underline{X} + 0.011\underline{Y} - 0.855\underline{Z} = -2.729$; $\underline{X}$, $\underline{Y}$, and $\underline{Z}$ are co-ordinates referred to orthonormal axes along $\underset{\sim}{a}$, $\underset{\sim}{b}$, and $\underset{\sim}{c}$.*

the co-ordinated carbon monoxide possesses appreciable π-acceptor properties [4].

TABLE 3

SELECTED INTERATOMIC DISTANCES AND ANGLES

Bond lengths (Å)			
Pt-Cl(1)	2.368(3)	P-C(6)	1.806(13)
Pt-Cl(2)	2.296(4)	C(2)-C(3)	1.529(21)
Pt-P	2.265(3)	C(4)-C(5)	1.546(20)
Pt-C(1)	1.855(14)	C(6)-C(7)	1.507(20)
P-C(2)	1.830(13)	O-C(1)	1.124(19)
P-C(4)	1.840(14)		
Bond angles (°)			
Cl(1)-Pt-Cl(2)	89.0(1)	Pt-P-C(2)	111.4(4)
Cl(1)-Pt-C(1)	88.4(4)	Pt-P-C(4)	113.3(4)
P-Pt-Cl(2)	87.9(1)	Pt-P-C(6)	111.2(4)
P-Pt-C(1)	94.7(4)	C(2)-P-C(4)	109.3(6)
Cl(1)-Pt-P	177.0(1)	C(2)-P-C(6)	105.3(6)
Cl(2)-Pt-C(1)	176.9(4)	C(4)-P-C(6)	106.0(6)
P-C(2)-C(3)	113.6(9)	P-C(6)-C(7)	113.6(9)
P-C(4)-C(5)	110.9(10)	Pt-C(1)-O	176.5(12)
Torsion angles (°)			
Cl(2)-Pt-P-C(2)	58(1)	Pt-P-C(2)-C(3)	62(1)
Cl(2)-Pt-P-C(4)	-178(1)	Pt-P-C(4)-C(5)	-176(1)
Cl(2)-Pt-P-C(6)	-59(1)	Pt-P-C(6)-C(7)	-62(1)

cis- And trans-influence of ligands in cis-[$PtCl_2(PEt_3)L$] complexes

Accurate crystallographic studies are now available for eight complexes of the type cis-[$PtCl_2(PEt_3)L$], where the ligands L display a wide range of electronic properties. Both strong and weak σ-donors, such as PEt_3 and Cl^-, and also strong and weak π-acceptors, such as CO and carbenoid, are represented. The bond lengths in these complexes are listed in Table 4, together with the ^1J(Pt-PEt_3) coupling constants. They enable us to examine in some detail the dependence of metal-ligand bonding upon the nature of the ligands L.

TABLE 4

BOND LENGTHS (Å) AND COUPLING CONSTANTS (Hz) in cis-[$PtCl_2(PEt_3)L$] COMPLEXES

L	Pt-P	Pt-Cl (cis to L)	Pt-Cl (trans to L)	^1J (Pt-PEt_3)	Ref.
Cl^-	2.215(4)	2.382(4)	2.301(3)[a]	3704	6
$C(NPhCH_2)_2$	2.234(3)	2.381(3)	2.362(3)	3720[b]	8
CNPh	2.238(8)	2.365(11)	2.333(12)	3049[c]	9
C(OEt)NHPh	2.239(8)	2.367(7)	2.361(5)	-	7
PEt_3	2.259(2)[a]	2.361(6)[a]	2.361(6)[a]	3515[d]	10
CO	2.265(3)	2.368(3)	2.296(4)	2754[c]	This work
$P(OPh)_3$	2.269(1)	2.355(2)	2.344(2)	3210[d]	12
PF_3	2.272(3)	2.357(3)	2.305(3)	2760	11

[a] Mean value. [b] Ref. 16. [c] Ref. 9. [d] Ref. 17.

The Pt-Cl(trans to L) bond lengths in Table 4 display a variation of about 0.07Å and increase along the series $CO \simeq Cl^- \simeq PF_3 < CNPh \leq P(OPh)_3 < PEt_3 \simeq C(OEt)NHPh \simeq C(NPhCH_2)_2$. This series reflects the increasing σ-basicity and decreasing π-acidity of the ligands and it is therefore compatible with current views on the trans-influence of ligands in transition metal complexes [1,18,19]

The platinum-ligand bonds cis to L are also affected by the nature of L. The Pt-P distances vary by about 0.06Å, almost as much as the Pt-Cl(trans to L) distances. The variation in Pt-Cl(cis to L) distances is smaller, ca. 0.03Å, but still statistically significant. In addition, we note that the

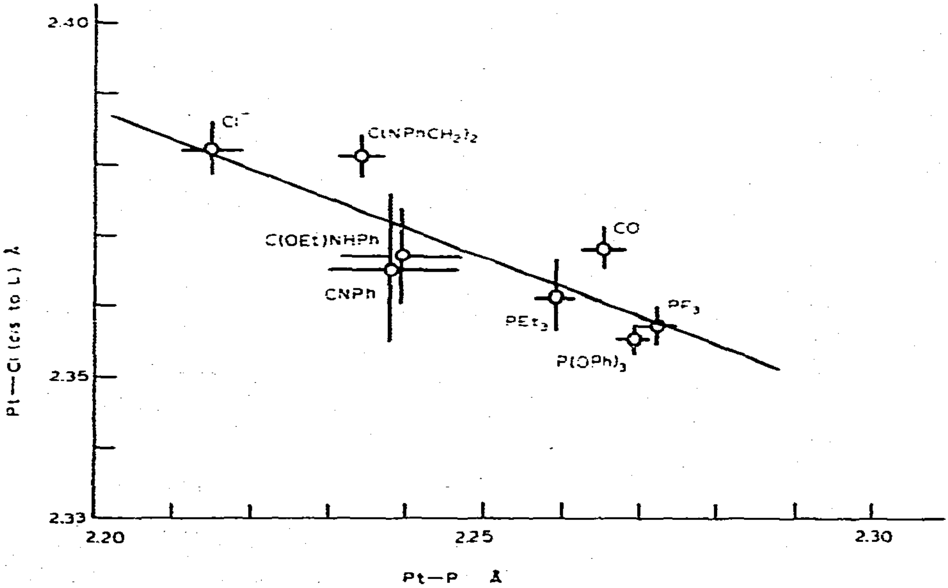

Figure 2. A plot of Pt-Cl(cis to L) versus Pt-P bond lengths in cis-$[PtCl_2(PEt_3)L]$ complexes (see Table 4). The ligands L and the unweighted least-squares trend line are shown. The errors indicated are standard deviations.

Pt-Cl(cis to L) distances display a consistent trend, illustrated in Figure 2: they decrease as the Pt-P distances increase (linear correlation coefficient -0.9).

Considering the cis-influence of ligands as their ability to weaken the cis-metal-ligand bonds, it is obvious that in cis-$[PtCl_2(PEt_3)L]$ complexes the ligands L can be arranged in a cis-influence series on the basis of either the Pt-P or Pt-Cl(cis to L) bond lengths. The Pt-P distances, which display greater variability, increase along the series $Cl^- < C(NPhCH_2)_2 \simeq CNPh \simeq C(OEt)NHPh < PEt_3 \simeq CO \simeq P(OPh)_3 \simeq PF_3$. This, of course, is approximately a reversal of the series of increasing Pt-Cl(cis to L) distances.

The cis-influence of ligands L may arise either from their steric or electronic properties, or perhaps from a combination of both. It is now recognised that in severely overcrowded platinum(II) complexes the steric repulsions between ligands can lead to considerable lengthening of Pt-P bonds. Thus in trans-$[PtI_2\{P(C_6H_{11})_3\}_2]$ [20] the Pt-P bonds are about 0.06Å longer than in trans-$[PtBr_2(PEt_3)_2]$ [21], and this is attributed mainly to the change in steric demands of the ligands in the two complexes. In the less crowded cis-$[PtCl_2(PEt_3)L]$ molecules discussed here the steric interactions of ligands are expected to be considerably weaker. To what extent, if at all, they affect the length of the Pt-P bonds is difficult to establish, since the force constants required for molecular mechanics calculations are not known. In this predicament we note that the observed cis-influence series bears little relationship to the size of ligands L, as measured, in the absence of a less crude estimate, by Tolman's cone angle (95,102,104,130 and 132° for CO, Cl^-, PF_3, $P(OPh)_3$ and PEt_3, respectively) [22]. Ligands of similar size, such as Cl^-, CO and PF_3, occur at opposite ends of the series, while ligands of different size, such as CO, PF_3, $P(OPh)_3$ and PEt_3, exert similar *cis*-influences. Furthermore, on steric grounds one might expect both bonds *cis* to L to lengthen as L becomes larger, thus leading to a positive correlation between the Pt-P and Pt-Cl(*cis* to L) distances. The observed correlation is, however, negative. We therefore consider that the steric properties of L are at most a minor factor in determining their position in the *cis*-influence series and, consequently, that the *cis*-influence of L is predominantly an electronic effect.

Another important observation emerges from the bond length data in Table 4: *cis*- and *trans*-influence of L are not related to each other, for the Pt-P and Pt-Cl(*cis* to L) distances show no correlation with the Pt-Cl(*trans* to L) distances. This indicates that *cis*- and *trans*-influence are transmitted through different electronic mechanisms in the molecular framework. Current theories emphasize that only those ligands which are strong σ-bases exert high *trans*-influence [1,18,19]. From the observed *trans*-influence series of ligands L, PEt_3 is expected to be a stronger base than Cl^-, $P(OPh)_3$, or PF_3. The same relative basicities of the three phosphorus-donor ligands are evident from i.r. and u.v. spectroscopic data [22]. The ordering of Cl^-, PEt_3, $P(OPh)_3$, and PF_3 in the *cis*-influence series is then obviously not related to their σ-basicities. This is consistent with Syrkin's theory [23], which considers that interactions between mutually *cis* σ-bonds are of minor importance, and which has been followed in most subsequent discussions of *trans*-influence of ligands. Zumdahl and Drago however have predicted, on the basis of extended Hückel molecular orbital calculations, that *cis*- and *trans*-influence transmitted through σ-bonds are of comparable magnitude [24].

The $^1J(Pt-PEt_3)$ coupling constants, which are thought to measure the *s*-component of the Pt-P σ-bond [25], display a range of _ca_. 1000 Hz in _cis_-[$PtCl_2(PEt_3)L$] complexes (Table 4). However, they show only an indifferent correlation with the Pt-P bond lengths, which reflect the overall Pt-P bond order. In the complexes with L = PEt_3 and CO, the Pt-P bond lengths are equal to within experimental error despite a difference in the coupling constants of 761 Hz. It therefore appears that, although both the overall and _s_-electron Pt-P bond orders are sensitive to the nature of the _cis_-ligand, there is no simple correspondence between the two quantities.

In the _cis_-influence series of L the ordering of ligands shows an obvious tendency: ligands which are considered to be strong π-acids, notably CO and PF_3, occur at the upper end of the series, while weak π-acids, such as Cl^- and carbenoid, occur at the lower end of the series. We therefore suggest that the _cis_-influence of L may reflect its π-acceptor properties. The lengthening of the Pt-P bonds can then be rationalized on the basis of an increasing competition between the L and PEt_3 ligands for the metal atom d_π-electrons. A necessary assumption here is that the PEt_3 ligand is a π-acid, albeit a weak one. The Pt-Cl(_cis_ to L) bond lengths may also be directly affected by the ligands L, increased Pt→L backdonation leading to enhanced electrostatic attraction between platinum and the chloride ligand. Alternatively, it may be considered that the ligand L influences the _cis_-Pt-Cl bond only indirectly, by modifying the _trans_-influence of the phosphine.

In conclusion we note that the Pt-P bond is more sensitive to the nature of the _cis_-ligands than the Pt-Cl bond. It then follows that platinum-phosphorus bond lengths, coupling constants or stretching frequencies will provide a valid measure of _trans_-influence of ligands only if in the complexes compared the ligands _cis_ to phosphorus are always the same. This precaution is less important if Pt-Cl bond parameters are used as a measure of _trans_-influence.

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References

1 T.G. Appleton, H.C. Clark and L.E. Manzer, Coordin. Chem. Rev., 10(1973) 335, and references therein.

2 Lj. Manojlović-Muir, K.W. Muir and R. Walker, J. Organometal. Chem., 66(1974) C21.

3 Lj. Manojlović-Muir, K.W. Muir and R. Walker, Acta Crystallogr., 31(1975) S145.

4 Lj. Manojlović-Muir, K.W. Muir and R. Walker, J. Chem. Soc. Dalton, (1976) 1279.

5 D.R. Russell, P.A. Tucker and S. Wilson, J. Organometal. Chem., 104(1976) 387.

6 G.W. Bushnell, A. Pidcock and M.A.R. Smith, J. Chem. Soc. Dalton, (1975) 572.

7 E.M. Badley, K.W. Muir and G.A. Sim, J. Chem. Soc. Dalton, (1976) 1930.

8 Lj. Manojlović-Muir and K.W. Muir, J. Chem. Soc. Dalton, (1974) 2427.

9 E.M. Badley, Ph.D. Thesis, University of Sussex, 1969.

10 Lj. Manojlović-Muir, K.W. Muir and T. Solomun, to be published.

11 P.B. Hitchcock, B. Jacobson and A. Pidcock, personal communication.

12 A.N. Caldwell, Lj. Manojlović-Muir and K.W. Muir, J. Chem. Soc. Dalton, in the press.

13 Lj. Manojlović-Muir, J. Chem. Soc.(A) (1971) 2796; K.W. Muir, J. Chem. Soc.(A), 1971(2663).

14 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, Great Britain, 1974.

15 M.A. Bush, A.D.U. Hardy, Lj. Manojlović-Muir and G.A. Sim, J. Chem. Soc.(A), (1971) 1003.

16 D.J. Cardin, B. Cetinkaya and M.F. Lappert, J. Organometal. Chem., 72(1974) 139.

17 G. Anderson, R.J. Cross and D.S. Rycroft, personal communication.

18 R. McWeeny, R. Mason and A.D.C. Towl, Discuss. Faraday Soc., 47(1969) 20; R. Mason and A.D.C. Towl, J. Chem. Soc.(A), (1970) 1601.

19 Lj. Manojlović-Muir and K.W. Muir, Inorg. Chim. Acta, 10(1974) 47.

20 N.A. Alcock and P.G. Leviston, J. Chem. Soc. Dalton, (1974) 1834.

21 G.G. Messmer and E.L. Amma, Inorg. Chem., 5(1966) 1775.

22 C.A. Tolman, Chem. Rev., 77(1977) 313.

23 Y.K. Syrkin, Bull. Acad. Sci. U.S.S.R., (1948) 69.

24 S.S. Zumdahl and R.S. Drago, J. Amer. Chem. Soc., 90(1968) 6669.

25 A. Pidcock, R.E. Richards, and L.M. Venanzi, J. Chem. Soc.(A),(1966) 1707; G.G. Mather, A. Pidcock and G.J.N. Rapsey, J. Chem. Soc. Dalton, (1973) 2095.