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PRELIMINARY COMMUNICATION

A *cis*-INFLUENCE IN SQUARE-PLANAR PALLADIUM AND PLATINUM COMPLEXES

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The *trans*-effect of ligands (their ability to promote the substitution reactions of the group *trans* to themselves in square-planar and octahedral complexes) is observed to increase in the following order[1-3]:

$$NH_3 \sim RNH_2 < py < R_3As < R_3P \qquad (1)$$

for a few ligands of present interest. Their ability to weaken the *trans* bond in the ground state of the molecule, which has been termed[4] their *trans*-influence, generally follows the same trend. Methods which have been used to monitor the *trans*-influence of ligands include observation of the stretching frequencies of the *trans* metal—ligand bond, ^{195}Pt—^{31}P spin—spin coupling constants, and chemical shifts of ^{1}H, ^{19}F and ^{31}P atoms in *trans* ligands[1-5].

These quantities vary, to a smaller extent, also according to the nature of the *cis* ligand. However, the smallness of the IR frequency shifts and uncertainty about the relation of the NMR parameters to bond strength have prevented characterization of the *cis*-influence of ligands (*i.e.* their ability to weaken the *cis* bond in the ground state of the molecule). We report that the ^{35}Cl nuclear quadrupole resonance (NQR) frequency ν_Q of a coordinated chlorine group is sensitive to the nature of *cis* ligands, and can provide a measure of their *cis*-influence.

The ^{35}Cl NQR frequencies observed for some square-planar d^8 *trans*-L_2MCl_2 complexes (M = Pd^{II} Pt^{II}) are given in Table 1. The strengths of the signals are shown as varying from very weak (vw), meaning just detectable above the background noise, through weak (w) to medium (m), meaning a signal-to-noise ratio of 8/1 with 3 g of sample and a 10 sec recording time-constant. The number of signals observed is expected to be the same as the number of chlorine atoms in the asymmetric unit of the crystallographic cell. For *trans*-$(NH_3)_2PtCl_2$, *trans*-$(Et_3P)_2PtCl_2$ and $(PhCN)_2PdCl_2$, there is one chlorine atom per asymmetric unit, and only one NQR signal appears in each case.

According to the semi-empirical treatment of Townes and Dailey[6], the covalent character σ of the metal–chlorine σ-bond is given by the approximate expression[7]:

$$e^2Qq_{\text{mol}}/e^2Qq_{\text{at}} = (1-s)\sigma-\tfrac{1}{2}\pi \qquad (2)$$

where e^2Qq_{mol} is the Quadrupole Coupling Constant for the chlorine atom in the free molecule, and e^2Qq_{at} that for the free chlorine atom. s is the degree of s-hybridisation of the chlorine σ-bonding orbital, and π is the degree of π-character of the metal–chlorine bond, as defined in ref. 7. The ionic character of the bond is $1-\sigma-\pi$. Only one experimental quantity is available, the NQR frequency, so we reduce the number of unknowns by making the following assumptions: (a) the M–Cl π-bond character is small (since all M and Cl π orbitals are filled) and may be neglected, *i.e.* $\pi = 0$; (b) in consequence of (a), the asymmetry parameter η is close to zero, so e^2Qq_{mol}/h may be replaced by $2\nu_Q$ (see eqn. 10 of ref. 7); (c) eqn. (2) for the free molecule may be applied to the molecule in the crystal; in fact, crystal splitting of up to 2% in the value of ν_Q is observed (see Table 1), so this assumption may be rather severe.

Substituting the value $e^2Qq_{\text{at}}/h = 109.7$ MHz[8] for ^{35}Cl then reduces eqn. (2) to:

$$\nu_Q = \tfrac{1}{2}(109.7)\,(1-s)\sigma \text{ MHz} \qquad (3)$$

We must now ask ourselves to what extent the observed changes in ν_Q are to be apportioned between changes in s and σ. According to Bersohn and Shulman[9], s is small in transition metal chloro compounds, and is much less than the value $s = 0.15$ predicted by Townes and Dailey's rule[6]. Further, s is unlikely to change appreciably among the compounds here considered, in view of their similar electronic structure and stereochemistry. Yet ν_Q varies by up to 25% (see Table 1). Consequently we feel it is reasonable to set s to some arbitrary low value, and to attribute the observed changes in ν_Q among these compounds principally to variations in σ. For simplicity we put $s = 0$. Values for σ derived on this basis, using the mean ^{35}Cl NQR frequency at 0°, are given in Table 1. The ionic character of the bond, and hence the negative charge on the chlorine, is $(1-\sigma)$, since π is taken as zero. (In comparing values in Table 1 with those for the isoleptic complexes studied by Kubo, Nakamura and coworkers[7], it should be remembered that they took $s = 0.15$).

Because of the number of assumptions made, the values given in Table 1 for the covaiency and the negative charge on the chlorine atoms can be regarded as only approximate, but conclusions based on comparisons within a series should still be valid. From Table 1 it is seen that the M–Cl bond is progressively weakened in *trans*-L_2MCl_2 compounds as the *cis* ligand L is changed from left to right in the following order:

For M = Pd^{II} L = PhCN, EtCN, n-Bu_3P, n-Bu_3As, py, piperidine (4)
For M = Pt^{II} L = n-Bu_3P, py, $(CH_3)_2NH$, NH_3

Thus the *cis* influence of these ligands increases from left to right.

This weakening of the M–Cl bond in the ground state appears to assist nucleophilic substitution reactions of the chlorine, for the rate of replacement of chlorine in *trans*-L_2PtCl_2 by weak nucleophiles has been observed[10] to increase in the similar order:

$$L = Et_3P < Et_3As < py < \text{piperidine}. \qquad (5)$$

TABLE 1

^{35}Cl NQR FREQUENCIES OBSERVED FOR SOME SQUARE-PLANAR d^8 *trans*-L_2MCl_2 COMPLEXES

trans-Compound	^{35}Cl NQR frequencies in MHz at 0° [a]	Covalency of M–Cl bond, σ	Charge on chlorine atoms $-(1-\sigma)$
(piperidine)$_2$PdCl$_2$	16.11 w 16.31 w	0.30	-0.70
py$_2$PdCl$_2$	17.72 m [b]	0.32	-0.68
(n-Bu$_3$As)$_2$PdCl$_2$	18.23 w 18.59 vw	0.33_5	-0.66_5
(n-Bu$_3$P)$_2$PdCl$_2$	18.37 w 18.50 w		
	18.58 w 18.63 w	0.34	-0.66
(EtCN)$_2$PdCl$_2$	20.30 w	0.37	-0.63
(PhCN)$_2$PdCl$_2$	20.58 w	0.38	-0.62
(NH$_3$)$_2$PtCl$_2$	17.30 w	0.32	-0.68
[(CH$_3$)$_2$NH]$_2$PtCl$_2$	18.16 w	0.33	-0.67
Py$_2$PtCl$_2$	19.63 m	0.36	-0.64
(n-Bu$_3$P)$_2$PtCl$_2$	20.90 w		
	21.04 w (doublet)	0.38	-0.62
	21.08 w		
(Et$_3$P)$_2$PtCl$_2$	20.99 m [b]	0.38	-0.62

[a] Measurements on Decca NQR spectrometer; quench sidebands were suppressed, and frequencies are reliable to ± 0.01 MHz. [b] The ^{37}Cl resonances (vw) have been detected at frequencies which, multiplied by the usual factor 1.269, coincide with the ^{35}Cl frequencies given.

For replacement by strong nucleophiles this order is not preserved. This supports the postulate[11] that the transition state for weak nucleophilic attack involves considerable Pt–Cl bond dissociation (reaction profile (a) of ref. 11), whereas for strong nucleophilic attack passage to the transition state entails little dissociation of the Pt–Cl bond (reaction profile (b) of ref. 11).

A significant feature of the above orders of *cis*-influence (4), and of *cis*-effect for weak nucleophiles (5), is that they are virtually the reverse of the order of *trans*-influence and *trans*-effect given in (1). One possible explanation for this is that the π-acceptor abilities of the ligands in series (1) increase from left to right, resulting in an increased *trans*-effect in the same order[2], whereas the total charge donated by ligands (σ donation less π withdrawal) increases from left to right in series (4) and (5), allowing the *cis*-M–Cl bond to become increasingly polarised. A second explanation is that ligands which weaken the *trans* bond simultaneously strengthen the *cis* bond. An effect of this type is predicted by Syrkin's theory[12] of *trans* influence, and has been observed[13] in a comparison of the force constants of the Pt–Cl bonds in the $[COPtCl_3]^-$ and $[NH_3PtCl_3]^-$ ions, though it did not emerge in a recent MO treatment of *trans* influence[5]. Further work is in hand to determine the validity of these explanations.

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