Correlation of Chlorine-35 Nuclear Quadrupole Resonance Frequencies with Platinum–Chlorine Bond-lengths in Platinum(II) Complexes

By C. W. FRYER

(*Imperial Chemical Industries Ltd., Petrochemical and Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire*)

Summary A comparison of *cis* and *trans* influences by ligands on the chlorine-35 n.q.r. frequency and the Pt–Cl bond-length in Pt^{II} complexes provides support for the σ-bonding mechanism of *trans* influence suggested by Syrkin.

THE chlorine-35 n.q.r. frequencies $^{35}\nu$ of chlorine ligands in some square-planar complexes of Ni^{II}, Pd^{II}, and Pt^{II} have recently been reported.[1–4] The purpose of this communication is to compare available values of the Pt–Cl bond-length in Pt^{II} complexes with $^{35}\nu$ values, and to draw conclusions about the mechanism of the *cis* and *trans* influence of ligands (*i.e.* their ground-state labilizing influence on *cis* and *trans* bonds).

In Figures 1 and 2, $^{35}\nu$ values at 0° are plotted against the Pt–Cl bond-lengths r obtained from recent accurate X-ray structure determinations. The full circles apply to the compounds in Section I of the Key, for which both $^{35}\nu$ and r values are available. The open circles represent less reliable correlations, for which $^{35}\nu$ applies to the compound given first in Section II of the Key, and r to the structurally similar compound given second. An uncertainty in the bond-lengths of two standard deviations is shown in the Figures. The three points at lowest frequency in Figure 2 apply to chlorines in asymmetric bridges; the length of the shorter, stronger bond has then been taken. For compounds c, d, f, and g, the two or three observed frequencies have had to be assigned to particular chlorines. Following the general pattern, the lower $^{35}\nu$ values have been assigned to the longer Pt–Cl bonds.

In Figure 1, the *trans*-ligand is specified against each point. For the points in Figure 2, the *trans*-ligand is the same in each case, namely chlorine. These points have been put in a separate Figure for the sake of clarity, and their general trend, given as a line in Figure 2, is reproduced as a broken line in Figure 1. The main observations to be made from these Figures are:

(i) there is a general tendency for $^{35}\nu$ to decrease as r increases,

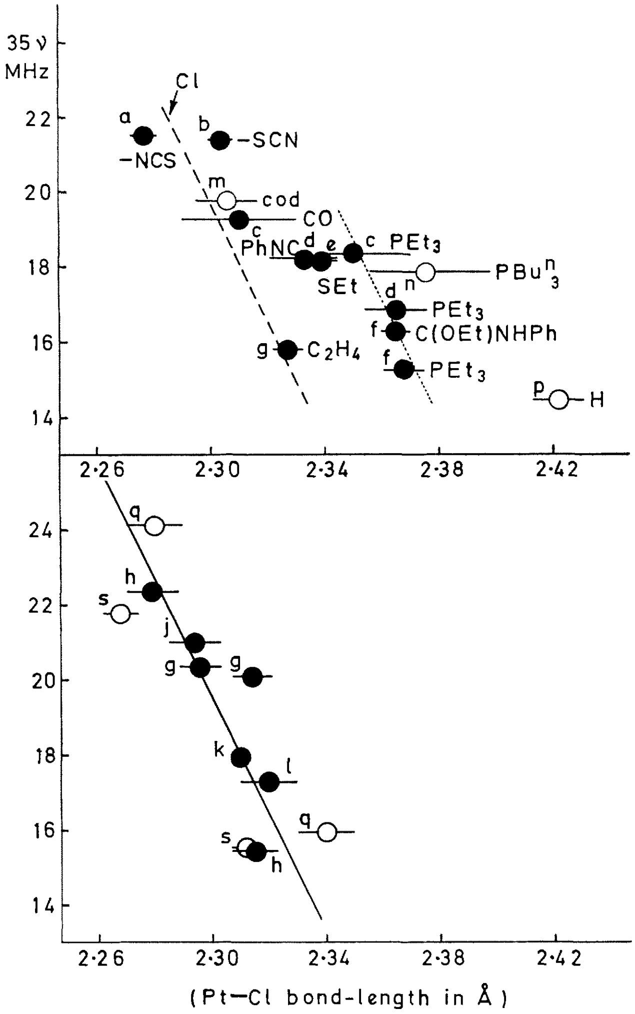
(ii) for a given range of $^{35}\nu$ values, the spread of r values is much greater when the *trans*-ligands are changed (as in Figure 1) than when the *cis*-ligands are changed (as in Figure 2),

(iii) if the *trans*-ligand is kept constant, as in Figure 2, the decrease in $^{35}\nu$ with increase in r is quite well represented by a straight line.

Observation (i) shows that the principal factor determining $^{35}\nu$ for a chlorine bonded to $\mathrm{Pt^{II}}$ is the Pt–Cl σ-bond order. Variation of the other factors that influence $^{35}\nu$ according to the Townes–Dailey theory,[5] namely Pt←Cl($3p$) or Pt→Cl($3d$) π-bonding, or hybridization of the $3s$ with the $3p_\sigma$ orbital, would produce the opposite result to that of observation (i). Consequently there is no evidence that *cis* or *trans* influences operate *via* a π-component of the Pt–Cl bond. A σ-bond mechanism of *cis* and *trans* influence is hence indicated, such as that suggested by Syrkin,[6] or Langford and Gray.[7,8]

From the conclusion of the previous paragraph, observation (ii) is seen to signify that a greater increase in r is obtained by changing the *trans*- than the *cis*-ligands even when the same reduction in Pt–Cl σ-bond order occurs. Langford and Gray's mechanism does not account for this, but an explanation can be provided in terms of Syrkin's theory. As a ligand forms a progressively stronger link to $\mathrm{Pt^{II}}$, the Pt employs a hybrid orbital of greater $6p_\sigma$ and lesser $5d_\sigma$ and $6s$ character for the *trans*-bond, while the reverse applies to the *cis*-bonds. In consequence the increase in r brought about through inductive displacement of charge towards a chlorine on increasing the σ-donor ability of a ligand is augmented by an expansion of Pt covalent radius along the Pt–Cl bond when that ligand is *trans* to the chlorine, and conversely reduced by a contraction of Pt covalent radius when it is *cis*.

Observation (iii) enables *cis* and *trans* influences of ligands to be separated. If ligands have a similar *cis* influence irrespective of the nature of the *trans*-ligand, the variation of $^{35}\nu$ with r may be represented in Figure 1 by a series of lines parallel to that established for *trans*-chlorine (*i.e.* to the broken line), one for each *trans*-ligand, displaced further to the right the greater is the *trans* influence of the ligand. This prediction is confirmed by the three points available for a *trans*-$\mathrm{PEt_3}$ ligand, as shown by the dotted line. The further down the appropriate line that the point



FIGURES 1 (top) and 2 (bottom). *Variation of chlorine*-35 *n.q.r. frequency* $^{35}\nu$ *at* 0° *with* Pt–Cl *bond-length* r *in* $\mathrm{Pt^{II}}$ *complexes. Figure* 1, *chlorines* trans *to the ligand specified. Figure* 2, *chlorines* trans *to another chlorine ligand.*

KEY

Section I

a	β-$\mathrm{Pt_2Cl_2(SCN)_2(PPr^n_3)_2}$
b	α-$\mathrm{Pt_2Cl_2(SCN)_2(PPr^n_3)_2}$
c	*cis*-$\mathrm{PtCl_2(CO)(PEt_3)}$
d	*cis*-$\mathrm{PtCl_2(PhNC)(PEt_3)}$
e	*cis*-$\mathrm{Pt_2Cl_2(SEt)_2(PPr^n_3)_2}$
f	*cis*-$\mathrm{PtCl_2\{C(OEt)NHPh\}(PEt_3)}$
g	$\mathrm{K[PtCl_3(C_2H_4)]H_2O}$
h	*trans*-$\mathrm{Pt_2Cl_4(PPr^n_3)_2}$
j	*trans*-$\mathrm{PtCl_2(PEt_3)_2}$
k	$\mathrm{K_2PtCl_4}$
l	*trans*-$\mathrm{PtCl_2(NH_3)_2}$

Section II

m	$\mathrm{Pt(cyclo\text{-}octadiene)Cl_2}$; $\mathrm{C_{10}H_{14}O_3PtCl_2}$
n	*cis*-$\mathrm{PtCl_2(PBu^n_3)_2}$; *cis*-$\mathrm{PtCl_2(PMe_3)_2}$
p	*trans*-$\mathrm{PtHCl(PMe_2Ph)_2}$; *trans*-$\mathrm{PtHCl(PEtPh_2)_2}$
q	$\mathrm{Pt_2Cl_4(CH_3CH{=}CH_2)_2}$; $\mathrm{Pt_2Cl_4(Me_2C{=}C{=}CMe_2)_2}$
s	$\mathrm{Pt_2Cl_4(AsEt_3)_2}$; $\mathrm{Pt_2Cl_4(AsMe_3)_2}$

for a complex lies, the greater is the *cis* influence of the *cis*-ligands. From Figure 2 it appears that olefine, arsine, and phosphine ligands have a smaller *cis* influence than chlorine or ammine, in contrast to their greater *trans* influence, which is further evidence in favour of Syrkin's theory.

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