# $^{195}$Pt Chemical Shifts in Platinum(II) Complexes of π-Bonding Ligands

By W. McFARLANE

(*Chemistry Department, Sir John Cass College, Jewry Street, London, E.C.3*)

THE chemical shifts of the heavier elements are potentially valuable because their extension over a wide range can provide information about relatively small changes of environment. Previously, measurements have been difficult because of detection problems associated with low magnetogyric ratios, low abundances, and unfavourable relaxation times. However, the application of double resonance techniques can alleviate many of the difficulties.[1] We report here $^{195}$Pt ($I = \frac{1}{2}$, abundance = 34%) chemical shifts determined by this method in some square-planar complexes of platinum(II) containing phosphorus or chalcogen ligands.

Proton spectra were obtained on a Varian HA-100 instrument modified for heteronuclear double resonance,[2] using concentrated solutions of the complexes in methylene dichloride. Extended studies of solvent effects are not yet complete, but it appears that they are small compared with the total range of $^{195}$Pt chemical shifts observed. The precision of the measurements depends on the signal-to-noise ratio of the recorded proton line, and the complexity of the $^{195}$Pt spectrum; that attained in a favourable case can be judged from Figure 1.

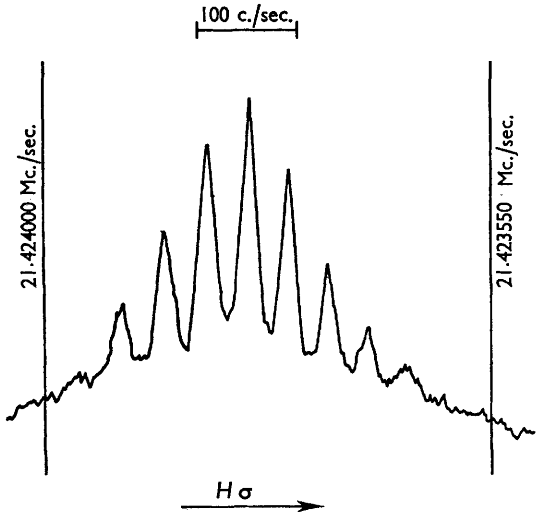

FIGURE 1. $^{195}$Pt *Inter-nuclear double resonance* (INDOR) *spectrum obtained by monitoring low-field satellite in the proton spectrum of* trans-$(Me_2S)_2PtCl_2$. (The frequencies are corrected to a field strength such that $Me_4Si$ would give a resonance at exactly 100 Mc./sec., and the assymmetry is due to the progressive-regressive character of the transitions involved.)

The $^{195}$Pt chemical shifts extend over a range of more than 1600 p.p.m. (Figure 2), which suggests that they are dominated by the paramagnetic shielding contribution. This view is supported by an apparent correlation between colour and chemical shift. The yellow complexes (*i.e.* those in which the energy separation, $\Delta E$, between the ground state and an excited level is relatively small) have low-field chemical shifts, whereas the colourless ones (with larger $\Delta E$) have high-field chemical shifts. The paramagnetic contribution to the shielding is inversely proportional[3] to $\Delta E$, so the changes are in the expected direction. A similar correlation has been noted for octahedral cobalt(III) complexes.[4]

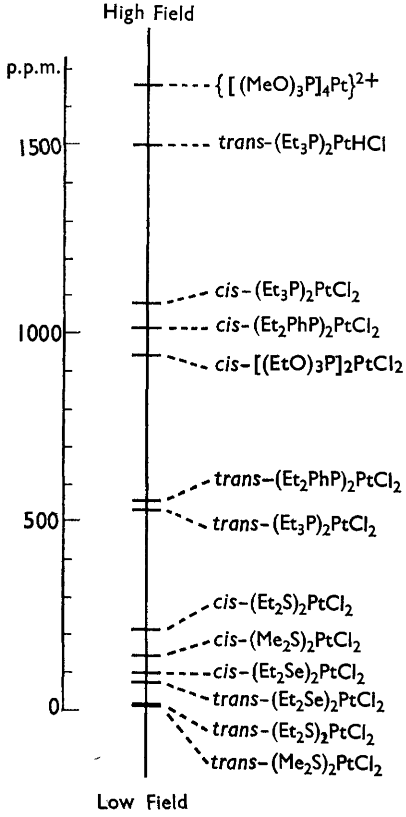

FIGURE 2. $^{195}$Pt *Chemical shifts in square-planar platinum complexes.*

The *trans*-effects[5] of the ligands used in the present study decrease in the order $(RO)_3P > R_3P > R_2S > R_2Se$, and it is evident that no precise correlation exists between this parameter and the $^{195}$Pt chemical shifts. However, it does appear that large differences between *cis*- and *trans*-isomers are found only when a ligand with a large *trans*-effect is involved. It is known[6] that Pt–P coupling constants in complexes of this type are not much affected by the nature of other non-$\pi$-bonding ligands attached to the platinum; the present figures for *trans*-$(Et_3P)_2$PtHCl show that this is not true of the $^{195}$Pt chemical shifts, and further studies to elucidate the factors involved are under way.

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