Ligand Exchange in Solutions of Complex Hydrides of Platinum(II)

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Summary Ligand exchange has been observed for the complexes *trans*-L_2PtHX in solution; line-width changes due to temperature and addition of free ligand L are reported.

BROAD hydridic resonances were initially reported by Chatt *et al.*[1] and Powell and Shaw[2] for complexes of the type *trans*-L_2PtHX where L = Et_3P, Et_3As and X = –NCS, –NCO. The n.m.r. spectra of these complexes indicated that isomers coexisted in solution. Both cyanate and thiocyanate are potentially ambidentate ligands. Powell and Shaw suggested quadrupole coupling with the ^{14}N nucleus in order to explain the broadness of the hydridic signals and also to allow the assignment of resonances to specific isomers. Other workers have accepted the concept of quadrupole broadening in the study of similar platinum complexes.[3] Recent work[4] has shown that the cyanate complexes exist as only one isomer, the *N*-bound form.

We report herein ligand exchange in solution which appears to be almost solely responsible for the observed broadening of the n.m.r. hydridic resonances of the complexes where L = Et_3P, $Bu^n{}_3P$, Ph_2EtP, Ph_3P, (*p*-tolyl)$_3$P, and Et_3As and X = – NCS and –NCO. This ligand exchange may also result in broadening when X = Cl. Br, I, CN, SCN, NO_2, and N_3.

The addition of tertiary phosphine to solutions of complex hydrides of platinum(II) containing the same phosphine results in dramatic changes in the line-widths of the hydridic resonances. *E.g.*, at 35 °C, the hydridic resonance of pure *trans*-$(Ph_3P)_2PtHCN$ in $CDCl_3$ consists of three broad resonances which do not exhibit any phosphorus–hydrogen coupling. The addition of an equimolar quantity of triphenylphosphine causes a half line-width change from 12 to 2 Hz. The addition of free $Bu^n{}_3P$ to *trans*-$[(Bu^n{}_3P)_2PtH(NCS)/(SCN)]$, results in collapse of all the triplets to singlets.

In general, hydridic resonance line-width changes are observed on the addition of any tertiary phosphine to these platinum complex hydrides in solution. The possible reactions are given in equations (1)—(3). Complexes of the type $[(Ph_3P)_2PtH]^+X^-$, where X^- = NO_3^-, Cl^-, ClO_4^-, and BF_4^-, have been characterised by Cariati *et al.*[5] and the similar triethylphosphine derivatives by Clark and Nixon.[6]

$$L_2PtHX + L' = LL'PtHX + L \qquad (1)$$

$$L_2PtHX = [LPtHX] + L \qquad (2)$$

$$L_2PtHX + L' = [L'L_2PtH]^+X^- \qquad (3)$$

On the addition of a large excess of tertiary phosphine to solutions of the platinum hydride complexes the usual set of hydridic n.m.r. resonances disappeared and a new set appeared which exhibited a *trans*-phosphorus–hydrogen coupling.[7] For instance, the addition of an excess of tri-n-butylphosphine to *trans*-$[(Bu^n{}_3P)_2PtH(CNS)/(SCN)]$ results in a doublet (*trans* $^2J_{P-H}$ 155 Hz) at τ 16·5 due to the hydridic protons attached to platinum atoms with zero spin and two doublets due to platinum atoms with spin $I = \frac{1}{2}$ (J_{Pt-H} 900 Hz). The n.m.r. spectrum of this complex reverts to that originally observed for *trans*-$[(Bu^n{}_3P)_2PtH(NCS)/(SCN)]$ on removal of tri-n-butylphosphine by vacuum distillation.

Mixing *trans*-$[(Ph_3P)_2PtH(NCS)/(SCN)]$ and *trans*-$[(Ph_2EtP)_2PtH(NCS)/(SCN)]$ in chloroform results in appearance of new hydride resonances which can only be attributed to a complex containing mixed tertiary phosphine ligand, *i.e.* *trans*-$[(Ph_3P)(Ph_2EtP)PtH(NCS)/(SCN)]$.

The effect of temperature on the n.m.r. spectra of complex hydrides of platinum is to alter the line-widths in the hydridic resonance region. For instance, the spectrum of pure *trans*-$(Ph_3P)_2PtHCN$ at 35 °C in $CDCl_3$ exhibits three broad resonances with no phosphorus–hydrogen coupling. However, on cooling the sample to −60 °C, a triplet is observed, J_{P-H} 13·7 Hz, $\omega_{\frac{1}{2}}$ 2 Hz. On raising the temperature to 110 °C, the broad hydridic resonances sharpen to $\omega_{\frac{1}{2}}$ 2 Hz.

It appears, from the temperature-dependent line-width changes and the phosphine-exchange broadening discussed above, that the use of quadrupole broadening to assign resonances to specific isomers of the thiocyanate platinum hydride complexes is not acceptable.

(*Received, October* 11*th*, 1971; *Com.* 1764.)

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