cis-trans Isomerisation and Ligand Exchange Reactions of an Isoquinoline–Platinum(II) Complex

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Summary The previous postulate[1] of a high-energy barrier to rotation about the Pt–N bond in *trans*-[$PtCl_2(C_2H_4)$(isoquinoline)] is shown to be incorrect.

It was recently proposed, on the basis of ^1H n.m.r. data, that *trans*-[$PtCl_2(C_2H_4)$(isoquinoline)] (I) exists in two forms.[1] In one the isoquinoline was postulated to be coplanar with the co-ordination plane with solvolysis of the isoquinoline ligand by $CDCl_3$ being fast on the n.m.r. time scale (no ^{195}Pt coupling to H^α or $H^{\alpha'}$ at room temperature).[1] In the other the plane of the isoquinoline ligand is vertical to the co-ordination plane with solvolysis being slow on the n.m.r. time scale (^{195}Pt–H^α and $H^{\alpha'}$ coupling in $CDCl_3$ at room temperature).[1] Since the interconversion of the two isomers takes *ca.* 3 days at room temperature,[1] the above postulate infers an unusually large energy barrier to rotation about the Pt–N bond. We here report studies of (I) that show the above proposals to be incorrect.

The ^1H n.m.r. spectrum of freshly prepared (I) in $CDCl_3$ at room temperature is shown in Figure (a). On standing for 24 h very broad ^{195}Pt satellites to H^α and $H^{\alpha'}$ are observed together with a new ethylene proton resonance of low intensity [see Figure (b)]. On further standing the ^{195}Pt satellite of H^α and $H^{\alpha'}$ sharpen and the new ethylene resonance grows to the equilibrium situation shown in Figure (c). The observation of a progressive change in the line shape of the ^{195}Pt satellites of H^α and $H^{\alpha'}$ indicates a gradual change in the rate of isoquinoline exchange for the complex molecules in solution. For the proposal of Orchin and Spaulding to be correct the ^{195}Pt satellites would have grown in intensity during the 3 days but would not have undergone changes in line shape. The new ethylene proton resonances [see Figure (c)] we assign to the second isomer which is not very soluble in $CDCl_3$. If a high initial concentration of (I) in $CDCl_3$ is used this second isomer precipitates from solution. Far i.r. studies show this isomer to be *cis*-[$PtCl_2(C_2H_4)$(isoquinoline)] (II) [ν_{Pt-Cl} (Nujol) 309, 294 cm^{-1}; *trans*-isomer (I) ν_{Pt-Cl} 345 cm^{-1}]. As previously reported[1] heating (I) converts it into (II).

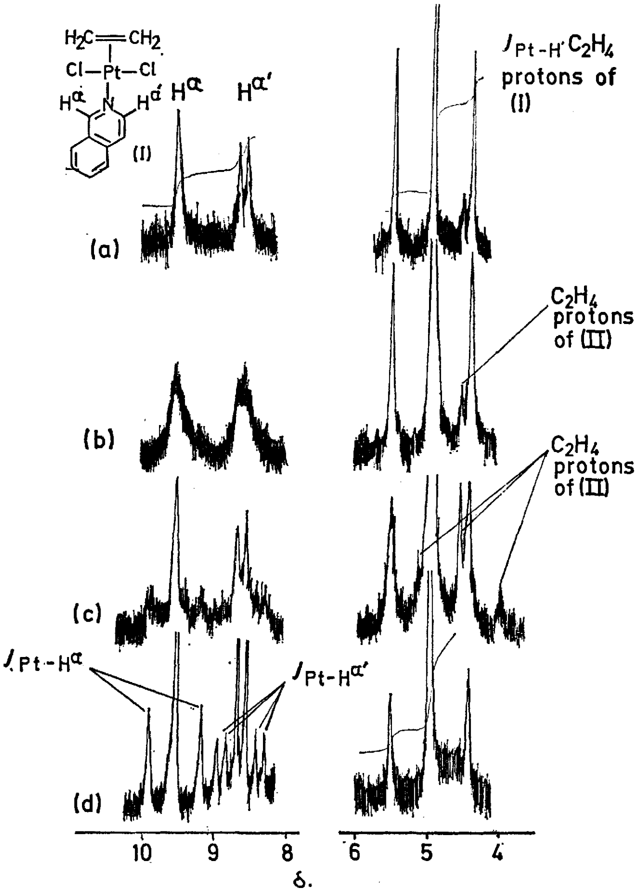

Figure. 60 MHz ^1H *N.m.r. spectra recorded at* 34° *in* $CDCl_3$: (a) *freshly prepared* (I) (0·2M); (b) *same solution after standing at* 20° *for* 24 h; (c) *same solution after standing at* 20° *for* ca. 3 *days*; (d) *freshly prepared* (I) *in the presence of a* 10% *molar quantity of* [$PtCl_2(C_2H_4)]_2$.

Formation of the *cis*-isomer (II) inhibits isoquinoline exchange in (I). The complex $[PtCl_2(C_2H_4)]_2$ is very effective in producing an immediate inhibition of isoquinoline exchange in (I)—see Figure (d). (^{195}Pt coupling to H^{α} and $H^{\alpha'}$ is clearly resolved indicating that isoquinoline exchange is slow on the n.m.r. time scale). Conversely the addition of isoquinoline to freshly prepared (I) in $CDCl_3$ at −60° induces collapse of the ^{195}Pt satellites of H^{α} and $H^{\alpha'}$. The addition of isoquinoline also increases the rate of isomerization of (I) into (II). These observations may be accounted for by the following scheme:

$$\mathit{trans}\text{-}PtCl_2(C_2H_4)L^* + S \rightleftharpoons \mathit{trans}\text{-}[PtCl_2(C_2H_4)S] + L^* \qquad (1)$$

$$\mathit{trans}\text{-}PtCl_2(C_2H_4)L + L^* \overset{\text{v. fast}}{\rightleftharpoons} \mathit{trans}\text{-}[PtCl_2(C_2H_4)L^*] + L \qquad (2)$$

$$\mathit{trans}\text{-}PtCl_2(C_2H_4)L + L \overset{\text{slow}}{\rightleftharpoons} \mathit{cis}\text{-}[PtCl_2(C_2H_4)L] + L \qquad (3)$$

$$\mathit{cis}\text{-}PtCl_2(C_2H_4)L + L \rightleftharpoons \mathit{cis}\text{-}[PtCl(C_2H_4)L_2]Cl \qquad (4)$$

SCHEME. L = isoquinoline; S = solvent.

Solvolysis of (I) (equation 1) generates a small amount of free isoquinoline. Loss of ^{195}Pt coupling to H^{α} and $H^{\alpha'}$ in freshly prepared $CDCl_3$ solutions of (I) is due to a fast S_N2 exchange of free and co-ordinated isoquinoline (equation 2). A slow isoquinoline catalysed isomerization of (I) into (II) (equation 3) introduces equilibrium (4) which has the effect of reducing the concentration of free isoquinoline in the system {Addition of $[PtCl_2(C_2H_4)]_2$ has the same effect as (4)}. This results in a decrease in the rate of isoquinoline exchange in (I) (equation 2) and thus accounts for the gradual resolution of the ^{195}Pt satellites of H^{α} and $H^{\alpha'}$. The formation of a new species containing two isoquinolines per Pt has been confirmed by n.m.r. studies of (I), in the presence of excess of isoquinoline, at −60° though a complete structural characterization of this species has not as yet been achieved. The equations (1)—(4) are similar to those proposed to account for PR_3 exchange and *cis–trans* isomerization of the complexes $[MCl_2(PR_3)_2]$ (M = Pt, Pd).[2,3]

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[3] D. G. Cooper and J. Powell, *Canad. J. Chem.*, 1973, **51**, 1634.