trans-Effect Order for Alkene, Alkyne, Phosphine, Arsine, Stibine, and Sulphide Ligands from Studies of Diethylamine Exchange Reactions of L,$PtCl_2$,[^{14}C]$NHEt_2$ in Various Solvents

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THE position of alkynes in the *trans*-effect series for platinum(II) complexes has not been reported, nor have the relative positions of substituted phosphines, arsines, and stibines been established.

We report the results of kinetic studies of diethylamine exchange reactions at 25° in complexes of the type *trans*-L,$PtCl_2$[^{14}C]$NHEt_2$ (L = ligand) in methanol (Figure 1), n-hexane (Figure 2), and benzene. The reaction products have been shown by spectra to be identical with the starting material.

The order of decreasing *trans*-effect for various ligands 'L' is now established as follows:

$C_2H_4 \sim Pr^iCH = CHMe \sim Me_2C(OH)C{\equiv}C{-}C(OH)Me_2 >> Et_3Sb > Ph_3Sb > Me_3P > Et_3P > Pr^n{}_3P > Ph_3P > Et_3As > Ph_3As >> Pr^n{}_2S$. The kinetic form for the exchange reactions is different in methanol to that found in the hydrocarbon solvents, suggesting that different mechanisms for exchange are operating.

In all solvents the reactions where L = alkene and alkyne were complete in less than 30 sec. and could not be followed by the reported method,[1] even at $-15°$. In methanol, no reaction was observed for three weeks for L = Pr^n_2S.

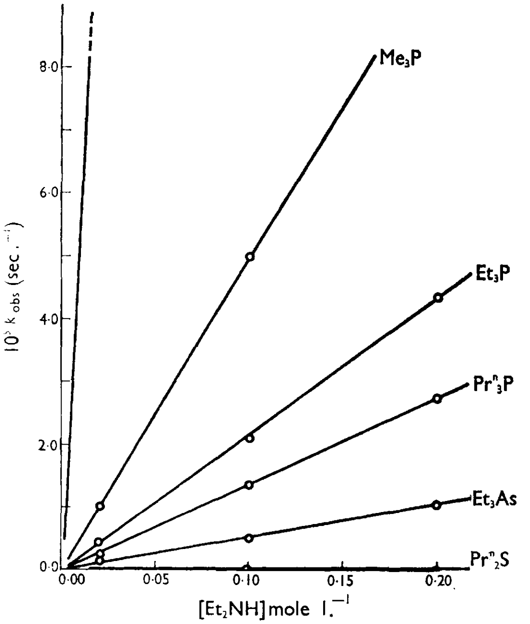

FIGURE 1. *Diethylamine exchange in* L,$PtCl_2$,[^{14}C]-$NHEt_2$ *in methanol at 25°.*

From our results we make the following observations:

(i) The alkyne ligand exhibits a very high *trans*-effect comparable to that for alkenes;

(ii) Substituted phosphines, arsines, and stibines may now be placed in decreasing order of *trans*-effect thus: $R_3Sb > R_3P > R_3As$ with $Et_3M > Ph_3M$ in each case;

(iii) All reactions of measurable rate in methanol (Figure 1) appear zero-order in reagent[1] whereas those in n-hexane (Figure 2) and benzene give rates which are first-order in ligand and have no reagent-independent contribution;[1]

(iv) The *trans*-effect order in methanol is thus obtained from k_{sol} values (a contribution to the rate attributed to the solvent) and the same order is obtained from studies in hydrocarbon solvents, where a different mechanism is operating, using the k_Y values (rate constant attributable to direct bimolecular attack by the nucleophile Y). Where L = Ph_3M, no n-hexane studies were possible because the complexes are too insoluble;

(v) Where L = Pr^n_2S, a slow exchange is observed in n-hexane in contrast to the behaviour in methanol;

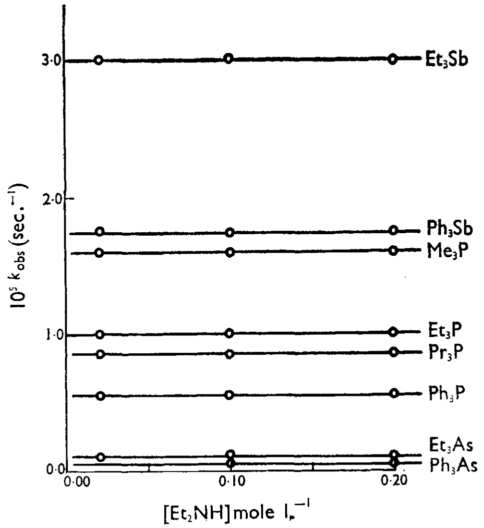

FIGURE 2. *Diethylamine exchange in* L,$PtCl_2$,[^{14}C]-$NHEt_2$ *in n-hexane at 25°.*

(vi) The order $Me_3P > Et_3P > Pr^n_3P$ agrees with that established from k_{sol} values found[2] for reactions of the bisphosphine complexes *cis*-$(R_3P)_2PtCl_2$ in ethanol although the rates in methanol in the present work are lower by a factor of *ca.* 10^3 (see ref. 1);

(vii) The ratio of k_{sol} values in methanol for L = Et_3M to those for L = Ph_3M is approximately constant at 1·8 : 1;

(viii) Rates of reactions in n-hexane are about four times faster than those in benzene;

(ix) All complexes, except where L = Pr^n_3P are new; details of their preparation and analysis will be published.

We suggest that the apparent absence of direct diethylamine attack in methanol is due in part to the complex adopting a pseudo-octahedral configuration[1,3] in the polar solvent and, in part, to the co-ordination of the smaller methanol molecule at the reaction centre, both of which effects will hinder the approach of the bulky solvated amine molecule.

Reactions in hydrocarbon solvents apparently involve direct attack by diethylamine which is now possible because solvation of both complex and reagent are now unimportant, and also because of the loss of the pseudo-octahedral configuration resulting from the greater affinity of the hydrocarbon chains of the complex for the nonpolar solvent. The observed zero value for k_{sol} indicates that a dissociative mechanism is not operating since the alternative explanation of solvent attack is improbable. The slower rates in benzene may be attributed to weak solvation effects.

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