Evidence of Trigonal Bipyramidal Transition State in Amine Substitution Reactions of R^1_3P,PtX_2,NHR^2_2 Complexes

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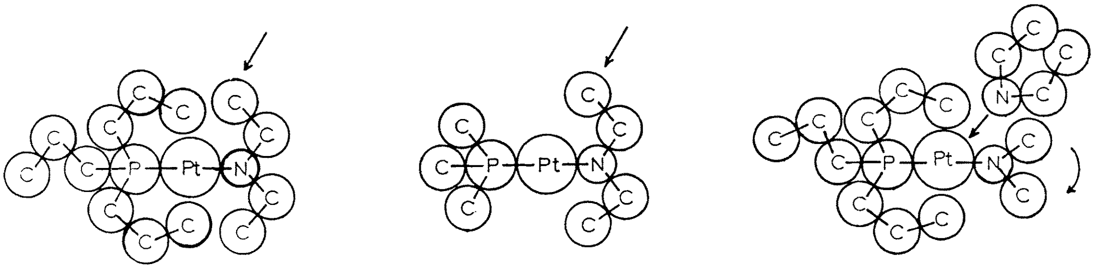
IT is generally accepted[1,2] that an associative mechanism operates in substitution reactions of Pt^{II} complexes. It is not, however, clear whether the five-co-ordinate transition state should be described as a trigonal bipyramid or a tetragonal pyrimid, although observations such as the trigonal bipyramidal structures[3] of stable five co-ordinate Pt^{II} complexes and the greater sensitivity of rate to *cis*-blocking as opposed to *trans*-blocking,[1,4] suggest that the former is more likely.

We report the results (Table) of further studies[5,6] of sterically hindered amine substitution reactions of the type $R^1_3P,PtX_2,[^{14}C]NHR^2_2 + R^3_2NH \rightleftharpoons R^1_3P,PtX_2,NHR^3_2 + [^{14}C]R^2_2NH$ in methanol and n-hexane at 25° in which it has been found that with shorter alkyl chains, R^2, of the co-ordinated amine molecule a significantly greater increase in the rate of substitution results than does a comparable, or even greater, reduction in the size of the phosphine chains, R^1.

This greater sensitivity of the rate of substitution to steric crowding in the vicinity of the leaving group indicates that amine attack occurs at an angle acute to the leaving group, which presumably then moves to a position below the square plane, and so results in the formation of a trigonal bipyramidal transition-state (Figure). On the contrary, attack perpendicular to the square plane which results in the formation of a tetragonal pyramid should show comparable susceptibility of rate to steric modifications on either side of the molecule. This behaviour is not observed.

The observed acceleration factor of 60, in n-hexane with



trans-$Pr_3{}^nP,PtCl_2,NHEt_2$ *trans*-$Me_3P,PtCl_2,NHEt_2$ *trans*-$Pr_3{}^nP,PtCl_2,NHMe_2$

FIGURE. *Diagram showing attack by* Et_2NH *at acute angle to the amine leaving group, viewed along the* Cl–Pt–Cl *axis with the hydro-carbon chains orientated so as to produce maximum steric hindrance.*

Rates of amine substitution reactions in methanol and n-hexane solvents at 25°

Pt^{II} complex	Reagent	$10^5 k_s$ (sec.$^{-1}$)[a]	$10^5 k_y$ (M^{-1} sec.$^{-1}$)[a]	Ratio k_s[a]	$10^4 k_y$ (M^{-1} sec.$^{-1}$)[b]	Ratio k_y[b]	E_{act} (kcal./mole)[d]	log A[b,d]
$Pr^n_3P, PtCl_2,NHEt_2$	Et_2NH[c]	0·86	0	1·0	1·4	1·0	15·2±0·3	6·35
$Et_3P,PtCl_2,NHEt_2$	Et_2NH[c]	1·01	0	1·25	2·1	1·5		
$Me_3P,PtCl_2,NHEt_2$	Et_2NH[c]	1·59	0	0·1	3·6	2·5	15·0±0·3	6·65
$Pr^n_3P,PtCl_2,NHMe_2$	Et_2NH	13·5	7·5	15·7	85	60·5	14·3±0·3	7·45
$Pr^n_3P,PtCl_2,NHEt_2$	Me_2NH	0·86	4	1·0	66	47		
$Pr^n_3P,PtI_2,NHEt_2$	Et_2NH	0·52	0	0·65	0·4	0·27	15·5±0·3	6·00
$Pr^n_3P,PtI_2,NHMe_2$	Et_2NH	10·8	2·5	12·8	23			

[a] Methanol results; [b] n-hexane results; [c] k_s, k_y values from data reported graphically in ref. 5; [d] log A values from rates measured at 25° for complex concentration of 5×10^{-3}M and reagent concentration of 0·1M.

shorter amine hydrocarbon chains is seen, from ΔE_{act} and log A values in the Table, to be due to a comparatively small activation-energy change (rate factor of 4) and a larger change in frequency factor (rate factor of 15). This data is consistent with the view that this acceleration is due largely to the removal of steric hindrance.

We also note that rates (k_y values) of direct substitution of co-ordinated Et_2NH by Me_2NH are similar to those for the reverse reaction, which further supports the postulate of the formation of a trigonal bipyramidal transitions state, in which it is considered that in this configuration the entering and leaving amine groups occupy similar positions.[2]

The expected small *cis*-effects are observed in the cases of isomeric di-iodo-complexes.

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