Steric Influences in Amine Substitution Reactions of *trans*-Dichloro(diethylamine)(tri-n-propylphosphino)platinum(II) in Methanol

By A. L. ODELL* and H. A. RAETHEL

(*Urey Radiochemical Laboratory, Chemistry Department, University of Auckland, Auckland, New Zealand*)

NUCLEOPHILIC substitution reactions of Pt^{II} complexes in solution generally take place according to a two-term rate law[1] in which the first-order rate constant k_{obs} is given by

$$k_{obs} = k_S + k_Y[Y]$$

The rate constant k_S is attributed to a solvent contribution to the rate and k_Y to direct bimolecular attack by the nucleophile, Y.

We report the results of amine substitution reactions,

$$trans\text{-}(Pr^n{}_3P)PtCl_2(NH[^{14}C]Et_2) + \text{amine} \rightleftharpoons$$
$$trans\text{-}(Pr^n{}_3P)PtCl_2(\text{amine}) + [^{14}C]Et_2NH \quad (1)$$

in methanol at 25°, in which the rates were followed by measuring the loss of ^{14}C-activity from the complex. The free amine and solvent were separated by vacuum transfer. Quantitative studies indicate that no side reactions take place.

The results are shown in the Figure and from these we note the following:—

(i) The values of k_S and k_Y are both depressed by a factor of *ca.* 1000 compared with amine attack on other Pt^{II}-complexes containing $Pr^n{}_3P$ *trans* to the leaving group;[2] *e.g.* pyridine attack on *cis*-$(Pr^n{}_3P)_2PtCl_2$ in EtOH has k_S $0{\cdot}83 \times 10^{-2}$ sec.$^{-1}$ (*cf.* $0{\cdot}86 \times 10^{-5}$, Figure) while k_Y is $1{\cdot}66$ mole.$^{-1}$ l.sec.$^{-1}$ (*cf.* $0{\cdot}63 \times 10^{-3}$). This suggests that the attack on $(Pr^n{}_3P)PtCl_2(NHEt_2)$ is highly sterically hindered. A molecular

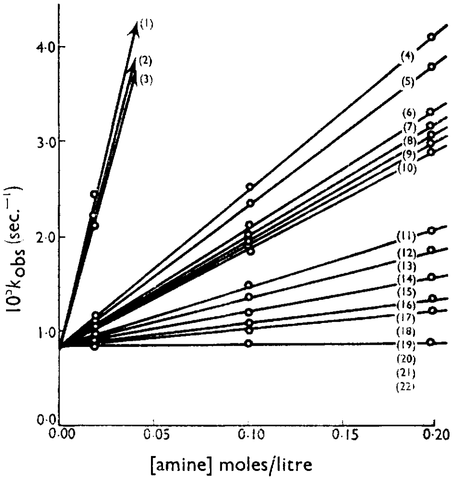

FIGURE. *trans*-$(Pr^n{}_3P)PtCl_2,(NHEt_2)$* + *amine in methanol at 25°. Amine reagents (those marked with asterisk react to give new compounds):* (1) 4-*methylpyridine;** (2) 3-*methylpyridine;** (3) *pyridine* (4) *methylamine;* (5) *aziridine;** (6) *ethylamine;* (7) *isobutylamine;** (8) *pyrrolidine;** (9) *n-butylamine;** (10) ***ammonia;*** (11) *isopropylamine;** (12) *s-butylamine;** (13) 2-*methylpyridine;** (14) *piperidine;* (15) *dimethylamine;* (16) 2,4,6-*trimethylpyridine;** (17) *t-butylamine;** (18) *diethylamine;* (19) *di-isobutylamines;** (20) (21) *di-isobutylamine;** (22) 2,4,6-*trimethylpiperidine.**

model of the complex clearly shows that the hydrocarbon chains from both the phosphine and amine can fold inwards above and below the square plane so as to block the 5th and 6th positions completely. Such complexes have been called[3] "pseudo-octahedral".

(ii) k_S Has the same value for all reagents.

(iii) The magnitude of k_Y for a series of aliphatic amines appears to be determined by the effective size of the entering amine molecule and shows no correlation with the base strength. Thus primary amines react faster than secondary amines and in those cases where the size of the amine molecule is large, *e.g.* Et_2NH or $Bu^s{}_2NH$, the path represented by the term $k_Y[Y]$ has been eliminated in contrast to the behaviour reported[4] for reactions

$$Pt(bipy)Cl_2 + amine \rightleftharpoons Pt(bipy)Cl(amine)^+ + Cl^- \qquad (2)$$

in methanol at 25° where the complex is not sterically hindered.

(iv) Tertiary amines give no measureable reaction, *e.g.* with Me_3N, Et_3N, and quinuclidine, even with a one hundred-fold excess of amine. Complexes containing these tertiary amines were prepared in good yield by the reaction[5]

$$(Pr^n{}_3P)_2Pt_2Cl_3 + 2R_3N \rightarrow 2\,(Pr^n{}_3P)PtCl_2(NR_3) \qquad (3)$$

in methanol, which demonstrates their stability. Studies of the reaction of Et_2NH with $(Pr^n{}_3P)PtCl_2(N[^{14}C]Et_3)$ in methanol at 25° show that it proceeds essentially to completion, indicating that lack of reaction with tertiary amines in reaction (1) is the result of an unfavourable equilibrium.

(v) Aromatic heterocyclic amines react significantly faster than their alicyclic amine analogues, which is in contrast with the behaviour reported[4] for reaction (2). Compounds not previously reported are formed by reaction (1) with several of the amines (Figure). These have also been synthesised by reaction (3).

(*Received, July 22nd*, 1968; *Com.* 976.)

---

[1] F. Basolo, "Mechanisms of Inorganic Reactions", ed. R. F. Gould, Advances in Chemistry Series 49, American Chemical Society, Washington, 1965, ch. 4.

[2] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

[3] C. H. Langford and H. B. Gray, "Ligand Substitution Processes", Benjamin Inc., New York 1965, ch. 2.

[4] L. Cattalini, A. Orio, and A. Doni, *Inorg. Chem.*, 1966, **5**, 1517.

[5] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 3858.