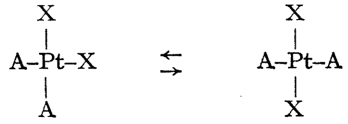
The Mechanism of Catalysed Isomerization of Tetragonal Planar Complexes

By PAUL HAAKE* and RICHARD M. PFEIFFER
(*Hall-Atwater Laboratories of Chemistry, Wesleyan University, Middletown, Connecticut,* 06457)

Summary The kinetics, activation parameters, solvent effects, and catalytic activities in the isomerization of *cis*-$[Pt(Bu^n{}_3P)_2Cl_2]$ indicate that the mechanism does not involve consecutive displacements; pseudorotation of a pentaco-ordinate intermediate should be considered.

THE *cis–trans*-isomerization of tetragonal planar complexes



(I) *cis* (II) *trans*

is an interesting topological conversion which is known to occur both photochemically[1] and thermally.[2] The photochemical process appears to proceed *via* a tetrahedral state.[1,3] The equilibrium studies of the thermal process[2] in benzene solution indicated *trans* predominance at equilibrium due to an increase in entropy over the *cis*-isomer in complexes with X = halogen and A = phosphine, stibine, or arsine. These thermal isomerizations were interpreted by a mechanism involving consecutive displacements:[4]

$$cis\text{-}PtA_2X_2 + A \rightarrow [PtA_3X]^+X^- \rightarrow trans\text{-}PtA_2X_2 + A.$$

A displacement mechanism has also been suggested for isomerization of palladium(II) complexes.[5]

We report here the first kinetic studies† of thermal, catalysed isomerization of platinum(II) complexes. Our results indicate that new ideas concerning the mechanism are required. In the isomerization of (I; A = $Bu^n{}_3P$, X = Cl) in cyclohexane, there is rapid isomerization in the presence of added $Bu^n{}_3P$, but in the absence of added $Bu^n{}_3P$ isomerization is immeasurably slow. Isomerization is first order in both *cis*-complex and $Bu^n{}_3P$; at 25°, $k_2 = 4{\cdot}49 \times 10\ \text{M}^{-1}\ \text{sec.}^{-1}$ (there is no solvent path[6]), $\Delta G^‡ = 13{\cdot}9$ kcal./mole, $\Delta H^‡ = 2{\cdot}9$ kcal./mole, and $\Delta S^‡ = -36{\cdot}9$ eu. The spectrum of the reaction mixture after 10 half-lives is identical to a spectrum of the *trans*-isomer indicating >99% *trans*-isomer at equilibrium. A good isosbestic point at 232 nm indicates that only isomerization is experimentally important.

The displacement mechanism requires formation of $[PtA_3X]^+X^-$ as an intermediate, and, therefore, solvents of higher polarity might be expected to accelerate isomerization. However, we find that the rate of isomerization is significantly reduced if small amounts of polar solvents, *e.g.*, $CHCl_3$, MeCN, or Et_2O are added to the cyclohexane used as solvent in our experiments. In contrast, the rates of displacement reactions of similar platinum(II) compounds increase in more polar solvents.[7] Also, the magnitude of the rate constant and the activation parameters observed here appear inconsistent with known data for displacement at platinum(II).[8] It therefore appears that a mechanism involving consecutive displacements is not a likely explanation for these platinum(II) isomerizations.

An alternative mechanism for isomerization involves pseudorotation of a pentaco-ordinate intermediate. Association ($PtA_2X_2 + A \rightleftarrows PtA_3X_2$) would explain the $\Delta S^‡$ barrier which we observe. By pseudorotations, the X–Pt–X angle of 90° in the *cis*-isomer could expand so that dissociation of PtA_3X_2 could produce *trans*-PtA_2X_2.

Holmes has estimated the barrier to pseudorotation of $SbCl_5$ to be accessible at room temperature.[9] According to the selection rules for isomerization of metal complexes formulated by Eaton,[10] pseudorotation of a trigonal bipyramidal d^8 species is thermally favoured. We are now testing this hypothesis for isomerization more extensively.

(*Received, July 21st,* 1969; *Com.* 1090.)

---

† Rates were evaluated by spectrophotometry. At 265 nm, the *trans*-isomer has ϵ_{max} 9850 and the *cis*-isomer ϵ_{max} 1990.

[1] P. Haake and T. A. Hylton, *J. Amer. Chem. Soc.*, 1962, **84**, 3774.
[2] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 1952, 273, 4300; 1953, 70; 1956, 525.
[3] P. Haake and S. H. Mastin, unpublished results.
[4] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1st edn., Wiley, New York, 1958, pp. 249—254; see also 2nd edn., pp. 423—427.
[5] L. Cattalini and M. Martelli, *J. Amer. Chem. Soc.*, 1969, **91**, 312.
[6] H. B. Gray and C. H. Langford, "Ligand Substitution Processes," Benjamin, New York, 1965.
[7] U. Belluco, M. Martelli, and A. Orio, *Inorg. Chem.*, 1966, **5**, 582.
[8] U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, 1966, **5**, 1123.
[9] R. R. Holmes and R. M. Deiters, *Inorg. Chem.*, 1968, **7**, 2229.
[10] D. R. Eaton, *J. Amer. Chem. Soc.*, 1968, **90**, 4272.