dicted for methanolysis of a B_9H_{15} hydride. Direct determination of the molecular weight of the new hydride proved impossible owing to its low thermal stability. To demonstrate that the hydride retained the nine boron unit of the initial salt, a toluene solution of the hydride was allowed to decompose in the presence of a large excess of acetonitrile, and a quantitative yield of $B_9H_{13} \cdot CH_3CN$ was recovered from the reaction mixture. The product was identified by comparison of its X-ray powder pattern with that calculated for the compound from the single crystal data of Wang, et al.[2]

The [11]B n.m.r. spectrum was recorded using a Varian DP60 nuclear magnetic resonance spectrometer operating at 19.3 Mc./sec. Throughout the determination of the spectrum the sample was maintained between -40 and $-60°$ using standard Varian accessories. The spectrum was substantially simpler than that of the previously isolated B_9H_{15}.[3] The spectrum consisted of a very broad low-field doublet ($\delta = 5$ p.p.m., $J = 136$ c.p.s.) and two overlapping high-field doublets ($\delta = 31$ p.p.m., $J = 163$ c.p.s.; $\delta = 44$ p.p.m., $J = 163$ c.p.s.). The integrated ratio of the high-field doublets to the low-field doublet was only 1.9, compared to the expected value of 2.0, but was somewhat uncertain owing to the extreme broadness of the downfield doublet. This spectrum strongly suggests a structure with approximate C_{3v} symmetry derived by removal of a triangle of borons from an icosahedron.

Only for the case of $B_{16}H_{22}$ has isomerism previously been observed in the binary boron hydride series. No sound theoretical reasons exist for the lack of a more general series of isomers, although considerable differences in stability may be expected. It is interesting to note that the rearrangement from the unstable iso form to the more stable normal form does not occur to a measurable extent. If the above structure is correct, migration of a boron atom would be required.

It should be noted that under very different conditions reaction of a $B_9H_{14}^-$ salt with polyphosphoric acid has been shown to form hexaborane(10).[4]

(2) F. E. Wang, P. G. Simpson, and W. N. Lipscomb, Jr., *J. Chem. Phys.*, **35**, 1335 (1961).

(3) A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

(4) H. A. Beall and W. N. Lipscomb, *ibid.*, **3**, 1783 (1964).

Jerry Dobson, Philip C. Keller, Riley Schaeffer

Department of Chemistry
Indiana University, Bloomington, Indiana
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Isotopic Exchange of a Hydridoplatinum(II) Complex with Deuterium Oxide

Sir:

We wish to describe a kinetic study of a novel substitution reaction of a square-planar complex, involving the isotopic exchange

$$trans\text{-}PtHCl(PEt_3)_2 + D_2O \longrightarrow trans\text{-}PtDCl(PEt_3)_2 + HDO \tag{1}$$
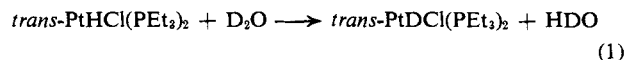
trans-PtHCl(PEt$_3$)$_2$ was prepared by the method of Chatt and Shaw[1] and its isotopic exchange with D_2O

(1) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 5075 (1962).

examined in D_2O–acetone solutions. The kinetic measurements were made by removing samples of the reaction mixture periodically, adding them to benzene containing an excess of ammonia to quench the reaction, freeze-drying the resulting mixture, and extracting the residual solid with benzene to dissolve the $PtHCl(PEt_3)_2$ and $PtDCl(PEt_3)_2$. The infrared spectrum of the benzene solution was recorded and the extent of isotopic exchange determined from the decrease in the absorbance of the Pt–H stretching band at 2196 cm.$^{-1}$, relative to the constant absorbance at 2876 cm.$^{-1}$ corresponding to one of the C–H stretching frequencies of the triethylphosphine which was unaffected by the exchange reaction. Using this procedure the kinetics of the exchange reaction were determined at 30° in D_2O–acetone solutions containing 25 and 10 vol. % D_2O. Among the kinetic variables examined were the effects of the concentrations of D^+ and Cl^-, each of which was varied from 0 to 6.4×10^{-3} M (using ClO_4^- and Li^+, respectively, to hold the ionic strength constant at 6.4×10^{-3} M).

Isotopic exchange, according to reaction 1, was found to be very slow (corresponding to a first-order rate constant of less than 10^{-5} sec.$^{-1}$) in the absence of added acid, but was accelerated by $DClO_4$ and, even more markedly, by DCl. The acceleration by DCl is in accord with the earlier qualitative observation of Chatt and Shaw.[1]

The rate law for the exchange reaction in 25% D_2O–75% acetone was found to be

$$-d[PtHCl(PEt_3)_2]/dt = (k_1 + k_2[Cl^-])[D^+][PtHCl(PEt_3)_2] \tag{2}$$

where $k_1 = 4.1 \times 10^{-2}$ M^{-1} sec.$^{-1}$ and $k_2 = 6.0$ M^{-2} sec.$^{-1}$.

The rates of both the Cl^--independent and Cl^--dependent paths exhibited an inverse dependence on the D_2O content of the solvent mixture, the effect being much greater for the latter path. On reducing the D_2O content to 10 vol. %, the rates of both paths remained first order in D^+, whereas the apparent kinetic dependence of the Cl^--dependent path on the Cl^- concentration became higher than first order. The empirical rate law under these conditions was found to be
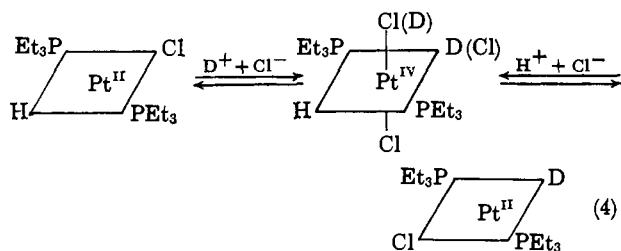
$$-d[PtHCl(PEt_3)_2]/dt = (k_1 + k_2'[Cl^-]^{1.4})[D^+][PtHCl(PEt_3)_2] \tag{3}$$

where $k_1 = 7.3 \times 10^{-2}$ M^{-1} sec.$^{-1}$ and $k_2' = 36$ $M^{-2.4}$ sec.$^{-1}$.

The acid catalysis of the exchange of *trans*-PtHCl(PEt$_3$)$_2$ with D_2O is somewhat unexpected in view of the generally accepted assignment of anionic character to the exchanging hydride ligand.[2] The most likely site of protonation of the complex is considered to be the platinum atom and, in line with this, the following mechanism involving reversible oxidation of the platinum(II) is proposed for the exchange path which is first order in both D^+ and Cl^-. The Cl^--independent path may be accounted for by an analogous mechanism involving a solvent molecule in place of the Cl^- ion.

The postulated intermediate of the mechanism depicted by eq. 4, which may have either a *cis* or *trans* configuration, was not detected under our conditions.

(2) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

$$\text{Et}_3\text{P}\underset{\text{H}}{\overset{\text{Cl}}{\diagup\hspace{-0.5em}\text{Pt}^{\text{II}}\hspace{-0.5em}\diagup}}\text{PEt}_3 \underset{\text{D}^+ + \text{Cl}^-}{\overset{\text{D}^+ + \text{Cl}^-}{\rightleftharpoons}} \text{Et}_3\text{P}\underset{\text{H}}{\overset{\text{Cl(D)}}{\diagup\hspace{-0.5em}\text{Pt}^{\text{IV}}\hspace{-0.5em}\diagup}}\text{PEt}_3 \underset{\text{H}^+ + \text{Cl}^-}{\overset{\text{H}^+ + \text{Cl}^-}{\rightleftharpoons}}$$

$$\text{Et}_3\text{P}\underset{\text{Cl}}{\overset{\text{D}}{\diagup\hspace{-0.5em}\text{Pt}^{\text{II}}\hspace{-0.5em}\diagup}}\text{PEt}_3 \quad (4)$$

Presumably it corresponds to the compound [PtH$_2$Cl$_2$-(PEt$_3$)$_2$], prepared by Chatt and Shaw[2] by passing dry HCl through an ether solution of *trans*-PtHCl(PEt$_3$)$_2$ and reported by them to decompose by loss of HCl to regenerate *trans*-PtHCl(PEt$_3$)$_2$ on heating or on treatment with water. We are presently attempting to prepare the isotopically substituted compound [Pt-HDCl$_2$(PEt$_3$)$_2$] by the corresponding reaction with DCl, to establish its structure, and to examine its decomposition.

No explanation is available for the apparently higher than first-order kinetic dependence of the Cl$^-$-dependent exchange path in solvents of low D$_2$O content. A difficulty connected with the interpretation of these results is that ionic dissociation is probably incomplete under these conditions so that the apparent kinetic dependence on the Cl$^-$ concentration may include the effects of ionic association equilibria (possibly involving HCl$_2^-$).

The above interpretation predicts that the Cl$^-$-catalyzed exchange between *trans*-PtHCl(PEt$_3$)$_2$ and D$_2$O should be accompanied by exchange of the Cl ligand of the complex with isotopically labeled Cl$^-$ in the solution. Experiments with ^{36}Cl$^-$ (designed to test this) revealed that, under the conditions of these experiments, chloride exchange occurs much more rapidly than hydrogen exchange, apparently by a direct mechanism which does not involve acid catalysis. This is consistent with earlier observations[3,4] that the chloride ligand of *trans*-PtHCl(PEt$_3$)$_2$ is rapidly substituted by pyridine in ethanol solution. The results of the chloride-exchange experiments are thus consistent with, but provide no supporting evidence for, the mechanism proposed for the hydride exchange.

(3) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961).
(4) C. D. Falk and J. Halpern, *J. Am. Chem. Soc.*, 87, 3003 (1965).

Charles D. Falk, Jack Halpern
Department of Chemistry, University of Chicago
Chicago, Illinois

Propagation Mechanism in Strong Base Initiated Polymerization of α-Amino Acid N-Carboxyanhydrides

Sir:

The mechanism in the strong base initiated polymerization of α-amino acid N-carboxyanhydrides (NCA's) has been the subject of much controversy.[1]

(1) C. H. Bamford and H. Block, "Polyamino Acids, Polypeptides

A plausible initial step for N-unsubstituted NCA's involving the removal of the N–H proton by the base to produce an N-carboxyanhydride anion (NCA$^-$) was proposed by Bamford[1] and established by Goodman and Arnon.[2]

Two propagating routes have been postulated. Bamford[1] contended that the NCA$^-$ ion attacks the carbonyl of an NCA molecule to create a dimer, I, terminated by a carbamate ion. This ion, he suggested, can remove a proton from another monomer molecule, recreating NCA$^-$, or it can abstract a proton from the protonated base (in the tertiary amine initiated case). Both possible reactions convert compound I to the corresponding carbamic acid which loses carbon dioxide to produce an amine-terminated dimer, II.

Bamford considered that this amine group could propagate by carbonyl attack on monomer molecules. Such a mechanism could not account for the observed high rate. However, he also proposed a possible propagating step in which the activated monomer (NCA$^-$) attacks the NCA terminal group of II, opening the ring and producing compound III. The resulting carbamate ion again reacts with NCA to create NCA$^-$ and carbon dioxide. Repetition of these rapid steps produces the polypeptide.

The alternative suggested by Blout[3] would simply have the carbamate ion I act as a nucleophile instead of a base. It attacks the NCA carbonyl to yield a mixed carboxylic–carbamic anhydride IV containing a carbamate ion at the chain end. Elimination of carbon dioxide is proposed to occur rapidly from such a mixed anhydride.

Work carried out by Goodman and Arnon[4] showed that polymerization initiated by sodium N-benzyl-carbamate gives identical kinetics with those of a strong base such as sodium methoxide. This appeared to support Blout's carbamate propagation route.

$$\text{RHC}\overset{\text{O}}{\underset{|}{\diagdown}}\text{C}\quad\text{I}$$
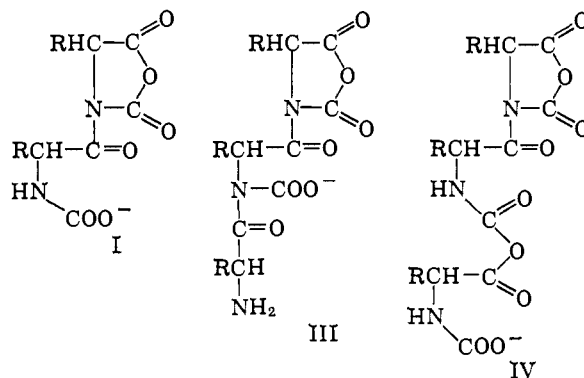
In order to distinguish between the Blout and Bamford proposals we extended the Goodman and Arnon carbamate experiments to include initiation by ^{14}C-labeled sodium N-benzylcarbamate. Blout's proposal would be established if the polymer contained all the radioactive initiator fragments. Recently, in an excellent review on the subject of NCA polymerization,[5]

and Proteins," M. A. Stahmann, Ed., University of Wisconsin Press, Madison, Wis., 1962, p. 65.
(2) M. Goodman and U. Arnon, *Biopolymers*, 1, 500 (1963).
(3) M. Idelson and E. R. Blout, *J. Am. Chem. Soc.*, 80, 2387 (1958).
(4) M. Goodman and U. Arnon, *ibid.*, 86, 3384 (1964).
(5) M. Szwarc, *Advan. Polymer Sci.*, 4, 1 (1965).