[Contribution from the Richardson Chemistry Laboratory of Tulane University]

The Factors Affecting the Directive Influence of the Nitro Group in the Nitro Complexes of Palladium(II). II. Dichlorodiaminepalladium(II) Complexes

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An investigation of the transelimination reactions of PdA_2Cl_2 with sodium nitrite to form the corresponding $PdA_2(NO_2)_2$, where A represents ethylamine, diethylamine and *n*-propylamine, is described. It has been shown that the basicity and the size of the amine affect this reaction very markedly. An explanation is offered for these observations in terms of previously postulated reaction mechanisms.

Introduction

As a result of the postulation of planar complex ions by Werner, geometrical isomerism offered an explanation for the different chemical and physical properties of the various platinum(II) and palladium(II) complexes. In an attempt to predict the formation of *cis–trans* isomers in planar complexes, Tschernaiev[1] formulated his rule of trans-elimination. Mann, *et al.*,[2] observed a reversal of Tschernaiev's rule in the formation of the dinitrodiamminepalladium(II) complex from the tetramminepalladium(II) ion.

As a result of a study of the factors contributing to the formation of the isomers of dinitrodiamminepalladium(II) from dichlorodiamminepalladium(II), Jonassen and Cull[3] postulated a reaction mechanism which was in harmony with Tschernaiev's rule of transelimination.

The purpose of this investigation was to determine the effect of varying the amine group on the formation of the *cis–trans* isomers of $[PdA_2(NO_2)_2]$ from the corresponding $[PdA_2Cl_2]$. A represents ethylamine, diethylamine, *n*-propylamine and hydroxylamine.

Experimental

A. **Reagents.**—The palladium(II) chloride used in the preparation of the complexes was prepared by the procedure outlined by Gutbier and Fellner.[4] All other reagents were of standard C.P. quality.

B. **Preparations.** 1. **Preparation of Dichlorodiethylaminepalladium**(II).—This procedure was a modification of Mann's preparation of $[Pd(NH_3)_2Cl_2]$.[5]

Palladium(II) chloride (3 g.) was placed in the thimble of a Soxhlet extractor and then 100 ml. of a 33% ethylamine solution added to the flask. The solution was refluxed on a steam-bath for 2 hr. Some color changes in the ethylamine was observed during refluxing which seemed to indicate that a slight decomposition of the amine was occurring. The solution was filtered while hot and the filtrate made just acid to litmus with 6 *M* hydrochloric acid. After standing for 20 min. the light yellow precipitate of dichlorodiethylaminepalladium(II) was removed from the mother liquor by filtration. The precipitate was then washed with two 10-ml. portions of water followed by 10 ml. of ethanol. The precipitate was dried for 2 hr. at 100–110°. The yield was about 90%. Analysis of $[Pd(C_2H_5NH_2)_2Cl_2]$: calcd. Pd, 39.8; found Pd, 39.9.

2. **Preparation of Dichlorobisdiethylaminepalladium**(II).—To 4.24 g. of $PdCl_2$ was added a solution of 30 ml. of diethylamine in 300 ml. of water. The solution was heated to boiling and filtered while hot. To the residue was added 100 ml. of water and 10 ml. of diethylamine. The resulting suspension was heated to boiling for 3 min. before filtering. The two filtrates were combined and made just acid to litmus with 6 *M* hydrochloric acid. A cream colored precipitate formed which was removed by filtration. It was washed with two 10-ml. portions of water followed by 10 ml. of ethanol. The crystals were dried at 100–110° for 2 hr. The yield was 65%. Analysis of $[Pd\{(C_2H_5)_2NH\}_2Cl_2]$: Calcd. Pd, 32.9; found Pd, 32.9.

3. **Preparation of Dichlorodi-*n*-propylaminepalladium** (II).—Using a modification of the Mann method,[2] $PdCl_2$ (8.40 g.) was added to a solution containing 30.7 ml. of *n*-propylamine in 120 ml. of water. The resulting solution was refluxed for about 3 hr. during which time it became black in color. The solution was filtered while hot and the filtrate made just acid to litmus with 6 *M* hydrochloric acid. After standing for 30 min. a dark yellow precipitate of dichlorodi-*n*-propylaminepalladium(II) settled from the solution. The yield was collected by filtration and washed with two 20-ml. portions of water followed by 20 ml. of ethanol. The crystals were dried in a desiccator over calcium chloride. The yield was about 54%. Analysis of $[Pd(n\text{-}C_3H_7NH_2)_2Cl_2]$: calcd. Pd, 36.0; found Pd, 36.2.

4. **Preparation of *cis*-Dinitrodiethylaminepalladium**(II).—Three grams of *cis*- or *trans*-$[Pd(C_2H_5NH_2)_2Cl_2]$ was dissolved in 35 ml. of a 33% ethylamine solution. The resulting solution was filtered and 20 ml. of a 4 *M* sodium nitrite solution was added. Upon standing in a desiccator over concentrated sulfuric acid at 10–12°, the first crop of crystals that formed had the *cis* configuration. These crystals were collected by filtration and washed with 10 ml. of water followed by 10 ml. of ethanol. Each precipitate was dried at 100–110°. The yield was only about 5%. Analysis of $[Pd(C_2H_5NH_2)_2(NO_2)_2]$: calcd. Pd, 36.9; found Pd, 36.8.

5. **Preparation of *trans*-Dinitrodiethylaminepalladium**(II).—The *trans* isomer was formed in the same manner as the *cis* complex with the exception that, after the addition of sodium nitrite, the resulting solution was placed in a desiccator over concentrated sulfuric acid at 35–40°. The yield was approximately 90%. Analysis of $[Pd(C_2H_5NH_2)_2(NO_2)_2]$: calcd. Pd, 36.9; found Pd, 36.7.

6. **Preparation of *trans*-Dinitrodi-*n*-propylaminepalladium**(II).—Five grams of *cis*- or *trans*-$[Pd(n\text{-}C_3H_7NH_2)_2Cl_2]$ was dissolved in 1.5 l. of 0.2 *M* *n*-propylamine. To this solution was added 50 ml. of 4 *M* sodium nitrite. The resulting solution was placed in a desiccator over concentrated sulfuric acid at room temperature (25–30°). Light yellow crystals formed from the solution after it had been standing for 30 days. The crystals were collected, washed with 15 ml. of ethanol and dried over calcium chloride. The yield was 50%. Analysis of $[Pd(n\text{-}C_3H_7NH_2)_2(NO_2)_2]$: calcd. Pd, 33.7; found Pd, 33.8.

It was observed that when a more concentrated solution of *n*-propylamine was used in this preparation, a white precipitate separated from the solution almost immediately. This precipitate was found to be tetra-*n*-propylaminepalladium(II) chloride. The yield of this salt increased greatly as the ratio of the concentration of Pd^{++} to the *n*-propylamine decreased. A yield of 60% of $[Pd(n\text{-}C_3H_7NH_2)_4Cl_2]$ was obtained when 3 g. of $[Pd(n\text{-}C_3H_7NH_2)_2Cl_2]$ was allowed to react with 30 ml. of *n*-propylamine in 15 ml. of water.

7. **Preparation of Dichlorodihydroxylaminepalladium**(II).—The dichlorodihydroxylaminepalladium(II) complex was prepared according to the procedure outlined by Goremykin.[5] Palladium(II) chloride (1.7 g.) was dissolved in 40 ml. of hot water. The solution was filtered to remove the undissolved $PdCl_2$. A solution of 1.7 g. of potassium chloride in 20 ml. of water was added to the filtrate. Ethanol

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(1) I. Tschernaiev, *Ann. inst. platine* (*U.R.S.S.*), **4**, 243 (1926).

(2) F. G. Mann, D. Crowfoot, D. C. Gattiker and N. Wooster, *J. Chem. Soc.*, 1642 (1935).

(3) H. B. Jonassen and N. L. Cull, This Journal, **73**, 274 (1951).

(4) A. Gutbier and C. Fellner, *Z. anorg. allgem. Chem.*, **95**, 129 (1916).

(5) V. I. Goremykin, *Compt. rend. acad. sci.* (*U.R.S.S.*), **32**, 633 (1941).

(250 ml.) was added to the solution and dark yellow crystals of potassium tetrachloropalladite precipitated. The crystals were collected and dissolved in a minimum amount of water (about 2 ml.). To the solution of K_2PdCl_4 20 ml. of a saturated solution of hydroxylamine hydrochloride was added. The resulting solution was then cooled in an ice-bath, and a strong solution of sodium hydroxide was added slowly until the solution was basic to litmus. The $[Pd(NH_2OH)_2(OH)_2]$ precipitated at this point. The crystals were filtered off and dissolved in a few ml. of dilute hydrochloric acid. When an excess of hydrochloric acid was added, $[Pd(NH_2OH)_2Cl_2]$ formed. The yellow precipitate was collected by filtration and washed with 20 ml. of ethanol followed by 20 ml. of diethyl ether. The crystals were stored in a desiccator over calcium chloride. The yield was about 30%. Analysis of $[Pd(NH_2OH)_2Cl_2]$: calcd. Pd, 44.0; found Pd, 44.0.

8. **Preparation of *trans*-Dinitrobisdiethylaminepalladium(II).**—To 4.60 g. of *cis*- or *trans*-$[Pd\{(C_2H_5)_2NH\}_2Cl_2]$ was added 330 ml. of water containing 32 ml. of diethylamine. The combined solutions were heated just to boiling and filtered while hot. When the filtrate cooled, a small precipitate of $[Pd\{(C_2H_5)_2NH\}_4]Cl_2$ appeared. This salt was removed by filtration, and to the filtrate was added a solution of 7.2 g. of sodium nitrite in 12 ml. of water. The resulting solution was placed in a desiccator over concentrated sulfuric acid at 35–40°. As crystals formed, they were removed by filtration, washed with two 10-ml. portions of ethanol followed by two 10-ml. portions of diethyl ether. The precipitate was dried over calcium chloride. The yield was about 60%. Analysis of $[Pd\{(C_2H_5)_2NH\}_2(NO_2)_2]$: calcd. Pd, 30.9; found Pd, 30.7.

9. **Attempted Study of the Reaction of Dichlorodihydroxylaminepalladium(II) with Sodium Nitrite.**—Pure hydroxylamine was prepared by the method outlined by Hurd and Brownstein.[6] The hydroxylamine was stored in a sealed bottle at −10° no longer than two days before use.

Dichlorodihydroxylaminepalladium(II) (2 g.) was added to about 5 ml. of water. To the partially dissolved complex was added a solution of 4 g. of hydroxylamine in 2 ml. of 4 *M* sodium nitrite. The resulting solution was diluted to 30 ml. with water. A dark gray precipitate formed immediately and was removed by filtration. The filtrate was placed in a desiccator over concentrated sulfuric acid at 10–12°. After 24 hr. a brownish-gray precipitate had formed but no constant analysis for Pd was obtained. The increasing dark color of the crystals indicated partial reduction of the palladium to the metallic state.

10. **Determination of the Solubility of the *trans* Forms of $[Pd(NH_3)_2(NO_2)_2]$, $[Pd(C_2H_5NH_2)_2(NO_2)_2]$, $[Pd\{(C_2H_5)_2NH\}_2(NO_2)_2]$ and $[Pd(C_3H_7NH_2)_2(NO_2)_2]$ in Water at 30°.**—Water solutions of the above *trans* complexes were saturated and brought to equilibrium at 30°. Three ml. of each solution was pipetted off into a crucible and analyzed for Pd. From the amount of Pd present the solubilities were calculated, which are shown in Table I.

TABLE I

SOLUBILITIES OF THE *trans*-DINITRO ISOMERS

Complex	Solubility In 1000 ml. of soln., *M*	 In 1000 ml. of soln., g.
$[Pd(NH_3)_2(NO_2)_2]$	1.4×10^{-2}	3.3
$[Pd(C_2H_5NH_2)_2(NO_2)_2]$	4.4×10^{-3}	1.3
$[Pd\{(C_2H_5)_2NH\}_2(NO_2)_2]$	1.06×10^{-3}	0.37
$[Pd(C_3H_7NH_2)_2(NO_2)_2]$	6.3×10^{-4}	0.2

C. **Tests Used to Differentiate between the *cis*- and *trans*-Dinitrodiaminepalladium(II) Isomers.**—The tests used to distinguish between the *cis*- and *trans*-dinitrodiaminepalladium(II) isomer were essentially the same as those employed by Mann[2] and Jonassen and Cull[3] for the dinitrodiamminepalladium(II) isomer.

A yellow precipitate of diiododiaminepalladium(II) was formed when an aqueous solution of either the *cis*- or *trans*-$[PdA_2(NO_2)_2]$ was treated with a saturated aqueous solution of KI (A = ammonia, ethylamine, *n*-propylamine or diethylamine). The solution above the precipitate turned red within an hour for the *trans* isomers. However, when the *cis*-dinitrodiamine or *cis*-dinitrodiethylamine palladium(II) was used in the reaction, the solution above the precipitate remained essentially colorless even after standing for two hours.

The ignition of samples of *cis*-dinitrodiamminepalladium(II)[3] and dinitrodiethylaminepalladium(II) resulted in an even decomposition leaving a dark gray, compact residue. All the *trans* complexes except the *trans*-*n*-propylamine isomer decomposed exothermically, and rather violently, leaving a gray, spongy deposit. The *trans*-dinitrodi-*n*-propylaminepalladium(II) isomer melted into a yellowish liquid which immediately decomposed with violence and caused excess spattering.

Both these tests were used in assigning the *cis* or *trans* configuration to each set of crystals.

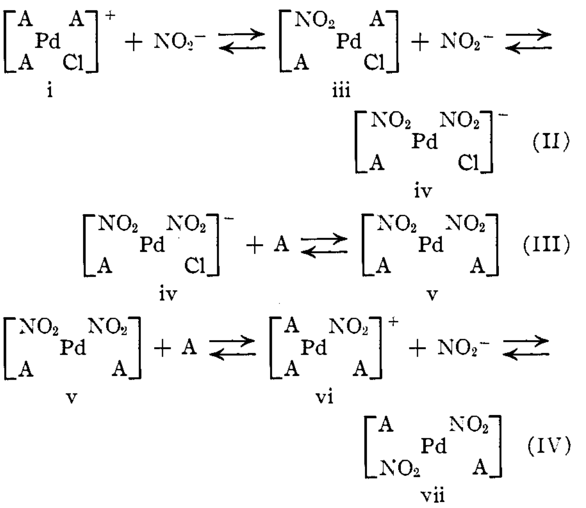
All attempts to characterize the *cis* and *trans* isomer of this series of palladium complexes by precipitation methods using thiourea or sodium oxalate have proven unsuccessful.[3]

Discussion

Reaction Mechanism.—From a consideration of the relative solubilities of the components present at equilibrium in the reaction mechanism postulated by Jonassen and Cull,[3] it was possible to explain qualitatively the results obtained in this investigation.

The reaction mechanism involves the steps (A represents ethylamine or *n*-propylamine)

$$[Pd(A)_2Cl_2] + A \rightleftharpoons \underset{i}{[PdA_3Cl]^+} + A \rightleftharpoons \underset{ii}{[PdA_4]^{++}} \qquad (I)$$



$$\underset{i}{\begin{bmatrix} A & & A \\ & Pd & \\ A & & Cl \end{bmatrix}^+} + NO_2^- \rightleftharpoons \underset{iii}{\begin{bmatrix} NO_2 & & A \\ & Pd & \\ A & & Cl \end{bmatrix}} + NO_2^- \rightleftharpoons \underset{iv}{\begin{bmatrix} NO_2 & & NO_2 \\ & Pd & \\ A & & Cl \end{bmatrix}^-} \qquad (II)$$

$$\underset{iv}{\begin{bmatrix} NO_2 & & NO_2 \\ & Pd & \\ A & & Cl \end{bmatrix}^-} + A \rightleftharpoons \underset{v}{\begin{bmatrix} NO_2 & & NO_2 \\ & Pd & \\ A & & A \end{bmatrix}} \qquad (III)$$

$$\underset{v}{\begin{bmatrix} NO_2 & & NO_2 \\ & Pd & \\ A & & A \end{bmatrix}} + A \rightleftharpoons \underset{vi}{\begin{bmatrix} A & & NO_2 \\ & Pd & \\ A & & A \end{bmatrix}^+} + NO_2^- \rightleftharpoons \underset{vii}{\begin{bmatrix} A & & NO_2 \\ & Pd & \\ NO_2 & & A \end{bmatrix}} \qquad (IV)$$

B. **Solubility Effects.**—As expected from solubility consideration, the amount of precipitation of the dinitrodiethylamine palladium(II) complex decreased with an increase in the temperature of the reaction (Table II).

However, in the reaction involving *n*-propylamine an increase in the amount $[Pd(n\text{-}C_3H_7NH_2)_2(NO_2)_2]$ was obtained with an increase in the temperature of the reaction. The extreme insolubility of tetra-*n*-propylaminepalladium(II) chloride demonstrated in preparation (5) is due to the larger organic component of the tetrammine ion. Since the salt of *n*-propylamine corresponding to (ii) precipitated, the concentration of soluble (i) was small, which in turn led to the formation of little of either the *cis*- or *trans*-dinitro isomers (v) or (vii), respectively. Consequently, any condition which increased the concentration of (ii), and hence (i), increased the tendency to form the $[Pd(n\text{-}C_3H_7NH_2]_2(NO_2)_2]$ complex.

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[6] C. Hurd and H. J. Brownstein, THIS JOURNAL, **47**, 67 (1925).

Table II

Amounts of *cis*- and *trans*-Dinitro Isomers Isolated in the Reaction of PdA_2Cl_2 with $NaNO_2$

These data were obtained by mixing the various components and allowing them to stand in a desiccator over concentrated sulfuric acid. The various fractions were collected as they precipitated at the various temperatures (see, for example, section B, preparation 4). The amounts listed are averages from several runs.

Temp., °C.	*cis*, %	*trans*, %	Transition *p*H
	A = ethylamine		
10–12	10.3	77.2	10.87
25–30	0.0	76.3	. . .
35–40	.0	74.1	. . .
	A = diethylamine		
10–12	.0	69.8	. . .
25–30	.0	64.0	. . .
35–40	.0	60.0	. . .
	A = *n*-propylamine		
10–12	.0	20.3	. . .
25–30	.0	50.2	. . .
35–40	.0	38.6	. . .
	A = ammonia[3]		
10–12	59.1	38.8	10.99
25–30	52.3	27.2	9.70
35–40	0.0	77.6	. . .

By increasing the temperature of the reaction, the solubility of (ii) was increased which led to a very noticeable increase in the formation of $[Pd(n\text{-}C_3H_7NH_2)_2(NO_2)_2]$ (Table II).

Although the solubility of the $[Pd(n\text{-}C_3H_7NH_2)_2(NO_2)_2]$ was also increased with an increase in the temperature of reaction, the increase in the solubility of (ii) was much greater. Since it is well known experimentally that the *cis* isomer is more soluble than the corresponding *trans* isomer, equilibrium IV is thus displaced toward the formation of the *trans* isomer (vii).

C. Effect of the Solubility of the *trans*-Dinitro Complexes.—The solubility of the *trans* complexes of the ammonia, the monoethylamine and diethylamine complexes are shown in Table I. These results explain the decrease in the amount of *cis* compound that is isolated from ammonia in comparison with the mono- and diethylamine. The greater insolubility of the mono- and diethylamine complexes drive the reaction toward the formation of the *trans* isomer and the amount of *cis* isolated decreases correspondingly, as can be seen from Table II at the various temperatures. Again the normal propylamine complex cannot be compared, since tetra-*n*-propylaminepalladium(II) chloride is so insoluble.

D. Effect of Change in the Basicity of the Basic Ionization Constants.—The basic ionization constants of diethylamine (1.26×10^{-3} at 25°) and ethylamine (5.6×10^{-4} at 25°) are larger than that of ammonia (1.8×10^{-5} at 25°). This may be the explanation for the higher transition *p*H in the formation of the *trans*-dinitro isomer as shown in reaction IV when the ammonia is compared with mono- and diethylamine.

Unfortunately, due to the insolubility of the tetra-*n*-propylaminepalladium(II) chloride no comparison can be made with this complex.

E. Effect of the Size of the Group Attached to the Nitrogen Donor Atom from Ammonia to Ethylamine to Diethylamine.—From steric considerations it becomes obvious that more and more strain is introduced in the *cis* complex as the groups attached to the nitrogen donor atom become larger. This will decrease the amount of the *cis* isomer which can be isolated (see Table II).

F. Results of the Study of the Reaction of Dichlorodihydroxylamine–Palladium(II) with Sodium Nitrite.—In the attempted study of the reaction of a hydroxylamine solution of $[Pd(NH_2OH)_2Cl_2]$ with sodium nitrite, reduction occurred at all temperatures (10–12°, 25–30° and 35–40°). No constant analysis for palladium on what was thought to be $[Pd(NH_2OH)_2(NO_2)_2]$ was obtained.

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