the other in the intermediate ion. This may occur intramolecularly or with the aid of the solvent; the present data give no means of distinguishing between the two. A similar problem has arisen previously in the mechanism of acetone exchange, which is both general acid and hydroxyl ion catalyzed.[6]

Summary

1. From experiments demonstrating that benzil exchanges with heavy oxygen water much more rapidly in alkaline than in neutral solution, it is concluded that the first step in the benzilic acid rearrangement is a rapid, reversible addition of hydroxyl ion to benzil, the rate-controlling step being rearrangement of the ion thus formed.

2. This mechanism is entirely consistent with organic evidence and with the theory of reactivity of organic compounds as a function of electron displacements developed by English workers.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Coördination Compounds of Palladous Chloride[1]

BY M. S. KHARASCH, R. C. SEYLER AND FRANK R. MAYO

Coördination compounds of ethylene derivatives with platinous chloride of the type $(Un\cdot PtCl_2)_2$, where Un represents an ethylene derivative, have been described by Anderson[2] and by Kharasch and Ashford.[3] Anderson prepared the compound of ethylene by refluxing ethylene with sodium chloroplatinate, and has recently succeeded in exchanging the bound ethylene for ethylene derivatives. Kharasch and Ashford prepared similar compounds by treating ethylene derivatives with platinic chloride. Their paper reviews briefly the previous work in the field and proposes a new structure for such compounds.

For reasons which will be discussed in a later publication, we became interested in ascertaining whether similar compounds with palladium are possible. Kondakov, Balǎs and Vít[4] claim to have prepared an addition compound of trimethylethylene and palladous chloride by allowing these substances to react in a sealed tube at room temperature in the presence of a trace of a basic substance. They consider the compound to have the formula $Un\cdot PdCl_2$.

Preparation of Palladous Chloride Compounds.—We were unable to obtain any compound of palladous chloride by direct interaction with the following unsaturated compounds: ethylene, isobutylene, cyclohexene, styrene, camphene. Numerous changes in procedure were of little avail. In some cases, the components were kept in a sealed tube for twenty-four hours. At all times a large excess of the unsaturated component was used. Neither acidic (hydrogen chloride) nor basic substances (pyridine, triethylamine) were effective in bringing about a combination. Solvents such as benzene, ether, and acetone did not appear to promote the reaction. Water was not used for it is claimed by Phillips[5] that in its presence palladous chloride is reduced to palladium by olefins.

It was quite obvious that a new approach to the problem was necessary. The preparative method indicated by the following equations was then found to be successful

$$PdCl_2 + 2C_6H_5CN \longrightarrow (C_6H_5CN)_2\cdot PdCl_2 \quad (1)$$

$$2(C_6H_5CN)_2\cdot PdCl_2 + 2Un \longrightarrow (Un\cdot PdCl_2)_2 + 4C_6H_5CN \quad (2)$$

The nitrile palladous chloride compounds are not described in the literature. For our study, we prepared the dibenzonitrile palladous chloride in 88–95% yield by heating palladous chloride in benzonitrile until solution took place. The method is the same as used by Kharasch and Ashford[6] to obtain the dibenzonitrile platinous chloride compound. Incidentally, this method of preparing the nitrile compounds of platinous chloride is superior to that of Hofmann and Bugge,[7] who treated benzonitrile in ether with an aqueous solution of potassium chloroplatinite

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[1] Abstracted from a dissertation submitted by Ralph C. Seyler to the Faculty of the Division of the Physical Sciences of the University of Chicago in 1937, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Anderson, *J. Chem. Soc.*, 971 (1934); 1042 (1936).

[3] Kharasch and Ashford, THIS JOURNAL, **58**, 1733 (1936).

[4] Kondakov, Balǎs and Vít, *Chem. Listy*, **23**, 579 (1929); **24**, 1, 26 (1930); *C. A.*, **24**, 3454 (1930).

[5] Phillips, *Am. Chem. J.*, **16**, 265 (1894).

[6] Kharasch and Ashford, unpublished work.

[7] Hofmann and Bugge, *Ber.*, **40**, 1772 (1907).

TABLE I

COMPOUNDS OF PALLADOUS CHLORIDE WITH OLEFINS AND BENZONITRILE

Olefin or nitrile	Color of compound	Formula of compound	Anal. for Pd[a] Calcd.	Anal. for Pd[a] Found	Stability
Cyclohexene	Light brown	$(C_6H_{10}PdCl_2)_2$	41.09	41.16	Stable 2–3 days in desiccator; dec. rapidly in acetone or alcohol
Styrene	Light red-brown	$(C_8H_8PdCl_2)_2$	37.88	36.76[b]	Like cyclohexene compound
Ethylene	Light canary-yellow	$(C_2H_4PdCl_2)_2$	51.88	51.28	Between cyclohexene and isobutylene compounds
			C, 11.66	11.69	
			H, 1.96	1.73	
Isobutylene	Brick-red	$(C_4H_8PdCl_2)_2$	45.66	45.56	Extremely unstable
Pinene	Complex obtained but not examined				
Camphene	Complex obtained but not examined				Decomposed on filter in 1–2 minutes
Dichloroethylene Stilbene Dipentene	Gave no isolable compounds				
Benzonitrile	Orange-yellow	$(C_7H_5N)_2PdCl_2$	27.81	27.65	Stable
			N, 7.38	7.11	

[a] Analyses for palladium are by ignition to the metal. [b] Low palladium content attributed to presence of styrene polymer.

for fourteen days at room temperature. Ramberg[8] shortened the time by employing a higher temperature (60°). The method of Kharasch and Ashford leads to practically quantitative yields in the course of a few minutes.

Strikingly enough the dibenzonitrile palladous chloride compound reacted very rapidly at room temperature with olefins to yield the desired derivatives. When a benzene solution of dibenzonitrile palladous chloride was treated with an excess of an olefin, a crystalline compound, $(Un{\cdot}PdCl_2)_2$, usually separated. For reasons mentioned in the experimental part, the displacement reaction is thought to take place quantitatively. However, the actual yields seldom exceeded 70% due to the experimental difficulties in the isolation of small quantities of materials. Table I is a summary of the analyses and some properties of the compounds prepared by us.

It is of interest to note that while the dibenzonitrile palladous chloride reacts with olefins to give compounds of the type $(Un{\cdot}PdCl_2)_2$, the nitrile platinous chloride compounds $(RCN)_2{\cdot}PtCl_2$ do not react with olefins. As a matter of fact the nitrile platinous chloride compounds can be formed from the olefin derivatives and a nitrile.

Properties of Palladous Chloride–Olefin Compounds.—All of the palladous chloride olefin compounds which we investigated were colored, rather insoluble in the common organic solvents, and unstable. Cyclohexene gave the most stable compound. While palladium analysis showed that the compound underwent little change during three days in a desiccator at atmospheric pressure, the palladium content had increased by 12–15% after three weeks. Most of the compounds were slightly soluble in benzene, chloroform and ether, insoluble in petroleum ether and acetic acid. All were less stable in solution than in the solid crystalline state and a limited number of observations indicates that some were less stable in acetone or alcohol solution (in which some were slightly soluble) than in the other solvents.

Because of the low stability and solubility of these substances in solution, precise determination of their molecular weights was very difficult. The most satisfactory results were obtained with the styrene compound. Determinations in benzene solution by the freezing-point method gave a value of 409, intermediate between 282 for the monomeric and 564 for the dimeric form of $C_8H_8{\cdot}PdCl_2$. We favor the dimeric formula, however, for the following reasons. (1) A substantial proportion of the compound decomposed with precipitation of palladium during the determination. Decomposition of the monomolecular form should give one molecule of hydrocarbon with no change in the apparent molecular weight while complete decomposition of the bimolecular form should give two molecules of hydrocarbon and an apparent molecular weight half that of the dimer. (2) By analogy with the platinum compounds we should expect the palladium compounds to have similar formulas. We therefore propose the following general formula for the compound of the ethylene derivative RCH=CHR' with palladous chloride

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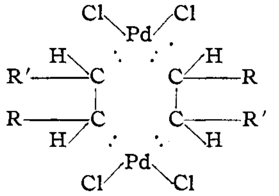
(8) Ramberg, *Ber.*, **40**, 2578 (1907).



This formula corresponds to that suggested by Kharasch and Ashford[3] for the platinum derivatives.

Since some compounds of palladium were more stable than others, it might be expected that an ethylene derivative forming a more stable compound would displace another olefin from its compound. Such is the case in solution. Cyclohexene formed the most stable compound and no other ethylene derivative was found to displace it. The derivative of ethylene underwent displacement with cyclohexene but was not affected by styrene. Styrene was displaced by either cyclohexene or ethylene. That the ethylene compound in the dry state is shown by Table I to be less stable than the styrene compound is probably due to the volatility of ethylene.

Experimental

Preparation of Palladous Chloride.—Palladium metal was purchased from the Thomas J. Dee Co. of Chicago. It contained 99.8% palladium and 0.2% gold and platinum. It was dissolved in aqua regia and converted to chloride by repeated evaporation with hydrochloric acid. The dark red palladous chloride was dried at 150–180° in a stream of dry chlorine. It was not deliquescent when free from nitrate.

Preparation of Dibenzonitrile Palladous Chloride.—About 2 g. of palladous chloride was dissolved in a minimum volume of benzonitrile, approximately 30 cc. being required at 100°. The solution was filtered and cooled, yielding a heavy precipitate. This was collected on a filter. More precipitate was obtained by diluting the filtrate with low-boiling petroleum ether. After thorough washing with the same solvent, the combined precipitates were dried over calcium chloride at 9–10 mm. for one hour. The yield was about 90%.

Preparation of Palladous Chloride–Olefin Compounds.—Most of the compounds were easily obtained by the following method. One-half gram of dibenzonitrile palladous chloride was dissolved in 10 cc. of benzene and the solution was filtered. An excess of the ethylene derivative was then added. Crystals of the ethylene derivatives precipitated rapidly and the quantity could be increased by dilution of the solution with petroleum ether. The product was collected on a filter, washed with petroleum ether, dried for about one hour over calcium chloride at 9–10 mm. and analyzed. Phosphorus pentoxide and sulfuric acid were not satisfactory as drying agents.

The ethylene compound was prepared by passing ethylene gas through a benzene solution of dibenzonitrile palladous chloride for one-half hour. Attempts to prepare the isobutylene compound by a similar method gave only negligible yields. The latter product was prepared by passing isobutylene into a chloroform suspension of dibenzonitrile palladous chloride at −78°.

It is our opinion that the reaction between the dibenzonitrile palladous chloride and an ethylene derivative goes practically to completion. Although the nitrile compound could be precipitated completely from the usual benzene solution by the addition of petroleum ether, none was precipitated in the presence of an excess of the ethylene derivative as demonstrated by the purity of the ethylene compounds. Because of the difficulties inherent in handling the small quantities of material involved, the usual yield of the ethylene compound was only 60–70% on the dibenzonitrile palladous chloride used.

Summary

1. Dibenzonitrile palladous chloride can be prepared in excellent yield by the direct action of benzonitrile on palladous chloride.

2. By the action of ethylene derivatives on dibenzonitrile palladous chloride, compounds containing one mole of ethylene, isobutylene, cyclohexene, or styrene per mole of palladous chloride have been obtained.

3. These complex ethylene derivatives are apparently bimolecular and a general structural formula for them has been proposed.

4. The stability of the palladous chloride–olefin compounds was found to decrease in the order cyclohexene, ethylene, styrene. An olefin forming a more stable compound was found to react with the less stable compound of another olefin to give a new compound and the other olefin.

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