[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TULANE UNIVERSITY]

Olefin Coördination Compounds. III. Coördination Compounds of Butadiene with Platinum(II), Palladium(II) and Copper(I) Halides[1]

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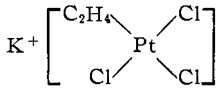
The complexes potassium sexachloro-μ-butadienediplatinum(II), 1,3-bis-(butadiene)-2,4-dichloro-μ-dichloroplatinum(II), tetrachloro-μ-bis-(butadiene)-dipalladium(II), dichloro-μ-butadienedicopper(I) and dibromo-μ-butadienedicopper(I) were prepared by treating liquid butadiene with various compounds of platinum(II), palladium(II) and copper(I). The complexes were thermally decomposed under vacuum to compare their relative stabilities. Infrared spectrograms indicate that 1,3-bis-(butadiene)-2,4-dichloro-μ-dichloroplatinum(II) has a chlorine bridged structure while in all other compounds butadiene is the bridge.

Coördination complexes of mono-olefin hydrocarbons with platinum(II), palladium(II) and copper(I)[2-11] as well as with other metallic salts,[12,13] have been studied with increasing interest during the past few years. Fewer reports are recorded, however, where a diolefin such as 1,3-butadiene[14,15] or similar compounds are used as complexing agents.

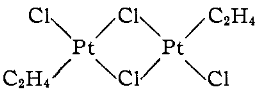
This study was undertaken in an effort to expand the knowledge of diolefin complexes and to attempt the preparation of compounds in which the olefinic bonds were coördinated to the metallic ion in a *cis* position.

A total of five complexes were prepared: $K_2(Pt_2Cl_6C_4H_6)$, potassium sexachloro-μ-butadienediplatinum(II); $(PtCl_2C_4H_6)_2$, 1,3-bis-(butadiene)-2,4-dichloro-μ-dichloroplatinum(II); $(PdCl_2C_4H_6)_2$, tetrachloro-μ-bis-(butadiene)-dipalladium(II); $(Cu_2Cl_2C_4H_6)$, dichloro-μ-butadienedicopper(I); $(Cu_2Br_2C_4H_6)$, dibromo-μ-butadienedicopper(I). Attempts to reproduce Hel'man's[14] butadiene platinous chloride dimer were unsuccessful; however, an isomer for which a chloride bridged structure is proposed has been isolated.

Several different types of inorganic complex ions can be prepared by treating a metallic salt with an unsaturated hydrocarbon. Ethylene, the primary member of the olefin series, can form either mononuclear units such as



or the dimer



The possibility of a structural isomer exists for the dimer when an aliphatic diolefin is used as the ligand. The bridging unit can then be either the chloride ion as in the ethylene dimer[16] or a hydrocarbon bridge involving both double bonds of the olefin.

The infrared spectrum of each complex is presented and an order of thermal stability is proposed.

Experimental[17]

A. **Preparation of Complexes.** 1. **Preparation of Potassium Sexachloro-μ-butadieneplatinum (II).**—One gram of dry K_2PtCl_4 was dissolved in 10 to 15 ml. of a 5% aqueous solution of HCl and placed in an atmosphere of butadiene under a pressure of about 100 cm. of mercury. The pressure gradually decreased to one atmosphere after a few hours and additional amounts of butadiene had to be added several times during the reaction.

After 1.5 to 2 days, the red solution had turned light yellow, indicating the completion of the reaction. Beautiful orange crystals of the complex were obtained by slow evaporation of the solution in a desiccator over KOH and $CaCl_2$. It was found that the *p*H of the solution had to be kept below 1 to prevent decomposition to metallic platinum. Yields were about 60% of the theoretical, based on K_2PtCl_4.

Anal. Calcd. for $K_2(Pt_2Cl_6C_4H_6)$: Pt, 53.1; Cl, 29.0. Found: Pt, 53.3; Cl, 30.2.

2. **Preparation of 1,3-Bis-(butadiene)-2,4-dichloro-μ-dichloroplatinum(II).**—About 0.5 g. of 1,3-bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum(II), prepared according to the method of Anderson,[2] was added to 10–15 ml. of liquid butadiene, obtained by the condensation of the gaseous hydrocarbon with a Dry Ice–trichloroethylene mixture. The reaction products were removed from the cold bath and warmed gradually to room temperature, allowing the excess diolefin to boil away. During this process, the orange ethylene complex changed to dark brick-red in color.

Anal. Calcd. for $(PtCl_2C_4H_6)_2$: Pt, 62.0; Cl, 22.2. Found: Pt, 61.4; Cl, 22.7.

This complex is not stable at room temperature. After one hour the color had changed to a very dark brown.

3. **Preparation of Dichloro- and Dibromo-μ-butadienedicopper (I).**—Two grams of anhydrous CuCl or CuBr was mixed with 10–15 ml. of liquid butadiene and the resultant mixture placed in an ice-salt bath at −10° for one hour. The excess butadiene was then permitted to evaporate at room temperature. Both complexes were pale yellow and quickly decomposed in air with the evolution of butadiene; however at −78° they were stable for several days.

Anal. Calcd. for $Cu_2Cl_2C_4H_6$: Cu, 50.8; Cl, 28.1. Found: Cu, 50.5; Cl, 28.7. Calcd. for $Cu_2Br_2C_4H_6$: Cu, 38.1; Br, 46.9. Found: Cu, 37.3; Br, 48.8.

4. **Preparation of Tetrachloro-μ-bis-(butadiene)-dipalladium(II).**—About 1.5 g. of benzonitrile palladous chloride, prepared by the procedure of Kharasch,[9] was dissolved in a minimum amount of benzene and the deep red solution filtered to remove any unreacted benzonitrile complex. A

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[1] Abstracted in part from the doctoral dissertation of P. E. Slade, Tulane University, 1955.

[2] J. S. Anderson, *J. Chem. Soc.*, 971 (1934).

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

[4] A. Hel'man and D. I. Riabchikov, *Compt. rend.* (*Doklady*) *Acad. Sci. URSS*, **33**, 462 (1941).

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[6] J. Chatt, *Ann. Rep. Prog. Chem.*, **43**, 120 (1946).

[7] J. Chatt, *J. Chem. Soc.*, 3340 (1949).

[8] J. Chatt, *Research*, **4**, 180 (1951).

[9] M. S. Kharasch, R. C. Seyler and F. R. Mayo, THIS JOURNAL, **60**, 882 (1938).

[10] H. Tropsch and W. J. Mattox, *ibid.*, **57**, 1102 (1935).

[11] E. R. Gilliland, *et al.*, *ibid.*, **61**, 1960 (1939).

[12] R. W. Keller, *Chem. Revs.*, **28**, 229 (1941).

[13] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).

[14] A. Hel'man, *Compt. rend.* (*Doklady*) *Akad. Sci. URSS*, **23**, 532 (1939).

[15] M. A. Lur'e, *et al.*, *Sint. Kauchuk*, **3**, 19 (1934).

[16] J. N. Dempsey and N. C. Baenziger, THIS JOURNAL, **77**, 4984 (1955).

[17] Carbon and hydrogen analyses were performed by the Microtech Laboratories, Skokie, Illinois.

steady stream of butadiene was passed through the solution and the color changed slowly from red to yellow. After no further color change was observed, petroleum ether was introduced into the solution and a light yellow flocculent precipitate was formed. The mixture was filtered with suction and the residue washed with petroleum ether. The complex was then dried in air at room temperature.

Anal. Calcd. for $(PdCl_2C_4H_6)_2$: Pd, 46.1; C, 20.8; H, 2.6. Found: Pd, 45.5; C, 21.5; H, 2.9.

B. **Thermal Stability Data.**—Although it is well known that metal–olefin complexes as a general rule are not extremely stable compounds, stability data had not been systematically obtained previously. In this study the butadiene complexes were thermally decomposed in a simple vapor pressure system of a vacuum apparatus and the decomposition pressure with change in temperature was observed. The system had a volume of 54 ml. and was equipped with an absolute manometer using a vernier indicator capable of pressure readings with an accuracy of ±0.2 mm.

With the exception of potassium sexachloro-μ-butadienediplatinum(II), all complexes were manipulated in a similar manner. The compound was quickly weighed into a small tube fitted with a ground glass joint and immediately placed in Dry Ice to prevent decomposition. After attaching the sample to the vapor pressure system, the tube was evacuated while remaining at the Dry Ice temperature. When the pressure reached the minimum reading of less than 10^{-5} mm. the solid CO_2 was replaced with a trichloroethylene–Dry Ice slush bath in a round-bottom flask fitted with a side arm for a thermometer. Since a total immersion thermometer was used, corrections were made for emergent stem. By allowing the temperature to rise slowly at a rate of about 1° per minute, the decomposition pressures were observed. Above room temperature, an oil-bath was used to heat the reaction tube.

Because of the unusual stability of $K_2(Pt_2Cl_6C_4H_6)$, 25° was the lowest temperature observed. An oil-bath was used to 80° and a Wood's alloy bath up to 300°.

The decomposition products from $(PtCl_2C_4H_6)_2$ and $Cu_2X_2C_4H_6$ were indentified by vapor pressure, molecular weight and infrared data as butadiene in each case. The products from $(PdCl_2C_4H_6)_2$ and $K_2Pt_2Cl_6C_4H_6$ contained butadiene, chlorine, traces of other unidentified gases, and metallic platinum.

C. **Infrared Data.**—The infrared spectrum of each complex was recorded on a Perkin-Elmer Model 21 double beam infrared spectrophotometer equipped with sodium chloride optics. The solid complexes were suspended in a Nujol mull between rock salt discs for the measurements.

Discussion

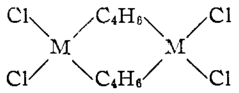
The platinum olefin complexes were prepared by modification of well established methods. Tetrachloro-μ-bis-(butadiene)-dipalladium(II) was prepared by the general methods given by Kharasch[9] for palladium–olefin complexes, and is the first butadiene–palladium complex on record. Cuprous chloride, or bromide, absorbs gaseous butadiene either as an anhydrous solid or when dissolved in a saturated ammonium chloride solution, but the solid–gas reaction is slow and, when the complex is made in solution, it contains four coördinated water molecules. The technique of reacting the anhydrous halide in liquid butadiene used in this work is rapid and leads to quantitative yields.

The palladium dimer is the most unusual of these complexes. The data indicate that this is a butadiene bridged compound in which the double bonds from two individual butadiene molecules are coördinated in *cis* positions in the palladium coördination plane. The complex is exceptionally stable not only in comparison with the other reported *cis* coördinated olefin complexes,[18] but also compared to other palladium–olefin compounds.

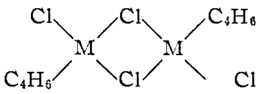
Thermal decomposition of the butadiene complexes studied gave the following order of thermal stability: $K_2(Cl_3PtC_4H_6PtCl_3) >> (PdCl_2C_4H_6)_2 > (PtCl_2C_4H_6)_2 \cong Cu_2Cl_2C_4H_6$ and $Cu_2Br_2C_4H_6$ as shown in Fig. 1.

The extremely stable character of the $K_2Pt_2Cl_6C_4H_6$ was expected, but the reversal of the usual order of stability in $(PtCl_2C_4H_6)_2$ and $(PdCl_2C_4H_6)_2$ was not anticipated. Since the compounds have the same general formula of $(MCl_2C_4H_6)_2$, where M is either platinum or palladium, a difference in the structure of the two seems indicated. Differences in stability would be expected if in one isomer a butadiene bridge linked the two metal ions whereas in the other, chloride ions formed the bridging units. This may be illustrated by the following typical structures, where M is the metal ion.

Structure 1

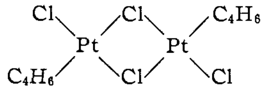


Structure 2

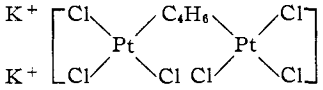


An attempt to distinguish between the two by infrared spectroscopy is possible since a strong transmission minimum corresponding to a conjugated carbon–carbon double bond stretching occurs in the 6.2 to 6.4 μ wave length region. The transmission is also decreased in this general region by a lone, or non-conjugated double bond although the intensity of the minimum varies considerably under different conditions of structure.

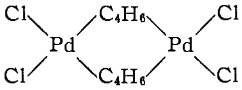
Only one complex, $(PtCl_2C_4H_6)_2$, showed a minimum in this region. This might possibly indicate the structure



These experimental data then seem to indicate that $(PtCl_2C_4H_6)_2$ is a possible isomer of the dimer reported by Hel'man.[14] Since $(PtCl_2C_2H_4)_2$ was used as a starting material, and ethylene was displaced by butadiene, it seems likely that the butadiene would occupy the same place in the structure originally held by ethylene. This should make it more likely to give a compound with a chloride bridge instead of one with a butadiene bridge as reported by Hel'man.[14] Since the compound produced by the displacement reaction was brick-red, while Hel'man's complex was described as having a green-brown color, it is quite possible that the two are isomers. Since the infrared data of the other four complexes indicate no minima in the 6.2 to 6.4 μ region, it is possible that they have a butadiene bridge structure as shown below



Potassium sexachloro-μ-butadienediplatinum(II)



Tetrachloro-μ-bis-(butadiene)-dipalladium(II)

$[X—Cu—C_4H_6—Cu—X]$ or $Cu^+ [CuX_2(C_4H_6)]^-$

Dibromo or Dichlorobutadienecopper(I)

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(18) J. Chatt and R. A. Wilkins, *J. Chem. Soc.*, 2622 (1952).

TABLE I

INFRARED TRANSMISSION MINIMA FOR BUTADIENE–METALLIC SALT COMPLEXES[a]

K_2-($Pt_2Cl_6C_4H_6$)	($PdCl_2$-C_4H_6)$_2$	$(PtCl_2C_4H_6)_2$	$Cu_2Cl_2C_4H_6$	$Cu_2Br_2C_4H_6$
2.34 w	2.35 w	2.34 vw	...	...
2.38 w	...	2.46 vw	...	...
3.71 vw	...	2.92 m	...	...
4.43 w	7.64 m	6.22 w	6.66 sh	6.62 sh
8.10 w	7.94 m	8.54 band	...	7.90 w
8.34 vw	8.14 w	9.36 band	...	...
8.58 vw	8.62 w	9.66 m	...	...
8.66 vw	9.23 w	9.82 m	9.91 w	9.91 w
9.65 s	10.15 w	10.00 m	10.51 w	10.49 vw
9.94 s	10.50 m	10.27 m	10.96 m	11.10 m
10.36 s	11.20 vw	10.38 m	...	...
11.80 s	11.32 w	11.78 band	...	...
12.39 w	11.56 w	12.34 w	...	...
	14.86 m	13.47 w	13.01 w	...

[a] w, weak; vw, very weak; s, strong; m, medium; sh, shoulder.

The complex compounds $Cu_2X_2C_4H_6$ are not very stable even though infrared data indicate the possibility of a butadiene bridge or a butadiene chelate ring in line with a coördination number of four for Cu(I) ion. However, this decrease in stability might also be due to the decreased coördinating tendency of the copper(I) ion toward olefins.[12]

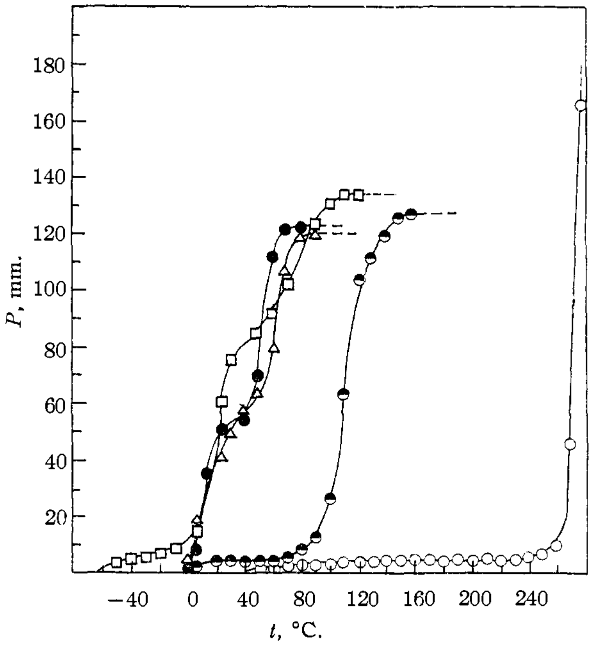

Fig. 1.—Thermal decomposition of butadiene complexes: ○, $K_2[Pt_2Cl_6C_4H_6]$; ◐, $(PdCl_2C_4H_6)_2$; △, $Cu_2Cl_2C_4H_6$; ●, $Cu_2Br_2C_4H_6$; □, $(PtCl_2C_4H_6)_2$.

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NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TULANE UNIVERSITY]

Olefin Coördination Compounds. IV. Platinum(II) Complexes with *cis*- and *trans*-2-Butene

BY HANS B. JONASSEN AND WARREN B. KIRSCH[1]

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1,3-Bis-(*cis*-2-butene)-2,4-dichloro-μ-dichlorodiplatinum(II) $(C_4H_8PtCl_2)_2$, (hereafter referred to as *cis*-2-butene platinous chloride), and 1,3-bis-(*trans*-2-butene)-2,4-dichloro-μ-dichlorodiplatinum(II) $(C_4H_8PtCl_2)_2$, (abbreviated to *trans*-2-butene platinous chloride) were prepared by the displacement of ethylene from 1,3-bis-(ethylene)-2,4-dichloro-μ-dichlorodiplatinum(II), (hereafter referred to as ethylene platinous chloride) $(C_2H_4PtCl_2)_2$. The infrared spectra of the two solids show that isomerization of the olefin does not occur. When the olefins are displaced from the complexes the corresponding *cis* and *trans* isomers are recovered with no rearrangement.

Introduction

The preparation of crystalline platinum–olefin complexes using both *cis* and *trans* isomers of a particular olefin, as the ligand has been questioned.[2,3] Usually one isomer gives a crystalline complex, and the other a tar. Anderson[3a] obtained a crystalline product using *trans*-2-pentene as the ligand, but Oppegard[3b] reported that a tar resulted. He was successful using *cis*-2-pentene and the infrared spectra of the tar and the crystalline complex differed. Oppegard assumed that this was evidence for the preservation of the rigid structure about the double bond.

A similar conclusion was reached by Winstein and Lucas,[4] using aqueous solutions of silver, in which the olefin was dissolved. Within experimental error, they found that no rearrangement of *cis* or *trans* isomers resulted.

In this study, crystalline coördination compounds of platinous chloride with *cis*-2-butene and with *trans*-2-butene have been prepared. Their infrared spectra show them to be different compounds. Decomposition of these two compounds with sodium cyanide yields the respective isomeric olefin without rearrangement.

Experimental

A. Materials.—Hydrocarbons; Phillips High Grade *cis*-2-butene and *trans*-2-butene (99 mole % minimum). Other chemicals were C.P. grade reagents.

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[1] Abstracted in part from the M.S. Thesis of Warren B. Kirsch, Tulane University, 1955.

[2] M. S. Kharasch and T. A. Ashford, THIS JOURNAL, **58**, 1733 (1936).

[3] (a) J. S. Anderson, *J. Chem. Soc.*, 971 (1934); (b) A. L. Oppegard and J. C. Bailar, private communications.

[4] S. Winstein and H. J. Lucas, THIS JOURNAL, **60**, 836 (1938).