TABLE II

SUMMARY OF DERIVED DATA

Substance	Formula	Mol. wt.	Density	$-\Delta U_B$, kcal. mole^{-1}	$-\Delta U_R$, kcal. mole^{-1}	$-\Delta H_R$, kcal. mole^{-1}	$-\Delta H_f^0$ kcal. mole^{-1}	$\Delta U_R/dT$ mole^{-1} cal.	$-\Delta F_f^0$ kcal. mole^{-1}
d-Alanine	$C_3H_7O_2N$	89.063	1.38	387.11 ± 0.11	386.86 ± 0.13	387.10 ± 0.13	134.81	38	88.99
l-Asparagine (anhyd.)	$C_4H_8O_3N_2$	132.078	1.44	461.36 ± 0.13	460.93 ± .17	460.63 ± .17	189.58	43	127.58
l-Asparagine (hyd.)	$C_4H_{10}O_4N_2$	150.094	1.54	458.64 ± .15	458.25 ± .19	457.95 ± .19	260.57	50	184.74
l-Aspartic acid	$C_4H_7O_4N$	133.063	1.66	383.47 ± .15	383.01 ± .19	382.57 ± .19	233.49	36	175.59
d-Glutamic acid	$C_5H_9O_4N$	147.078	1.54	537.85 ± .23	537.36 ± .28	537.31 ± .28	241.30	49	174.94
Creatine (anhyd.)	$C_4H_9O_2N_3$	131.094	1.33	555.59 ± .16	555.21 ± .20	555.06 ± .20	129.31	48	64.20
Creatinine	$C_4H_7ON_3$	113.079	1.31	558.62 ± .12	558.26 ± .16	558.11 ± .16	57.94	38	7.89

corrections and these corrected values are compared with our values in Table III. In the case of creatinine Emory and Benedict[10] calculated their result on the basis of the carbon dioxide found. We have corrected their reported value back to the mass basis which brings it into much better agreement with our value.

TABLE III

COMPARISON OF THE PRESENT DATA WITH VALUES FROM THE LITERATURE

Substance	Reference	Older data $-\Delta H_R$, kcal. mole^{-1}		New value $-\Delta H_R$, kcal. mole^{-1}		Difference %
d-Alanine	8	386.87	±0.19	387.10	±0.13	−0.06
d-Alanine	10	390.6	±1.2	387.10	± .13	.90
l-Asparagine (anh.)	11	462.3	±1.2	460.63	± .17	.37
l-Asparagine (hyd.)	10	458.4	±1.2	458.50	± .19	− .01
l-Aspartic acid	10	381.9	±1.1	382.57	± .19	− .18
l-Aspartic acid	9	384.7	±1.3	382.57	± .19	+ .48
d-Glutamic acid	9	541.7	±0.7	537.31	± .28	+ .82
d-Glutamic acid	10	536.6	±1.3	537.31	± .28	− .13
Creatine	11	558.4	±1.5	555.06	± .20	+ .54
Creatine	10	553.8	±1.3	555.06	± .20	− .23
Creatinine	10	556.4	±1.3	558.11	± .16	− .31

In a recent paper Zittle and Schmidt[12] report the heat of hydration of anhydrous *l*-asparagine as 2250 ± 200 calories. This compares favorably with the value of 2680 ± 330 calories as calculated from our combustion data on these two compounds. They do not state how the anhydrous material was obtained but it was very probably by treatment at 100° or above.

Summary

1. The experimental values of the heats of combustion at constant volume and at 25° of seven organic compounds are given.

2. From the experimental values the heat of combustion at constant pressure and the heat of formation have been calculated.

3. These new values for heats of formation have been used with existing entropy data to calculate more reliable free energy data.

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[12] Zittle and Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

PASADENA, CALIF. RECEIVED JUNE 30, 1936

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

Coördination Compounds of Platinous Halides with Unsaturated (Ethylene) Substances

BY M. S. KHARASCH AND T. A. ASHFORD[1]

Introduction

Platinum is an unusually versatile element. It has primary valences of two and four, and it forms two series of coördination compounds with both organic and inorganic substances. In these the metal exhibits the coördination numbers of four and six, respectively. Stereoisomers have been obtained in both series. Where the coördination number is six, the accepted view is that the valence bonds of the platinum atom are directed toward the corners of an octahedron; giving rise to the following two stereoisomeric configurations for compounds of the type PtX_4A_2.[2] Some compounds of the type PtX_2A_2 also exist in two stereoisomeric forms: *cis* and *trans*[2] (p. 338).

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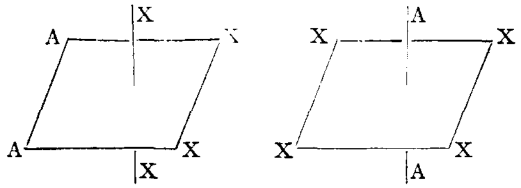
[1] This communication is an abstract of a dissertation submitted by T. A. Ashford in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Chicago.

[2] Werner, "Lehrbuch der Stereochemie," Gustave Fischer, Jena, 1904, p. 350.



Furthermore, Reihlen and Hühn[3] report that they have resolved into optical antipodes platinum compounds of coördination number four. It is still an unsettled question whether the configuration of these compounds is planar, tetrahedral or pyramidal.[4]

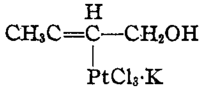
Several classes of coördination compounds of platinum, notably those with ammonia and with the amines, have been studied extensively. However, two important classes, namely, those with unsaturated substances and those with nitriles, have received scant attention because of the lack of satisfactory methods for preparing these complexes.

In the work reported in this paper a particularly simple general method has been developed for the preparation of organo-platinum complexes with unsaturated compounds. This method has been used to prepare a large number of compounds, the properties of which are herein described.

Previous Work

The literature contains references to complex salts of the type $K(Un{\cdot}PtX_3)$, in which Un is an unsaturated molecule containing an ethylene bond. The first compound of this series was obtained by Zeise,[5] who isolated a substance with the empirical formula $K(C_2H_4{\cdot}PtCl_3){\cdot}H_2O$, from a reaction mixture of chloroplatinic acid and alcohol. Birnbaum[6] prepared similar compounds with propylene and amylene, and Chojnacki[7] obtained $K(C_2H_4{\cdot}PtBr_3)$, with platinic bromide.

Biilmann and his collaborators[8] have extended the work to unsaturated substances other than hydrocarbons, and they have prepared compounds with unsaturated alcohols, acids and aldehydes. Pfeiffer and Hoyer[9] have prepared similar substances from allyl alcohol, allyl acetate, crotyl alcohol and crotyl aldehyde. The latter workers consider that in these compounds the platinum atom is coördinately bound directly to the carbon atom by a single bond; they propose the following structure.



$$\mathrm{CH_3C{=}\underset{PtCl_3\cdot K}{\overset{H}{C}}{-}CH_2OH}$$

This structure indicates that the compounds are derivatives of the metallic chloroplatinates, in which a chloride ion has been replaced by an unsaturated molecule. There is, however, no experimental evidence that the substances are monomolecular.

The series from which the compounds discussed above are derived is obviously $Un{\cdot}PtX_2$. As will be shown later, however, substances of this type are bimolecular and should be written $(Un{\cdot}PtX_2)_2$. Recently, Anderson[10] obtained $(C_2H_4PtCl_2)_2$ by refluxing ethyl alcohol with sodium chloroplatinate. This reaction is very complex, presumably involving at least four steps. Preliminary attempts to extend this method to other alcohols have not as yet proved successful.

General Method of Preparation

The most direct method for preparing a compound of the type $(Un{\cdot}PtCl_2)_2$ or $(Un{\cdot}PtBr_2)_2$ would be to combine a platinous halide with an unsaturated compound. However, attempts to apply this method have given unsatisfactory results. Platinous halides are very insoluble and inert substances; consequently platinic halides have been used.

The general method here described departs radically from that of Anderson since anhydrous platinic chloride or bromide in an anhydrous solvent is used instead of the metallic haloplatinates. It differs further in that the unsaturated compounds are used instead of the alcohols. The method is rapid as well as general. The reaction is complete in about an hour.

Although the reaction, as outlined above, and described in more detail in the experimental part, appears simple, it is probably more complex than might at first be supposed. Hydrogen halide is usually evolved during the reaction, and in some instances a small quantity of platinum separates. Halogenation of the unsaturated compound also has been demonstrated.

Physical and Chemical Properties

The coördination compounds $(Un{\cdot}PtCl_2)_2$ are well-defined crystalline substances. When heated

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(3) Reihlen and Hühn, *Ann.*, **489**, 42 (1931).

(4) *Cf.* Dwyer and Mellor, THIS JOURNAL, **56**, 1551 (1934).

(5) Zeise, *Pogg. Ann.*, **21**, 497 (1831).

(6) Birnbaum, *Ann.*, **145**, 67 (1869).

(7) Chojnacki, *Jahresber.*, 510 (1870).

(8) Biilmann, *Ber.*, **33**, 2196 (1900); Biilmann and Anderson, *ibid.*, **36**, 1565 (1903); Biilmann and Hoff, *Chem. Zentr.*, 88, I, 562 (1917).

(9) Pfeiffer and Hoyer, *Z. anorg. allgem Chem.*, **211**, 241 (1933).

(10) Anderson, *J. Chem. Soc.*, 971 (1934).

in a melting-point tube they do not melt sharply, but darken over a range of several degrees. They vary widely in stability. The greatest difference has been observed between the compounds obtained from *trans*-dichloroethylene and from dipentene. The former decomposes in a few days; the latter appears unchanged even after standing in the air for ten months.

The compounds are in general soluble in acetone, chloroform and alcohol; they are less soluble in benzene, and difficultly soluble or insoluble in glacial acetic acid. Those of low molecular weight are soluble in sodium chloride solution, presumably forming compounds analogous to Zeise's salt

$$[(CH_3)_2C{=}CH_2\cdot PtCl_2]_2 + 2NaCl \longrightarrow 2Na(CH_3)_2C{=}CH_2\cdot PtCl_3$$

When treated with pyridine the substances decompose, liberating the olefin and forming the pyridine platinous chloride.

$$[Un\cdot PtCl_2]_2 + 4C_5H_5N \longrightarrow 2Un + 2(C_5H_5N)_2\cdot PtCl_2$$

Concentrated hydrochloric acid decomposes them.

$$Un\cdot PtCl_2]_2 + 4HCl \longrightarrow 2Un + 2H_2PtCl_4$$

Bromine also decomposes these substances, forming the platinum halides and the bromine addition product of the unsaturated compound.

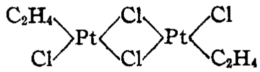
Molecular Weight

The coördination compounds of the series $(Un\cdot PtCl_2)_2$ are unstable at higher temperatures; consequently the ebullioscopic method for the determination of their molecular weights is inapplicable. For the same reason the Rast method cannot be used. With the exception of the compound obtained from isobutylene, these substances are also sparingly soluble in benzene. However, the depression of the freezing point of benzene by isobutylene platinous dichloride indicates that the substance is bimolecular, $[(CH_3)_2C{=}CH_2\cdot PtCl_2]_2$, and no doubt the other compounds of the same series are likewise.[11]

Structure of the Compounds of the Type $[(Un\cdot PtCl_2)]_2$

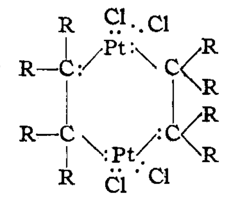
That these compounds are derivatives of platinous chloride seems fairly well established. Their analyses as well as their reactions with pyridine, with concentrated hydrochloric acid, and with bromine point to this conclusion. Furthermore, the compound prepared from dipentene and platinic chloride is the same as the one obtained by treating dipentene with platinous chloride in the presence of dry hydrogen chloride.

Anderson[10] has proposed for ethylene platinous chloride the formula

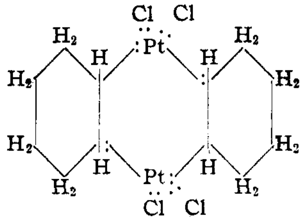


Against this formula, however, may be raised the serious objection that it makes a chlorine atom form two coördination bonds.

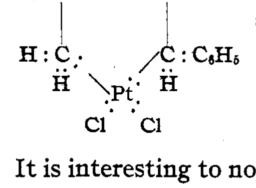
Consideration of the electron arrangement in the substance aids in deriving a structure. The general electronic configuration here proposed for all compounds of the type $(Un\cdot PtCl_2)_2$



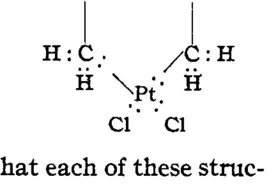
is specifically exemplified in the following formula for cyclohexene platinous chloride



When monosubstituted ethylenes are used, there is a possibility of structural isomerism. For instance, the compound derived from styrene might have either of the two structures shown by the formulas



and



It is interesting to note that each of these structural isomers contains two asymmetric carbon atoms, and can exist in three stereoisomeric forms. With more complex substituted ethylenes, the number of isomers becomes still greater. Further study of these substances is contemplated.

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[11] Anderson[10] has estimated the molecular weight of ethylene platinous chloride by the Barger–Rast method, and his results point to a bimolecular form.

Applicability of the Method

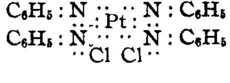
The method described above has been used to prepare coördination compounds from the following unsaturated substances: cyclohexene, dipentene, pinene, ethylene, isobutylene, styrene, stilbene and *trans*-dichloroethylene. No crystalline coördination compounds could be isolated from the following substances: allyl chloride, allyl bromide, allylbenzene, vinyl bromide, tridecene, isostilbene and *cis*-dichloroethylene. The latter substances react with the platinic chloride to give red solutions but no crystals separate. In all these cases red gums are obtained.

It is interesting that crystalline compounds have been isolated from *trans*-dichloroethylene and from *trans*-diphenylethylene, whereas all attempts to obtain crystalline substances from their *cis*-isomers have failed. It would be desirable to extend the work to other pairs of *cis–trans* stereoisomers, to determine how general this relation is. In this connection it should be noted that from cyclohexene, dipentene and pinene (which are *cis* compounds) crystalline substances have been isolated.

The method does not seem to be applicable to unsaturated acids and their esters. All attempts to prepare compounds with maleic anhydride, maleic and fumaric acids and their ethyl esters, and with cinnamic ester have failed. These substances do not appear to react at all with platinic chloride.

Coördination Compound of Platinic Chloride with Azobenzene

It might be expected that azo compounds which contain a double bond between two nitrogen atoms would form coördination compounds similar to those obtained from the olefins. However, the compound obtained from the interaction of platinic chloride and azobenzene has the empirical formula $(C_6H_5N{=}NC_6H_5)_2PtCl_4$. This compound is analogous to the coördination compounds of the type $(RCN)_2PtCl_4$ obtained from platinic chloride and nitriles. It appears that the azo group is equivalent to a nitrile group. For this compound the following formula is proposed



$$\begin{matrix} & \ddot{}\,Cl & Cl\,\ddot{} & \\ C_6H_5:\ddot{N} & & & \ddot{N}:C_6H_5 \\ & & Pt & \\ C_6H_5:\ddot{N} & & & \ddot{N}:C_6H_5 \\ & \ddot{}\,Cl & Cl\,\ddot{} & \end{matrix}$$

Here one pair of electrons from each azo group forms a coördination bond.

Experimental Part

Preparation of Anhydrous Platinic Chloride.—Anhydrous platinic chloride is prepared by a modification of the method of Rosenheim and Löwenstamm.[12] Chloroplatinic acid is prepared by the usual method. The acid melts at about 60° and still contains six molecules of water of crystallization. The melted acid is poured into a porcelain boat and the boat with its contents is placed in a glass tube contained in an electric furnace. A slow current of dry chlorine is passed through the apparatus. The temperature is raised gradually to 275° in the course of two hours; it is kept there for one-half hour and then is allowed to fall gradually. When the apparatus has cooled to about 150°, the boat is removed and the contents are pulverized while hot in an agate mortar. The powdered substance is again placed in the furnace in an atmosphere of chlorine at 275° for one-half hour. It is then allowed to cool and is placed in a glass-stoppered bottle in a desiccator over concentrated sulfuric acid.

Anal. Calcd. for $PtCl_4$: Pt, 57.9. Found: Pt, 57.7.

Platinic chloride thus prepared is a very hygroscopic red-brown substance. It is slightly soluble in nitrobenzene, glacial acetic acid and alcohol, very slightly soluble in chloroform and ether, and insoluble in benzene and in toluene.

Preparation of Platinous Chloride.—Platinous chloride is prepared by a modification of the method of Berzelius.[13] Pure chloroplatinic acid is heated over a free flame to about 150°. The resulting solid is placed in a boat, and the boat with its contents is placed inside the furnace. The temperature is raised to 360–380° for about two hours, while a slow current of air is passed through the apparatus. The greenish solid is then pulverized and is again placed in the furnace at 360° for about one hour. After cooling, the solid is boiled with water containing a few drops of hydrochloric acid to remove any unchanged platinic chloride. The platinous chloride, which is insoluble, is washed twice by decantation and again placed in the furnace at 360° for one-half hour.

Anal. Calcd. for $PtCl_2$: Pt, 73.4. Found: Pt, 73.2.

Platinous chloride is a greenish-gray solid. It is insoluble in benzene, chloroform, glacial acetic acid and alcohol.

General Method of Preparation of Complexes

The most direct method for preparing a compound of the type $(Un{\cdot}PtCl_2)_2$ or $(Un{\cdot}PtBr_2)$ would be to combine a platinous halide with an unsaturated compound. However, attempts to apply this method have given unsatisfactory results. Platinous halides are very insoluble and inert substances; consequently platinic halides have been used.

To prepare the chlorides 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid and 0.5 cc. (about 2–4 moles) of the unsaturated hydrocarbon is added (in the case of pinene 1 cc. is added). The mixture is warmed in the steam-bath for about ten minutes. During this period the platinic chloride goes into solution and the reaction is completed. Crystals of the chloride

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[12] Rosenheim and Löwenstamm, *Z. anorg. Chem.*, **37**, 403 (1903).

[13] Berzelius, *Schweigger's J.*, **7**, 55 (1813).

separate out from the filtrate with or without cooling and these are collected and washed with additional portions of the solvent. In the case of *cyclohexene* 1 g. of the chloride is triturated with 0.25 g. (1 mole) of the hydrocarbon in 15 cc. of glacial acetic acid and after a few minutes 1 cc. (3 moles) more of the cyclohexene is added, considerable heat being evolved and the reaction going to completion.

In the case of *stilbene* 0.25 g. of the hydrocarbon also is first added and the mixture is heated on the steam-bath, the platinic chloride being completely dissolved in about fifteen minutes to form a red solution. After filtration an additional 0.5 g. (2 moles) of stilbene is added.

Platinic bromide can also be used in place of the chloride and it has the advantage of being more soluble in glacial acetic acid. In the case of *cyclohexene* 0.2 g. of the bromide is dissolved in 5 cc. of glacial acetic acid and 1 cc. of cyclohexene is added. In a few minutes the deep red solution becomes pale orange and long needles separate.

In the case of *styrene* 2 cc. of the hydrocarbon is added to 0.5 g. of the bromide in 10 cc. of glacial acetic acid.

Preparation of Ethylene Platinous Chloride ($C_2H_4 \cdot PtCl_2)_2$.—About 1 g. of platinic chloride is suspended in about 25 cc. of anhydrous benzene. The suspension is kept at 70° for about one hour, while ethylene from a cylinder is bubbled through it. After standing at room temperature for twenty-four hours, the reaction mixture is again warmed to 70° and treated with ethylene. During these operations most of the platinic chloride goes into solution, and at the same time a considerable quantity of hydrogen chloride is evolved. The hot solution is filtered, and from the filtrate, upon cooling, orange crystals separate. They are crystallized from benzene.

This compound is identical with the one prepared by Anderson[10] by refluxing absolute alcohol with sodium chloroplatinate.

Preparation of Isobutylene Platinous Chloride $[(CH_3)_2C{=}CH_2 \cdot PtCl_2]_2$.—About 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid and the mixture is warmed to 50°. Isobutylene, prepared by heating *t*-butyl alcohol with oxalic acid, is then bubbled through the suspension. In the course of a few minutes the platinic chloride dissolves, giving a red solution. The solution is filtered. As more isobutylene is bubbled through the filtrate orange crystals separate. The crystals are washed with glacial acetic acid.

Molecular Weight.—The solubility of this compound in benzene permits an accurate determination of its molecular weight. The compound is found to be bimolecular: solute, 0.1330, 0.2406, 0.2406 g.; solvent, 8.742, 8.742, 17.484 g.; average depression, 0.119, 0.223, 0.107°. Calcd. for $(C_4H_8 \cdot PtCl_2)_2$: mol. wt., 644.4. Found: mol. wt., 654, 633, 658.

Reaction of Stilbene Platinous Chloride with Pyridine.—About 0.2 g. of stilbene platinous chloride is dissolved in 2 cc. of chloroform and 10 drops of pyridine added. A yellowish precipitate, presumably pyridine platinous chloride, separates. About 25 cc. of petroleum ether is added, and the filtrate is evaporated to dryness. A crystalline substance melting at 125° is obtained. A mixture of this substance with stilbene also melts at 125°. The reaction evidently proceeds according to the equation

$$(C_6H_5CH{=}CHC_6H_5PtCl_2)_2 + 4C_5H_5N \longrightarrow 2C_6H_5CH{=}CHC_6H_5 + 2(C_5H_5N)_2PtCl_2$$

Reaction of Stilbene Platinous Chloride with Concentrated Hydrochloric Acid.—About 0.1 g. of stilbene platinous chloride is dissolved in 10 cc. of benzene, and 20 cc. of concentrated hydrochloric acid is added. After shaking for about one hour the mixture is allowed to stand overnight. The benzene layer becomes colorless, while the aqueous layer becomes orange. The benzene layer upon evaporation gives colorless crystals, melting at 125°. A mixture of these crystals with stilbene also melts at 125°. The aqueous layer upon evaporation at 100° gives platinous chloride.

Reaction of Stilbene Platinous Chloride with Bromine.—About 0.3 g. of stilbene platinous chloride is dissolved in 20 cc. of chloroform and an excess of bromine in carbon tetrachloride is added. The solution is then evaporated under reduced pressure. The red mass is extracted with petroleum ether, and the solution after filtering is evaporated to dryness. The solid that is obtained and also a mixture with stilbene dibromide melts at 237°. The residue from the extraction is soluble in water, consisting presumably of platinic chloride and platinic bromide.

Cis-Phenylethylene; Isostilbene.—This substance is prepared by hydrogenation of tolane in methyl alcohol solution in the presence of platinum catalyst, until the theoretical amount of hydrogen is absorbed. Upon evaporation of the solvent an oil is obtained. This oil is dissolved in light petroleum ether (b. p. 30–35°), and placed in acetone–carbon dioxide mixture to precipitate any unchanged tolane. The cold solution is then filtered and the filtrate is evaporated, leaving the pure substance in the form of an oil.

All attempts to prepare crystalline coördination compounds with isostilbene have failed. Nitrobenzene, benzene, chloroform and glacial acetic acid have been used as solvents, and the temperature as well as the time of heating have been varied. In all cases the platinic chloride goes into solution while hydrogen chloride is evolved. Under all conditions red gums have been obtained.

Preparation of Trans-Dichloroethylene Platinous Chloride, ***trans*-($C_2H_2Cl_2 \cdot PtCl_2)_2$**.—About 0.5 g. of platinic chloride is suspended in 10 cc. of benzene, and 1 cc. of *trans*-dichloroethylene is added. The mixture is warmed to 40–50° for about three hours, during which most of the platinic chloride goes into solution and at the same time a considerable quantity of hydrogen chloride gas is evolved. The reaction mixture is then heated to the boiling point of benzene and filtered. From the filtrate amber crystals separate on cooling.

Cis-Dichloroethylene.—Several attempts to isolate a crystalline compound with *cis*-dichloroethylene have failed. As in the case of *cis*-diphenylethylene gums have been obtained.

Preparation of Di-azobenzene Platinic Chloride $(C_6H_5N{=}NC_6H_5)_2 \cdot PtCl_4$.—About 0.5 g. of platinic chloride is suspended in 10 cc. of glacial acetic acid, a gram of azobenzene added to the mixture and the whole warmed on a steam-bath. After about one hour the platinic chloride goes into solution and at the same time a brick-red solid separates. The compound is purified by washing successively with glacial acetic acid, benzene and petroleum ether.

Anal. Calcd. for $(C_6H_5N{=}NC_6H_5)_2 \cdot PtCl_4$: Pt, 27.84. Found: Pt, 27.5, 27.6.

TABLE I

ORGANO PLATINUM COMPOUNDS: ANALYSES, CHEMICAL, PHYSICAL AND OPTICAL PROPERTIES

Platinous chlorides	Color	Optical data[a] Form	Bire.	Ext. angle	Solubilities[b] CHCl₃	Ether	Bz	EtOH	Glac. HAc	Acetone	Water	NaCl soln.	M.p., °C.	Platinum, % Calcd.	Found	Found
Cyclohexene	sl. or.	l. silky needles[c]	. . .	par. sym. obl.	s.	s.	sl. s.	v. s.	ins.	v. s.	. . .	ins.	145–146	56.07	56.0	56.0[i]
Dipentene	f. yel.	biax. pr.[c]	low	34°	v. s.	ins.	v. sl.	ins.	ins.	s.	. . .	ins.	151–152	48.53	48.4[d]	48.3[e,j]
Pinene	f. yel.	prisms[c]	high	6°	v. s.	sl.	s.	sl.	sl.	s.	. . .	ins.	138–141	48.53	48.6	48.6
Ethylene	or.	tablets[c]	high	32°	s.	v. s.	s.	v. s.	ins.	v. s.	sl.[g]	sl.	170–180[f]	66.35	65.7	65.7
Isobutylene	or.	rhb. pl.	. . .	18°	v. s.	v. s.	v. s.	v. s.	sl.	v. s.	ins.[g]	v. s.	144–145	60.59	60.6	60.7
Styrene	or.	hex. pr.[c]	fair	30°	s.	s.	sl.	. . .	v. sl.	s.	ins.	v. sl.	169–171	52.73	52.6	52.6
Stilbene	or.	sm. hex. pr.[c]	high	30°	v. s.[h]	s.	v. sl.	v. sl.	ins.	v. s.	. . .	ins.	191–192	43.75	43.7	43.7[k]
trans-Dichloroethylene	or.	cryst.[c]	high	par.	s.[h]	. . .	s.	. . .	. . .	s.	. . .	. . .	155–160	53.77	54.6	54.7
Cyclohexene ·$PtBr_2$	or.	l. sl. need.[c]	fair	par.	s.	ins.	v. sl.	v. sl.	ins.	sl.	. . .	. . .	150–151	44.66	44.5	44.7
Styrene·-$PtBr_2$	rose	hex. pr.[c]	fair	32°	s.	ins.	sl.	ins.	ins.	sl.	. . .	ins.	153–154	42.52	42.4	42.5

[a] Abbreviations: par., parallel; sym., symmetrical; obl., oblique; ext., extinction; bire., birefringence; or., orange; yel., yellow; f., faint; l., long; sm., small; pl., plates; sl., slender; pr., prisms; hex., hexagonal. [b] Abbreviations: s., soluble; v., very; sl., slightly soluble; ins., insoluble. [c] Anisotropic. [d] Prepared from platinous chloride and dipentene. [e] Prepared from platinic chloride and dipentene. [f] After standing in air for about three weeks it decomposes at 125–130°. [g] Also in petroleum ether. [h] Also in nitrobenzene. [i] % Chlorine calcd.: 20.37. Found: 20.34 and 20.44. [j] % Chlorine calcd.: 17.63. Found: 17.7 and 17.7. [k] % Chlorine calcd.: 15.89. Found: 15.8 and 15.8.

The compound decomposes at 168–170°.

Solubility.—This compound is soluble in acetone, chloroform and ether; and slightly soluble in glacial acetic acid, alcohol and benzene.

Summary

1. It has been shown that anhydrous platinic halides react with ethylenic substances to give coördination compounds of the type $(Un{\cdot}PtX_2)_2$.

2. The behavior of these coördination compounds with various reagents has been described.

3. A ring formula has been proposed for the coördination compounds.

CHICAGO, ILL.

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The Orientation of *p*-Methoxydiphenyl in the Friedel and Crafts Reaction

BY L. F. FIESER AND CHARLES K. BRADSHER

In the course of certain synthetic work the occasion arose to investigate the condensation of *p*-methoxydiphenyl with succinic anhydride in the presence of aluminum chloride, and it was found that the reaction proceeds smoothly in nitrobenzene solution, giving a mixture of two isomers. As the higher melting keto acid forms a sparingly soluble sodium salt by means of which it can be removed from the mixture, a separation is easily accomplished. It was found that about two-thirds of the substitution occurs in the para position of the unsubstituted ring (I) and the remainder ortho to the methoxyl group (II). In establishing the structures the keto acids were first oxidized, best with permanganate in the case of I and with hypobromite for II, to the methoxydiphenyl carboxylic acids III and IV. The hydroxy acids obtained on demethylation corresponded in melting point to substances described in the patent literature, 4-hydroxy-4′-carboxydiphenyl having been obtained through the nitro derivative of the 4-carboxylic acid[1] and 3-carboxy-4-hydroxydiphenyl from the 4-hydroxy compound through the aldehyde[2] and by the Kolbe reaction.[3] In order to establish the structures completely exhaustive oxidations were conducted on the phenol III and the keto acid II. These yielded terephthalic acid and benzoic acid, respectively, in accordance with the formulation.

It was of interest to see whether the solvent in the Friedel and Crafts reaction plays any part in determining the ratio of homo- and hetero-nuclear substitution products, and as the condensation of *p*-methoxydiphenyl with succinic anhy-

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(1) French Patent 735,846; English Patent 390,556.

(2) American Patent 1,839,526.

(3) American Patent 1,941,207.