# COÖRDINATION COMPOUNDS OF OLEFINS WITH METALLIC SALTS

R. N. KELLER[1]

*Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois*

*Received December 13, 1940*

CONTENTS

I. Introduction ..... 229
II. Historical ..... 230
A. Compounds of the Group VIII metals ..... 230
1. Platinum-olefin compounds ..... 230
2. Palladium-olefin compounds ..... 234
3. Iron-olefin compounds ..... 235
4. Iridium-olefin compounds ..... 235
B. Compounds of other metals ..... 236
1. Aluminum-olefin compounds ..... 236
2. Zinc-olefin compounds ..... 237
3. Copper-olefin compounds ..... 237
4. Silver-olefin compounds ..... 237
5. Mercury-olefin compounds ..... 238
6. Miscellaneous compounds ..... 239
III. Discussion of methods of preparing metal-olefin compounds ..... 239
IV. Properties and reactions of metal-olefin compounds ..... 241
V. Technical applications of metal-olefin compounds ..... 244
VI. Structure of metal-olefin compounds ..... 246
VII. Conclusion ..... 261

## I. Introduction

The metal-olefin compounds have received considerable attention recently,—in part because of their practical importance, but primarily because of the many challenging problems centering around their structure. From the time the very first of these compounds was prepared, the mode of linkage of the double bond to the metal has been the subject of much speculation. While the ability to combine with olefins is quite widely distributed among the metals, it is most strongly exhibited by platinum. The formation of such compounds is not limited to hydrocarbons alone. Analogous substances containing unsaturated alcohols, acids, aldehydes, and esters are known, and in each of these the unsaturated molecule seems to occupy only one coördination position in the complex.

[1] Present address: Department of Chemistry, University of Wisconsin, Madison, Wisconsin.

## II. Historical

### A. COMPOUNDS OF THE GROUP VIII METALS

#### *1. Platinum–olefin compounds*

The credit for preparing the first compound of this type is to be given, perhaps, to Zeise, who in 1827 published a note concerning the research which was being done on platinum compounds in his laboratory (125). Three years later this work was published in Latin (126), and the following year a condensed form appeared in German (127). Berzelius (8) in 1830, however, had reported that by refluxing a mixture of alcohol and sodium chloroplatinate a very acid solution was obtained, which, when concentrated with potassium chloride, yielded yellow crystals. Qualitative analysis of this substance indicated it to be a double salt of potassium chloride and platinous chloride, along with an "atherartigen Substanz." When Zeise's investigation appeared shortly thereafter, Berzelius concluded (9) that his product was identical with that obtained by Zeise.

Zeise discovered that when platinic chloride was boiled with alcohol an acid solution resulted. By treating this solution with potassium chloride he obtained a compound in which potassium, platinum, chlorine, and the constituents of ethylene were present. The composition of the anhydrous substance was indicated to be $KCl \cdot PtCl_2 \cdot C_2H_4$. These analyses were immediately challenged by Liebig (70), who maintained that the anhydrous salt still contained the components of one-half a molecule of water for the simplest formula. He thought that the radical $C_4H_{10}O$ was present and that the correct formulation of the compound should be $2KCl \cdot 2PtCl_2 \cdot C_4H_{10}O$. Repetition of the analysis by Zeise (128) simply served to confirm his original contention that ethylene was present.

Zeise considered that he had obtained the basic compound of this series of substances, $PtCl_2 \cdot C_2H_4$, by treating the ammonium salt (prepared similarly to the potassium salt) with chloroplatinic acid. His product, however, was probably the more or less decomposed acid $H[PtCl_3 \cdot C_2H_4]$, now generally referred to as "Zeise's acid." The potassium and ammonium salts he obtained were probably $K[PtCl_3 \cdot C_2H_4] \cdot H_2O$ and $NH_4[PtCl_3 \cdot C_2H_4] \cdot H_2O$. Zeise apparently also prepared the non-ionic compound $[PtCl_2 \cdot NH_3 \cdot C_2H_4]$.

Griess and Martius (32), in 1861, not only confirmed Zeise's formula but also demonstrated that ethylene was liberated when Zeise's compound was thermally decomposed. These workers also prepared compounds analogous to Zeise's salt but containing aniline hydrochloride, diphenylamine hydrochloride, and ethylenediamine hydrochloride, instead of ammonium chloride and potassium chloride. The structures which Griess and Martius proposed for these compounds are mainly of historical interest at present.

Hoping to settle conclusively the question as to whether these substances actually contained ethylene, Birnbaum (13) undertook to synthesize such compounds by a method different from any heretofore employed. The reaction of alcohol on platinic chloride is apparently quite a complicated process, as evidenced by the great variety of products obtained. For this reason Zeise was unable to clarify completely the course of the reaction. Birnbaum contended that the fact that Griess and Martius had observed ethylene as one of the decomposition products of Zeise's salt was not proof that ethylene as such was present in the molecule originally; it might be simply a secondary decomposition product. This seemed even more plausible when it was considered that the thermal decomposition of the salt gave not only platinous chloride and ethylene but also an appreciable quantity of metallic platinum and carbonaceous decomposition products. Birnbaum reasoned that if the complexes could be synthesized from ethylene as a starting material, all ambiguities as to the resulting structure would be eliminated. He succeeded in making not only ethylene but also several of its homologs combine with platinous chloride dissolved in hydrochloric acid. Treatment of the resulting solution with potassium chloride gave a substance which proved to be Zeise's salt, $KCl \cdot PtCl_2 \cdot C_2H_4 \cdot H_2O$. The corresponding propylene compound was obtained in the same way. Amylene was found to react under similar conditions, but the compound formed was very unstable. The amylene compound was also obtained by employing Zeise's method, i.e., refluxing amyl alcohol with platinic chloride. The results indicated to Birnbaum that the coördinating abilities of propylene and amylene are certainly less than that of ethylene.

Since an aldehyde was detected as one of the products of the reaction of an alcohol with platinic chloride, Birnbaum proposed the following equation as the probable course of the primary reaction:

$$PtCl_4 + 2C_2H_5OH \rightarrow PtCl_2 \cdot C_2H_4 + CH_3CHO + H_2O + 2HCl$$

Zeise (129) had also demonstrated the presence of an aldehyde in his distillate. Moreover, he had isolated ethyl chloride, which was formed as a secondary product, and literally expressed the above equation in words.

An attempt by Birnbaum to prepare Zeise's salt by the reaction of ethylene on a potassium chloroplatinite solution was unsuccessful. When platinic chloride was refluxed with methyl alcohol, partial reduction of the platinic chloride to platinous chloride appeared to take place, but no further reaction occurred.

Using Zeise's original method, Chojnacki (18) prepared the ethylene–platinous bromide compound $KBr \cdot PtBr_2 \cdot C_2H_4 \cdot H_2O$, which was entirely analogous to Zeise's salt.

Jorgensen (61) sought to improve the yields of these olefin compounds

by a modification of Berzelius' method (8). Apparently only one attempt (96) had been made to repeat Berzelius' experiment, and this had resulted in failure. Jorgensen found that the reaction was slow and that refluxing with absolute alcohol for about 10 hr. was necessary. The solution became acidic and some reduction to metallic platinum occurred. The very soluble potassium salt of Zeise's acid could be obtained from the resulting yellow solution, but Jorgensen more conveniently isolated the acid as its tetrammine platinous salt, the formula of which he indicated as

$$\begin{array}{ll} & \cdot NH_3 \cdot NH_3 \cdot Cl \cdot Cl \cdot Pt \cdot C_2H_4Cl \\ Pt & \\ & \cdot NH_3 \cdot NH_3 \cdot Cl \cdot Cl \cdot Pt \cdot C_2H_4Cl \end{array}$$

The primary reaction for this method was given as follows:

$$Na_2PtCl_6 + 2C_2H_5OH \rightarrow 2NaCl + H[PtCl_3 \cdot C_2H_4] + HCl + CH_3CHO + H_2O$$

Biilmann (10) demonstrated that the same general type of compound can be made from an unsaturated alcohol. Allyl alcohol reacted readily with a warm aqueous solution of potassium chloroplatinite according to the equation

$$C_3H_5OH + K_2PtCl_4 \rightarrow K[PtCl_3 \cdot C_3H_5OH] + KCl$$

This alcohol did not react, however, with the acid $H_2PtCl_4$. The compound $K[PtBr_3 \cdot C_3H_5OH]$ was obtained in a strictly analogous manner (11) from potassium bromoplatinite.

Unsaturated acids were found (12) to form complex compounds with platinum, according to the general reaction[2]

$$K_2PtCl_4 + Un \rightarrow K[PtCl_3 \cdot Un] + KCl$$

Interestingly enough, acids with the double bond in the $\alpha$-position with respect to the carboxyl group did not form complexes; however, acids in which the double bonds were in the $\beta$-position or farther removed from the carboxyl group formed complexes, although it was observed that the rate of reaction of the latter class was slower than with allyl alcohol.

When a suspension of platinous chloride in trimethylethylene is saturated with gaseous hydrogen chloride, a brown liquid is obtained from which a platinous chloride–trimethylethylene complex, $2PtCl_2 \cdot C_5H_{10}$, may be isolated (68). The reaction is slow. The true molecular weight of the substance was not determined.

A number of compounds analogous to Zeise's salt, containing unsatu-

[2] Un = olefinic molecule.

rated acids, esters, alcohols, and aldehydes, were obtained from potassium chloroplatinite by Pfeiffer and Hoyer (94). The course of these reactions was followed by a color change of the solution from red to yellow as the potassium chloroplatinite was converted into the complex. Inasmuch as Pfeiffer and Hoyer were unsuccessful in obtaining complexes of olefinic substances with aluminum bromide, stannic chloride, etc., they suggested that the olefin bond might conceivably be a specific coördinating group for platinous salts.

Anderson (3) succeeded in isolating the primary member of the ethylene series, $PtCl_2 \cdot C_2H_4$, from the solution obtained by reducing sodium chloroplatinate with alcohol by evaporation below 50°C. in a high vacuum. A brown, tarry, strongly acid mass was obtained, from which the ethylene–platinous chloride was separated by extraction with chloroform, followed by recrystallization from benzene. The analogous compound, styrene–platinous chloride, $PtCl_2 \cdot C_6H_5CH{=}CH_2$, was also obtained (4). A significant reaction was utilized in this preparation: styrene was found to displace ethylene quantitatively from $PtCl_2 \cdot C_2H_4$ in a vacuum at room temperature. Employing the same method, Anderson readily obtained potassium styrenetrichloroplatinite, $K[PtCl_3 \cdot C_6H_5CH{=}CH_2]$, from Zeise's salt. The corresponding indene compound was found to be much less stable, and while the cyclohexene compound could not be isolated, its formation was indicated. The only compounds obtained which were comparable in stability to Zeise's ethylene compounds were styrene–platinous chloride and potassium styrenetrichloroplatinite.

As a result of this systematic investigation, Anderson drew the interesting conclusion that the coördinating abilities of the olefins decrease in the order $CH_2{=}CH_2$ > $C_6H_5CH{=}CH_2$ > indene > cyclohexene > $(C_6H_5)_2C{=}CH_2$ and $\begin{array}{l} C_2H_5 \diagdown \\ \qquad\qquad C{=}CH_2 \\ CH_3 \diagup \end{array}$. Although no pure compounds of the type $PtCl_2 \cdot 2C_6H_5CH{=}CH_2$ could be isolated, Anderson found evidence for their existence.

A somewhat radical departure was made by Kharasch and Ashford (64) in the method of preparing compounds of the type $PtCl_2 \cdot Un$. Anhydrous platinic chloride or bromide was treated in an anhydrous solvent with the olefinic substance. The method is a rapid one and seems quite general. The reactions involved are not well understood and are probably complex. Hydrogen halide is usually evolved during the reaction, and in some instances a small quantity of platinum separates. Halogenation of the unsaturated compound may also occur. As pointed out by Kharasch and Ashford, the most direct method would be to combine a platinous halide

with an unsaturated compound, but attempts to apply this method have been less satisfactory, owing to the insolubility and inertness of these platinous compounds.

The method of Kharasch and Ashford gave compounds with chloro-substituted olefins but did not seem applicable to unsaturated acids and their esters. It is interesting to note that *trans*-dichloroethylene and *trans*-diphenylethylene formed crystalline coördination compounds with platinum, whereas the corresponding *cis*-isomers failed to react.

Chernyaev and Hel'man (17, 37) prepared Zeise's salt by passing ethylene for 15 days through a concentrated aqueous solution of potassium chloroplatinite containing 3 to 5 per cent of hydrochloric acid, precipitating the tetrammine salt, $[Pt(NH_3)_4][PtCl_3 \cdot C_2H_4]_2$, with aqueous $[Pt(NH_3)_4]Cl_2$, and regenerating $K[PtCl_3 \cdot C_2H_4]$ with potassium chloroplatinite. Compounds of the general formula $[PtRX_2 \cdot C_2H_4]$ were also prepared. In this series R equals thiourea, ammonia, pyridine, and quinoline, and X equals CN, NCS, $NO_2$, I, Br, and Cl.

Hel'man examined (39) the interesting question as to whether the presence of two double bonds, as in butadiene, makes it possible for such a substance to occupy two coördination positions and thus form a five-membered ring. The evidence seems to indicate that no ring is formed and that each double bond functions separately. Only one coördination position is therefore taken up in such compounds as $[PtCl_2 \cdot C_5H_5N \cdot C_4H_6]$ and $[PtCl_2 \cdot NH_3 \cdot C_4H_6]$.

### *2. Palladium–olefin compounds*

The palladium–olefin compound $PdCl_2 \cdot C_5H_{10}$ was reported (68) to be formed when palladous chloride, trimethylethylene, and a trace of some basic substance were allowed to react in a closed tube at room temperature. Kharasch, Seyler, and Mayo (65) were completely unsuccessful in their attempts to prepare the same and analogous compounds by this method. A quite different approach to the problem by these workers, however, resulted in the development of a very effective and general method for the preparation of these compounds. Palladous chloride was converted into the dibenzonitrile–palladous chloride derivative, which, strikingly enough, reacted very rapidly at room temperature with olefins to yield the desired derivatives. The steps in such a preparation are indicated below:[3]

$$PdCl_2 + 2C_6H_5CN \rightarrow (C_6H_5CN)_2PdCl_2$$

$$2(C_6H_5CN)_2PdCl_2 + 2Un \rightarrow [PdCl_2 \cdot Un]_2 + 4C_6H_5CN$$

[3] See page 249 for the proof of the dimeric structure of $[PdCl_2 \cdot Un]_2$.

The displacement of the benzonitrile was thought to take place practically quantitatively, but, because of the experimental difficulties involved, the yields seldom exceeded 70 per cent. By the use of this method compounds containing ethylene, isobutylene, cyclohexene, and styrene were obtained.

### *3. Iron–olefin compounds*

Kachler (62) reported the preparation of the compound $FeCl_2 \cdot C_2H_4 \cdot 2H_2O$ and pointed out that it corresponds to the ethylene–platinous chloride compound $PtCl_2 \cdot C_2H_4$. This substance was said to form when ferric chloride in ether in the presence of a small quantity of phosphorus was heated in a sealed tube. The following equation was given for the reaction:

$$2C_2H_5OC_2H_5 + 2FeCl_3 \rightarrow 2C_2H_4 \cdot FeCl_2 + 2C_2H_5OH + Cl_2$$

Efforts to prepare the compound from alcohol instead of ether were not successful.

An attempt was made by Chojnacki (18) to prepare the compound reported by Kachler, starting with ferrous chloride and ethylene. This corresponds to the method used by Birnbaum in preparing ethylene–platinous chloride from ethylene and platinous chloride. Chojnacki was not successful in this, but claimed that he did prepare the corresponding ethylene–ferrous bromide compound whose composition he gave as $C_2H_4 \cdot FeBr_2 \cdot 2H_2O$. He also stated that a solution of this compound, when treated with a concentrated solution of potassium bromide and evaporated slowly, deposited almost colorless crystals which upon analysis were shown to contain iron, bromine, potassium, and ethylene. No formula was advanced for this substance.

Manchot and Haas (75) were unable to repeat the work of Kachler and Chojnacki. They claimed that Kachler's supposed ethylene–ferrous chloride was really a partially decomposed ether addition compound.

The long heating of iron pentacarbonyl with butadiene was reported (97) to give the complex $Fe(CO)_3 \cdot C_4H_6$, in which two of the five carbon monoxide molecules of the carbonyl had been replaced by one molecule of butadiene. The unsaturated hydrocarbon occupies one or two coördination positions of the iron atom. Less well-defined compounds approximating to $Fe(CO)_3 \cdot (C_5H_8)_3$, $Fe(CO)_3 \cdot (C_5H_8)_2$, and $Fe(CO)_3 \cdot (C_6H_{10})_2$ were obtained with isoprene and with $\beta,\gamma$-dimethylbutadiene (also see page 236).

### *4. Iridium–olefin compounds*

Sadtler (100) reported the preparation of the iridium chloride–ethylene complex $IrCl_2 \cdot C_2H_4$ by the treatment of iridic chloride with absolute

alcohol. The equation for the reaction was said to be similar to that for the preparation of the corresponding platinum compound. When the resulting solution was treated with potassium chloride or ammonium chloride, mixtures of substances resulted. The following complexes were said to have been identified in these mixtures:

$$IrCl_2 \cdot C_2H_4 \cdot NH_4Cl \cdot H_2O \quad \text{or} \quad NH_4[IrCl_3 \cdot C_2H_4] \cdot H_2O$$

$$IrCl_2(C_2H_4)_2 \cdot 2NH_4Cl \quad \text{or} \quad (NH_4)_2[IrCl_4(C_2H_4)_2]$$

$$IrCl_2 \cdot C_2H_4 \cdot 2KCl \cdot XH_2O$$

No compounds of iridium could be obtained by passing ethylene through an iridium chloride solution, nor did a reaction occur when iridium chloride was treated directly with ethylene.

If the above complexes are true chemical individuals, the compound $(NH_4)_2[IrCl_4(C_2H_4)_2]$ has no counterpart in the platinum series. However, the above experimental work does not appear convincing, and these substances would bear further investigation.

## B. COMPOUNDS OF OTHER METALS

### *1. Aluminum–olefin compounds*

The product obtained by cracking petroleum with aluminum chloride under certain conditions consists largely of saturated hydrocarbons. On the theory that the aluminum chloride combines with any unsaturated hydrocarbons formed and holds them back from the distillate, Henderson and Gangloff (42) studied the reaction of aluminum chloride with various unsaturated molecules. Direct reaction of the unsaturated molecule with anhydrous aluminum chloride proved to be unsatisfactory as a means of obtaining compounds which approached definite compositions. A fairly nice crystalline product was obtained from a solution of aluminum chloride in absolute alcohol into which ethylene was passed. This substance was extremely difficult to analyze because of its instability and hygroscopic character, but seemed to correspond to the formula $AlCl_3 \cdot 3C_2H_4 \cdot H_2O$. Later (27) a second product was obtained with ethylene, which appeared to be either $AlCl_3 \cdot 3C_2H_4 \cdot 2H_2O$ or $AlCl_3 \cdot C_2H_4 \cdot 2C_2H_5OH$. In a similar way these investigators were able to prepare compounds of aluminum chloride with other unsaturated hydrocarbons as well as with unsaturated acids, aldehydes, and alcohols.

Very similar results were obtained with ferric chloride, although the reactions were less vigorous and not so complete. Ferric chloride and amylene in methyl alcohol gave $FeCl_3 \cdot C_5H_{10} \cdot CH_3OH$.

From the results of a study of the reactions of aluminum chloride and

unsaturated hydrocarbons, Stanley (111) concluded that any explanation for such reactions must take into account the formation of an aluminum chloride–hydrocarbon complex. Results of an earlier study led Szayna (115) to somewhat similar conclusions.

### *2. Zinc–olefin compounds*

There seems to be some evidence (67, 68) for the existence of addition compounds of zinc chloride and amylene, various formulas having been reported, such as $ZnCl_2 \cdot C_5H_{10}$ and $2ZnCl_2 \cdot C_5H_{10}$. These apparently have been little studied and their exact nature is not clear.

### *3. Copper–olefin compounds*

Berthelot (7) observed that a hydrochloric acid solution of cuprous chloride absorbed ethylene to the extent of 0.17 mole ethylene to 1 mole of cuprous chloride. Propylene was absorbed to a slightly greater extent, the ratio being 0.25 to 1.

It was reported by Manchot and Brandt (74) that cuprous chloride and ethylene combine to form an unstable compound in which 1 mole of ethylene unites with 1 mole of cuprous chloride. The combination did not occur in the absence of water. The compound was too unstable to isolate, and these investigators considered that the combination between these two molecules occurs not through specific atoms but through "latent affinities" of the entire molecule.

Ethylene under pressure was found to give with *solid* cuprous chloride an addition compound (117) which contained 1 mole of ethylene to 1 mole of cuprous chloride, $CuCl \cdot C_2H_4$. It is interesting to note in this connection that no polymerization of ethylene was observed in the presence of cuprous chloride at pressures of 65 to 80 atmospheres and temperatures of 100 to 200°C.

Later (30) it was shown that such a reaction is not limited to ethylene and cuprous chloride. Ethylene, propylene, and isobutylene are absorbed by solid cuprous chloride, and ethylene is absorbed by cuprous bromide. Under suitable conditions olefins may be recovered from gaseous or liquid mixtures by the use of solid cuprous halides.

Cuprous chloride also forms a complex with butadiene (72). This is a rather stable pale yellow powder having either the composition $Cu_2Cl_2 \cdot C_4H_6 \cdot 4H_2O$ or $Cu_2Cl_2 \cdot C_4H_6$, depending upon the conditions under which it is prepared.

### *4. Silver–olefin compounds*

By means of a distribution method, Winstein and Lucas (123) have studied the coördination complexes which the silver ion forms with various olefinic substances. The method consists essentially in distributing the

unsaturated compound between carbon tetrachloride and aqueous silver nitrate, or between carbon tetrachloride and mixtures of silver nitrate and potassium nitrate, and comparing the quantities of the organic substance dissolved in the aqueous layer under these circumstances with the quantity dissolved in the aqueous layer when the latter contains only potassium nitrate.

The unsaturated compounds used were certain monoölefins, diolefins, and unsaturated oxygenated compounds, such as allyl alcohol and crotonaldehyde. The reaction to form a complex was found to be rapid and reversible. Three types of complexes were observed: (*1*) combination of one silver ion with one unsaturated molecule, (*2*) combination of two silver ions with one unsaturated molecule, and (*3*) combination of one silver ion with two unsaturated molecules. In most cases only solutions of these complexes were obtained, although in the cases of two hydrocarbons solid silver complexes were isolated.

According to Winstein and Lucas, probably the first step in the chemical change which takes place when a silver–olefin complex is formed is the replacement of a coördinated water molecule by the ethylenic molecule, as follows:

$$\mathrm{Un} + (\mathrm{H_2O})_2 \cdot \mathrm{Ag}^+ \rightleftarrows \mathrm{Un}(\mathrm{H_2O})\mathrm{Ag}^+ + \mathrm{H_2O}$$

Therefore, it follows that if the strength of the coördinate bond holding a water molecule is much greater than the strength of the silver–olefin bond, there will be little or no tendency for the olefinic substance to form a complex with the silver ion. Of the ten metallic ions studied in this work, silver ion was the only one which entered into complex formation. In aqueous solution the following ions failed to form complexes with an olefin: $Cd^{++}$, $Co^{++}$, $Cr^{+++}$, $Cu^{++}$, $Fe^{+++}$, $Ni^{++}$, $Pb^{++}$, $Tl^{+}$, and $Zn^{++}$.

### *5. Mercury–olefin compounds*

The compounds of olefinic substances with mercuric salts have been more extensively studied than any other class of olefin–inorganic salt complexes. These compounds seem for the most part to be of a somewhat different type[4] from those of platinum, palladium, silver, etc.

Mercury compounds have been made containing ethylene and its homologs, both aliphatic and aromatic unsaturated alcohols, and unsaturated acids. The gaseous olefins react readily with mercuric salts to form compounds (20, 46, 102, 103) from which the olefins may be regenerated by the action of hydrochloric acid. The corresponding reaction of the higher olefins is frequently accompanied by reduction of the mercury to the mercurous state with simultaneous oxidation of the hydrocarbon. If alcoholic

[4] The structures of the mercury–olefin compounds are discussed on page 258.

solvents are employed, the solvent sometimes enters into the reaction and the final products then contain alkoxyl groups. Tausz (116) has described compounds of mercuric acetate with cyclohexene, methylcyclohexene, and the terpenes. He also prepared double compounds of amylene and hexene. Hugel and Hibou (50) have reported that for each olefin the addition compounds with mercuric salts have variable compositions depending on the experimental conditions.

As a class, the mercury–olefin compounds are useful as intermediates in organic syntheses.

### 6. *Miscellaneous compounds*

In connection with the compounds of olefins with inorganic salts, the work of Hofmann and von Narbutt (47) should be mentioned. These investigators reported an unusual reaction which appears to involve direct addition across the double bond. The reaction between dicyclopentadiene and potassium chloroplatinite in propyl alcohol yielded a product, $PtCl_2 \cdot C_{10}H_{12}$, which probably should be formulated as $PtCl \cdot C_{10}H_{12}Cl$. This compound is said to differ very markedly (4) in properties from the ethylene– and styrene–platinous chlorides.

Other unsaturated hydrocarbon–metallic salt complexes have been reported. These do not fall within the province of this survey and will therefore be considered only very briefly. Acetylene complexes of aluminum and copper salts are known. Typical of these are the following: $AlCl_3 \cdot 3C_2H_2 \cdot H_2O$ (42), $2CuCl \cdot C_2H_2$, and $KCl \cdot 4CuCl \cdot C_2H_2$ (121). A number of complexes of aluminum chloride and aluminum bromide with benzene and substituted benzenes have been prepared. Of these the following are representative: $AlCl_3 \cdot 3C_6H_6$ (121), $Al_2Cl_6 \cdot 2sym\text{-}C_6H_3(C_2H_5)_3 \cdot HCl$, $Al_2Br_6 \cdot sym\text{-}C_6H_3(C_2H_5)_3$, and $Al_2Br_6 \cdot C_6H_5CH_3$ (84). Investigations seem to indicate that the stability of such complexes increases as the number of alkyl groups present increases. Antimony pentachloride forms compounds with several aromatic hydrocarbons; the reaction with anthracene to give an intensely green precipitate has been suggested as a qualitative means of identifying this hydrocarbon (43). Antimony trichloride is reported (99) to form the complex $3SbCl_3 \cdot C_6H_6$. The compound $Ni(CN)_2 \cdot NH_3 \cdot C_6H_6$ results (45) when a strongly ammoniacal solution of nickelous cyanide is shaken with benzene. Similar compounds containing phenol, aniline, thiophene, and pyrrole instead of benzene have also been obtained (44).

## III. Discussion of Methods of Preparing Metal–Olefin Compounds

From the foregoing survey it is evident that most of the satisfactory methods for the preparation and isolation of metallic salt–olefin complexes are concerned with platinum and palladium compounds. For this reason

the following discussion of the relative merits of the more important preparatory methods is confined to the compounds of these two metals.

*Method A.*—The reduction of platinic chloride by a saturated primary alcohol (Zeise's original method) seems to involve many side reactions, and the yields of the corresponding olefinic complex are never high.

*Method B.*—The reaction in which sodium chloroplatinate is reduced by a saturated primary alcohol likewise is very complex and is none too satisfactory for other than ethyl alcohol.

Both methods A and B give, obviously, only the $\alpha$-unsaturated complexes.

*Method C.*—In reactions of olefinic compounds with potassium chloroplatinite in aqueous alcohol solution, the unsaturated molecule enters the coördination sphere and displaces one chloride ion:

$$K_2PtCl_4 + Un \rightarrow K[PtCl_3 \cdot Un] + KCl$$

This displacement proceeds at room temperature or slightly above but is slow, owing to the insolubility of the chloroplatinite in alcohol. Reactions of this type are reversible (4), and in carrying out preparations by this method an equilibrium must be attained. Zeise's salt is stable enough to be recrystallized unchanged in the presence of an excess of potassium chloride or hydrochloric acid, while with other olefin complexes under the same conditions recrystallization may lead only to potassium chloroplatinite (13). Anderson points out that the extent to which the olefin-containing complex anion is formed in this reaction may thus afford some qualitative measure of the coördinating power of the olefin.

*Method D.*—In some cases olefins add directly to platinous chloride dissolved in an absolute alcohol-hydrochloric acid mixture (4). Since the system is homogeneous, the reaction proceeds quite rapidly but usually is incomplete, owing to the presence of the necessarily high concentration of hydrochloric acid.

*Method E.*—A significant method of preparation is by the direct replacement of one olefin by another either under reduced pressure or in solution.

(*1*) Under reduced pressure: As Anderson points out (4), the factors involved here are the relative stabilities of the salts, i.e., the relative coördinating tendencies of the olefins, and the relative volatilities of the olefins under reduced pressure. Styrene readily displaces ethylene from Zeise's salt, yet the styrene complex is definitely less stable than the ethylene salt.

(*2*) In solution: In some cases this method might be of some importance. It was found to be applicable to the palladium-olefin compounds (65), but as a means of preparing these complexes was of only secondary importance.

*Method F.*—Undoubtedly the most satisfactory method of preparing complexes of the type $[PtX_2 \cdot Un]_2$ is the method in which the platinic halide is treated in an anhydrous solvent, such as benzene or glacial acetic acid, with the unsaturated compound. The reaction proceeds smoothly and good yields are obtained. In general, platinic bromide is somewhat better for these reactions, probably because the bromide is more soluble than the chloride.

*Method G.*—Palladous chloride–olefin derivatives can be prepared by the action of the olefin on dibenzonitrile–palladous chloride. The reaction takes place readily and gives good yields.

It is interesting to note in this connection that while dibenzonitrile–palladous chloride reacts with olefins to give compounds of the type $[PdCl_2 \cdot Un]_2$, the 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.

## IV. Properties and Reactions of Metal–Olefin Compounds

The coördination compounds $PtCl_2 \cdot Un$ (usually formulated as $[PtCl_2 \cdot Un]_2$)[5] are well-defined crystalline substances. They are decomposed by water, but in general are soluble in ether, chloroform, alcohol, and acetone. They are difficultly soluble or insoluble in glacial acetic acid, and only moderately soluble in cold benzene. Most of these compounds do not possess sharp melting points but darken over a range of several degrees. Their stabilities vary widely: the compound obtained from *trans*-dichloroethylene decomposes in several days, while that from dipentene remains unchanged after standing in the air for ten months (64).

The ethylene complex $[PtCl_2 \cdot C_2H_4]_2$ (3) and the isobutylene complex $[PtCl_2 \cdot (CH_3)_2C{=}CH_2]_2$ (64) are said to dissolve in aqueous potassium chloride or sodium chloride, presumably forming compounds analogous to Zeise's salt:

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

The ethylene–platinum compound $[PtCl_2 \cdot C_2H_4]_2$ decomposes without melting and does not combine with a further molecule of ethylene. This is in contrast to the reaction of $PtCl_2 \cdot CO$, which with carbon monoxide readily forms $PtCl_2 \cdot (CO)_2$.

A further interesting and possibly significant reaction of the ethylene–platinous chloride compound is the fact that it is rapidly and quantitatively reduced by hydrogen at room temperature to platinum, hydrogen chloride, and ethane (3):

$$[PtCl_2 \cdot C_2H_4]_2 + 4H_2 \rightarrow 2Pt + 4HCl + 2C_2H_6$$

[5] See page 249 for proof of dimeric structure.

The analogous styrene–platinous chloride, $[PtCl_2 \cdot C_6H_5CH{=}CH_2]_2$, is likewise reduced with extreme ease, reacting with hydrogen below 50°C. At higher temperatures incandescence may accompany the reaction (4).

When these substances are treated with pyridine, decomposition of the complex occurs and the olefin and pyridine–platinous chloride result (64):

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

Concentrated hydrochloric acid causes decomposition in the following manner:

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

Bromine also decomposes these compounds; the liberated olefin in turn is brominated:

$$[PtCl_2 \cdot Un]_2 + 2Br_2 \rightarrow 2UnBr_2 + 2PtCl_2$$

As previously mentioned, styrene and amylene can displace ethylene from $[PtCl_2 \cdot C_2H_4]_2$ at room temperature under reduced pressure (4).

The potassium salts $K[PtCl_3 \cdot Un]$ are usually too soluble to be obtained in the pure state and are more conveniently isolated as salts of $[Pt(NH_3)_4]^{++}$, strychnine, brucine, $[Coen_2(C_2O_4)]^+$, and *trans*-$[Coen_2Cl_2]^+$. The last two ions are in general more satisfactory than $[Pt(NH_3)_4]^{++}$ in forming well-crystallized and difficultly soluble salts of $[PtCl_3 \cdot Un]^-$. According to Anderson (3), the quinolinium salts of the olefintrichloroplatinites are characterized by relatively high stability and low solubility. Quinolinium ethylenetrichloroplatinite is sufficiently stable to be recrystallized from boiling water; in the presence of one molecular quantity of quinoline, it is converted into the non-electrolyte, quinoline–ethylene–platinous chloride:

$$C_9H_7NH[PtCl_3 \cdot C_2H_4] \underset{HCl}{\overset{C_9H_7N}{\rightleftharpoons}} [C_9H_7N \cdot PtCl_2 \cdot C_2H_4]$$

Hot 2 *N* hydrochloric acid reverses this reaction.

Potassium cyanide effects the vigorous decomposition of $K[PtCl_3 \cdot C_2H_4]$, ethylene being liberated quantitatively according to the equation

$$K[PtCl_3 \cdot C_2H_4] + 4KCN \rightarrow K_2Pt(CN)_4 + 3KCl + C_2H_4$$

Anderson points out (3) that other reagents capable of forming complex platinites, $K_2PtX_4$, have a tendency to react similarly. However, the extent to which ethylene is displaced at room temperature depends on the nature of the complex. Anderson postulates that the reaction may proceed by an initial metathesis to a complex $K[PtX_3 \cdot C_2H_4]$, which may then break down spontaneously in the presence of an excess of reagent. When X equals CN this breakdown is immediate and quantitative; for X equals

$NO_2$, however, only a fraction of the ethylene is displaced at room temperature. The evolution of ethylene with potassium thiocyanate is intermediate between that of cyanide and that of nitrite.

If ethylene–platinous chloride, $[PtCl_2 \cdot C_2H_4]_2$, is dissolved in hydrobromic acid and warmed, Chojnacki's acid, $H[PtBr_3 \cdot C_2H_4]$, is formed. This can be isolated as the quinolinium salt, which is decomposed by hot water and is consequently less stable than the corresponding chloro compound. From such considerations Anderson concludes that compounds of the general type $K[PtX_3 \cdot C_2H_4]$ appear to decrease in stability in the order $X = Cl > Br > NO_2 > NCS > CN$.

Above 90°C. Zeise's salt undergoes the following reaction with water (3):

$$K[PtCl_3 \cdot C_2H_4] + H_2O \rightarrow KCl + 2HCl + Pt + CH_3CHO$$

The corresponding styrene compound is somewhat less stable; dissociation occurs slowly at room temperature in aqueous solution, with the liberation of styrene and the deposition of platinous chloride.

Ethylene is almost quantitatively expelled from Zeise's salt by anhydrous pyridine (3):

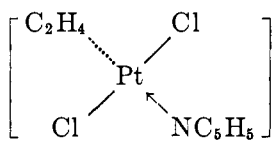
$$K[PtCl_3 \cdot C_2H_4] + 2C_5H_5N \rightarrow [PtCl_2(C_5H_5N)_2] + KCl + C_2H_4$$

Excess aqueous pyridine ultimately transforms Zeise's salt into tetrapyridinoplatinous chloride:

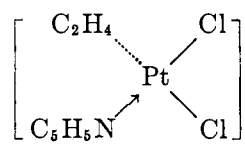
$$K[PtCl_3 \cdot C_2H_4] \xrightarrow[\text{pyridine}]{\text{aqueous}} [PtCl_2 \cdot C_2H_4 \cdot C_5H_5N] \rightarrow$$

$$[PtCl_2(C_5H_5N)_2] \rightarrow [Pt(C_5H_5N)_4]Cl_2$$

The non-ionic complex $[PtCl_2 \cdot C_2H_4 \cdot C_5H_5N]$, which is the product of the first step in the above reaction, is thought to have a *trans*-configuration (formula I). Aqueous ammonia gives a similar compound. If, however, the compound $K[PtCl_3 \cdot C_5H_5N]$ is treated with ethylene, an isomer of the product of the above reaction is obtained (16, 17). This is presumably the *cis*-form (formula II).




I




II

When 1 mole of Zeise's salt reacts with 2 moles of sodium nitrite, ethylene splits out and $Na_2[PtCl_2(NO_2)_2]$ is formed (41):

$$K[PtCl_3 \cdot C_2H_4] + 2NaNO_2 \rightarrow Na_2[PtCl_2(NO_2)_2] + C_2H_4 + KCl$$

If the proportions are mole for mole, the product is $Na[PtCl_2(C_2H_4)(NO_2)]$. This substance is very soluble but reacts with $[Pt(NH_3)_4]Cl_2$ to give $[Pt(NH_3)_4]\ [PtCl_2(C_2H_4)(NO_2)]_2$. The $C_2H_4$ and $NO_2$ groups in this complex are said to be in the *trans*-positions.

Substitution about the double bond in olefinic substances seems to lower greatly the stability of the coördination compounds of the type $K[PtCl_3 \cdot Un]$ (4). On the other hand, the water-solubility of the compounds derived from substituted olefins is higher than that of the ethylene compounds.

All of the palladium compounds obtained by Kharasch, Seyler, and Mayo (65) were colored, unstable, and rather insoluble in the common organic solvents. All were less stable in solution than when solid and were evidently less stable in acetone and alcohol than in other solvents. As a class, these compounds are less stable than the corresponding platinum compounds.

It might be expected that an olefin capable of forming a more stable compound would be able to displace the olefin from a less stable palladium–olefin complex. This appears to be the case (65). Cyclohexene formed the most stable compound and no other olefin was found to displace it from a solution of the cyclohexene–palladous chloride. The ethylene complex underwent displacement with cyclohexene but was not affected by styrene. The stabilities of the palladous chloride–olefin compounds in solution are therefore in the order cyclohexene > ethylene > styrene. The ethylene compound in the dry state apparently is less stable than the styrene compound, but this is believed to be due to the greater volatility of the ethylene.

Comparatively little information is available regarding the properties and reactions of other metallic salt–olefin complexes. In most cases these substances are decidedly less stable than the platinum and palladium compounds and some of them are known only in solution.

## V. Technical Applications of Metal–Olefin Compounds

There seems to be little doubt that the metallic salt–olefin complexes are of great significance in many syntheses and processes involving olefinic substances. However, a scarcity of pure research and of pertinent journal and patent literature along this line makes it difficult even to speculate on the extent of the usefulness of these substances. Many compounds which are classed as catalysts for certain polymerization, hydration, and hydrogenation reactions may function by means of intermediate complex formation. The following brief survey indicates the general types of substances used in these and other reactions. Some are definitely known to form olefin complexes. Many of them, however, apparently have never been investigated from this standpoint.

The gaseous olefins are readily absorbed by aqueous solutions of cuprous, silver, mercuric, and platinous salts (26, 79). Complex compounds are probably formed. The olefins can be removed from these solutions by warming or by reducing the pressure. Scrubbing coal gas with an acid solution of silver nitrate under ordinary or increased pressures at 0–10°C. has been proposed (48, 49, 59, 114) as a method of removing ethylene and other olefins. These olefins may be subsequently recovered by heating the solution to 50–70°C. An ammoniacal solution of a cuprous salt was suggested (31, 60, 120) as a means of absorbing olefins (mainly ethylene) and carbon monoxide from coal gas, coke oven gases, and similar gases under 150 to 250 atmospheres pressure. The gases released from the ammoniacal solution may be scrubbed with either a solution of silver nitrate to absorb olefins or an ammoniacal solution of cuprous formate (5). Dubois (24) reported that both acid and ammoniacal solutions of cuprous chloride absorb olefins practically quantitatively from mixtures with other gases. Diolefins can be recovered from mixtures also containing monoölefins by taking advantage of the fact that the diolefins form insoluble complexes with certain heavy-metal salts (36). The more unsaturated constituents are removed from cracked oils by heating with ferric chloride solution (52), and hydrocarbon oil fractions of low boiling point are purified by treatment with aluminum chloride below 35°C. (113).

In the preparation of butadiene, advantage has been taken of the complex-forming ability of olefins (57). Butane is catalytically dehydrogenated to butylene. This is separated from the reaction mixture by solutions or suspensions of salts that absorb olefins, as, for example, silver nitrate, cupric nitrate, or mercurous nitrate. The butylene is easily recovered by heating the solution or reducing the pressure and is further dehydrogenated to butadiene. The latter can be removed by a solution of cuprous chloride containing ammonium chloride (72) or by other salts of the heavy metals of Groups I and II.

Of the many inorganic halides which have been found effective for condensing or polymerizing olefins, aluminum chloride is without doubt the most popular (81). The exact rôle that aluminum chloride plays in its reactions with olefins is uncertain. In the broadest sense it is looked upon as a catalyst. Olefins in the presence of aluminum chloride are said to polymerize, isomerize, cyclicize, and form paraffins and more highly unsaturated compounds (25).

Aluminum chloride has been used for converting gaseous and high-boiling olefins into low-boiling liquids (98), viscous oils (80, 106), synthetic lubricating oils (90), and synthetic resins (19). A patent (54) has been issued covering the process for preparing a double compound of ethylene and aluminum chloride. This compound is used for condensing hydro-

carbons. Aluminum fluoride has also found some application in these processes (56).

Boron halides, especially boron fluoride, have also been used extensively for polymerizing olefins. With boron fluoride, polymers of high molecular weight (86), rubber-like substances (21), and oils which compare favorably with petroleum lubricating oils (85) have been obtained. Boron halides are reported to form complexes with olefins; these complexes are useful in effecting the polymerization of olefins (28).

It seems not unlikely that the Friedel–Crafts reactions may proceed by means of an intermediate halide salt-complex. Aluminum chloride is the common catalyst for these reactions, but many other halides have been used (82).

Carbonyl compounds of metals such as tungsten, molybdenum, and those of Group VIII of the Periodic System have been used for converting high-boiling hydrocarbons into lower boiling forms by hydrogenation under pressure (55).

Metallic salt–olefin complexes are probably important intermediates in some stages of synthetic rubber manufacture, but, here again, detailed information is lacking. The polymerization of butadiene or of its derivatives is effected by boron fluoride (35), aluminum chloride (130), heavy-metal carbonyls such as those of iron, nickel, cobalt, chromium, etc. (2, 53), and by certain metal–organic compounds, such as iron phthalocyanine sulfonic acid (58). Cuprous chloride solutions appear to be employed commercially (14, 66) to dimerize acetylene to vinylacetylene. This is the first step in making 2-chloro-1,3-butadiene, which in turn is readily polymerized to an excellent rubber.

The hydration of olefins in aqueous acid solutions is frequently greatly accelerated by the presence of certain metal salts. This may be another instance in which olefin complexes are important intermediates. Of the many compounds which have been useful in aiding these hydration reactions, compounds of the metals of Groups I, II, IV, V, and VIII are most frequently mentioned (23, 33, 78, 83, 109, 110, 119). Usually soluble catalytic salts such as sulfates, chlorides, and cyano complexes (77) are employed directly. In some cases, however, insoluble compounds may be added to the solution and then converted into soluble complexes by passing carbon monoxide or nitric oxide through the mixture (78).

## VI. Structure of Metal–Olefin Compounds

It seems evident that in a complex compound of an olefinic substance with a metallic salt the double bond is actually functioning in the metal–olefin union. Pfeiffer and Hoyer (94) arrived at this conclusion because they found that unsaturated alcohols, acids, and aldehydes form sub-

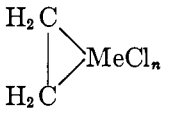
stances analogous to Zeise's salt, whereas the corresponding saturated compounds are completely incapable of reacting similarly. Winstein and Lucas (123), although admitting that the unsaturation of the coördinating molecule appears to be responsible for complex formation, point out that this interpretation is not entirely unambiguous, especially in those cases where the complex is composed of one metal ion and two unsaturated oxygenated molecules.

The interest and importance of this group of complexes center around the nature of the bond joining the metal and olefinic molecule. While these compounds differ in no marked way chemically from other types of complex salts (61), the mechanism of complex formation is obscure, in that the coördinating group possesses no "lone pair" of electrons with which to form the coördinate link.

The electron-pair theory is generally accepted as offering the best picture of the formation of a coördinate bond and the most satisfactory explanation of the many properties of coördination compounds. This view, however, is not universally accepted. Samuel and Hunter (101) point out that it is not altogether clear how a closed $s^2$ electron-pair can be shared with a second atom. They believe that the conception of the lone pair of electrons as an agent for true chemical linkage is not entirely in harmony with the results of band spectroscopy experiments. The acceptance of the electron-pair theory demands, in turn, the presence of a "lone pair" of electrons in order that an atom may exhibit "donor" functions. These are not apparent in the usual formulation of olefinic substances. In the opinion of some authorities the formation of complex compounds of the olefins with metallic salts supplies an interesting test of the application of the lone-pair bond theory.

Pfeiffer (91, 92) disposed of the structural problems associated with these compounds with the vague statement that the unsaturated carbon atoms of the olefinic molecule form the center of a region which, as a whole, is capable of exhibiting a kind of "secondary" valence. This so-called secondary valence may be satisfied by various ions or molecules. On this basis Zeise's salt is indicated as $K[C_2H_4 \ldots . PtCl_3]$.

Hantzsch (34) objected to this formulation on the ground that it represents carbon as having a coördination number of 5 instead of 4. To avoid this, he suggested a symmetrical structure (III) for these complexes:

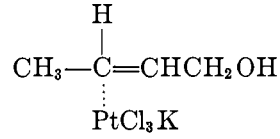



III

He entirely neglected, however, to elucidate the nature of the bonds between the hydrocarbon molecule and the metal.

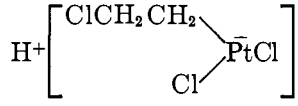
Biilmann (10) suggested that with a properly substituted olefinic substance the potassium salt $K[PtCl_3 \cdot Un]$ might contain an asymmetric carbon atom; however, he believed that resolution was probably not possible because of the instability of the compound.

Pfeiffer and Hoyer (94) offered no explanation of the structure. They pointed out the possibility that an asymmetric carbon atom can be present in certain of these compounds and gave a formula as follows:



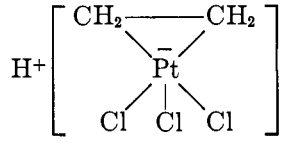
IV

Drew, Pinkard, Wardlaw, and Cox (22) proposed the following structure for Zeise's acid:



V

In their opinion this compound is analogous to the corresponding ammonia and pyridine compounds, in which they believed that substantial evidence points to the presence of $NH_3Cl$ and $C_5H_5NCl$ groups. They stated that in the case of Zeise's acid it is not possible, owing to the quadrivalency of carbon, to write the group $ClCH_2CH_2$ in any other manner, since the alternative formula would be that of a platinic instead of a platinous compound:



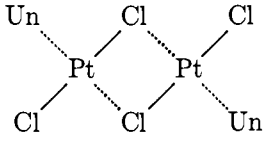
VI

A considerable amount of evidence seems to justify the formulation of these compounds as derivatives of bivalent platinum. The more significant points are as follows: (*1*) Zeise's salt and its analogs can be prepared by direct reaction of the unsaturated substance on potassium chloroplatinite in aqueous alcohol solution (94). (*2*) Zeise's acid is formed by the direct absorption of ethylene by platinous chloride in alcoholic hydrogen chloride (13). (*3*) The reactions of these compounds with pyridine, hydrochloric acid, bromine, and potassium cyanide (pages 242–243)

indicate the presence of platinous platinum. (*4*) The compound prepared from dipentene and platinic chloride, for example, is the same as the one obtained by treating dipentene with platinous chloride in the presence of dry hydrogen chloride (64).

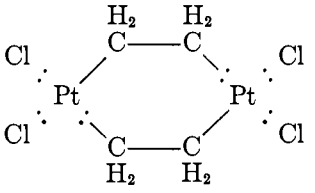
The platinum–olefin and palladium–olefin compounds of the general type $MCl_2 \cdot Un$ probably possess a doubled molecular formula in order to maintain the coördination number of 4 for these metals. The coördination compounds of this series are unstable at higher temperatures, and consequently the ebullioscopic method for the determination of their molecular weights is not satisfactory. An approximate molecular weight determination, however, by the Barger–Rast method points to the dimeric form for ethylene–platinous chloride (3). Kharasch and Ashford report (64) that the solubility of isobutylene–platinous chloride in benzene permits an accurate determination of the molecular weight of this compound. Results indicate that it is bimolecular. Precise determinations of the molecular weights of the corresponding palladous–olefin compounds were not possible, but an approximate molecular weight of 409 was obtained for styrene–palladous chloride by the freezing-point method in benzene solution. This is intermediate between 282 for the monomeric and 564 for the dimeric form of $PdCl_2 \cdot C_6H_5CH{=}CH_2$.

Pfeiffer (93) has proposed a formula for ethylene–platinous chloride in which platinum is tetracovalent, the ethylene molecule occupies one coördination position about the platinum atom, and two of the chlorine atoms serve as bridging atoms in the dinuclear complex (formula VII). Anderson (3) accepts this formula.



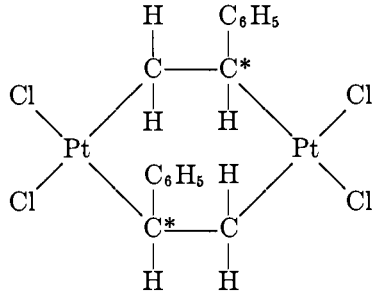

VII

Kharasch and Ashford (64) have objected to such a formula on the basis that it postulates the formation of two coördinate bonds by one chlorine atom. They have proposed a ring structure for compounds of the type $[MCl_2 \cdot Un]_2$, in which the *olefin* molecule acts as a bridging unit between the metal atoms:

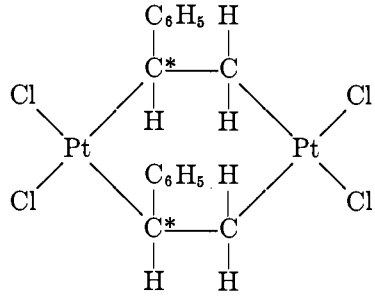



VIII

With such a structure there are interesting possibilities of structural isomerism. As pointed out by Kharasch and Ashford, the compound derived from styrene, for instance, might have either of the two structures shown by the formulas IX and X:



IX



X

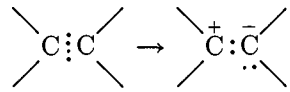
Each of these structural isomers contains two asymmetric carbon atoms and can exist in three stereoisomeric forms. The number of isomers would become still greater, of course, with more highly substituted ethylenes.

Kharasch and Ashford's objection to Pfeiffer's formula need not be given too much weight, since stable compounds are known in which halogen atoms act as bridging groups. A number of examples of such compounds have been described by Mann and Purdie (76), Gibson and Simonsen (29), Palmer and Elliott (88), and Wells (122).

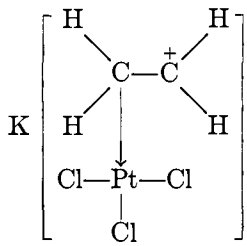
An objection may be raised to Kharasch and Ashford's formula, in that platinum does not appear to be truly in the platinous state. This might seem difficult to reconcile with their statement that it is well established that these compounds are derivatives of platinous platinum. It seems more difficult, however, to understand the mutual ease with which one olefin can replace another if the structure is of the type shown in formula VIII. In the opinion of Anderson (3), any formulation involving quadrivalent platinum introduces covalences linking the hydrocarbon to the platinum atom, and the resulting complex must necessarily be represented as an alkyl platinum derivative. Winstein and Lucas (123) feel that from a purely chemical point of view one would hardly expect these compounds to undergo so many reactions typical of compounds having a coördinate link if the carbon-to-metal bond is a metallo-organic type as in formula VIII.

As a matter of fact, it is perhaps pointless to attempt to label platinum in a cyclic compound such as proposed by Kharasch and Ashford as platinous or platinic. A structure of this type is unique and the usual terms pertaining to valence and linkages can not be used here appropriately.

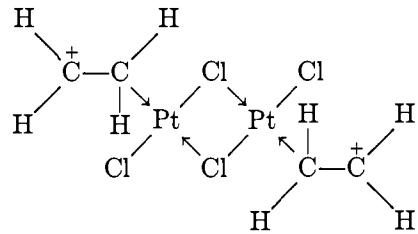
Kharasch and Ashford's method of formulating the structures of the bimolecular compounds $[MCl_2 \cdot Un]_2$, is hardly applicable to compounds of the type $K[PtCl_3 \cdot Un]$. It seems very improbable that the latter substances are other than unimolecular, since the platinous platinum has its normal coördination number of 4. Kharasch and Ashford (64), nevertheless, point out that there is no experimental evidence to support this contention. It is generally agreed that in the compounds $K[PtCl_3 \cdot Un]$ the olefinic molecule occupies only one position in the coördination sphere (3, 61, 92, 94). By our classical concepts, then, something must happen whereby a pair of electrons becomes available for coördinating purposes in the olefinic molecule. One possible mechanism by which such a pair of electrons may be produced in ethylene and similar compounds or in an aromatic nucleus has been proposed by Bennett and Willis (6). They suggest that a lone pair may be produced by a complete transfer of one pair of electrons from the double bond to one carbon, resulting in a polarized state of the molecule, and converting it at the same time into a potential "donor" molecule:



The structures of Zeise's salt and of Pfeiffer's and Anderson's ethylene–platinous chloride would then presumably become as shown in formulas XI and XII.



XI



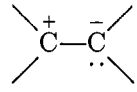
XII

Anderson (4) critically examined the applicability of this theory to the platinum–olefin type compounds, and, while admitting that such a mechanism seems the only means whereby a lone pair of electrons can be produced at one olefinic carbon atom, indicated that it is not altogether free from objections on physical grounds. This hypothetical polarized state of the bond represents an excited state of the molecule, and it is questionable whether such an excitation would occur under the conditions used for preparing these compounds. If, on the other hand, the activation takes place in the field of the platinum atom, the reactions must still involve a

high energy of activation. If an excitation or polarization of the olefinic molecule occurs, then an abnormally low value for the net heat of formation of the coördinate link might be expected as compared with the value found for the coördination of compounds already having a free pair of electrons. In so far as the strength of a coördinate bond can be taken as a measure of its heat of formation, the linkage Pt←olefin must be associated with a smaller heat of formation than the linkage Pt←$NR_3$. A low heat of coördination, however, is not necessarily an indication that internal rearrangement preceded coördination.

Another objection to the mechanism discussed above is that the opening of the double bond leaves one of the carbon atoms with a sextet of electrons. Such a mechanism would be expected to provide ample opportunity for polymerization and rearrangement. In fact, a reversible process in which the double bond is opened by coördination to a metal should actually promote polymerization. Anderson reports that polymerization occurred occasionally but quite irregularly. Lucas states that polymerization was not observed and that not the slightest rearrangement of olefins occurred.

If a polarized intermediate such as

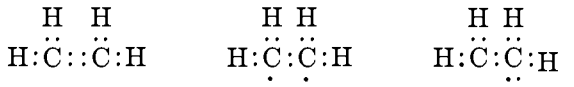


is formed in the coördination of an olefin to a metal, unsymmetrical substitution about the double bond should be a factor influencing the ability of olefins to coördinate (4). This seems to be borne out by Anderson's observation that styrene coördinates much more readily than cyclohexene. The phenyl group in styrene confers on the double bond an appreciable dipole moment ($0.37 \times 10^{-18}$ E.S.U.) (87). If the polar influence of this group is associated in some way with the relatively high coördinating ability of styrene, the insertion of another phenyl group on the same carbon might well lead to an even greater coördinating tendency. Anderson found the exact reverse of this to be the case. If unsymmetrical diphenylethylene formed coördination compounds with platinous chloride, they were too unstable to be isolated.

These apparent contradictions as to the rôle that dissymmetry about the double bond plays in promoting or retarding coördination have been explained by Anderson on the basis of the steric factors involved. He concludes that in the case of unsymmetrical diphenylethylene the augmented dissymetry of the double bond may be outweighed by the steric effect of the two phenyl groups. These two bulky groups may effectively "block" any attachment to the carbon atom.

It is interesting to note in this connection that ethylene, which forms some of the most stable metal–olefin compounds, has been found to have

zero dipole moment (108). Lewis (69) supposed that the average state of ethylene is a composite of three states as indicated below:

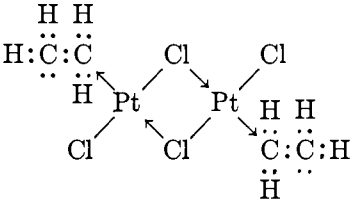


At any given instant some molecules may approximate any one of these states, but the great majority of them must be nearest to the first structure, as shown by the phenomenon of *cis–trans* isomerism in olefinic molecules. Such stereoisomerism is generally ascribed to the lack of free rotation about the double bond.

The relationship, if any, between *cis*- and *trans*-configurations and coördinating ability seems somewhat obscure. Kharasch and Ashford (64) isolated crystalline compounds from *trans*-dichloroethylene and from *trans*-diphenylethylene, but could not obtain compounds from the *cis*-isomers. They did, however, obtain coördination complexes of the *cis*-compounds cyclohexene, dipentene, and pinene. Rather similar erratic results were obtained by Anderson (4), who found that both of the *cis*-compounds indene and cyclohexene coördinate, whereas *trans*-phenylmethylethylene does not. However, the *trans*-form of pentene-2 coördinates rather strongly.

One fact which stands out and seems quite general is that progressive substitution about the double bond greatly reduces the coördinating ability of the olefins.

In attempting to overcome the necessity for assuming the existence of a trivalent carbon atom and yet retain the advantages of Pfeiffer's formula for ethylene–platinous chloride, Stiegman (112) proposed a formula (XIII) in which platinum acts as the "donor" atom and the activated or polarized olefin the "acceptor" molecule:

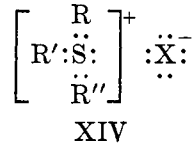


XIII

The assumption is made that in some manner the two electrons needed for the platinum–olefin bond are "called out" from the electron shells of the platinum atom. This is indicated, or implied at least, in the ring formula of Kharasch and Ashford.

In Stiegman's formulation each carbon atom has a complete octet of

electrons, but one pair of these electrons is "unshared". Whether such a structure could have a stable existence is debatable. It is conceivable that under the influence of the pair of electrons donated from the platinum to one carbon atom the pair of unshared electrons on the other carbon atom would act much as a fourth group about this atom. This situation would be quite comparable to the case of sulfur in sulfonium salts:

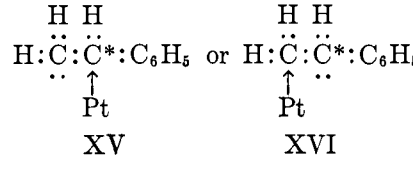


XIV

Properly substituted sulfur compounds of this type have been resolved (95, 107), indicating that the valences of the sulfur atom possess a tetrahedral distribution and that the unshared pair of electrons acts as the fourth group.

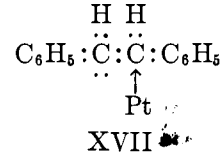
Another factor which may have some bearing on whether a structure as given above for the platinum–olefin compounds could exist is that the carbon holding the unshared pair of electrons possesses a residual negative charge.

When a properly substituted olefin is used in preparing a compound analogous to that shown in formula XIII, one or more asymmetric carbon atoms might well result. In the case of styrene–platinous chloride, the platinum can donate a pair of electrons to either of the two carbon atoms:



XV XVI

In formula XV the starred carbon atom is asymmetric because of the presence about it of four different groups. In formula XVI the starred atom is again asymmetric if the pair of unshared electrons can function as the fourth group. In the case of stilbene only one structure is possible:



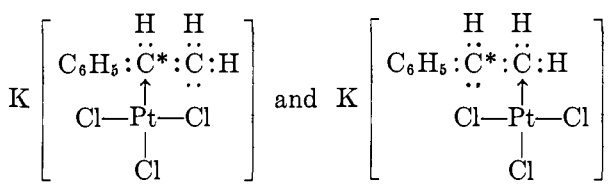
XVII

However, since these compounds are non-ionic and possess no functional groups, the usual methods of resolution are not applicable. Using the method of selective adsorption of one isomer by finely divided optically

active quartz in contact with the racemic solution (118), Stiegman (112) obtained some evidence of optical activity with the styrene– and stilbene–platinous chloride complexes. A more thorough study of the quartz method for the resolution not only of the above platinum–olefin compounds but also of compounds definitely known to be resolvable by other means casts some doubt on the reliability of this method (63). For this reason the results obtained by Stiegman must be regarded as somewhat inconclusive. Moreover, from the standpoint of the stereochemical possibilities involved, a positive resolution of these compounds by the quartz method would not distinguish between the formula suggested by Stiegman (formula XIII) and the ring structure proposed by Kharasch and Ashford (formula VIII).

An analog of Zeise's salt has been studied with a view to determining whether the ion $[PtCl_3 \cdot Un]^-$ can be resolved when a properly substituted olefin is present in the coördination sphere (63). The styrene complex was used because it appeared to be the most stable of the complexes which satisfy the stereochemical requirements of the problem. Since it is reasonably certain that the ion $[PtCl_3 \cdot Un]^-$ is monomolecular (see, however, page 251), it was thought that the ambiguities associated with compounds of the type $[PtCl_2 \cdot Un]_2$ and the rather uncertain method of resolution would be eliminated.

If the platinum acts as a "donor" atom, the styrene analog of Zeise's salt can be formulated in two ways (formulas XVIII and XIX):



XVIII and XIX

In either event an asymmetric carbon atom is present (starred), and the anion exists in enantiomorphic forms. Since the compound is ionic, the usual methods of resolution can be employed. While the preliminary attempts to resolve the above compound have been unsuccessful, they are not to be taken as conclusive, and the above formulation cannot be definitely discarded.

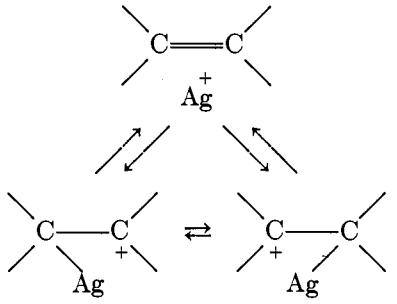
Hel'man (40) has proposed a unique explanation of the bond formation between an olefin and platinum. By virtue of the high *trans* influence (15, 38) of this group of compounds, the platinum first functions as an electron donor to the activated olefin, and then becomes an acceptor. This, according to Hel'man, results in the formation of a four-electron

covalent bond and a high activity of the inner sphere. Such a mechanism is difficult to comprehend.

Little insight into the structure of these compounds has been obtained from absorption spectra data. Anderson (4) examined the absorption spectra of the styrene and indene salts $K[PtCl_3 \cdot Un]$ over the range 2800–4300 Å. on a reflection grating spectrograph and found them to conform closely to those of other platinous complexes. Apparently no study of the infrared absorption spectra of these compounds has been made.

Winstein and Lucas (123), using their distribution method, have concluded that complex formation with silver ions in solution is a general property of ethylenic compounds. They state that the silver–olefin coördinate bond is probably similar in character to the coördinate bonds of other metals with olefins. Their observations indicate that complex formation is rapid and reversible. They found no rearrangement of isomeric forms of substituted olefins during their work.

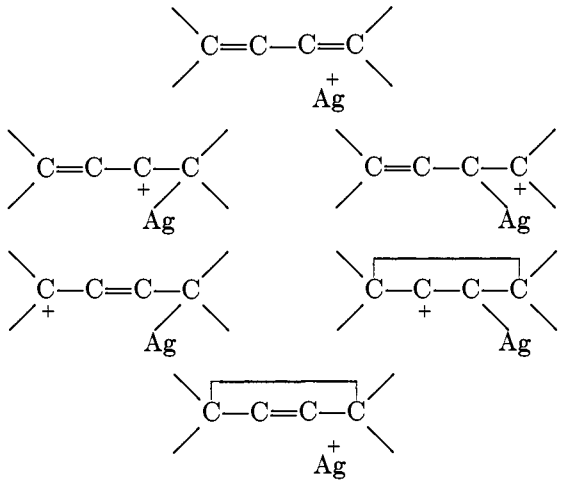
From a consideration of their results, Winstein and Lucas propose a structure for these metal–olefin complexes which involves equilibria among three forms:



XX

They call attention to the fact that a structure made up of contributions from these three forms need not result from an intermediate containing an activated double bond. Resonance among the three forms prevents the complex from behaving as a molecule having a carbon with just a sextet of electrons. Thus the facts of rapid reversible reactions but no polymerization or rearrangement are adequately explained, and the characteristic properties of these complexes seem reasonable. Also, they maintain, any objection to the formation of what amounts to a three-membered ring on the basis of strain involved is not serious, since the carbon–carbon–metal bond angle will be considerably greater than the 60° angle of cyclopropane, and the resonance energy is enough greater than the strain energy that a structure of moderate stability is to be expected.

On the basis of the same mechanism, Winstein and Lucas consider the following forms as contributing to the structures of the diene–monosilver complexes:



XXI

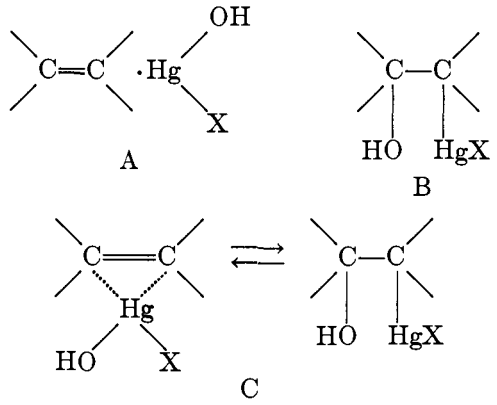
By extending the concept of resonance to the Zeise series of salts, $K[PtCl_3 \cdot Un]$, three electronic forms corresponding to those on page 256 (XX) are obtained. In the case of complexes of the type $[PtCl_2 \cdot Un]_2$, the possibility of resonance among nine electronic forms is a factor which, according to Winstein and Lucas, enhances the stability of these compounds.

Winstein and Lucas agree with Anderson that the influence of the structure of the olefinic molecule upon the stability of the resulting complexes is steric. Observations made during their study of silver–olefin complexes indicate that the stability of the complex is less, the more deeply the double bond is buried in the carbon chain.

It is interesting at this point to recall Anderson's comments (3) with regard to the reaction of Zeise's salt with water (page 243). He states that the products of decomposition of this salt by water might be expected to contain either (*a*) ethylene glycol (or possibly ethylene chlorohydrin) if the ethylene double linkage were in some manner symmetrically coördinated (34, 91, 92) to the platinum atom, or (*b*) acetaldehyde if the coördinate link is formed by one of the carbon atoms. The reaction indicates that acetaldehyde is formed. Perhaps more helpful information could be obtained from a study of the reaction between water and a Zeise-type salt containing an unsymmetrical olefin such as propylene.

Of the mercury–olefin compounds, those with ethylene have been most

investigated. A lively controversy has centered about the structure of these and substituted ethylene derivatives. Mainly because of the ease with which the olefin can be regenerated from its combination with a mercuric salt, Manchot (73) regarded these substances as double salts or "molecular addition compounds" represented by structure A (XXII). The more common theory is that they are "true addition compounds" of type B. Sand (103), on the other hand, preferred to consider them as representing an equilibrium mixture between a molecular addition compound and the ordinary type of addition compound. He illustrated these




XXII

tautomeric forms as in C. Adams, Roman, and Sperry (1) have discussed the relative merits of these three structures and indicate their preference for type B. This structure is generally accepted at the present time and is rather conclusively supported by the fact that optically active mercury compounds with olefins of the type RR′C=CRR′ have been prepared (105). There are indications (104, 124), however, that in addition to products of type B, molecular or coördination compounds of olefins with mercuric salts of type A may also exist.

Using the distribution method (123), Lucas, Hepner, and Winstein (71) found that the mercuric ion forms rather stable complexes with cyclohexene. This hydrocarbon dissolves readily in aqueous mercuric nitrate, forming an acid solution. Two reactions which seem significant in the formation of the mercury–cyclohexene complex in solution are:

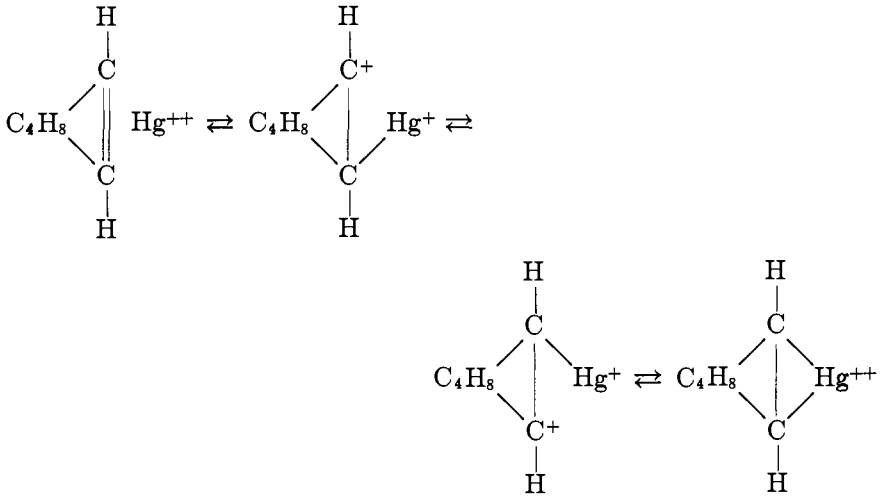
$$C_6H_{10} + Hg^{++} \rightleftarrows C_6H_{10}Hg^{++}$$

$$C_6H_{10} + Hg^{++} + HOH \rightleftarrows C_6H_{10}HgOH^{+} + H^{+}$$

The first reaction is probably strictly analogous to the reaction of silver ion and an olefin. However, in the case of mercuric ion and cyclohexene

the reaction proceeds principally according to the second equation. Experimental data point to the formation of the 1:1 complexes $C_6H_{10}Hg^{++}$ and $C_6H_{10}HgOH^+$.

The conclusion was reached (123) that coördination complexes of mercuric ion with cyclohexene can be formulated in much the same way as the analogous silver–olefin complexes. The various resonating forms of the "cyclohexene-mercurinium" ion can be represented in simplified form as:



XXIII

The "cyclohexene-mercurinium hydroxide" ion, $C_6H_{10}HgOH^+$, can be represented in a similar way, the mercury atom holding one hydroxyl radical. During the course of the above investigation there were indications that secondary reactions, not well understood, were occurring. One of these reactions presumably led to the formation of a compound of type B (XXII).

Lucas and coworkers admit that the discovery of coördination complexes of an olefin and mercuric ion adds confusion to our knowledge of this type of compound. The equilibria between the olefin, the mercuric salt, the compound of type A (XXII), and the compound of type B (XXII), are apparently complex, and it is entirely possible that some of the products which have been obtained in the past were actually of the coördination type.

The steps through which resonating systems pass, according to the theory advanced by Winstein and Lucas, can be pictured with the aid of three-dimensional diagrams. Figure 1 represents the *trans*-form of a substituted

olefin. The opening of the double bond can be considered as giving rise to a molecule in which one carbon atom possesses a sextet of electrons, as shown in figure 2. This, in effect, is a representation in model form of the "polarized" or "excited" state previously mentioned. However, Winstein and Lucas prefer to consider that this is *not* an intermediate in their theory of the formation of olefin–metal bonds. The resonating forms which they postulate may be represented by the diagrams shown in figure 3. What is actually being said, apparently, when Winstein and Lucas state that there is no rearrangement during the above resonance process is that the pair of electrons indicated can in some manner "resonate" or shift position (figure 3, A) from the apex of carbon atom 1, for example, to the "unoccupied" apex of carbon atom 2 and back again before group A or group B can move to the position on carbon atom 1 which is left unoccupied

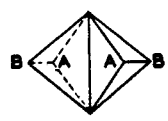



FIG. 1

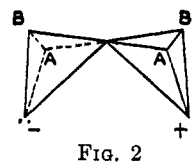



FIG. 2

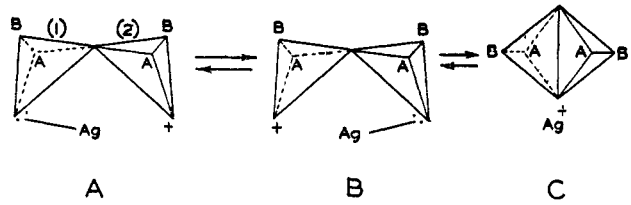



FIG. 3

by the resonating pair of electrons. If group A or group B does shift position, isomerization or rearrangement takes place. This, however, appears not to occur. For this reason Winstein and Lucas believe that the structure shown in figure 2 should not be postulated as an intermediate, because if this polarized form had more than a fleeting existence, rearrangement would certainly be expected.

It is interesting to speculate on the stereochemical possibilities of the above structures. At the instant the carbon–silver bond is in the position pictured in A of figure 3, carbon atom 1 holds four different groups and is consequently asymmetric. The same applies to the second carbon atom in figure 3, B. With a properly substituted olefin, carbon atom 1 would never be identical with carbon atom 2, and optical activity for the whole complex should result. However, such optical activity seems very unlikely when all of the forms in such a resonating system are more closely

examined. Considering a platinum–olefin complex in which four unlike groups are situated about the double bond, it is seen from figure 4 that a total of five forms is possible:

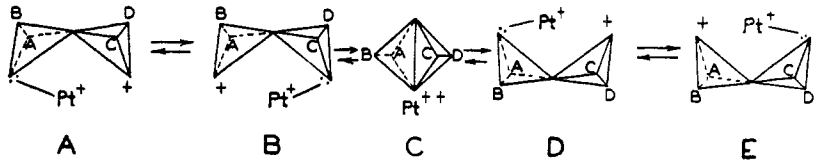



FIG. 4

When the double bond of figure 4 C "opens up," it can do so in either of two ways; in one case structures A and B (figure 4) are formed, while in the other case structures D and E (figure 4) result. However, structure A is a mirror image of structure D, and structure B is a mirror image of structure E. If the dextro- and levo-isomers of each pair of enantiomorphs are present in equal amounts, the complex is, of course, optically inactive.

It is a matter of conjecture as to whether properly chosen groups about the double bond could exert some sort of steric or polar effect and thus shift the above equilibria predominantly one way, or, in other words, cause the double bond to "open up" in one way preferentially. In this event optical activity might result. If such a situation is possible, it certainly must involve much more complex molecules than any of those discussed here.

## VII. CONCLUSION

Perhaps no one theory has been advanced which satisfactorily explains all of the questions relating to the various inorganic salt–olefin compounds. It is entirely possible that the metal–olefin bonds in these complexes are not all of the same type; in that case any one theory concerning the mechanism of their formation would obviously be inadequate. The character of the metal ion involved must undoubtedly play some part in the nature and stability of the bond formed; yet it would be comforting to feel that the double bond in olefinic substances is not versatile in the manner in which it coördinates with metal ions.

Of the mechanisms proposed to explain the mode of attachment of an olefin to a metal ion, that of Winstein and Lucas seems to be of most general application. However, if cases of optical activity among these compounds are positively demonstrated, even this explanation is inadequate. A question which can logically be raised concerning this mechanism is whether or not, with the resonating type of bond suggested, the olefinic molecule truly occupies the equivalent of *only one* coördination position in the coördination sphere. Perhaps the real point of difficulty here is

lack of a clear-cut understanding of what is meant by a "coördination position". If this term implies an area or region about the central atom in which the valence bond has a certain tolerance of direction, then the above criticism may not be warranted.

The structure proposed by Winstein and Lucas resembles in some respects that suggested by Hantzsch (compare XXIII and formula III), the latter probably being equivalent, in modern terms, to a structure having single-electron bonds. It is clearly questionable, however, whether the conditions for the formation of single-electron bonds obtain in these compounds (89). The nature of the bonds in Hantzsch's formula can be explained even less satisfactorily on the basis of covalence. Either alternative—two single-electron bonds or two covalent bonds—is difficult to reconcile with the apparently well-established fact that the olefinic molecule occupies only one position in the coördination sphere.

The mechanisms proposed by Stiegman and by Kharasch and Ashford demand that a pair of electrons for the coördinate bond be supplied in some manner by the platinum. Hel'man's theory carries somewhat the same requirement. In discussing the applicability of this theory, Hel'man points out that complex compounds containing unsaturated molecules are formed only by bivalent platinum and generally by metals in their lowest state of oxidation. This would seem to imply that in some way the bivalent condition of platinum is associated with the availability of those electrons needed in forming the bond between the platinum and olefin. Since the difference in valence between platinous and platinic platinum is 2, it is conceivable that a "calling out" of two electrons, as demanded by the above theories, might be possible. However, it is exceedingly difficult to understand how any such thing could occur in the cases of $Ag^{+}$, $Fe^{++}$, $Fe^{+++}$, $Al^{+++}$, $Cu^{+}$, and $Hg^{++}$ ions. No such assumption is necessary in applying Winstein and Lucas' theory of resonating structures.

The theory involving a polarized intermediate molecule would hardly explain the general absence of polymerization and rearrangement of the olefins. Such an intermediate might be expected to *promote* these changes. This identical theory, as a matter of fact, was used by Hunter and Yohe (51) in explaining the catalytic activity of aluminum chloride in polymerization reactions. They assumed that an intermediate "activated" complex might be formed in which one carbon atom is momentarily three-covalent. On the other hand, Winstein and Lucas' theory might appear incapable of explaining this tendency of aluminum chloride to cause polymerization. However, one must remember in this connection that these polymerization reactions are usually carried out at somewhat elevated temperatures. As previously noted, Gangloff and Henderson (27, 42) obtained crystalline addition products of aluminum chloride and various

olefinic substances at room temperature. Some polymerization at higher temperatures was noticed by Stiegman while preparing platinum–olefin compounds, and Anderson has reported occasional instances of polymerization.

It is altogether possible that at higher temperatures the resonating type of bond shifts over to an activated complex type, or the olefin receives enough energy so that it may be expelled as an activated or polarized molecule which in this excited state enters into polymerization reactions. The fact that aluminum chloride tends to induce polymerization to a greater extent than platinum and other metal ions need not be due to a fundamentally different type of metal–olefin bond but may be associated rather with a difference in the character of the metals themselves. The tendency to eliminate an olefin in an activated or polarized state or the tendency to form an activated addition complex with increase of temperature may merely be more pronounced in the case of aluminum chloride.

From theoretical considerations Winstein and Lucas (123) believe that the reactivity of these complexes is greater (*a*) the smaller the coördinated metal atom and (*b*) the more electronegative the coördinated metal atom. They feel that the relatively low reactivities of the silver and platinum complexes in terms of absence of polymerization and isomerization may be due to the comparatively large sizes of these metal atoms.

The formula of Drew, Pinkard, Wardlaw, and Cox for compounds of the type $K[PtCl_3 \cdot Un]$ does not seem satisfactory in view of the ready replacement of one olefin by another. Also, it gives platinum the unusual coördination number of 3. The structure in which the unsaturated molecule occupies one coördination position in the complex through a resonating type of bond seems preferable.

The dinuclear formula suggested by Pfeiffer for compounds of the general type $[MCl_2 \cdot Un]_2$ is preferred to that advanced by Kharasch and coworkers. Here, also, the resonating type of bond is believed preferable to that suggested by Stiegman. Such a resonating bond, however, would eliminate the possibility of optical isomerism in these dimeric compounds, unless they are of the type suggested by Kharasch and Ashford.

No definite decision can be made as to whether or not all metal–olefin bonds are of exactly the same type. Nevertheless, there seems to be no evidence to indicate that the mechanism of attachment of the olefinic molecule to the metal ion is not fundamentally the same in every case. Any variation in the properties of the resulting complexes can apparently be attributed to differences in character of the metals involved.

The author wishes to acknowledge his indebtedness to Professor John C. Bailar, Jr., for suggesting a review of this subject and to express his

gratitude for the many valuable suggestions and criticisms offered by Professor Bailar during the preparation of the manuscript.

## REFERENCES

(1) ADAMS, ROMAN, AND SPERRY: J. Am. Chem. Soc. **44**, 1781 (1922).
(2) AMBROS, REINDEL, EISELE, AND STOEHREL (to I. G. Farbenindustrie A.-G.): U. S. patent 1,891,203 (December 13, 1932).
(3) ANDERSON: J. Chem. Soc. **1934**, 971.
(4) ANDERSON: J. Chem. Soc. **1936**, 1042.
(5) ANTHES (to I. G. Farbenindustrie A.-G.): German patent 540,896 (May 27, 1922).
(6) BENNETT AND WILLIS: J. Chem. Soc. **1929**, 256.
(7) BERTHELOT: Ann. chim. phys. **23**, 32 (1901).
(8) BERZELIUS: Jahresber. **9**, 162 (1830).
(9) BERZELIUS: Jahresber. **12**, 300 (1833).
(10) BIILMANN: Ber. **33**, 2196 (1900).
(11) BIILMANN AND ANDERSON: Ber. **36**, 1565 (1903).
(12) BIILMANN AND HOFF: Rec. trav. chim. **36**, 306 (1916).
(13) BIRNBAUM: Ann. **145**, 67 (1869).
(14) BURK, THOMPSON, WEITH, AND WILLIAMS: *Polymerization and its Applications in the Fields of Rubber, Synthetic Resins and Petroleum*, p. 76. Reinhold Publishing Corporation, New York (1937).
(15) CHERNYAEV: Ann. inst. platine (U. S. S. R.) No. **5**, 118 (1927).
(16) CHERNYAEV AND HEL'MAN: Compt. rend. acad. sci. U. R. S. S. [N.S.] **4**, 181 (1936).
(17) CHERNYAEV AND HEL'MAN: Ann. secteur platine, Inst. chim. gén. (U. S. S. R.) No. **14**, 77 (1937).
(18) CHOJNACKI: Jahresber. **23**, 510 (1870); Z. Chem. [2] **6**, 419 (1870).
(19) DAYTON SYNTHETIC CHEMICALS, INC.: German patent 651,668 (October 18, 1937).
(20) DENIGÈS: Compt. rend. **126**, 1145, 1868 (1898).
(21) DE SIMO AND HILMER (to Shell Development Co.): U. S. patent 2,085,524 (June 29, 1937).
(22) DREW, PINKARD, WARDLAW, AND COX: J. Chem. Soc. **1932**, 997.
(23) DREYFUS: British patent 397,187 (August 21, 1933).
(24) DUBOIS: Przemysl Chem. **14**, 313 (1930).
(25) EGLOFF, WILSON, HULLA, AND VAN ARSDELL: Chem. Rev. **20**, 345 (1937).
(26) ELLIS: *The Chemistry of Petroleum Derivatives*, p. 142. The Chemical Catalog Company, Inc., New York (1934).
(27) GANGLOFF AND HENDERSON: J. Am. Chem. Soc. **39**, 1420 (1917).
(28) GERHART AND HULL (to Standard Oil Company of Indiana): U. S. patent 2,148,115 (February 21, 1939).
(29) GIBSON AND SIMONSEN: J. Chem. Soc. **1930**, 2531.
(30) GILLILAND, SEEBOLD, FITZHUGH, AND MORGAN: J. Am. Chem. Soc. **61**, 1960 (1939).
(31) GORDON AND HUGHES (to Imperial Chemical Industries, Ltd.): British patent 304,345 (October 17, 1927).
(32) GRIESS AND MARTIUS: Ann. **120**, 324 (1861); Compt. rend. **53**, 922 (1861).
(33) GUTYRYA AND BUINITSKAYA: Azerbaĭdzhanskoe Neftyanoe Khoz. **1937**, No. 1, **50**.

(34) HANTZSCH: Ber. **54**, 2632 (1921).
(35) HARMON (to E. I. du Pont de Nemours and Co.): U. S. patent 2,151,382 (March 21, 1939).
(36) HEBBARD AND LLOYD (to Dow Chemical Co.): U. S. patents 2,188,899 and 2,189,173 (February 6, 1940).
(37) HEL'MAN: Sci. Repts. Leningrad State Univ. **2**, No. 2, 5 (1936).
(38) HEL'MAN: Compt. rend. acad. sci. U. R. S. S. **16**, 351 (1937).
(39) HEL'MAN: Compt. rend. acad. sci. U. R. S. S. **23**, 532 (1939).
(40) HEL'MAN: Compt. rend. acad. sci. U. R. S. S. **24**, 549 (1939).
(41) HEL'MAN AND LITVAK: Ann. secteur platine, Inst. chim. gén. (U. S. S. R.) **1939**, No. 16, 29.
(42) HENDERSON AND GANGLOFF: J. Am. Chem. Soc. **38**, 1382 (1916).
(43) HILPERT AND WOLF: Ber. **46**, 2215 (1913).
(44) HOFMANN, HÖCHTLEN, AND ARNOLDI: Ber. **39**, 339 (1906).
(45) HOFMANN AND KÜSPERT: Z. anorg. Chem. **15**, 203 (1897).
(46) HOFMANN AND SAND: Ber. **33**, 1340, 1353, 2692 (1900).
(47) HOFMANN AND VON NARBUTT: Ber. **41**, 1625 (1908).
(48) HORSLEY (to Imperial Industries, Ltd.): Canadian patent 284,405 (October 30, 1928).
(49) HORSLEY (to Imperial Chemical Industries, Ltd.): U. S. patent 1,875,924 (September 6, 1933).
(50) HUGEL AND HIBOU: Chimie & industrie, *Special No.*, 296 (February, 1929).
(51) HUNTER AND YOHE: J. Am. Chem. Soc. **55**, 1248 (1933).
(52) I. G. FARBENINDUSTRIE A.-G.: British patent 276,427 (May 26, 1926).
(53) I. G. FARBENINDUSTRIE A.-G.: British patent 340,004 (August 12, 1929).
(54) I. G. FARBENINDUSTRIE A.-G.: British patent 345,334 (December 18, 1930).
(55) I. G. FARBENINDUSTRIE A.-G. (Zorn and Vogel, inventors): German patent 579,565 (June 29, 1933).
(56) I. G. FARBENINDUSTRIE A.-G.: British patent 478,601 (January 21, 1938).
(57) I. G. FARBENINDUSTRIE A.-G.: British patent 508,764 (July 5, 1939).
(58) I. G. FARBENINDUSTRIE A.-G. (Gumlich and Dennstedt, inventors): German patent 679,587 (August 9, 1939).
(59) IMPERIAL CHEMICAL INDUSTRIES, LTD.: French patent 662,099 (March 12, 1928).
(60) IMPERIAL CHEMICAL INDUSTRIES, LTD.: French patent 746,714 (June 3, 1933).
(61) JORGENSEN: Z. anorg. Chem. **24**, 153 (1900).
(62) KACHLER: Ber. **2**, 510 (1869); J. prakt. Chem. **107**, 315 (1869); Jahresber., p. 349 (1869).
(63) KELLER: Ph.D. Thesis, University of Illinois, 1940.
(64) KHARASCH AND ASHFORD: J. Am. Chem. Soc. **58**, 1733 (1936).
(65) KHARASCH, SEYLER, AND MAYO: J. Am. Chem. Soc. **60**, 882 (1938).
(66) KLEBANSKIĬ, TZYURIKH, AND DOLGOPOL'SHIĬ: Bull. acad. sci. U. R. S. S. **1935**, No. 2, 189; J. Research Assoc. Brit. Rubber Mfrs. **4**, 505 (1935).
(67) KONDAKOFF: J. Russ. Phys.-Chem. Soc. **24**, 309 (1892); Bull. soc. chim. [3] **7**, 576 (1892); J. Russ. Phys.-Chem. Soc. **25**, [1] 345, 456 (1893).
(68) KONDAKOV, BALAS, AND VIT: Chem. Listy **23**, 579 (1929); **24**, 1, 26 (1930).
(69) LEWIS: Trans. Faraday Soc. **19**, 456 (1923–24).
(70) LIEBIG: Ann. **9**, 1 (1834); **23**, 12 (1837).
(71) LUCAS, HEPNER, AND WINSTEIN: J. Am. Chem. Soc. **61**, 3102 (1939).
(72) LUR'E, MARUSHKIN, AFANAS'EV, AND PIMENOV: Sintet. Kauchuk **3**, No. 6, 19 (1934).

(73) MANCHOT: Ber. **53**, 984 (1920).
(74) MANCHOT AND BRANDT: Ann. **370**, 286 (1909).
(75) MANCHOT AND HAAS: Ber. **45**, 3052 (1912).
(76) MANN AND PURDIE: J. Chem. Soc. **1936**, 873.
(77) N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ: British patent 323,748 (July 9, 1928).
(78) N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ: British patent 336,603 (June 4, 1929).
(79) N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ: German patent 622,965 (December 10, 1935).
(80) N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ: British patent 479,632 (February 9, 1938).
(81) NATIONAL RESEARCH COUNCIL: *Twelfth Report of the Committee on Catalysis*, pp. 182–3. John Wiley and Sons, Inc., New York (1940).
(82) Reference 81, Chap. XIX.
(83) Reference 81, pp. 221–4.
(84) NORRIS AND INGRAHAM: J. Am. Chem. Soc. **62**, 1298 (1940).
(85) OTTO: Brennstoff-Chem. **8**, 321 (1927).
(86) OTTO AND MÜLLER-CUNRADI (to I. G. Farbenindustrie A.-G.): U. S. patent 2,130,507 (September 20, 1938).
(87) OTTO AND WENZKE: J. Am. Chem. Soc. **57**, 294 (1935).
(88) PALMER AND ELLIOTT: J. Am. Chem. Soc. **60**, 1852 (1938).
(89) PAULING: *The Nature of the Chemical Bond*, pp. 17, 239. Cornell University Press, Ithaca, New York (1939).
(90) PERQUIN (to Shell Development Co.): Canadian patent 380,056 (March 14, 1939).
(91) PFEIFFER: *Organische Molekülverbindungen*, p. 14. Verlag von Ferdinand Enke, Stuttgart (1922).
(92) PFEIFFER: *Organische Molekülverbindungen*, p. 18. Verlag von Ferdinand Enke, Stuttgart (1927).
(93) Reference 92, p. 209.
(94) PFEIFFER AND HOYER: Z. anorg. allgem. Chem. **211**, 241 (1933).
(95) POPE AND PEACHEY: J. Chem. Soc. **77**, 1072 (1900).
(96) PRECHT: Z. anal. Chem. **18**, 515 (1879).
(97) REIHLEN, GRUHL, HESSLING, AND PFRENGLE: Ann. **482**, 161 (1930).
(98) RICARD (to Soc. Ricard, Allenet et Cie.): U. S. patent 1,745,028 (January 28, 1930).
(99) ROSENHEIM AND STELLMANN: Ber. **34**, 3383 (1901).
(100) SADTLER: Chem. News **24**, No. 629, 280 (1871); Bull. soc. chim. **17**, 54 (1872).
(101) SAMUEL AND HUNTER: J. Chem. Soc. **1934**, 1180; Chemistry & Industry **1935**, 31, 635; Nature **138**, 411 (1936).
(102) SAND: Ber. **34**, 1385 (1901).
(103) SAND: Ann. **329**, 135 (1903).
(104) SAND AND BREEST: Z. physik. Chem. **59**, 424 (1907).
(105) SANDBORN AND MARVEL: J. Am. Chem. Soc. **48**, 1409 (1926).
(106) SIXT (to Consortium für elektrochemische Industrie G. m. b. H.): U. S. patent 2,183,154 (December 12, 1939).
(107) SMILES: J. Chem. Soc. **77**, 1174 (1900).
(108) SMYTH AND ZAHN: J. Am. Chem. Soc. **47**, 2501 (1925).
(109) SOCIÉTÉ DES CARBURANTS SYNTHETIQUES: French patent 733,601 (June 11, 1931).

(110) STANDARD ALCOHOL CO.: British patent 493,884 (October 17, 1938).
(111) STANLEY: J. Am. Concrete Inst. **49**, 349 (1930).
(112) STIEGMAN: Ph.D. Thesis, University of Illinois, 1937.
(113) STRANSKY AND HANSGIRG: British patent 267,959 (March 18, 1926).
(114) SYNTHETIC AMMONIA AND NITRATES, LTD., AND HORSLEY: British patent 291,186 (March 30, 1927).
(115) SZAYNA: Przemysl Chem. **12**, 637 (1928).
(116) TAUSZ: Chem.-Ztg. **37**, 1023 (1913). *Cf.* BALBIANO: Ber. **48**, 394 (1915).
(117) TROPSCH AND MATTOX: J. Am. Chem. Soc. **57**, 1102 (1935).
(118) TSUCHIDA, KOBAYASHI, AND NAKAMURA: J. Chem. Soc. Japan **56**, 1939 (1935); Bull. Chem. Soc. Japan **11**, 38 (1936).
(119) VAN PESKI AND LANGEDIJK (to Shell Development Co.): U. S. patent 2,055,269 (September 22, 1935).
(120) WATTS AND IMPERIAL CHEMICAL INDUSTRIES, LTD.: British patent 393,317 (December 2, 1931).
(121) WEINLAND: *Einführung in die Chemie der Komplex-Verbindungen*, p. 340. Verlag von Ferdinand Enke, Stuttgart (1924).
(122) WELLS: Z. Krist. **100**, 189 (1938).
(123) WINSTEIN AND LUCAS: J. Am. Chem. Soc. **60**, 836 (1938).
(124) WRIGHT: J. Am. Chem. Soc. **57**, 1994 (1935).
(125) ZEISE: Pogg. Ann. **9**, 632 (1827).
(126) ZEISE: Magaz. f. Pharm. **35**, 105 (1830).
(127) ZEISE: Pogg. Ann. **21**, 497 (1831); Schweiggers Journal der Chemie u. Physik **62**, 393 (1831); **63**, 121 (1831).
(128) ZEISE: Ann. **23**, 1 (1837); Pogg. Ann. **40**, 234 (1837).
(129) ZEISE: Pogg. Ann. **40**, 250 (1837).
(130) ZELINSHIĬ, DENISENKO, EVENTOVA, AND KHROMOV: Sintet. Kauchuk **1933**, No. 4, 11.