PLATINUM GROUP METAL-OLEFIN COMPLEXES

DISSERTATION

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By

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INTRODUCTION

Historical

Platinum-olefin Compounds

The first preparation of a compound containing a metal-olefin bond was that of Zeise\(^1\) in which he published a small note concerning an inflammable salt obtained during a reaction between platinic chloride and alcohol. These experiments\(^2\) were later published in greater detail. He also obtained a strongly acid solution when platinic chloride was refluxed with alcohol. When potassium chloride was added to the solution a yellow compound was obtained. The analysis of this compound was found to correspond to KCl.PtCl\(_2\).C\(_2\)H\(_4\) after it was dehydrated.

Meanwhile Berzelius\(^3,4\) found that refluxing a mixture of alcohol and sodium chloroplatinate resulted in a strongly


\(^{3}\)J. Berzelius, Jahresber., 2, 162 (1830).

\(^{4}\)Ibid., 12, 300 (1833).
acid solution which, when treated with potassium chloride and concentrated, gave yellow crystals considered to be identical to those of Zeise. From his analysis he postulated that the compound was a double salt of potassium chloride and platinous chloride, along with an "ethereal" substance. The salt obtained by these two workers has since been referred to as Zeise's salt. 

Liebig\(^5\)\(^6\) claimed that Zeise's analysis was incorrect and that the correct formulation was actually 2KCl\(\cdot\)2PtCl\(_2\)\(\cdot\)C\(_4\)H\(_{10}\)O.

Zeise\(^7\)\(^8\) repeated his experiments and merely recon-

\(^5\)J. Liebig, Ann., 2, 1 (1834).
\(^6\)Ibid., 23, 12 (1837).
\(^7\)W. C. Zeise, Ann., 23, 1 (1837).

firmed his earlier results. Further experiments were also carried out in an endeavour to prepare the primary member of the series, PtCl\(_2\)\(\cdot\)C\(_2\)H\(_4\). The ammonium salt (analogous to Zeise's salt) was allowed to react with chloroplatinic acid but later work has shown that this reaction would not give the desired product. From other experiments he described, Zeise apparently succeeded in forming the non-
ionic compound \([\text{PtCl}_2 \cdot \text{NH}_3 \cdot \text{C}_2 \text{H}_4]\). He concluded from this and other work that the yellow salt was best represented by the formula \(K[\text{PtCl}_3 \cdot \text{C}_2 \text{H}_4]H_2\text{O}\).

After the first initial surge of interest in these compounds it was some time before other workers took up the challenge of the problem, and carried out further work to settle the question of the composition of Zeise's salt. In 1861 Griess and Martius\(^9,\)\(^\text{10}\) confirmed Zeise's formula and also demonstrated that during thermal decomposition ethylene was evolved. A range of similar salts was prepared with the potassium chloride replaced by a series of amine hydrochlorides. They also suggested some possible structures for these types of compounds.

Birnbaum\(^11,\)\(^\text{12},\)\(^\text{13}\) also attempted to resolve the problem.

\(^\text{10}\)P. Griess and C. A. Martius, *Compt. rend.*, 52, 922 (1861).
\(^\text{13}\)K. Birnbaum, *Jahresber.*, 1867, 560.

As the reaction with alcohol must involve some complicated type of degradation, and the observation of evolution of ethylene was not conclusive, since ethylene could have been
a secondary product of the rather complicated thermal decom-
position, he decided to use ethylene in an attempt to pre-
pare the complex. Platinous chloride dissolved in hydro-
chloric acid was treated with ethylene, and Zeise's salt
was obtained on addition of potassium chloride. Using the
same procedure he prepared the corresponding compounds with
propylene and amylene, but found them to be less stable than
the ethylene compound. Birnbaum detected aldehyde as a
product of the reaction of platinic chloride with alcohol,
as did Zeise,\textsuperscript{14} and proposed the following equation to re-

\[ \text{PtCl}_4 + 2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{PtCl}_2 \cdot \text{C}_2\text{H}_4 + \text{CH}_3\text{CHO} + \text{H}_2\text{O} + 2\text{HCl}. \]

Birnbaum was not able to prepare Zeise's salt by the action of ethylene on a potassium chloroplat-
inate solution.

Chojnaki\textsuperscript{15,16} prepared the bromo analogue of Zeise's

\textsuperscript{14}W. C. Zeise, Pogg. Ann., 40, 250 (1837).

\textsuperscript{15}C. Chojnaki, Jahresber., 23, 510 (1870).


salt by refluxing a mixture of platinic bromide and alcohol,
adding potassium bromide and separating the yellow salt
which proved to be entirely analogous to Zeise's salt. The
formula was KBr.PtBr\textsubscript{2} \cdot \text{C}_2\text{H}_4 \cdot \text{H}_2\text{O}.
After a lapse of time, interest in this study was revived by Jorgensen,¹⁷ who attempted to improve the yields so far achieved. The method he used was a modification of that of Berzelius, and similar to that attempted previously by Precht,¹⁸ but he did not meet with any success. The reaction required ten hours refluxing and some reduction to metallic platinum occurred. He preferred to isolate the tetrammine platinous salt \([Pt(NH_3)_4][PtCl_3C_2H_4]_2\) as it was not as soluble as the potassium salt. The primary action for this method was given as,

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

Biilmann¹⁹ demonstrated that the reaction of an unsaturated alcohol was identical to that of a simple olefin, as allyl alcohol reacted with a warm aqueous solution of potassium chloroplatinite to form \(K[PtCl_3.C_2H_5OH]\). The analogous bromo salt was also prepared.²⁰


¹⁹E. Biilmann, Ber., 32, 2196 (1900).

²⁰E. Biilmann, and A. C. Andersen, Ber., 36, 1565 (1903).
This work was followed by the preparation of platinum-olefin compounds containing unsaturated acids with double bonds in the β-position, or those further removed from the carboxyl group. If the double bond was in the α-position no reaction occurred.  


The first preparation of a metal-olefin complex involving a cyclic olefin was that of Hofmann and Narbutt.  


Platinous chloride and di-cyclopentadiene were allowed to react in methanol and a stable compound, PtCl.C₆H₆.CH₃, was isolated. If ethanol was used as a solvent the corresponding ethoxy derivative was obtained, but propyl alcohol did not form an alkoxy-compound and the compound PtCl₂.C₁₀H₁₂ was isolated. These complexes were lighter in colour than any previous olefinic complexes and also exhibited other different characteristics.

Kondakov, Balas and Vit 23, 24 prepared the trimethyl-  

24 Ibid., 24, 1 (1930).
ethylene complex by dissolving platinous chloride in alcohol saturated with hydrogen chloride, and shaking with an excess of trimethylethylene for four months. A platinous chloride-trimethylethylene complex, 2PtCl₂·C₅H₁₀, was isolated from the resulting brown liquid. When platinous chloride was shaken directly with trimethylethylene no reaction took place in one year.

Pfeiffer and Hoyer²⁵ prepared a large number of compounds analogous to Zeise's salt by allowing unsaturated acids, esters, alcohols and aldehydes to react with potassium chloroplatinite. The reaction was considered to be complete when the characteristic red colour of the potassium chloroplatinite had been changed to the yellow solution of the complexes. Attempts to prepare olefinic complexes with other metal halides were unsuccessful and a certain specificity of olefinic complexes towards platinous salts was suggested.

The primary member of the series, PtCl₂·C₂H₄, was finally prepared by Anderson,²⁶ from the solution obtained


after refluxing sodium chloroplatinate with alcohol and evaporating below 50°C in a high vacuum. The brown, strongly acid tarry mass was extracted with chloroform and the extracted material was recrystallised from benzene. Zeise's salt was readily prepared from the above alcoholic solution by the addition of potassium chloride. The following observations were used as evidence that the platinum was present in the bivalent state:

1. Zeise's salt and the analogous carbonyl compound $K\{\text{PtCl}_3\text{CO}\}\text{H}_2\text{O}$, which was known to contain bivalent platinum, had similar properties.

2. $\text{PtCl}_2\text{C}_2\text{H}_4$ was reduced rapidly to metallic platinum by hydrogen gas, one mole of hydrogen being used for each formula weight.

3. An excess of pyridine reacted to form $\text{PtCl}_2\cdot\text{C}_2\text{H}_5\text{CN}$. From the extent of the reaction of Zeise's salt with potassium salts to form the corresponding complex platinites and to liberate ethylene, a sequence of stabilities of the compounds $K\{\text{PtX}_3\cdot\text{C}_2\text{H}_4\}$ was proposed. The stability was found to decrease in the order, chloro, bromo, nitro, thiocyanato and cyano.

Subsequently$^{27}$ the styrene complex $\text{PtCl}_2\cdot\text{C}_6\text{H}_5\text{CH}═\text{CH}_2$

was prepared by displacing ethylene from ethylene platinous chloride in vacuum at room temperature by the less volatile styrene. The same method was also used to replace the ethylene in Zeise's salt by styrene.

The method proved to be very general and could be applied to other olefins. Indene and cyclohexene compounds were prepared but were less stable than the ethylene and styrene compounds. From these investigations Anderson concluded that the coordinating ability of the olefins examined in this study, decreased in the order ethylene, styrene, indene, cyclohexene, α-diphenyl ethylene and α-methyl-α-ethylethylene. However the above order was based, to some extent, on the displacing power of one olefin toward the other and the relative volatilities of the respective olefins tended to confuse the results. Of significance was the observation that the compound PtCl₂·2C₅H₅CH=CH₂ was present in the reaction products when styrene was used to replace ethylene from the ethylenic complex. This compound could not be isolated in a pure state, but it was undoubtedly present and this was the first observation of a compound with two olefinic groups attached to one metal atom. A formal analogy between the carbonyl and olefinic complexes had been assumed but Anderson showed that the bonding strengths must have been radically different since styrene did not replace the carbonyl group in the [PtCl₃·CO]⁻ ion even after prolonged heating in vacuum.
A novel method of preparation of platinum-olefin complexes was presented by Kharasch and Ashford.\textsuperscript{28} Anhydrous platinic halides were treated with the corresponding olefin in glacial acetic acid for approximately one hour at room temperature; the complexes separated and were filtered off and recrystallised from benzene. The course of the reaction was apparently involved and no explanation was given. Hydrogen chloride was evolved during the reaction and some metallic platinum usually separated out. With this method the following olefinic complexes of platinum were prepared: cyclohexene, dipentene, pinene, ethylene, isobutylene, styrene, stilbene and trans-dichloroethylene. Allyl chloride, allyl bromide, allylbenzene, vinyl bromide, tridecene, isostilbene, cis-dichloroethylene and unsaturated acids or their esters did not yield any crystalline compounds that could be isolated. It was noted that cis-ethylenic complexes had never been isolated but that trans-ethylenic complexes were readily obtained. Molecular weight determinations were carried out on the isobutylene complex and showed that it was bimolecular.

Shortly after the entry of English and American workers into this field a large volume of work appeared in the
Russian literature. Chernyaev and Helman\textsuperscript{29,30} utilised two significant reactions to prepare the isomers of $[\text{PtCl}_2\cdot\text{C}_2\text{H}_4\cdot\text{Am}]$. When Zeise's salt was reacted with ammonia or pyridine, the entering group invariably occupies the trans position to the ethylene, but when ammonia or pyridine chloroplatinate was treated with ethylene the compound that was formed had a cis configuration which demonstrated the trans directing influence of the ethylenic group. This work was followed up by demonstrating that other ligands also exerted the same strong trans effect.\textsuperscript{31,32} Thiourea, ethylene, propylene, butylene, styrene and carbonyl were examined and found to possess this property.

Chernyaev and Helman\textsuperscript{33} found that Zeise's salt could
be prepared by passing ethylene for two weeks into a concentrated aqueous solution of potassium chloroplatinite, containing 3 to 5 per cent concentrated hydrochloric acid. The salt formed was found to be stable in dilute hydrochloric acid solutions but was decomposed by hot water, sulphuric acid and alkalies. When ammonia was added carefully to Zeise's salt, one of the chloro groups was replaced, and the neutral molecule PtNH₃.C₂H₄.Cl₂ was formed with the entering group trans to the ethylene. With hydrogen chloride this gave a reversible reaction between the neutral molecule and the ammonium analogue of Zeise's salt NH₄[Pt.C₂H₄.Cl₃]. The reactions of pyridine were of the same nature as the above reactions with ammonia. When thiourea, ammonia, pyridine, quinoline, bromide, iodide, nitrite, thiocyanate and cyanide were added in excess, displacement of ethylene occurred. The stability of the ethylenic complexes was shown to depend on the other substituents in the order quinoline, pyridine, ammonia and thiourea, and decreased with acid groups in the order chloro, bromo, iodo, nitro, thiocyanato and cyano. It was assumed that ethylene had a trans effect equal to or greater than that of the iodo and nitro groups.

Helman modified the above preparation of Zeise's

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salt by precipitating the ethylene complex as \( [\text{Pt(NH}_3\text{)}_4] \) \( [\text{PtCl}_3 \cdot \text{C}_2\text{H}_4]_2 \) with the addition of \( \text{Pt(NH}_3\text{)}_4\text{Cl}_2 \) to the reaction mixture of potassium chloroplatinite and ethylene. The precipitate was washed and the Zeise's salt regenerated by the addition of potassium chloroplatinite.

A relative order of stability in platinum-unsaturated complexes was published by Helman\textsuperscript{35} and she proposed the order of decreasing stability as carbonyl, styrene, ethylene, propylene and butylene. Apart from the relative positions of ethylene and styrene this order is the same as that proposed by other workers. Of note in the reaction of chloroplatinite ion in dilute acid solution with ethylene was the observation that the reaction was catalysed by the presence of propylene.

Chatt and Hart\textsuperscript{36} observed that the rate of reaction, in the preparation of platinum-olefin complexes, was affected by the presence of other platinum group metals. The reaction time was thirty to forty hours with pure platinum, but the introduction of iridium, palladium, or rhodium
reduced the reaction time between five and fifteen hours, depending on the metal present as impurity. This may explain the wide variations in reaction times suggested by earlier workers and also the variations in the decomposition temperatures reported.

By using butadiene as an olefinic ligand the problem as to whether the two double bonds could possibly occupy two coordination positions and form a five-membered ring was investigated. However, the evidence indicated that the double bonds reacted separately and no ring formation occurred. The reason for this was explained as the lack of free rotation in the butadiene molecule due to the proximity of the two double bonds. A variety of complexes were prepared with butadiene as ligand and they exhibited the strong trans influence as with the mono-olefinic ligands.

Helman and Litvak attempted to synthesise a non-ionic complex containing ethylene and nitro groups. When one mole of Zeise's salt was treated with two moles of sodium
nitrite, ethylene was replaced and the salt Na₂[Pt(NO₂)_2Cl₂] formed. If they reacted in equi-molar proportions the trans salt Na[PtC₂H₄NO₂Cl₂] formed and the latter reacted with pyridine to form [PtC₂H₄PyCl₂] as the ethylene group exerts a greater trans-labilising effect than the nitro group. Attempts to prepare the non-ionic complex by reaction between [PtNH₃C₂H₄Cl₂] and sodium nitrite, or by treatment of NH₄[NH₃PtNO₂Cl₂] with ethylene were unsuccessful.

A series of unsaturated molecules was reacted with sodium chloroplatinate in an aqueous solution. Nitric oxide gave no reaction but carbon monoxide, ethylene and butadiene reacted to give the complex Na[PtUnCl₃], where Un represents the unsaturated ligand. The mechanism of the formation of the complex was explained by a series of reactions which first involved the reduction of sodium chloroplatinate to the chloroplatinite followed by complex formation with the unsaturated molecule. The three complexes prepared above exhibited identical reactions when treated with pyridine followed by reaction with hydrochloric acid.

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With complexes of the type PyH[PtUnCl₃]₄⁰ an extended series of coordination tendencies of unsaturated ligands was proposed. The stability decreased in the following order: nitric oxide, carbon monoxide, styrene, butadiene and ethylene, and propene and butene of equal tendency. Complexes with more than one unsaturated molecule were stated to be unobtainable.

A radical departure from previous reactions with Zeise's salt was to treat it with ethylenediamine⁴¹ and to observe whether two chloro ligands could be replaced and a complex formed with ethylenediamine occupying two coordinate positions around the platinum atom. The reaction did not proceed in this way because a complex was formed with two platinum atoms connected by one molecule of ethylenediamine as indicated by the formula C₂H₄·Cl₂Pt·NH₂CH₂CH₂NH₂·PtCl₂·C₂H₄. When this complex was treated with hydrochloric acid a salt was formed, enH₂[PtCl₃·C₂H₄]. The butadiene analogue of Zeise's salt was also treated with ethylenediamine and a polymer was formed which also reacted with hydrochloric acid, similarly to the ethylene complex, to form a salt.

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Helman\textsuperscript{42,43} used the strong trans effect of ethylene to prepare two isomers containing four different ligands attached to the platinum atom. By reacting Zeise's salt with potassium bromide and then ammonia the compound \([C_2H_4PtBrClNH_3]\) was prepared with the two halogen atoms trans to each other. The compound \(NH_4[\text{NH}_3PtCl_3]\) treated with potassium bromide followed by ethylene gave the isomer with the halogen atoms in the cis position. It was found impossible to form the ammonium salt of the \([C_2H_4PtClBrI]\)^- ion as the action of sodium iodide on the \([C_2H_4PtClBr_2]\)^- ion caused displacement of the ethylene. The synthesis was even more difficult if chloride or bromide ion was introduced into a complex containing a metal-olefin bond.

There were some conflicting ideas concerning the valency of platinum in these ethylene complexes, and Helman and Ryabchikov\textsuperscript{44} subjected Zeise's salt and Cossa's salt, \(NH_4[PtNH_3Cl_3]\), to electrometric titration with potassium permanganate. Cossa's salt, which was known to contain

\textsuperscript{42} A. D. Helman, Doklady Akad. Nauk S.S.S.R., 38, 327 (1943); C.A., 32, 6579 (1943).

\textsuperscript{43} A. D. Helman, Compt. rend. acad. sci. U.R.S.S., 38, 310 (1944); C.A., 38, 526 (1944).

\textsuperscript{44} A. D. Helman and D. I. Ryabchikov, Compt. rend. acad. sci. U.R.S.S., 33, 412 (1941); C.A., 38, 6226 (1944).
bivalent platinum, oxidised normally and a jump in the potential was observed at the transition point. However no such titration curve was obtained with Zeise's salt and because of its large initial potential, which is characteristic of tetravalent platinum salts, it was concluded that the platinum in Zeise's salt was tetravalent.

Following the failure of ethylenediamine to react with Zeise's salt and produce a complex with ethylene in the cation, Helman and Meilakh\textsuperscript{45} were successful in preparing a relatively stable product $[\text{PtCl}_2\text{C}_5\text{H}_5\text{N}\cdot\text{NH}_3\cdot\text{C}_2\text{H}_4]\text{NO}_3$. When silver nitrate was added to cis-$[\text{PtCl}_2\cdot\text{C}_2\text{H}_4\cdot\text{NH}_3]^-$, a nitrato-chloro compound was obtained in which the nitrato group could be easily hydrolysed. The aquo complex was unstable but in the presence of pyridine it reacted to form $[\text{PtCl}_2\cdot\text{C}_5\text{H}_5\cdot\text{NH}_3\cdot\text{C}_2\text{H}_4]\text{NO}_3$, which was isolated and crystallised. If chloride or bromide was introduced into the aqueous solution of this cation the reaction was reversed to displace the pyridine or water molecule and form the starting material. By treatment of the aquo-cationic complex with potassium chloride,\textsuperscript{46} the third isomer of bromo-


chloroethyleneammineplatinum(II) was prepared with the chloro group trans to the ethylene.

It was found that a relatively simple synthesis of alkyl platinum complexes could be used, based on reaction of Zeise's salt with Grignard reagents. This synthesis

\[ \text{Zeise's salt} + 	ext{Grignard reagents} \rightarrow \text{alkyl platinum complexes} \]

was also used as evidence for the tetravalency of platinum in the salt as the alkyl compounds prepared in this manner were also known to contain tetravalent platinum. However, these workers realised that replacement of the ethylene by ammonia, pyridine and other ligands definitely gave bivalent complexes of platinum.

With the ligand, allylamine, which contains an unsaturated and an amine group, it was found that by varying

\[ \text{allylamine} + \text{potassium chloroplatinite} \rightarrow \text{complex} \]

the conditions of the reaction it was possible to vary the position of coordination in the ligand to the metal atom. When allylamine reacted with potassium chloroplatinite the double bond was not used in bonding as the complex prepared was stable to heat and to alkaline conditions. The complex which was prepared when the reactants were associated in a

\[ \text{complex} \]
strongly acid medium exhibited all the properties of the metal-olefin bond, such as the production of a platinum mirror when heated in water.

The preparation of a compound with two olefin groups attached to one platinum atom was finally solved by Chatt and Wilkins. Ethylene was passed into a solution of ethylene platinous chloride in acetone, which was cooled to -70°C. Yellow material separated which was considered to be the monomeric trans-bichlorobisethyleneplatinum(II). The complex was unstable because of the strong trans-labilising effect of the ethylenic group combined with a weak coordinating affinity. At -10°C the yellow complex reverted to the dimer (ethylene platinous chloride) which is orange, and the evolution of ethylene was observed. The presence of the ketone appeared to aid in the formation of the monomer and facilitated entry of the ethylene by opening the chloro bridge between the two platinum atoms. Some evidence was presented for the cis-isomer of the monomer, which was unstable, had different properties from those of the trans-isomer, and was greyish in colour. The variation in colour between the isomers was compared to that of the known carbonyl complexes and was found to be analogous.

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Flynn and Albert\(^{51}\) bubbled propylene through a solution of ethylene platinous chloride in acetone and considered that they had prepared a complex with two different olefinic ligands attached to the one platinum atom, \(\text{PtCl}_2 \cdot \text{C}_2\text{H}_4 \cdot \text{C}_3\text{H}_6\). The dipentene complex was prepared by Chatt and Wilkins by displacement of ethylene from ethylene platinous chloride, but was found to differ in properties from the complex obtained by reacting dipentene with platinic chloride in glacial acetic acid. The complex formed from the displacement reaction appeared to be monomeric, whereas the other was too insoluble to allow the molecular weight to be determined.

Chatt and Duncanson\(^{52}\) developed a method of preparation for Zeise's salt and for ethylene platinous chloride which gave rather high yields of pure product. Potassium chloroplatinitite, in a 3 per cent hydrochloric acid solution, was shaken for ten days in an atmosphere of ethylene. The resulting solution was filtered, cooled, and crystals of Zeise's salt appeared and could be removed if required.
The solution was then evaporated over containers of sulphuric acid and potassium hydroxide pellets, the residue extracted with acidified alcohol, the solution filtered and evaporated to dryness under reduced pressure to give the ethylene platinous chloride. The material prepared in this way was relatively pure but if higher purity was required it could be purified by recrystallisation from toluene. 53


The action of a halogen molecule on ethylene platinous chloride was studied by various workers. 54, 55 At room temperature the halogen molecule added to the complex, but at higher temperatures the halogenated olefin was formed. Thus at room temperature,

\[ \text{PtCl}_2 \text{Un} + \text{X-X} \rightarrow \text{PtCl}_2 \text{X}_2 \text{Un}. \]

Doyle and Jonassen 56 re-examined the preparation of

the dicyclopentadiene complex. From the properties of the complex and infrared observations they postulated that one molecule of the ligand occupied two coordinate positions around the metal atom. They observed, as before, that one chloro group could be replaced by an alkoxy group but it was impossible to prepare a complex with two alkoxy groups present. The trans effect of the two platinum-olefin bonds labilises the chloro groups and they were readily replaced by iodo groups. Apparently steric considerations prevented the formation of the bi-alkoxy compound.

The use of poly-olefins as ligands was also examined by Jensen.\textsuperscript{57,58} The complex formed by adding 1.5-hexadiene

\begin{itemize}
\item\textsuperscript{57}K. A. Jensen, Acta Chem. Scand., 7, 866 (1953).
\item\textsuperscript{58}Ibid., 7, 868 (1953).
\end{itemize}

(biallyl) to an aqueous solution of potassium chloroplatin-ite was a pale yellow compound with the formula \(\text{PtCl}_2 \cdot \text{C}_6\text{H}_{10}\). As the complex was monomeric it was assumed that the bi-olefin must have taken up two coordinate positions. The high dipole moment was consistent with the above assumption that the complex was substituted in cis-positions by the bi-olefin. Diallyl ether and cyclooctatetraene also formed similar monomeric compounds with platinous chloride and it appeared that bonding occurred through the two olefinic groups situated on opposite sides of the ligands. It was
thought that more than one coordinate position could only be taken up by a poly-olefin when the distance between the participating double bonds had a certain value.

The replacement of one of the chloro groups in Zeise's salt by a series of ligands according to the reversible reaction

$$[\text{C}_2\text{H}_4\text{PtCl}_3]^- + L \rightleftharpoons \text{trans-}[\text{C}_2\text{H}_4\text{I} \text{PtCl}_2]^- + \text{Cl}^-$$

was utilised\(^{59}\) to determine the stability constants of a series of ligands. The reaction was carried out in 0.2N perchloric acid, to prevent the formation of the hydroxy-complex which was unstable and rapidly decomposed. The free chloride concentration was determined by means of silver-silver chloride electrodes and the stability constants determined for a large range of ligands. These were found to decrease in the sequence thiocyanato, iodo, bromo, chloro and fluoro. For most metals the order of stability is reversed but the above phenomenon appears to be typical of those metals that form metal-olefin complexes. Chatt and Gamlen\(^{60}\) also made use of the following typical reaction


amine-platinous complexes, \([\text{C}_2\text{H}_4\text{PtCl}_3^-]+\text{am} \rightarrow \text{trans} -[\text{C}_2\text{H}_4\text{amPtCl}_2^-]\text{Cl}^-.\) From pH determinations and other measurements they were able to calculate the desired stability constants. The results showed that simple tertiary alkylamines had a very low affinity for the platinous ion. They managed however, to isolate two tertiary alkylamine complexes, namely \(\text{C}_2\text{H}_4\cdot\text{NMe}_3\text{PtCl}_2\) and its 1-methylpyridine analogue.

Chatt, Vallarino and Venanzi\(^6\) re-examined the diene-alkoxy derivatives of Hofmann and Narbutt and other workers. The diene complex was first prepared by allowing the diene to react with sodium chloroplatinite in propan-1-ol at room temperature for two days. Crystals of the diene product settled out and were then dissolved in the appropriate alcohol and a weak base such as sodium carbonate was added to form the general complex \([(\text{diene OR})_2\text{Pt}_2\text{X}_2]\). The complexes were examined by various reactions and by infrared analysis, and the simple diene complexes were presumed to be monomeric and to have the cis-configuration. The alkoxy complexes were dimeric and bridging through the halogen atoms was proposed. The alkoxy group was presumed to add across one of the double bonds in each diene while the other double bond was untouched. Boiling the alkoxy complex with

hydrochloric acid yielded the simple diene complex. Di-
cyclopentadiene and 1,5-cyclooctadiene were found to form
very stable complexes but those of dipentene and 1,5-hexa-
diene were more difficult to prepare and the latter did
not exhibit the same stability.

Jonassen and coworkers\textsuperscript{62,63} prepared a series of
platinum olefin complexes and examined their thermal sta-
bilities and infrared spectra. The thermal stability of the
butadiene analogue of Zeise's salt was greater than that
of butadiene platinous chloride which was in turn much more
stable than the copper complex. Slade and Jonassen\textsuperscript{63}
claimed that replacement of the ethylene in the dimer, ethylene
platinous chloride, by butadiene gave a dimeric structure
with chloro-bridging, but the preparation of the butadiene
complex from platinous or platinic salts resulted in a
structure involving bridge formation through the butadiene.

The first definite preparation of a complex of both
cis- and trans-olefins was that of Jonassen and Kirsch.\textsuperscript{64}

\textit{79}, 1275 (1957).

\textsuperscript{63} P. E. Slade Jr., and H. B. Jonassen, J. Am. Chem.

\textsuperscript{64} H. B. Jonassen and W. B. Kirsch, J. Am. Chem. Soc.,
\textit{79}, 1279 (1957).
They replaced the ethylene in ethylene platinous chloride with the cis- and trans-2-butene and obtained crystalline complexes. When the complexes were decomposed the olefins were found to retain their configuration and from the infrared data it was presumed that the olefins showed no signs of isomerisation.

**Palladium-olefin Compounds**

The preparation of a palladium-olefin compound was reported\(^5\) to have resulted from the reaction of trimethyl-


ethylene, palladous chloride and a trace of base in a closed tube at room temperature. Kharasch, Seyler and Mayo\(^6\) attempted to repeat the preparation but isolated no complex and stated that no compound could be obtained by the direct reaction of palladous chloride with an olefin. Palladium-olefin complexes were prepared by an indirect means which proved to be general for a series of olefins. Palladous chloride was reacted with benzonitrile to form the complex \((C_6H_5CN)_2\cdot PdCl_2\), which gave the corresponding olefin complex when the olefin was added at room temperature.
The ethylene, isobutylene, cyclohexene and styrene complexes were formed by this method but only the latter two olefins gave complexes of any stability. Molecular weight determinations on the complexes were not entirely conclusive but the compounds were considered to be dimeric.

The method of preparation was used\textsuperscript{67} to prepare the

\begin{flushright}
\end{flushright}

biallyl complex with the composition \(\text{PdCl}_2 \cdot \text{C}_6\text{H}_6\), and also to prepare the butadiene complex,\textsuperscript{68} which was found to be very stable thermally, when compared with the corresponding platinum complex. This difference in stability was considered to be due to a difference in structure. The platinum complex is known to be dimeric with the bridging through the two chloro groups but it was thought that the bridging in the palladium complex may have been through the butadiene groups.

Chatt, Vallarino and Venanzi\textsuperscript{69} extended their work on

\begin{flushright}
\end{flushright}

the diene and diene alkoxy platinum complexes to the
corresponding palladium complexes. In the preparation of the diene complexes it was not necessary to prepare the benzonitrile intermediate since direct reaction of sodium chloropalladite in acetone gave the desired products. The alkoxy derivatives were formed by an identical method to that used to prepare the platinous series. The palladium complexes were found to be more deeply coloured, less stable and more reactive; this evidence pointed to identical bonding with that obtained in the platinum complexes.

**Iridium-olefin Compounds**

Sadtler\(^70\) prepared the complex \(\text{IrCl}_2 \cdot \text{C}_2\text{H}_4\) by treating iridic chloride with absolute alcohol. Addition of potassium chloride gave greenish-brown crystals \(\text{IrCl}_2 \cdot \text{C}_2\text{H}_4 \cdot 2\text{KCl} \cdot x\text{H}_2\text{O}\), but ammonium chloride gave a mixture of salts which could not be definitely separated. Direct treatment of ethylene with iridium chloride, in solution or in the solid state, did not give rise to any complex formation. No further work has appeared on the iridium ethylene complexes and it is doubtful what complexes were really isolated. A complex in which the bonding was not between the metal atom and one particular unsaturated linkage was prepared by

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Cotton, Whipple and Wilkinson,\textsuperscript{71} by allowing iridium acetyl-

\textsuperscript{71}F. A. Cotton, R. O. Whipple and G. Wilkinson, 

acetonate to combine with the Grignard reagent, cyclopenta-
dienyl magnesium bromide, followed by treatment with 
Reinicke's salt to separate the salt of the complex formed.

\textbf{Rhodium-olefin Compounds}

The rhodium complex of cyclopentadiene was prepared\textsuperscript{72}

\textsuperscript{72}Ibid.,

with the same method of preparation as above. The simple 
bromide could be isolated and it had the formula \((C_5H_5)_2 \cdot \text{RhBr}_3\). 
These complexes are stable in acid and neutral 
solutions but are rapidly decomposed under alkaline condi­
tions.

The strongly chelating diolefin, 1,5 -cyclooctadiene, 
was used\textsuperscript{73,74} to prepare a series of rhodiumolefin complexes.

\textsuperscript{74}J. Chatt and L. M. Venanzi, \textit{J. Chem. Soc.}, \textbf{1957}, 
4735.

Rhodium chloride (RhCl\textsubscript{3}) and the above ligand in boiling 
ethanol produced a stable yellow crystalline solid with the
formula $C_8H_8\cdot RhCl$, which was dimeric and was considered to have the chloro-bridged structure with the olefin occupying the two free coordination positions that were left over in the square planar arrangement. Amines split the bridge structure to give the complex $C_8H_2\cdot RhClAm$, in similar manner to the reaction with platinum complexes. When the dimeric species was treated with cyclopentadienyl sodium a complex was obtained with the formula $C_8H_2\cdot RhC_5H_5$, in which the bonding between the metal atom and the cyclopentadienyl ion was of the same type as in ferrocene.

Structure of Platinum-olefin Complexes

Jorgensen was one of the first to discuss the bonding of the metal to the olefin group in Zeise's salt.\textsuperscript{75} The

\textsuperscript{75}S. M. Jorgensen, Z. anorg. Chem., 24, 160 (1900).

complexes obtained did not differ in a marked way chemically from other types of complex salts, but the mechanism of complex formation must have been obscure as the coordinating group was usually considered to possess a lone pair of electrons and this could not be associated with ethylene without complete polarisation and charge separation. A mechanism of this nature was suggested by Bennett and Willis\textsuperscript{76}

\textsuperscript{76}G. M. Bennett and G. H. Willis, J. Chem. Soc., 1929, 256.
who proposed that a lone pair was produced by complete transfer of one pair of electrons from the double bond to one carbon atom, resulting in a polarised state of the molecule and producing a potential "donor" molecule.

Biilmann\textsuperscript{77} proposed that if a properly substituted olefin was present in the salt K[PtCl\textsubscript{3}.Un], it would contain an asymmetric carbon atom, but resolution was thought to be impossible because of the instability of the compound.

Pfeiffer\textsuperscript{78} first described the complex with the vague statement that the unsaturated carbon atoms of the olefinic molecule formed the centre of a region which was capable of exhibiting a "secondary" valence and he wrote Zeise's salt as K[C\textsubscript{2}H\textsubscript{4}⋯.PtCl\textsubscript{3}]. He also arrived at the conclusion that the double bond must still be functioning in the complex as unsaturated alcohols, acids and aldehydes formed complexes whereas no such similar complexes could be formed by the corresponding saturated compounds.\textsuperscript{79} He pointed out the possibility that an asymmetric carbon atom could

\textsuperscript{77} E. Biilmann, Ber., \textbf{33}, 2196 (1900).

\textsuperscript{78} P. Pfeiffer, "Organische Molekularverbindungen", Verlag von Ferdinand Enke, Stuttgart, 1921, p.14.

be present in certain of these compounds and gave a representation.

\[
\begin{align*}
\text{CH}_3 & - C \equiv \text{CHCH}_2\text{OH} \\
\text{PtCl}_3K
\end{align*}
\]

As this formulation represented carbon as having a coordination of five instead of four, a symmetrical structure was suggested for these complexes.\textsuperscript{80}

\[
\begin{align*}
\text{H}_2 & \quad \text{MeClm.} \\
\text{H}_2 & \quad \text{C}
\end{align*}
\]

\textsuperscript{80}A. Hantzsh, \textit{Ber.}, \textbf{54}, 2632 (1921).

From analogous ammonia and pyridine complexes in which \(\text{NH}_3\text{Cl}\) and \(\text{C}_5\text{H}_5\text{NCl}\) groups were believed to be present, a structure for Zeise's acid was proposed by Drew, Pinkard, Wardlaw and Cox\textsuperscript{81} as.

\[
\begin{align*}
\text{H}^+ & \quad \left[\begin{array}{c}
\text{ClCH}_2\text{CH}_2 \\
\text{Pt}^\text{2+}\text{Cl}
\end{array}\right]
\end{align*}
\]


This formulation satisfied the growing evidence that in Zeise's salt the platinum was present in the bivalent state and any alternative formula would suggest that the metal was present in the tetravalent state.
The compounds of the general formula PtCl₂.₂₄ were thought to possess a doubled molecular formula in order to maintain the coordination number of four. Pfeiffer proposed a formula in which the platinum is tetracovalent, the ethylene molecule occupies one coordination position about the platinum atom and two of the chloro groups act as bridging atoms in the binuclear complex.

\[ \text{C}_2\text{H}_4 \quad \text{Cl} \quad \text{Pt} \quad \text{Cl} \quad \text{Pt} \quad \text{Cl} \quad \text{C}_2\text{H}_4 \]

Anderson accepted the formula and confirmed the dimeric structure of ethylene platinous chloride by molecular weight determination according to the Barger-Hast method as the instability of the complex at elevated temperatures prevented determination by the ebullioscopic method. The correctness of the above formula, is supported by the mutual ease with which one olefin can replace another, but in spite of these facts Kharasch and Ashford objected.

to the structure and proposed a ring system in which the olefin molecule acts as a bridging unit between the metal atoms.

\[
\begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{CH}_2\text{CH}_2
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl}
\end{array}
\begin{array}{c}
\text{CH}_2\text{CH}_2
\end{array}
\]

Their main objection to the previous structure was the postulation of formation of two coordinate bonds by one chlorine atom, but there are many instances of chloro-bridging in the literature. If the styrene derivative of platinous chloride were to have this structure, the possibility of structural isomerism would arise with the \(\alpha\)-carbon atoms closest to one metal atom or one at each metal atom. Also as there are two asymmetric carbon atoms present in such a structure, which can exist in three stereoisomeric forms, the number of isomers would be large. As yet no separation of isomers has been definitely accomplished.

Anderson\(^{85}\) examined the possibility of a lone pair being formed on one of the carbon atoms by polarisation. Although this is the only means by which the "lone-pair" theory of bonding could be satisfied, the theoretical polarised state represents an excited state and it was

\(^{85}\text{J. S. Anderson, J. Chem. Soc., 1936, 1042}\)
difficult to see how such excitation could have occurred under the conditions used in preparation of these compounds. Also, if polarisation had occurred, one of the carbon atoms would be left with a sextet of electrons, which would encourage polymerisation and rearrangement, whereas neither of these phenomena occur to any extent.

Winstein and Lucas\textsuperscript{86} proposed a structure for metal olefinic complexes involving equilibria between three forms, two of which are the polarised double bond with the metal ion bonded to the carbon atom with the lone pair of electrons, and the third with the positive ion midway between the two carbon atoms still doubly bonded. They claimed that this structure explained the reversible reactions, lack of polymerisation, and the strain that would be introduced if a rigid three membered ring were postulated.

The styrene analogue of Zeise's salt was studied\textsuperscript{87} to observe whether it could be resolved; as it was stable and as the salt is monomolecular the ambiguities of the dimeric type of complex would be avoided. If the platinum acts as a "donor" or "acceptor" atom there would be two ways of


\textsuperscript{87}R. N. Keller, Ph.D. dissertation, University of Illinois, 1940.
formulating the type of complexing, depending on whether the platinum was bonded to the terminal or the carbon atom next to the benzene ring; and in both cases an asymmetric carbon atom would be present. The attempt to separate the enantiomers was not successful.

A unique explanation of the bond formation between platinum and olefin was that of Helman, in which the platinum first acts as an electron donor to the activated olefin and then becomes an acceptor, resulting in the formation of a four-electron covalent bond and a high activity of the inner sphere.

Bokii and coworkers made an x-ray study of the structure of cis-[PtNH₂·C₂H₄·Cl₂]₂ and found that it existed as a dimer with the Pt-Pt bond distance 1.4Å. The reason for the abnormally small intermetallic distance was considered to be due to an "intravalent" or "dimetallic" bond.
involving the deeper-lying 5d electrons that are not used in normal bonding to form the monomer.

Chatt\textsuperscript{92} reviewed the previous structures and ruled out any possibility of an alkyl type of structure or bridging by olefinic groups. He favoured a "side on" association in which the metal atom lies in the plane of, or originally occupied by, the pi electrons. No evidence for unpaired electrons was found by magnetic measurements and the dimeric structure of $[\text{PtCl}_2 \cdot \text{Un}]$ was confirmed as was the monomeric structure of the $[\text{Am.C}_2\text{H}_4 . \text{PtCl}_2]$ species. Shortly after this, a suggestion was made\textsuperscript{93} that the hydrogen atom in ethylene can become labile under suitable conditions and than an ethylidene complex can result.

\begin{center}
\begin{tikzpicture}
  \node (Pt) at (0,0) {Pt};
  \node (Cl1) at (-0.5,-1) {Cl};
  \node (Cl2) at (0.5,-1) {Cl};
  \node (CH2) at (-1,-1.5) {CH$_2$};

  \draw (Pt) -- (Cl1);
  \draw (Pt) -- (Cl2);
  \draw (Pt) -- (CH2);

  \draw (CH2) -- (Pt) -- (Cl2);

  \node (K+) at (-2,-2) {K$^+$};
  \draw (K+) -- (Pt);
\end{tikzpicture}
\end{center}

The platinum is still in the dsp\textsuperscript{2} hybridised state, but in addition there is pi bonding through a d orbital to the carbon atom giving a total of two d, one s, and two p orbitals used. The evidence cited for this type of structure was that displacement reactions are merely a reversal


\textsuperscript{93} J. Chatt, \textit{Research (London)}, 4, 180 (1951).
of combination so that the liberated ethylidene rearranges to the original olefin, ethylene complexes are similar to carbonyl complexes, and the olefin platinous complexes are resistant to oxidation as are the platinic ammines. When the infrared spectral data were examined\textsuperscript{94} the double bond


was still found to be present but was lowered by 143 cm\textsuperscript{-1}, due to coordination to the metal, from that of the double bond in ethylene. This bond was rather weak as the ethylene molecule was symmetrical. The position of the carbon hydrogen stretching frequencies was further evidence for the unsaturated nature of the ethylene. These observations immediately disproved the ethylidene structure, and another structure was proposed in an attempt to explain the mode of bonding between the metal and the olefin. It was postulated that a sigma bond was formed by overlap of the dsp\textsuperscript{2} hybrid orbital of the platinum atom with the pi orbital of the olefin, and a pi-type bond by overlap of a filled 5d orbital of the metal atom with the antibonding pi molecular orbital of the olefin. The pi-type bond was also considered to be strengthened by the hybridisation of the 5d orbital with the vacant 6p orbital of the platinum atom to give a dp hybrid with a more suitable shape than the unhybridised 5d orbital to give larger overlap with the antibonding orbitals of the
olefin. Spatially the atoms in \([\text{C}_2\text{H}_4\text{PtCl}_3]^-\) would be arranged with the platinum and the chloro groups in one plane and the ethylene group placed vertically to this plane and symmetrical above and below it. The hydrogen atoms would be expected to be repelled slightly by repulsion of the platinum atom.

Wunderlich and Mellor\textsuperscript{95,96} determined the crystal structure of Zeise's salt by x-ray analysis. They found essentially the same structure as proposed by Chatt with the three chloro groups and the platinum atom in the same plane. The axis of the carbon atoms was found to be perpendicular to the plane. As the two platinum-carbon distances are the same, the ethylene was distributed evenly above and below the square planar structure. One aspect of note was that the chloro group trans to the ethylene was abnormally long and this is of particular interest in view of the known trans effect of ethylene.

\textbf{Square Planar Complexes}

From carbon chemistry the coordination number of four has been associated with a tetrahedral arrangement about the central atom. The first evidence of any other arrangement than the classical one was that the preparation of the
complex \([\text{Cl}_2(\text{NH}_3)_2\text{Pt}]\), by different methods, gave complexes that exhibited different properties.\(^{97,98}\)

\(^{97}\) M. Peyrone, Ann., 51, 15 (1845).

\(^{98}\) I. Reiset, Compt. rend., 18, 1103 (1844).

Werner\(^{99}\) explained this phenomena by considering that the ligands must have been coplanar, but the metal atom would not necessarily be in the same plane, to give this structural isomerism.

Mills and coworkers\(^{100,101}\) attempted to supply more evidence for the nature of the complexes of platinum(II) and palladium(II) by preparing the complexes with isobutylenediamine and mesostilbenediamine as ligands. If the arrangement was tetrahedral the complex would have a centre of symmetry and if the arrangement was planar optical isomers would be possible. They were able to separate the optical isomers in both cases and thus concluded that the ligands were arranged in a coplanar arrangement.


The x-ray study of the compounds potassium chloroplatinite and potassium chloropalladite showed that all the atoms were actually in the same plane.  

\[ \text{102 R. G. Dickinson, J. Am. Chem. Soc., 44, 2404 (1922).} \]

Pauling carried out a wave-mechanical treatment to explain the formation of the square planar structure. As the d orbitals have energy levels close to the higher s and p orbitals, hybridisation of one d, one s and two p orbitals can occur to give hybrid orbitals, directed to the four corners of a square, after the d electrons are paired leaving the one vacant d orbital. His calculations showed that the dsp\(^2\) orbitals had a 34 per cent greater bond strength than the sp\(^3\) tetrahedral orbitals and thus the energy used to pair the d electrons was easily recompensed by the additional bond strength obtained with the square planar configuration.

Crystal field theory has been applied recently to square planar complexes by Orgel and others, \(^{104-106}\) and their

\[ \text{104 L. E. Orgel, J. Chem. Soc., 1952, 4756.} \]
\[ \text{105 R. J. Gillespie and R. S. Nyholm, Quart. Rev., 11, 339 (1957).} \]
\[ \text{106 J. S. Griffith and L. E. Orgel, Quart. Rev., 11, 381, (1957).} \]
results were complimentary to those of Pauling. Crystal field theory deals with the non-bonding d orbitals which have different shapes as opposed to the s and p orbitals. When the free metal ion, with all d orbitals degenerate, is placed in the field of negative ligand ions or polarised molecules, the influence of the field causes splitting of the energy levels of the various d orbitals. Due to the splitting of the levels, and if the field is sufficiently strong to give a large enough energy difference between the levels, pairing of the electrons becomes possible. In an octahedral field the five d orbitals are split into a lower triplet and an upper doublet, but if there are more than six electrons present at least one electron must occupy the upper doublet and deformation from the octahedral case leads to further splitting of the previously degenerate levels.

Square planar configurations are possible in the d⁷, d⁸ and d⁹ cases but d⁸ is the most common, e.g. nickel(II), palladium(II), platinum(II), and gold(III). Of these the platinum(II) complexes have received the most attention due to their stability. A known example of a d⁷ square planar complex is cobalt(II) and for d⁹, copper(II).
**Infrared Stretching Vibrations**

The forces between atoms in molecules cause oscillation about an equilibrium position and are called the stretching vibrations. These vibrations give rise to absorption bands in the infrared region. The vibrations are considered to obey Hooke's law approximately.

For a mass \( m \) which is at a distance \( x \) from its equilibrium position the force is given by

\[
F = -kx
\]

where \( k \) is the force constant. But also

\[
F = ma
\]

where \( a \) is the acceleration.

\[
F = m \frac{d^2x}{dt^2}
\]

\[-kx = m \frac{d^2x}{dt^2}\]

The solution of this differential equation is given by

\[
x = x_0 \sin \left( \frac{2\pi \nu_{osc} t + \Theta}{2\pi} \right)
\]

where \( x_0 \) is rest position, \( \nu_{osc} \) is the frequency of oscillation, and \( \Theta \) is a constant. \( \nu_{osc} \) is given by

\[
\nu_{osc} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}
\]

For two atoms of mass \( m_1 \) and \( m_2 \), the force on each other is approximately proportional to the change of the internuclear distance.
\[ \frac{m_1}{\mu} \frac{d^2 r_1}{dt^2} = -k (r - r_e) \]
\[ \frac{m_2}{\mu} \frac{d^2 r_2}{dt^2} = -k (r - r_e) \]

where \( r \) is the total distance between atoms, and \( r_e \) is the equilibrium distance between atoms.

Combining these two equations and substituting for the reduced mass \( \mu \), where

\[ \mu = \frac{m_1 m_2}{m_1 + m_2} \]

\[ \mu \frac{d^2 (r - r_e)}{dt^2} = -k (r - r_e) \]

and from the simple case

\[ \nu_{osc} = \frac{1}{2 \pi} \sqrt{\frac{k}{\mu}} \]

\[ \nu_{osc} = \frac{c}{\lambda} \]

where \( \nu_{osc} \) is given vibrations per second, \( c \) is the speed of light, \( \lambda \) is the wave length in cm. and \( \frac{1}{\lambda} \) is the wave number \( \nu \).

\[ \nu = \frac{\nu_{osc}}{c} \]

\[ \nu = \frac{1}{2 \pi} c \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \]

\[ = 1307 \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \]
where \( k \) is used as a pure number corresponding to the number of dynes per cm by \( 10^5 \).

Examination of known spectra show that the force constant for single bonds lies within a relatively narrow range of values as does the force constant of multiple bonds. Thus for a carbon-carbon double bond the force constant can be determined from the known spectra of simple olefins. When the stretching frequency is lowered due to a particular substitution or complex formation, a calculation of the force constant gives a value for the relative bond order for the new bond.
STATEMENT OF THE PROBLEM

Earlier work in metal-olefin complexes has tended to be largely qualitative and a variety of complexes with various olefinic ligands have been prepared but with little correlation. The relative positions of the atoms in the molecule have been thoroughly investigated and a reasonable explanation of the type of bonding suggested.

It is proposed to obtain some quantitative data by studying the kinetics of the preparation of Zeise's salt and then to study the effect of the electron density of the ethylenic group on the metal-olefin bond by the use of conveniently substituted styrenes. It is also hoped to extend the complexes of ethylene to other platinum group metals by use of high pressures.
EXPERIMENTAL

Preparation of Zeise's Salt and Ethylene Platinous Chloride

Of the previous methods of preparation, that of Chernyaev and Helman\(^7\) gave the greatest yield with the maximum ease of handling. The only disadvantage of their method was the extended reaction and the large quantities of ethylene used, when the reaction was carried out by merely bubbling ethylene through an acidic solution of potassium chloroplatinite. The reaction was attempted in a closed system under various pressures of ethylene.

The reaction vessel is shown in Figure 1 and was constructed from a 24/40 Pyrex glass joint. The gas inlet used in this vessel allowed it to be rocked in any position without loss of liquid. A reaction vessel of the dimensions shown will accommodate about 20 ml. of solution. The vessel was wrapped in two places, with asbestos tape, to maintain its position in a steel bomb normally used for high pressure hydrogenation. A pad of glass wool was placed in the bottom of the bomb and the reaction vessel was held firmly in place by a spring placed between the glass vessel and the cover of the steel bomb.

A. 24/40 standard taper Pyrex joint
B. Gas inlet
C. Asbestos tape

Figure 1. Reaction Vessel
One gram of potassium chloroplatinitite was dissolved in 20 ml. of a hydrochloric acid solution prepared by mixing one part by volume of hydrochloric acid (specific gravity 1.18) and nine parts of double distilled water. The solution was transferred to the clean reaction vessel and the vessel mounted in the steel bomb. Grease was omitted from the ground glass joint to prevent reduction of the platinum complex to the metal when the product was poured from the vessel.

The system was flushed once with the nitrogen, twice with ethylene, the pressure of the ethylene adjusted, and the bomb-rocking mechanism started. The reaction was considered complete when the red solution of the potassium chloroplatinitite turned yellow. Table I shows the effect of ethylene pressure on the reaction time.

**Table I**

**EFFECT OF ETHYLENE PRESSURE ON REACTION TIME**

<table>
<thead>
<tr>
<th>Pressure (lbs./sq. in.)</th>
<th>Reaction Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>49</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>150</td>
<td>6</td>
</tr>
<tr>
<td>500</td>
<td>2.5</td>
</tr>
<tr>
<td>900</td>
<td>1.5</td>
</tr>
</tbody>
</table>
The yellow solution was evaporated to small volume in a vacuum desiccator containing concentrated sulphuric acid and a separate container of potassium hydroxide pellets. Yellow crystals of Zeise's salt separated and could be filtered and washed with a small volume of cold water.

If ethylene platinous chloride was required the yellow solution was evaporated to dryness and treated with a mixture of 20 ml. of ethanol (95 per cent) and one ml. of hydrochloric acid (specific gravity 1.18). Potassium chloride and any unreacted potassium chloroplatinitine were filtered off and the filtrate evaporated under reduced pressure to give rose-red crystals of ethylene platinous chloride. If the filtrate is evaporated to dryness the product is sufficiently pure for use in further reactions involving displacement of the ethylene with lower boiling olefins. The yield was about 95 per cent and this material may be purified by the method of Chatt and Searle.¹⁰⁸ The product was stored in a desiccator to avoid decomposition by water vapour.

Kinetics and Mechanism of Formation
of Zeise's Salt

Theory of Second Order Reactions

If the reaction is represented by

\[ \text{K}_2\text{PtCl}_4 + \text{C}_2\text{H}_4 \rightarrow \text{K}[\text{Pt.C}_2\text{H}_4\cdot\text{Cl}_3] + \text{HCl} \]

Let \( b \) be the initial concentration of potassium chloroplatinite, \( a \) the initial concentration of ethylene and \( x \) the concentration of Zeise's salt at time \( t \). Thus, the concentrations at time \( t \) of potassium chloroplatinite and ethylene will be \( b-x \), and \( a-x \) respectively. Hence the rate expression will be

\[
\frac{dx}{dt} = k(a-x)(b-x)
\]

for the rate of formation of Zeise's salt.

\[
\frac{dx}{(a-x)(b-x)} = kdt
\]

Using partial fractions to solve the lefthand side

\[
\frac{1}{(a-x)(b-x)} = \frac{1}{(a-b)} \left[ \frac{1}{b-x} - \frac{1}{a-x} \right]
\]

Integrating the rate equation gives

\[
\frac{1}{(a-b)} \left[ \ln(a-x) - \ln(b-x) \right] = kt + c
\]

To evaluate the constant \( c \), when \( t = 0 \), \( x = 0 \) and hence

\[
c = \frac{1}{(a-b)} \ln \frac{a}{b}
\]
\[
kt = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)}
\]

If the ethylene concentration is kept constant by controlling the pressure of the gas over the liquid phase, the term \((a-x)\) in the above equation would be constant as are \(a\) and \(b\). Hence the plot of \(t\) versus the logarithm of the concentration of the potassium chloroplatinate remaining should be a straight line.

If there is a physical property of the reacting species such that the property is a linear function of the concentration of the species, and if this property varies appreciably with the reactants and products, it is possible to calculate the proportions of the species at all times. In order to follow the concentration of potassium chloroplatinite and Zeise's salt, the ultraviolet absorption spectra were used. At the wavelengths used, neither ethylene nor hydrochloric acid absorb to any extent.

Letting \(b\) be the original concentration of the potassium chloroplatinite and \(x\) the amount of Zeise's salt formed,

\[
A = \log_{10} \frac{I_0}{I} = \ell ml
\]

where \(A\) is the absorbance, \(I_0\) the incident light, \(I\) the transmitted light, \(\ell\) the molar absorptivity, \(m\) the molarity of the species, and \(l\) the path length in cm. which is one in this case.

\[
A = A_a + A_b
\]
where $A$ is the total absorbance or the measured absorbance at any time, $A_a$ is absorbance of the potassium chloroplatinite and $A_b$ is absorbance of the Zeise's salt present

$$A = \varepsilon_a (b-x) + \varepsilon_b x$$

where $\varepsilon_a$ is the molar absorptivity of potassium chloroplatinite and $\varepsilon_b$ is the molar absorptivity of Zeise's salt.

$$x = \frac{A - b\varepsilon_a}{\varepsilon_a - \varepsilon_b}$$

Thus from the absorbance of the mixture and the molar absorptivities of the reactant and product the concentration of each species can be determined, provided that the absorbance is a linear function of the concentration and if the species when mixed show no enhancement of the absorption.

**Kinetic Order Based upon Platinum**

The spectra of potassium chloroplatinite and Zeise's salt, measured in a 10 per cent concentrated hydrochloric acid solution, were determined with a Beckman DU Spectrophotometer and are shown in Figure 2. For concentrated solutions the absorbance at 400 mu was used to determine the relative concentrations of the species and for more dilute solutions the absorbance at 330 mu was used.

A master solution was prepared by dissolving 1.000 gm. of dry potassium chloroplatinite (Fisher Scientific Company, purified) in 25 ml. of 1M hydrochloric acid in double distilled water. Any subsequent dilutions were made in the
Figure 2. Absorption Spectra of $K_2PtCl_4$ and Zeise's Salt.
same solvent. The linearity of absorbance with concentration (i.e., test for Beer's law) was examined at 400 μm with a series of dilutions and a slit width of 0.06 mm. The results are shown in Table II.

**TABLE II**

**ABSORBANCE OF VARIOUS CONCENTRATIONS OF K₂PtCl₄**

<table>
<thead>
<tr>
<th>Conc. of K₂PtCl₄, Moles/Litre</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01927</td>
<td>1.04</td>
</tr>
<tr>
<td>0.00964</td>
<td>0.546</td>
</tr>
<tr>
<td>0.00482</td>
<td>0.277</td>
</tr>
<tr>
<td>0.00193</td>
<td>0.101</td>
</tr>
</tbody>
</table>

The Beer's law plot is shown in Figure 3, which shows that the absorbance is linear to the concentration within the concentrations used.

To test for any enhancement of the reactant and product a series of mixtures of 0.00385 M potassium chloroplatinum and its product after reaction with ethylene for an extended period were prepared and the absorbance measured at 330 and 400 μm.
Figure 3. Beer's Law Plot for K$_2$PtCl$_4$

Figure 4. Test for Enhancement of Product and Reactants
TABLE III

ABSORBANCE OF MIXTURES OF K₂PtCl₄ AND ZEISE'S SALT

<table>
<thead>
<tr>
<th>Per Cent K₂PtCl₄</th>
<th>Per Cent Zeise's Salt</th>
<th>Absorbance 330 µm</th>
<th>Absorbance 400 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0.310</td>
<td>0.218</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>0.464</td>
<td>0.205</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>0.618</td>
<td>0.187</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>0.775</td>
<td>0.172</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>0.925</td>
<td>0.156</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>1.07</td>
<td>0.136</td>
</tr>
</tbody>
</table>

The plot of absorbance versus proportion of reactant and product are shown in Figure 4, page 57, demonstrate that any mutual enhancement of the spectra was negligible.

Ten ml. of the master solution of potassium chloroplatinitie was placed in the clean dry reaction vessel described in the preparation of Zeise's salt. This was introduced into the steel bomb and the pressure after flushing, adjusted to 50 lb. per square inch with ethylene (The Matheson Company, Chemically pure) and the vessel set rocking. At regular intervals one ml. samples were removed and diluted to five ml. with 1M hydrochloric acid and the absorbance measured at 400 µm. From the spectral data the
concentration of potassium chloroplatinite remaining in the diluted sample could be calculated and the results are shown in Table IV.

TABLE IV

KINETIC DATA BASED UPON PLATINUM

<table>
<thead>
<tr>
<th>Time (hrs.)</th>
<th>Absorbance (1 cm. cell)</th>
<th>Conc. K₂PtCl₄ Moles/Litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.04</td>
<td>0.01927</td>
</tr>
<tr>
<td>2.75</td>
<td>0.884</td>
<td>0.01204</td>
</tr>
<tr>
<td>5.75</td>
<td>0.789</td>
<td>0.00773</td>
</tr>
<tr>
<td>9.75</td>
<td>0.720</td>
<td>0.00455</td>
</tr>
<tr>
<td>13.0</td>
<td>0.679</td>
<td>0.00266</td>
</tr>
<tr>
<td>30.0</td>
<td>0.624</td>
<td>0.00014</td>
</tr>
<tr>
<td>78.0</td>
<td>0.621</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

The absorbance of the pure Zeise's salt was taken as 0.620 in the calculations and the data were plotted on semi-logarithmic paper to check whether the reaction was first order. The plot is shown in Figure 5 and it was found to be linear.

The order with respect to platinum was also checked with varying concentration of potassium chloroplatinite and varying pressures of ethylene. Using the same concentration
Figure 5: Plot of Logarithm of $K_2PtCl_4$ Conc. vs. Time
as above, the pressure was maintained constant by bubbling ethylene through 1M hydrochloric acid solution, to saturate the gas and prevent dehydration of the reaction mixture, then through a bubbler held in a constant temperature bath at 25°C., and finally through a bubbling device, in which mercury could be placed, to maintain a constant pressure in the reaction vessel. By this method the reaction was studied with pressures of 5.5 cm. and 32.5 cm. of mercury above atmospheric pressure. As before the plot of the logarithm of the concentration versus time was a straight line.

The initial concentration was varied between 0.01927 M and 0.00385 M and ethylene was passed through at a pressure of 5.5 cm. of mercury above atmospheric. This platinum data also showed that the reaction was behaving as first order.

Warburg Constant Volume Respirometer

The apparatus is shown in Figure 6, and it can be used to determine quantities of gases absorbed or evolved in any reaction. The various subdivisions of the cell also allow variations in the operations that can be carried out without opening the system. The flask of the equipment is placed in a constant temperature bath and is fitted to a shaking mechanism. The manometer is read from outside the bath after stopping the shaking action.
Figure 6. Warburg Constant Volume Respirometer

- F  Flask
- S  Sidearm
- G  Sidearm stopcock
- C  Center well
- M  Manometer
- R  Manometer fluid reservoir, fitted with clamp to adjust level of fluid
- T  Three-way stopcock
The system is calibrated so that from the observed pressure changes the amount of gas at 0°C. and 760 mm. can be calculated. The volume of the flask was calculated by filling with mercury, weighing it and dividing by the density at the temperature. The volume of the manometer to the reference point (usually 150 mm.) was determined by the use of a special Warburg calibrating device fitted with a calibrated micrometer and piston used to drive the liquid into the capillary tubing, and the volume of liquid read from the micrometer.

Let \( h \) be the observed change in the manometer (open side) in mm., \( x \) the microlitres of gas at 0°C. and 760 mm. Hg pressure, \( V_g \) the volume of gas phase in the flask, including the connecting tubes down to the reference point (150 mm. on closed arm of the manometer), \( V_f \) the volume of fluid in the flask, \( P \) the initial pressure in the vessel of gas involved in the determination, \( P_0 \) the standard pressure which is 760 mm. of mercury or 10,000 mm. of Brodie's fluid (sodium chloride 23 gm., sodium tauroglycocholate 5 gm. and Thymol Blue in 500 ml.), \( T \) the absolute temperature of the bath, \( \alpha \) the solubility in the reaction liquid of the gas involved (ml. gas/ml. liquid at 760 mm. mercury at temperature \( T \)) and \( p \) the vapour pressure of fluid at temperature \( T \).

The initial amount of gas in the gas space is given by

\[
V_g = \frac{273}{T} \frac{P-p}{P_0}
\]
and the initial amount of dissolved gas by

\[ V_f \alpha \frac{P-p}{P_0} \]

The final amount of gas in gas space is given by

\[ V_g \frac{273}{T} \frac{P-p+h}{P_0} \]

and final amount of dissolved gas by

\[ V_f \alpha \frac{P-p+h}{P_0} \]

The total amount of gas finally present is the amount initially present plus the amount \( x \) produced. Thus we have

\[
(V_g \frac{273}{T} + V_f \alpha) \frac{P-p+h}{P_0} = (V_g \frac{273}{T} + V_f \alpha) \frac{P-p}{P_0} + x
\]

\[ x = h \left[ V_g \frac{273}{T} + V_f \alpha \right] \frac{P-p+h}{P_0} \]

Thus the amount of gas \( x \) is proportional to the change in height of the manometer, and the proportionality constant can be readily determined by calibration of the vessel and from known values of \( P_0 \) and \( \alpha \).

As the manometer was open to the atmosphere, corrections have to be made for any change in atmospheric pressure, also small changes in pressure over the liquid in the vessel could occur as a result of the change in vapour pressure caused by minute changes in the temperature of the apparatus. To make these two corrections, a similar cell containing the
same solvent, was placed in the bath and any changes of pressure in this cell was applied as a correction to the cell in which the reaction was taking place.

**Kinetic Order Based upon Ethylene**

Ten ml. of 0.0964 M solution of potassium chloroplatinitite dissolved in 1 M hydrochloric acid was placed in a cell with a total volume of 19.059 ml. The bath temperature was maintained at $25 \pm 0.02^\circ$ C. and the vessel and contents were allowed to come to temperature equilibrium. Mercury was used as a manometric fluid, and the vessel was pretested for leaks by applying air pressure to the cell by means of the three-way stopcock and then allowing the system to remain for a period at least as long as the expected reaction time, to see whether any pressure change occurred. Ethylene was then swept rapidly through the cell; the right hand side of the manometer (i.e., the side attached to the cell) was adjusted to zero in this case and ethylene pressure applied so that the open side read the full 500 mm. which could be obtained with this system. The barometric pressure was determined at the start of the experiment and the comparison cell was adjusted to read zero pressure. These two readings can be used to calculate the pressure of the test cell at any time during the experiment. The cell was shaken to achieve good equilibrium between the ligand and gas phase. At regular intervals the shaking mechanism
was stopped, the closed side of the manometer adjusted to the zero mark, the pressure read from the open side of the manometer in mm. of mercury and the correct pressure calculated.

With these quantities of reactants the quantity of potassium chloroplatinitre present initially was $9.64 \times 10^{-3}$ moles and that of ethylene $3.825 \times 10^{-4}$ moles. Thus there was at least a tenfold excess of the platinum salt and a pseudo-order would be expected for the reactant present in the lower amount. Any order obtained from this series of experiments would be the order of the ethylene alone. As the concentration of ethylene in the solution is proportional to the pressure of ethylene, and if the reactant behaves as first order, the plot of the logarithm of the concentration versus time should be a straight line and hence the plot of the logarithm of the pressure should also be a straight line. The results are given in Table V.

The pressure of ethylene was determined by subtracting the vapour pressure of the solution at the temperature used from the total pressure, corrected for any change in atmospheric pressure or change in vapour pressure of the solvent resulting from small changes in temperature of the solvent.

These logarithms of the ethylene pressures were plotted versus time, and from Figure 7 it can be seen that a straight line was obtained and hence the reaction based upon ethylene is first order. The experiment was repeated with the
Figure 7. Plot of Logarithm of Ethylene Pressure versus Time
same quantities of platinum salt and ethylene and also with one-half the amount of platinum and in all cases the results indicated that ethylene was behaving as first order.

TABLE V

KINETIC DATA BASED UPON ETHYLENE

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>Pressure of Ethylene (mm. Hg)</th>
<th>Log. Press.</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>1028.0</td>
<td>3.0119</td>
</tr>
<tr>
<td>50</td>
<td>1011.9</td>
<td>3.0051</td>
</tr>
<tr>
<td>60</td>
<td>998.7</td>
<td>2.9994</td>
</tr>
<tr>
<td>80</td>
<td>979.5</td>
<td>2.9910</td>
</tr>
<tr>
<td>135</td>
<td>930.1</td>
<td>2.9685</td>
</tr>
<tr>
<td>170</td>
<td>896.4</td>
<td>2.9525</td>
</tr>
<tr>
<td>200</td>
<td>877.5</td>
<td>2.9432</td>
</tr>
<tr>
<td>265</td>
<td>823.6</td>
<td>2.9157</td>
</tr>
<tr>
<td>320</td>
<td>780.0</td>
<td>2.8921</td>
</tr>
<tr>
<td>350</td>
<td>759.4</td>
<td>2.8804</td>
</tr>
</tbody>
</table>

Kinetics of Reaction with Both Reactants Changing Concentrations

Quantities of potassium chloroplatinum and ethylene were used in the Warburg constant volume respirometer so that the concentration of both changed during the reaction. One ml. of a 1M hydrochloric acid solution containing 40 mg.
of potassium chloroplatinite was introduced into the cell, using the same procedure as in the last experiment and taking pressure readings at regular intervals.

In the kinetic expression for the second order reaction, units of concentration cancel and for convenience the total number of moles of the reactants were calculated at the start and at successive intervals during the reaction. The moles of potassium chloroplatinite were obtained from the molecular weight and the amount added initially. The amount of ethylene was determined from the volume of the vessel, the temperature, the solubility of the ethylene in the solution, the total pressure of the vessel and the vapour pressure of the liquid. The gas phase is equilibrated constantly with the liquid phase, and thus the system was considered as a whole. The amount of ethylene used at normal temperature and pressure was determined by the change in pressure at time \( t \) and the constants of the cell as described earlier. Mercury was used as manometric fluid. One mole of potassium chloroplatinite is used for every mole of ethylene, therefore the amount remaining could also be determined by subtraction. The results are shown in Table VI. These results are plotted in Figure 8, by calculating the slope of the curve, the rate constant \( k \) can be determined as

\[
k = \frac{\text{slope} \times 2.303}{(a - b)}
\]

\[
= 8.76 \times 10^{-4} \text{ litres moles}^{-1} \text{ min}^{-1}
\]
### TABLE VI

**KINETIC DATA BASED UPON ETHYLENE AND PLATINUM CONCENTRATIONS VARYING DURING REACTION**

<table>
<thead>
<tr>
<th>Time (mins.)</th>
<th>( x ) ml.</th>
<th>( x ) moles x 10(^4)</th>
<th>( (a-x) ) moles x 10(^4)</th>
<th>( (b-x) ) moles x 10(^4)</th>
<th>( \frac{b(a-x)}{a(b-x)} ) log.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6.993</td>
<td>0.963</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0.112</td>
<td>0.050</td>
<td>6.943</td>
<td>0.913</td>
<td>0.0200</td>
</tr>
<tr>
<td>210</td>
<td>0.251</td>
<td>0.112</td>
<td>6.881</td>
<td>0.851</td>
<td>0.0467</td>
</tr>
<tr>
<td>350</td>
<td>0.397</td>
<td>0.177</td>
<td>6.816</td>
<td>0.786</td>
<td>0.0770</td>
</tr>
<tr>
<td>420</td>
<td>0.444</td>
<td>0.201</td>
<td>6.792</td>
<td>0.762</td>
<td>0.0889</td>
</tr>
<tr>
<td>510</td>
<td>0.588</td>
<td>0.263</td>
<td>6.730</td>
<td>0.700</td>
<td>0.1217</td>
</tr>
<tr>
<td>630</td>
<td>0.647</td>
<td>0.289</td>
<td>6.704</td>
<td>0.674</td>
<td>0.1365</td>
</tr>
<tr>
<td>795</td>
<td>0.794</td>
<td>0.354</td>
<td>6.639</td>
<td>0.609</td>
<td>0.1762</td>
</tr>
<tr>
<td>1410</td>
<td>1.201</td>
<td>0.536</td>
<td>6.457</td>
<td>0.427</td>
<td>0.3183</td>
</tr>
<tr>
<td>1595</td>
<td>1.297</td>
<td>0.579</td>
<td>6.414</td>
<td>0.384</td>
<td>0.3614</td>
</tr>
<tr>
<td>1775</td>
<td>1.375</td>
<td>0.615</td>
<td>6.378</td>
<td>0.348</td>
<td>0.4015</td>
</tr>
<tr>
<td>1900</td>
<td>1.441</td>
<td>0.643</td>
<td>6.350</td>
<td>0.320</td>
<td>0.4361</td>
</tr>
<tr>
<td>2050</td>
<td>1.475</td>
<td>0.659</td>
<td>6.334</td>
<td>0.304</td>
<td>0.4672</td>
</tr>
<tr>
<td>2880</td>
<td>1.751</td>
<td>0.782</td>
<td>6.211</td>
<td>0.181</td>
<td>0.6734</td>
</tr>
</tbody>
</table>
Figure 8. Second Order Plot versus Time
Testing for Species Present During the Reaction

From the spectra of the product and the reactant Figure 2, page 55, it was observed that the two curves intersect at 378\(\mu\)u and were tangential to each other at 440 \(\mu\)u. If there were only two species present in any quantity, i.e., potassium chloroplatinite and Zeise's salt, and because ethylene gives no absorption in this region, these two isosbestic points should persist during the whole reaction.

A 0.0193 M solution of potassium chloroplatinite in 1M hydrochloric acid was treated with ethylene in an identical manner to that used in studying the kinetics of the platinum salt. Samples were removed at regular intervals and their spectra determined. The results are shown in Figure 9, which demonstrates the persistence of the two isosbestic points and thus the product and the reactant were the only two species present in any quantity during the reaction.

Discussion

From the kinetic data it is apparent that the reaction is taking place by means of a bimolecular process. The only two compounds in any quantity are potassium chloroplatinite and Zeise's salt, therefore an intermediate product which is unstable and decomposes almost immediately to Zeise's salt must be formed by a rate controlling process.
Figure 9. Check for Isosbestic Points

1. K₂PtCl₄ 0.0193M in 1 M HCl
2. Reacted 5 hrs.
3. Reacted 11 hrs.
4. Reacted 21 hrs.
5. Reacted 29 hrs.
6. Reacted 45 hrs.
7. Reacted 93 hrs. — Zeise's Salt.
Banerjea, Basola and Pearson\textsuperscript{109} have also examined reactions of square planar complexes, and found that if the entering group has any trans effect, the reaction is first order in both metal and ligand. This is consistent with the above findings. They also postulate some possible mechanisms for the course of the reaction on the basis of the directional characteristics of the d orbitals.

In solution, square planar complexes are considered to have two extra groups, one above and one below the plane, but at a greater distance from the primary ligands,\textsuperscript{110} and thus would be more labile than the primary ligands. In the system studied with a relatively high concentration of chloride ions these two extra groups would be expected to be chloro groups. Hence the species present at the commencement of the experiment would be $[\text{PtCl}_6]^{4-}$ and at the conclusion $[\text{rt.} \text{C}_2\text{H}_2\cdot \text{Cl}_5]^{3-}$. Many complicating equilibria with solvent and ligands could be postulated, but because the rate controlling process is the bimolecular addition, we would expect that at some stage a higher coordination number than the usual four would be attained to give an unstable
material which rapidly dissociates to the final product. If we neglect solvation or addition of chloride ion to give long unstable bonds, and possible equilibria, a simplified mechanism would be

\[ \text{K}_2\text{PtCl}_4 + \text{C}_2\text{H}_4 \xrightarrow{\text{slow}} \text{K}_2\text{PtCl}_4 \cdot \text{C}_2\text{H}_4 \xrightarrow{\text{fast}} \text{KPtCl}_3 \cdot \text{C}_2\text{H}_4 + \text{KCl}. \]

**Conclusions**

From the evidence presented during the preparation of Zeise's salt from potassium chloroplatinite the following conclusions have been drawn:

1. From the appearance of two isosbestic points, only the product and reactants were present in any appreciable concentration.
2. Since potassium chloroplatinite obeys Beer's law, the reaction can be followed spectrophotometrically.
3. Mutual enhancement of the spectra of product and reactant does not occur.
4. The reaction is first order based upon both the platinum salt and ethylene.
5. A five coordinate, unstable intermediate is formed during the reaction and the reaction must take place in at least two steps.
Platinum(II)-Styrene Complexes and the Effect of Substitution on the Trans Effect

Background of the Problem

Anderson\textsuperscript{111} prepared platinum-styrene complexes by replacing the ethylene in Zeise's salt, potassium trichloroethylene platinum(II), and in ethylene platinous chloride, 1,3-dichloro-2,4-bisethylene-uu-dichlorodiplatinum(II).

The styrene analogue of Zeise's salt was obtained in a pure form. Replacement of the ethylene in ethylene platinous chloride by styrene gave a mixture of the styrene analogue of the dimer and a proportion of the monomer, trans-dichlorodistyreneplatinum(II). The cause of the bridge rupture appears to be the strong trans effect of the olefinic ligand which labilises the group in the position trans to itself. The cause of this trans effect has been explained on different bases by some authors.\textsuperscript{112-117} This work attempts to


test the theory of Chatt, Duncanson and Venanzi,\textsuperscript{114} which proposes that the trans effect is due to the amount of pi-bonding between the metal and the ligand occurring when electrons from a filled d orbital of platinum are donated in part to a pi orbital in unsaturated ligands. By varying the electron density on the olefinic group the extra overlap of the metal orbital and the pi orbital of the olefin would increase the electron density between the metal and the ligand and hence the degree of pi bonding. It was proposed to prepare substituted styrenes with conveniently placed substituents so that a quantitative measure of the electron density could be obtained from the Hammet sigma values. If the extra pi bonding did in fact cause a higher degree of the trans effect we would expect that the chloro-bridge would be labilised and this would allow the bridge to break and an extra ligand could be introduced to form the monomer.

**Preparation of Ligands**

**Styrene.** Styrene (Eastman Organic Chemicals, stabilised with tert-butylcatechol) was washed twice with one part of 10 per cent sodium hydroxide to four parts of styrene, and
then with distilled water until the extract was alkaline free. The material was dried over white Drierite, the styrene redistilled under vacuum, and the product stored under refrigeration as were all the other ligands, to prevent polymerisation.

**Meta-chlorostyrene.** A nitrating mixture of 1.6 litres of concentrated sulphuric acid and 200 ml. of fuming nitric acid (specific gravity 1.50) was cooled to less than 10° C. in an ice bath. Benzaldehyde (250 gm., benzoic acid free) was added over a period of four hours and the reaction mixture left overnight. The product was isolated by pouring the mixture onto four kilograms of crushed ice and the yellow precipitate collected, washed with cold water and pressed dry. The cake was dissolved in 120 ml. of warm benzene, the water removed and the solution filtered. After concentrating the solution on a steam bath the m-nitrobenzaldehyde separated. Pure stannous chloride (900 gm.) was dissolved in 1.2 litres of concentrated hydrochloric acid and the solution was cooled to 5° C. When the m-nitrobenzaldehyde (200 gm.) was added rapidly the temperature rose slowly at first and then the red solution boiled vigorously. When the reaction had ceased the solution was cooled to 2° C. and a solution of sodium nitrite (92 gm.) in 300 ml. of water was added over a period of 90 min., making sure that the stem of the funnel was below the level of the reaction mixture and that the temperature did not exceed 5° C.
When a positive test was obtained with the starch-iodide test the addition was stopped. A cuprous chloride solution was prepared by dissolving copper sulphate (378 gm.) and sodium chloride (322 gm.) in 1,200 ml. of hot water and sodium hydroxide (54 gm.) in 600 ml. of water. The diazonium solution was added immediately to the warm cuprous chloride solution and the mixture swirled gently; concentrated hydrochloric acid (1680 ml.) was added and the mixture left to stand overnight. The m-chlorobenzaldehyde was obtained by steam distillation and then extracted with ether and dried over anhydrous calcium chloride. The ether solution was decanted and the solvent removed by evaporation; yield 65 gm., b.p. 90-94°C. at 12 mm. Methyl Grignard was prepared with the usual precaution of excluding any water, and the m-chlorobenzaldehyde dissolved in dry ether was added slowly, and then the mixture refluxed for one hour. The mixture was cooled and decomposed by dropwise addition of a 25 per cent solution of ammonium chloride in water. The ethereal layer was removed and dried over anhydrous magnesium sulphate, the ether removed and the residue vacuum distilled; yield 28 gm., b.p. 120-123°C at 15 mm.

Powdered fused potassium bisulphate (2.5 gm.) and picric acid (5 mgm.) used as a stabiliser, were placed in a modified Claisen flask maintained at 220-250°C. by a salt bath. The carbinol was added very slowly and a 20 cm. distillation column was maintained at a pressure of 125 mm. while the
temperature at the top was 110-120ºC. After the addition was complete and distillation had ceased, the pressure was reduced to 20 mm. and maintained until no more liquid distilled. The distillate was extracted with ether, dried over anhydrous magnesium sulphate and redistilled under reduced pressure; yield 15 gm. m-chlorostyrene, b.p. 63-65ºC. at 10 mm.

Ortho-hydroxystyrene. The method of Niederl, Smith and McGreal\textsuperscript{118} was used. Phenol (Merck, 49 gm.) was mixed with

\begin{footnote}
\end{footnote}

vinyl acetate (Matheson, Coleman and Bell, 86 gm., stabilised, 99.5 per cent pure) was cooled, and concentrated sulphuric acid (9.8 gm.) was added slowly with cooling. Water vapour was excluded from the reaction mixture with the use of a calcium chloride tube. The dark viscous liquid was dissolved in warm 10 per cent potassium hydroxide, the solution filtered and the ortho-hydroxystyrene precipitated by the addition of dry ice. After washing the product it was dried in air and then in a vacuum desiccator over anhydrous calcium chloride. The polymerised material was distilled under vacuum and the fraction boiling from 54-58ºC. at 4 mm. pressure was retained (47 gm.). Sulphur (0.3 gm.) was added and the styrene was redistilled; yield 34 gm., b.p. 52-53ºC. at 2 mm.
**Para-methoxystyrene.** Anisole (68 gm.) and acetyl chloride (59 gm.) were added to a mixture of a aluminum chloride (100 gm.) and carbon disulphide (156 gm.) and the temperature maintained below 10°C. The mixture was then refluxed for thirty minutes and the carbon disulphide was removed. The crude paramethoxyacetophenone was liberated by adding the mixture to ice and a little hydrochloric acid. The crude material was decanted and then distilled twice, b.p. 99-100°C at 4 mm., and then recrystallised from benzene (44 gm.). The ketone was reduced by sodium borohydride (25 gm.) dissolved in 150 ml. of methanol and left overnight. The adduct formed was decomposed with dilute sulphuric acid and the oil obtained, after removing the methanol, distilled from 97-99°C. at 4 mm. pressure (31 gm.).

The alcohol was dehydrated by adding it dropwise to fused potassium bisulphate in a Claisen flask maintained at 200-220°C., yield 18.5 gm., b.p. 70-82°C. at 4 mm. The product was then redistilled and 16 gm. of paramethoxystyrene was obtained from 74-76°C. at 4 mm. pressure.

**Ortho-and para-aminostyrene.** 2-Phenylethyl acetate (150 gm.) was added dropwise to a mixture of 650 ml. fuming nitric acid (specific gravity 1.50) and 315 ml. acetic anhydride, and the temperature was maintained between 35 and 40°C. The reaction mixture was left one hour and after addition to ice the nitro mixture was extracted with ether.
and the extracts were washed with dilute sodium hydroxide until all the acid had been removed. The liquid obtained was refluxed for six hours in methyl alcohol (600 ml.) containing hydrogen chloride gas (12 gm.). The methyl alcohol and acetate were removed under vacuum, the residue dissolved in ethyl alcohol and hydrogenated under pressure with a Raney nickel catalyst. The catalyst was filtered off, the solvent removed by vacuum distillation and when the residue was chilled the para isomer separated as a solid. It was filtered and recrystallised, after treatment with decolourising carbon, from a mixture of four parts benzene to one part of ethyl alcohol; yield 7.5 gm., m.p. 109°C. This was mixed with 10 gm. of finely powdered potassium hydroxide and heated under vacuum; yield 5 gm., b.p. 87-89°C, at 2 mm. The product turned yellow immediately it was exposed to air.

The oil obtained after removal of the para isomer was distilled to isolate the ortho isomer; yield 10 gm., b.p. 144-147°C. at 3 mm. This was added to 13 gm. of powdered potassium hydroxide and the product was distilled from 75-77°C. at 8 mm. pressure (6 gm.).

**Para-hydroxystyrene.** This was prepared in a small quantity but it polymerised very rapidly and could not be used in this study.
Preparation of Olefinic Complexes

Two methods of preparation were tried. The first was only used for some of the styrenes but the results were used as a comparison to the more general method which was satisfactory for all the ligands. The ethylene platinous chloride used was prepared by treating an aqueous acidified solution of potassium chloroplatinite with ethylene under pressure, as described earlier.

1. Ethylene platinous chloride (0.300 gm.) was dissolved in acidified ethanol and sufficient of the ligand was added to give a ratio of six moles per mole of the ethylene platinous chloride. The yellow solution turned red and when vacuum was applied ethylene boiled out vigorously. The solvent was removed in a vacuum rotary evaporator and excess ligand removed by heating for one hour at a temperature not greater than five degrees above the boiling point of the ligand at the reduced pressure of the vessel. The solid material was extracted with methanol, (because polymerised styrenes are insoluble) it was filtered and the solvent removed by vacuum evaporation. The complex was dissolved in the minimum quantity of hot benzene and left to crystallise. The crystals were filtered and washed with cold benzene.

2. Ethylene platinous chloride (0.100 gm.) was placed in a tube fitted so that vacuum could be applied. The same ratio of ligand was used as in method 1. The ligand was dissolved in two ml. of benzene, and then added to the solid.
When solution had occurred vacuum was applied and after the ethylene boiled out a precipitate of the complex was obtained. This was filtered, washed with chilled benzene and dried in the air. The remaining solution was evaporated under vacuum in a rotary evaporator and then heated for fifteen minutes at a temperature corresponding to the boiling point of the ligand at that pressure.

**Absorption Spectra**

Visible and ultraviolet spectra were obtained with a Beckman DU Spectrophotometer. The solvent used was ethanol and silica cells of 1 cm. light path were utilised.

Infrared absorption spectra were carried out with a Perkin Elmer, model 21, double beam spectrophotometer equipped with sodium chloride optics. The potassium bromide wafer technique was used with the solid complexes and the spectra of the ligands measured directly as a capillary film spread between two optical salt plates. The spectra were calibrated by means of the water vapor spectrum.

**Reduction of the Complexes with Hydrogen**

The Warburg apparatus and special cells were used to measure the quantity of hydrogen used in the reduction of the complexes. A method was devised whereby the complex could be placed in a small hole in a stopcock, placed directly under the centre well, Figure 6 page 62, the hydrogen gas was led into the main chamber of the cell and left to
come to equilibrium. By turning the stopcock slightly the hydrogen gas and the complex were brought into contact. A small pellet of potassium hydroxide was also placed in a side arm of the cell to remove the hydrogen chloride formed during the reduction. From the calibration of the cell and the change in pressure it was possible to calculate the quantity of hydrogen absorbed. The reduction was found to be extremely rapid after an initiation period, which varied greatly in time.

**Displacing Pressure of the Ligands**

Ethylene platinous chloride (0.5 mgm.) dissolved in ethanol was transferred to the main compartment of a Warburg cell and the ethanol removed by evaporation. A solution (0.5 ml.) of the ligand in methanol was prepared so that the mole ratio of the ligand to the ethylene platinous chloride would be 6 to 1, and this was placed in the side arm of the vessel. After the system had attained temperature equilibrium (30°C.), the cell was tipped, then it was mixed rapidly and returned to the bath. The pressure increase was measured after equilibrium was reached (6 to 24 hours). From the calibrations, temperature etc., it was possible to determine the amount of ethylene displaced at standard temperature and pressure.
Analysis

Analysis for C, H, Cl and platinum (ash) were carried out by Huffman Microanalytical Laboratories, Wheatridge, Colorado. The percentage of monomer and dimer were calculated from the analysis and the theoretical values for the pure monomer and dimer.

Results and Discussion

Using method 1 for the preparation the percentages of dimer and analysis for m-Chlorostyrene were - Calculated for 100 per cent \([(C_8H_7Cl)PtCl_2]_2\): C, 23.74; H, 1.73; Pt, 48.23. Found: C, 24.22; H, 2.08; Pt, 48.45.

Styrene - Calculated for 85 per cent \([(C_8H_8)PtCl_2]_2\), 15 per cent \((C_8H_8)_2PtCl_2\): C, 28.12; H, 2.33; Pt, 51.10. Found: C, 28.11; H, 2.39; Pt, 51.00.

p-Methoxystyrene - Calculated for 100 per cent \((C_9H_{10}O)PtCl_2\): C, 40.45; H, 3.77; Pt, 36.52. Found: C, 51.17; H, 5.39, Pt, 28.10.

Using method 2 as preparation, m-Chlorostyrene - Calculated for 100 per cent \([(C_8H_7Cl)PtCl_2]_2\): C, 23.74; H, 1.73; Pt, 48.23. Found: C, 23.45; H, 1.95; Pt, 47.25.

Styrene - Calculated for 97 per cent \([(C_8H_8)PtCl_2]_2\): C, 26.33; H, 2.20; Pt, 52.31. Found: C, 26.55; H, 2.20; Pt, 51.9.

p-Methoxystyrene - Calculated for 84 per cent \((C_9H_{10}O)PtCl_2\): C, 29.10; H, 2.72; Pt, 45.80; Found: C, 28.79; H, 2.76; Pt, 46.5.
p-Aminostyrene—Calculated for 100 per cent \((C_8H_9N)_2PtCl_2\):
C, 38.09; H, 3.60; Cl, 14.07; Pt, 38.70. Found: C, 40.22; H, 4.00; Cl, 14.27; Pt, 35.83.

o-Aminostyrene—Calculated for 100 per cent \((C_8H_9N)_2PtCl_2\):
C, 38.09; H, 3.60; Cl, 14.07; Pt, 38.70. Found: C, 38.07; H, 3.86; Cl, 14.52; Pt, 37.24.

o-Hydroxystyrene—Calculated for 40 per cent \([C_8H_8O]PtCl_2\)_2:
C, 32.74; H, 2.78; Pt, 43.24. Found: C, 32.47; H, 3.33; Pt, 43.20.

The percentages of the dimeric species are tabulated in Table VII along with the sigma constants.

**TABLE VII**

**PERCENTAGE OF DIMERIC SPECIES IN COMPLEXES**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Method of Preparation</th>
<th>sigma Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number 1</td>
<td>Number 2</td>
</tr>
<tr>
<td>m-chlorostyrene</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>styrene</td>
<td>85</td>
<td>97</td>
</tr>
<tr>
<td>p-methoxystyrene</td>
<td>*</td>
<td>84</td>
</tr>
<tr>
<td>p-aminostyrene</td>
<td>*</td>
<td>0</td>
</tr>
<tr>
<td>o-aminostyrene</td>
<td>*</td>
<td>0</td>
</tr>
<tr>
<td>o-hydroxystyrene</td>
<td>100</td>
<td>40</td>
</tr>
</tbody>
</table>

* Analysis showed in these cases that more than two ligands were present for each platinum atom.
The results for the o-hydroxystyrene are not comparable to other results as a prolonged reaction time was necessary to obtain any product. The slow reaction may have been due to some steric hindrance. The complex which was obtained was different in character from the other complexes. The amino-substituted ligands were also found to vary in their mode of complexing from that of other styrene ligands.

Negative sigma constants indicate that the electron density on the olefinic group is enhanced, and from the percentages of the dimer for the first three ligands in the table which cover a fairly wide range of sigma values it appears that the theory proposed earlier is correct.

The colour and melting or decomposition points of the complexes are shown in Table VIII.

From a comparison of the results in Table VII to those in Table VIII it was noted that the melting or decomposition points of the complexes were lowered by increasing amounts of the monomeric species present. The high thermal stability of the amino complexes as compared with the others is probably due to the absence of the metal-olefin bond. The colour of the o-hydroxystyrene complex was very intense; the crystals appear almost black but form an intensely red solution with ethanol in which decomposition slowly occurs to deposit metallic platinum.
TABLE VIII

COLOUR AND MELTING POINTS OF THE COMPLEXES

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Method 1 Colour</th>
<th>Method 1 M.P.</th>
<th>Method 2 Colour</th>
<th>Method 2 M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-chlorostyrene</td>
<td>orange</td>
<td>200 D</td>
<td>orange</td>
<td>190 D</td>
</tr>
<tr>
<td>styrene</td>
<td>orange</td>
<td>205 D</td>
<td>orange</td>
<td>235 D</td>
</tr>
<tr>
<td>p-methoxystyrene</td>
<td>orange-brown</td>
<td>85-90$^\circ$</td>
<td>orange</td>
<td>166-170$^\circ$</td>
</tr>
<tr>
<td>p-aminostyrene</td>
<td>brown</td>
<td>250 D</td>
<td>lemon-yellow</td>
<td>230 D</td>
</tr>
<tr>
<td>o-aminostyrene</td>
<td>light-brown</td>
<td>235-242$^\circ$</td>
<td>yellow-brown</td>
<td>215 D</td>
</tr>
<tr>
<td>o-hydroxystyrene</td>
<td>deep red</td>
<td>205 D</td>
<td>deep red</td>
<td>180 D</td>
</tr>
</tbody>
</table>

- Decomposes

The styrene complexes were all found to be much more stable towards decomposition by boiling water and dilute alkalies than the ethylene platinous chloride which gives a platinum mirror in boiling water and is decomposed immediately by dilute alkalies. Under similar conditions no decomposition occurred with the styrene complexes. Some of the complexes were rapidly reduced by hydrogen gas at room temperature and atmospheric pressure, which appears to be a function of the metal-olefin bond and thus complexes not reduced were considered not to have a simple metal-
olefin bond. Spectroscopic evidence also supported these results. When reduction occurred it was noted from the amount of hydrogen used that reduction of the benzene ring must have occurred and this could only have been made possible by the extremely reactive platinum catalyst formed when the metal-olefin bond was attacked, because no other type of platinum catalyst could cause reduction of the benzene ring so rapidly at the temperature and pressure used. Table IX gives the calculated and experimental quantities of hydrogen, (presuming that the benzene ring was reduced) for the various complexes calculated from the results of the elemental analysis.

TABLE IX

QUANTITY OF HYDROGEN USED IN REDUCTION OF COMPLEXES

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Calculated No. of moles $\times 10^6$</th>
<th>Experimental No. of moles $\times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>9.46</td>
<td>9.28</td>
</tr>
<tr>
<td>styrene</td>
<td>44.7</td>
<td>37.9</td>
</tr>
<tr>
<td>m-chlorostyrene</td>
<td>60.2</td>
<td>64.6</td>
</tr>
<tr>
<td>p-methoxystyrene</td>
<td>27.2</td>
<td>30.8</td>
</tr>
</tbody>
</table>

Neither of the aminostyrene complexes nor the o-hydroxy-styrene complex were reduced by hydrogen.
Ultraviolet and visible spectra. With the material produced by the second method of preparation, the ligands and complexes were dissolved in absolute alcohol and diluted to suitable concentrations. The styrene, m-chlorostyrene and p-methoxystryene complexes exhibit two peaks in the region of 250 and 280 millimicrons and this type of spectra has been observed for ethylene platinous chloride, see Figures 10, 11 and 12. The complexes prepared from the residue after filtering off the precipitated complexes showed similar spectra. The o- and p-aminostyrene complexes, Figures 13, 14 have their absorption bands in the same position as that in the ligand itself, but when the p-aminostyrene residue was heated to remove the ligand the absorption peak moves to a wavelength near that found with the complexes that are known to bond through the olefin group, Figure 13. This was assumed to be evidence that the position of bonding has changed from the amino to the olefin groups. This type of behaviour has been reported to occur with allylamine by Helman and Essen.\textsuperscript{119} The o-hydroxy-

Figure 10. Absorption Spectra of Styrene and Complex

- ○ Styrene, 0.000096 M
- □ Styrene complex, 0.0280 mg/ml
Figure II. Absorption Spectra of m-Chlorostyrene and Complex
Figure 12. Absorption Spectra of p-Methoxystyrene and Complex
Figure 13. Absorption Spectra of p-Aminostyrene and Complexes
Figure 14. Absorption Spectra of o-Aminostyrene and Complex
Figure 15. Absorption Spectra of o-Hydroxystyrene and Complex
ibility of ring formation involving the olefin and the hydroxyl group, but further work is difficult due to the instability of the complex.

**Infrared spectra.** The infrared spectra of the ligands and the complexes are shown in Figures 16 to 22. The principle absorption bands used to study the ligands and complexes were the carbon-carbon double bond stretching frequency at 1635 cm\(^{-1}\) and the two bands associated with the terminal vinyl group; one at 990 cm\(^{-1}\) due to the hydrogen deformation mode of the \(-\text{CH} = \text{C}-\) structure and the 910 cm\(^{-1}\) out of plane deformation of the hydrogens in the \(=\text{CH}_2\) group. When complex formation occurred between the platinum atom and the olefinic group of the ligands the double bond frequency was lowered approximately 120 cm\(^{-1}\), and the frequencies associated with the terminal vinyl group are replaced by one at 970 cm\(^{-1}\). From calculations of the force constant in the carbon—carbon double bond stretching frequency, the double bond character had been reduced to slightly over one and two-thirds bond character. With the \(m\)-chlorostyrene, \(p\)-methoxystyrene and styrene complexes the reduction in bond character was almost identical and this demonstrated that the extra electron density in the olefin group must be used in bonding with the platinum atom rather than being associated with the double bond. The principle bands are shown in Table X.
Figure 16. Infrared Spectra of Styrene and Complex
Figure 17: Infrared Spectra of m-Chlorostyrene and Complex
Figure 18. Infrared Spectra of p-methoxystyrene and Complex
Figure 19. Infrared Spectra of o-Aminostyrene and Complex
Figure 20. Infrared Spectra of p-Aminostyrene and Complex
Figure 21. Infrared Spectra of o-Hydroxystyrene and Complex

- o-hydroxystyrene
- o-hydroxystyrene complex
Figure 22. Infrared Spectra of p-Aminostyrene Complex (heated)
TABLE X

INFRARED SPECTRA BANDS (in cm\(^{-1}\)) OF LIGANDS AND COMPLEXES

<table>
<thead>
<tr>
<th></th>
<th>-C=C-</th>
<th>-CH=C-</th>
<th>=CH(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Styrene</strong></td>
<td>1634</td>
<td>995</td>
<td>910</td>
</tr>
<tr>
<td><strong>styrene complex</strong></td>
<td>1514</td>
<td>967</td>
<td></td>
</tr>
<tr>
<td><strong>m-chlorostyrene</strong></td>
<td>1638</td>
<td>992</td>
<td>918</td>
</tr>
<tr>
<td><strong>m-chlorostyrene complex</strong></td>
<td>1510</td>
<td>974</td>
<td></td>
</tr>
<tr>
<td><strong>p-methoxystyrene</strong></td>
<td>1632</td>
<td>995</td>
<td>904</td>
</tr>
<tr>
<td><strong>p-methoxystyrene complex</strong></td>
<td>1510</td>
<td>972</td>
<td></td>
</tr>
</tbody>
</table>

The amino-styrenes and their complexes were more difficult to interpret as the amino deformation frequencies occur in the same region as the carbon-carbon double bond stretching frequency region. However, from the appearance of the vinyl frequencies it appears that the bonding had taken place through the nitrogen atom. The sample of p-aminostyrene complex obtained by heating the residue to remove the ligand shows some reduction in the normally intense bands associated with the terminal vinyl group and this is considered to be added evidence of the rearrangement to bonding through the olefin group, see Figure 22.
The terminal vinyl frequencies in the o-amino styrene are weaker than in the other styrenes because of some steric hindrance or interaction of the two adjacent groups. In the complex the bonds are weakened in intensity but show up faintly. o-Hydroxystyrene shows almost no terminal vinyl frequencies due to the large interaction of the groups. The spectra of the complex shows only the hydroxy stretching frequency and the aromatic carbon-carbon frequency and could not be used for any diagnostic work.

Results obtained from the displacing power of the styrene ligands on the ethylene in ethylene platinous chloride are what was expected from the previous results, i.e., the displacing power is increased by the decrease in the sigma constant, showing that the ligand with the higher electron density has a greater tendency to coordinate.

By calculation the 0.5 mg. of ethylene platinous chloride contains 0.387 ml. of ethylene. The low value obtained for the o-hydroxystyrene fits in with the low reactivity found when trying to prepare its complex. It was noted that the p-aminostyrene first evolved ethylene but then reabsorbed all that was evolved. There seems to be no explanation for this behaviour, but a comparison of the elemental analysis of the two amino-styrene shows, from the higher carbon and hydrogen analysis for the para-aminostyrene over that of the ortho-aminostyrene prepared identically, that the ethylene could be reabsorbed in some fashion.
TABLE XI

DISPLACING POWER OF LIGANDS

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Increase in Press. cm</th>
<th>ml. Ethylene evolved at S.T.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-chlorostyrene</td>
<td>3.9</td>
<td>0.072</td>
</tr>
<tr>
<td>styrene</td>
<td>4.8</td>
<td>0.088</td>
</tr>
<tr>
<td>p-methoxystyrene</td>
<td>6.6</td>
<td>0.121</td>
</tr>
<tr>
<td>o-aminostyrene</td>
<td>9.1</td>
<td>0.167</td>
</tr>
<tr>
<td>p-aminostyrene</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>o-hydroxystyrene</td>
<td>0.7</td>
<td>0.011</td>
</tr>
</tbody>
</table>

After this section of the study had been completed a dissertation appeared\textsuperscript{120} whose title suggested that the work may have overlapped that done in this dissertation. He determined the stability constants of some substituted styrene complexes with platinum by determining the amounts of the species present when the platinum-dodecene complex was treated with the various styrenes. The results obtained were of the same order for increasingly negative sigma constants, but differed for positive sigma values. A possible explanation of this, is that his study does not

consider any possibility of two ligands attached to the one platinum atom, whereas, this study has demonstrated their importance.

Conclusions

A study of the properties of styrene-platinum complexes has indicated the following:

1. The extent of pi bonding depends on the electron density of the olefinic group as given quantitatively by the Hammett sigma constants.

2. The trans directing effect of the olefinic group is due to the extensive pi bonding.

3. Aminostyrenes bond through the nitrogen atom rather than the olefin group, but if the complex is heated rearrangement may occur to some extent and some of the ligand molecules rearrange to bond through the olefin group.

4. Reduction of the three centred metal-olefin bond creates an exceptionally active platinum catalyst, such that the benzene ring is reduced at room temperature and atmospheric pressure.

5. Bridge breaking by the styrene ligands is increased by the higher electron density on the olefin group.
Reaction of Ethylene with Other Metals

Palladium

The apparatus previously described, for the preparation of platinum ethylene complexes was used throughout these series of experiments, and all solutions were made up in double distilled water. Palladium(II) was considered to be more apt to give complex formation with ethylene, due to its electronic similarity to platinum(II), and to its similarity in other reactions.

Preparation of potassium chloropalladite ($K_2PdCl_4$).
Palladium chloride powder (Matheson, Coleman and Bell, 0.500 gm.) was dispersed in 50 ml. of water and 0.410 gm. of potassium chloride added. The solution was warmed until complete solution was complete. It was then evaporated until crystals appeared and then left to crystallise. The yellow-brown crystals were recrystallised from water.

Preparation of potassium chloropalladate ($K_2PdCl_4$).
A portion of the potassium chloropalladite, 0.200 gm. prepared above was dissolved in 10 ml. water, chlorine gas bubbled through and a bright red precipitate was obtained, which was washed with chlorine water, alcohol and then with ether. The material was then air dried.

Reaction of palladium with ethylene. Solutions of palladium(II) chloride were prepared with varying concentrations of hydrochloric acid so that the strength of the
palladium was 0.0056 M in all cases. When the solutions were allowed to react with ethylene at 400 lb. per square inch for 24 hours and the spectra measured from 240 to 750 μm, the only change found was the relative intensities as reduction to palladium metal had occurred to various extents. From measurements of the absorption at 470 μm the amounts of palladium chloride remaining after identical reaction times and ethylene pressures are given in Table XII.

**TABLE XII**

**AMOUNTS OF PALLADIUM(II) CHLORIDE REMAINING**

<table>
<thead>
<tr>
<th>Molarity of HCl</th>
<th>Per cent PdCl₂ Remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

Solutions of potassium chloropalladite were prepared in varying concentrations of hydrochloric acid and when these solutions were treated with ethylene under pressure the results were identical to those observed above with solutions of palladium(II) chloride. Solutions of potassium
chloropalladate were also prepared but the red solution formed was unstable and reverted to a yellow solution which reacted with ethylene to give reduction to the metal.

**Preparation of ethylene palladous chloride.** Previously no direct method of preparation was successful. However, by the use of ethylene under pressure and utilising benzene as solvent a direct method was obtained. Palladium(II) chloride (practically insoluble) was suspended in benzene and was treated with ethylene at 900 lb. per square inch for eight hours. A yellow solution was obtained, along with some metallic palladium and some yellow material. The solution was filtered and the residue extracted with benzene to give more yellow solution. This solution turned light brown after standing five hours. When the solution was evaporated to dryness in a rotary evaporator, under vacuum, a yellow-brown solid was obtained which evolved ethylene when added to acidified water. Its infrared spectra showed absorption bands that could only be associated with carbon-hydrogen or carbon-carbon bonds. This material was thought to be a mixture of ethylene palladium chloride and palladium(II) chloride.

When styrene was added to the freshly prepared yellow solution, the colour changed immediately to red. Application of vacuum caused ethylene to be evolved and the immediate
cooling effect of the evaporation allowed an orange material to separate. This material was filtered and washed with cold benzene. The infrared spectra resemble very closely the spectra of the styrene platinous chloride. It was analysed and found to be a mixture of the monomeric and dimeric species. Calculated for 60 per cent $[\text{PdCl}_2 (\text{C}_8\text{H}_8)]_2$ and 40 per cent $\text{PdCl}_2 (\text{C}_8\text{H}_8)_2$: C, 40.40; H, 3.35; Cl, 22.45; Pd, 33.78; Found: C, 40.44; H, 3.46; Cl, 22.25; Pd, 33.94.

Discussion. The experimental work showed that in aqueous solutions palladium(II) was reduced to the metal. This reduction could be retarded greatly by the addition of hydrochloric acid. An explanation for this retardation could be that the large excess of chloride ions (which have a relatively great coordinating tendency) competed too greatly to allow any attack by the ethylene. This suggests that reduction by the ethylene may take place by means of an unstable palladium-olefin intermediate. Addition of the known ethylene palladium chloride to an acidified aqueous media leads instantly to decomposition of the complex. Infrared evidence on the material obtained after evaporating the yellow benzene solution indicates strongly that it was a solution of ethylene palladium chloride, but it could not be obtained directly from this solution without some decomposition. The displacement of the ethylene in the complex by styrene gives much more tangible evidence,
as the material obtained was quite stable and elemental analysis as well as spectroscopic analysis demonstrated that it was a palladium-olefin complex. No complex was formed by direct reaction of styrene with palladium chloride. By analogy to the platinum reactions, the palladium-ethylene complex must have been formed directly.

Iridium

Preparation of potassium chloroiridate (K₂IrCl₆).
Iridium(IV) chloride (American Platinum Works) was treated with aqua regia to ensure that all the iridium was present in the plus four state. The solution was evaporated to dryness in a tared tube and the quantity of iridium(IV) chloride determined, 0.515 gm. This was dissolved in water and 0.229 gm. potassium chloride added. The solution was evaporated almost to dryness and the reddish black crystals that separated were filtered and washed.

Preparation of potassium chloroiridite (K₃IrCl₆).
Potassium chloroiridate, 0.200 gm., obtained above, was dissolved in 20 ml. of water and potassium oxalate monohydrate, 0.038 gm., was added. This mixture was heated on a hotplate until the solution had turned olive green and when the solution was further evaporated, pale crystals were obtained which were filtered and washed with alcohol.
Potassium chloroiridate was dissolved in water to give a 0.0021 M solution and when this reacted with ethylene at 150 lb. per square inch, the yellow-orange solution became colourless after 17 hours. The same strength solution in 1M hydrochloric acid took 40 hours at 900 lb. per square inch ethylene pressure, to complete the reaction. The ultraviolet spectra of the product was determined and it was found to be identical to that obtained by McBride\textsuperscript{122} when he treated iridium(IV) with ethylenediaminetetraacetic acid and other reducing agents and obtained iridium(\textsc{ii}). Solutions of potassium chloroiridite showed no reaction with ethylene.

\textbf{Rhodium}

It has been recognised that rhodium(\textsc{iii}) in aqueous solutions tends to solvate and convert slowly from an anionic form, $\text{RhCl}_6^{2-}$, to the cationic form $\text{Rh(H}_2\text{O)}_6^{+++}$.\textsuperscript{123} However, it was shown by Jorgensen\textsuperscript{124} that a steady state was obtained.


\textsuperscript{123}W. M. MacNevin and E. S. McKay, \textit{Anal. Chem.}, 29, 1220 (1957).

\textsuperscript{124}K. Jorgensen, \textit{Acta Chem. Scand.}, 10, 500 (1956).
in a 1M hydrochloric acid solution after one day and was found to be stable for at least 60 days. The species present was presumably RhCl₅(H₂O)ᵐ. In view of this it was decided to carry out all the work on solutions at least one day old and in 1M hydrochloric acid.

Preparation of K₂RhCl₅. Rhodium(III) chloride (American Platinum Works), 0.500 gm., was dissolved in 10 ml. of water and 0.400 gm. potassium chloride added. After two days pink-red crystals appeared, were filtered and washed with a little cold water.

Reaction with ethylene. A 0.0028 M solution of K₂RhCl₅ was prepared in 1M hydrochloric acid, and after standing one day, was allowed to react for 24 hours at 900 lb. per square inch pressure of ethylene. The pink solution turned yellow and the spectra of the initial and final material was determined, and is shown in Figure 23. Some of the resulting solution was evaporated to dryness, under vacuum, in a rotary evaporator and brown crystals were obtained. A portion of this material was redissolved in 1M hydrochloric acid and its spectra redetermined as shown in Figure 23. Another portion was analysed for carbon content.

Reduction of K₂RhCl₅ with hydrazine. Solutions of K₂RhCl₅ in 1M hydrochloric acid were treated with measured amounts of hydrazine dihydrochloride, in the same solvent, such that sufficient reducing material was present to give a one, two, three and four to one equivalent ratio of
1. 0.0028 M Rh

2. After reaction with ethylene

3. Evaporated and redissolved in 1 M HCl

Figure 23. Absorption Spectra of Rhodium (III) and Complex
hydrazine to each mole of rhodium. The reduction was slow at room temperature but after heating at 70° C. for 3 hours, and then leaving overnight, the reaction was apparently complete. For one equivalent of hydrazine, the reaction mixture was orange and for two or more the mixture was yellow. However, the spectra of the latter three were all identical, and all exhibited one maximum at 436 μ, which does not resemble that of the yellow solution obtained by the reaction with ethylene.

Discussion. The analysis for the material showed that there was 1.59 per cent of carbon present in the sample. This amount could not be correlated to any known formulation but suggests that a complex could have formed and that it was unstable. Under the conditions of the reaction it is difficult to see how the peak at 451 μ could arise without assuming some complex formation with ethylene. The hydrochloric acid concentration precludes the presence of a species more highly solvated than that present originally, and the spectra of the rhodium reduced with successively greater amounts of reducing agent precludes the chance that the species present after reaction with ethylene was simply rhodium in a lower oxidation state. It does not preclude the fact that rhodium could be reduced first, followed by complex formation. The chlorine content, 42.50 per cent, gives very strong evidence that reduction had occurred, as
$\text{K}_2\text{RhCl}_5$ requires 48.52 per cent chlorine, and $\text{K}_2\text{RhCl}_4$ requires 42.96 per cent chlorine.

**Osmium**

$\text{K}_2\text{OsCl}_6$ was prepared by treating 0.5 gm. of osmic oxide (OsO₄, Merck Reagent) with 10 ml. of concentrated hydrochloric acid. The mixture was refluxed for 30 minutes, followed by the addition of potassium chloride (0.300 gm.) and 10 ml. of alcohol. After evaporating to dryness the material obtained was recrystallised from dilute hydrochloric acid. The deep red crystals were filtered and washed with alcohol. A yellow solution was obtained when the crystals were dissolved in water, but on standing the solution turned a greenish colour and some black material precipitated. In 0.1M hydrochloric acid solutions the solution appeared quite stable.

A 0.00020 M solution of $\text{K}_2\text{OsCl}_6$ in 0.1 M hydrochloric acid was treated with ethylene at a pressure of 700 lb. per square inch for 96 hours. The ultraviolet spectrum did not change at all during this period and it was assumed that neither complex formation nor reduction had occurred to any measurable extent.

**Ruthenium**

$\text{K}_2\text{RuCl}_5$ was prepared by dissolving approximately 0.5 gm. of ruthenium(III) chloride (American Platinum Works) in 10 ml. of water. The actual amount weighed out was difficult
to determine as the material is highly deliquescent. The solution was acidified with hydrochloric acid and 0.400 gm. of potassium chloride added. The mixture was left to stand two days and then evaporated to about half the original volume. Red-brown crystals were obtained and they were filtered and washed with alcohol. A 0.00028 M solution in water was red-brown initially but darkened on standing. The same concentration of the ruthenium salt in 0.1 M hydrochloric acid appeared quite stable and did not change in colour over a period of one month.

When the acid solution was reacted with ethylene for 19 hours at a pressure of 750 lb. per square inch, the solution became almost colourless. It was also noticed that the addition of a reducing agent, hydrazine dihydrochloride gave an identical colour change. Mixtures were prepared to give a ratio of one, two, three and four equivalents of hydrazine dihydrochloride to each mole of the $\text{K}_2\text{RuCl}_5$. The solutions were allowed to react for 3 days at room temperature and the spectra were determined. The spectra of all four were identical, (hydrazine does not interfere at the wavelengths studied, 310-600 mu), and it was thought that the $\text{K}_2\text{RuCl}_5$ must have been reduced to $\text{K}_2\text{RuCl}_4$ and no further.

To confirm the extent of the reduction the same strength ruthenium solution was prepared in 0.3M hydrochloric acid and the reaction with ethylene took 43 hours at the same pressure to complete the reduction. The solution was evaporated
in a rotary evaporator and analysed for chlorine. The chlorine content found was 45.20 per cent compared to 44.1 per cent for $K_2 RuCl_4$, and 49.6 per cent for $K_2 RuCl_5$. The higher value than that calculated for the ruthenium(II) salt may have been due to incomplete reduction or reoxidation before the solution was dried.

Miscellaneous Solid Materials

An unstable compound was formed when solid copper(I) chloride, placed in a glass tube, was treated with ethylene at 60 atmospheres pressure.\textsuperscript{125} The isoelectronic zinc(II) chloride was tested along with cadmium(II) and mercury(II) chloride, which have the same outer electronic structure. The samples were allowed to react three days at 60 atmospheres pressure but no complex formation was observed. Platinum(II) chloride, powdered, was treated in the same manner and an increase in weight was observed. The sample was extracted with alcohol acidified with hydrochloric acid and a solution of ethylene platinous chloride was obtained. However, this is not as convenient a method of preparation as the one proposed earlier, as the rate and extent of the reaction is much lower, also the platinum(II) chloride is more difficult to prepare and handle.

Conclusions

The reaction of ethylene with a series of metals has shown that:

1. Aqueous solutions of potassium chloropalladite are reduced to the metal, the rate being dependent on the hydrochloric acid concentration.

2. The ethylene complex of palladium(II) can be prepared in a direct manner by using benzene as a solvent.

3. Potassium hexachloroiridate(IV) is reduced rapidly and quantitatively to iridium(III).

4. There is strong evidence for complex formation to an unstable compound with rhodium(III). Reduction occurs either before or after complex formation.

5. Potassium hexachlorooxomate(IV) does not react with ethylene.

6. Potassium pentachlororuthenate(III) is reduced to ruthenium(II).

7. Ethylene platinous chloride can be formed by the direct action of ethylene on platinum(II) chloride.
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