230. *Complex Compounds of the Olefins with Metallic Salts. Part II. Homologues of Zeise's Salt.*

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IN Part I (J., 1934, 971) the reactions of Zeise's salt, $K[PtCl_3,C_2H_4],H_2O$, were described, and it was shown that in all the compounds obtained, the ethylene molecule occupies one place in the co-ordination shell; *i.e.*, that, if the co-ordination number 4 for platinum is to be consistently maintained, the ethylene must be regarded as attached by one co-ordinate linkage. Evidence was brought forward supporting the view that, on chemical grounds, no intrinsic difference is discernible between the co-ordination of ethylene and that of neutral molecules such as ammonia.

The present contribution deals with compounds analogous to Zeise's salt, but derived from substituted ethylenes, and aims at tracing the influence of substitution upon the ability of olefins to co-ordinate with platinum. Compounds of this type, $K[PtCl_3,C_3H_6]$ and $K[PtCl_3,C_5H_{10}]$, containing propylene and amylene (probably the Δ^{α}-compound in view of the mode of preparation used), were described by Birnbaum (*Annalen*, 1869, **145**, 67), whose results show that the co-ordinating ability of propylene and amylene is certainly less than that of ethylene. Reaction of a different type—direct addition across the double bond—was observed by Hofmann and von Narbutt (*Ber.*, 1908, **41**, 1625) with di*cyclo*pentadiene. This, with potassium chloroplatinite in methyl and ethyl alcohols formed $PtCl{\cdot}C_{10}H_{12}{\cdot}OMe$ and $PtCl{\cdot}C_{10}H_{12}{\cdot}OEt$, but in propyl alcohol a compound $PtCl_2,C_{10}H_{12}$ (probably $PtCl{\cdot}C_{10}H_{12}Cl$) was formed. It is significant that the last differed markedly in properties from the co-ordination compounds $PtCl_2,C_2H_4$ and $PtCl_2,CHPh{:}CH_2$ described in this and the previous paper. Other examples of addition across the double bond have not been observed with certainty in the present work, and the case of di*cyclo*pentadiene appears to be abnormal and worth reinvestigation.

Attention has been mainly directed to aromatically substituted olefins, as likely to show more pronounced steric and polar effects than the aliphatic compounds. The hydrocarbons examined were: Monosubstituted, styrene; αα-disubstituted, αα-diphenylethylene, β-phenylpropylene; αβ-disubstituted (*cis*-), *cyclo*hexene, indene; αβ-disubstituted (*trans*-), α-phenylpropylene; trisubstituted, β-phenyl-Δ^{β}-butylene; tetrasubstituted, tetraphenylethylene, bisdiphenylene-ethylene. In addition, amylene was examined, as it appeared that its compounds might be of use in the preparation of other complexes, by the reaction (C) described below.

The effect of substitution is greatly to lower the stability of the complex salts formed. The solubility of salts derived from substituted olefins is higher than that of ethylene compounds, so that although Zeise's acid may readily be isolated as its not very soluble quinoline salt $C_9H_7NH[PtCl_3,C_2H_4]$, yet the corresponding *styrenetrichloroplatinite*, $C_9H_7NH[PtCl_3,CHPh{:}CH_2]$, is too soluble to be used as a convenient means of identifying the complex, and the potassium salt $K[PtCl_3,CHPh{:}CH_2]$ is extremely soluble. For these reasons, a number of the compounds were not characterised as their potassium salts, which can indeed be isolated only with difficulty in most cases, but as their tetramminoplatinous salts $[Pt(NH_3)_4][PtCl_3,X]_2$ or, better, as their 1 : 6-dichlorobisethylenediaminocobaltic salts $[CoCl_2en_2][PtCl_3,X]$. The latter, being in all cases less soluble than the corresponding chloroplatinite $[CoCl_2en_2]_2[PtCl_4]$, enabled the olefin complex to be separated by fractional precipitation.

The formation of complex salts containing olefins has been effected by several methods.

(A) Olefinic compounds react directly with potassium chloroplatinite, displacing one chlorine ion from the co-ordinated complex: $K_2PtCl_4 + C_nH_{2n} \longrightarrow K[PtCl_3,C_nH_{2n}] + KCl$. This reaction, observed by Biilmann (*Zentr.*, 1917, I, 562) with unsaturated acids, aldehydes, and ketones, takes place also with hydrocarbons. Reaction proceeds at room temperature in aqueous-alcoholic solution, and is slow owing to the insolubility of the chloroplatinite in alcohol. It was shown in Part I (*loc. cit.*, p. 973) that reactions of the above type are reversible. In the case of $K[PtCl_3,C_2H_4]$, the stability of the ethylenetrichloroplatinite ion is so high that Zeise's salt may be recrystallised unchanged in presence of an excess of potassium chloride or hydrochloric acid, although a variety of observations indicate that ethylene may be lost by dissociation in the same manner as styrene (see below). With other olefins, however, the stability may be so far lowered that, on recrystallisation, only potassium chloroplatinite is obtained (cf. Birnbaum, *loc. cit.*), while in carrying out the preparation of olefin complexes by the above method an equilibrium must be attained. Moreover, the insolubility of potassium chloroplatinite, and the solubility of the Zeise's salts in alcohol, tend to shift the equilibrium further to the left. The extent to which the olefin-containing complex anion is formed in this reaction thus affords some qualitative measure of the co-ordinating power of the olefin (see p. 1045). As a preparative method it is suitable only for the styrene salt, $K[PtCl_3,CHPh{:}CH_2]$.

(B) Similar in principle is the direct addition of olefins to platinous chloride dissolved in absolute-alcoholic hydrogen chloride. Reaction is more rapid than with (A), since the system is homogeneous, but the necessary high concentration of hydrogen chloride checks the reaction when only partly completed. In addition to the olefintrichloroplatinites there are also formed by this reaction by-products containing platinum, which are soluble in ether and do not react with potassium chloride. The nature of these substances, which have not yet been isolated, is unknown.

(C) Δ^{α}-Aliphatic olefin complexes may be readily prepared by the method of Zeise and Jörgensen, *i.e.*, by reduction of either platinic chloride or sodium chloroplatinate with the corresponding saturated alcohol.

(D) The most striking and significant mode of formation is by the direct replacement of one olefin by another. Thus, if an alcoholic solution of Zeise's salt is treated in a vacuum with styrene, a vigorous reaction takes place, and ethylene is liberated quantitatively. There remains a new, yellow, very soluble salt, *potassium styrenetrichloroplatinite*:

$$K[PtCl_3,C_2H_4] + CHPh{:}CH_2 = K[PtCl_3,CHPh{:}CH_2] + C_2H_4$$

Similarly, ethylene may be replaced by amylene, and amylene in turn by indene. The factor involved is not solely the relative stability of the salts (*i.e.*, the relative "residual affinities" of the olefins), since the styrene complex is definitely less stable than the ethylene complex, but the relative volatility of the olefins, as is shown by the effect of pressure. At atmospheric pressure the displacement of ethylene proceeds only slowly, if at all. On reducing the pressure, whereby ethylene is removed from the system, reaction proceeds at once to completion.

Similar behaviour is shown by ethyleneplatinous chloride, $PtCl_2,C_2H_4$. At room temperature in a vacuum, ethylene is replaced quantitatively by styrene, forming the analogous styreneplatinous chloride $PtCl_2,CHPh{:}CH_2$.

In view of the formal analogy between the co-ordination compounds of ethylene and of carbon monoxide, and the possible relationship in the mechanisms whereby the co-ordinate linkage is formed, it was of importance to examine whether styrene would displace co-ordinated carbon monoxide. It was found, however, that anilinium carbonyltrichloroplatinite $C_6H_5{\cdot}NH_3[PtCl_3,CO]$ (Mylius and Foerster, *Ber.*, 1891, **24**, 2424), selected as being soluble in alcohol without decomposition, could be warmed with styrene in a vacuum for prolonged periods without any measurable evolution of carbon monoxide. The inference must be drawn that the strength of the linkage olefin→Pt is distinctly less than that of the links $CO \rightarrow Pt$ or $NH_3 \rightarrow Pt$ in, *e.g.*, Cossa's salt, and that some dissociation probably occurs. The latter conclusion is borne out by the decomposition of the styrene salt in solution (see below).

The importance of the demonstration of the mutual replaceability of the olefins lies in the conclusive evidence it affords that in such compounds one is dealing with true molecular compound formation, and not, as has been suggested (cf. Drew, Pinkard, Wardlaw, and Cox, J., 1932, 997), with compounds of such a type as $K[\begin{smallmatrix}Cl\\Cl\end{smallmatrix}{>}Pt\text{-}CH_2{\cdot}CH_2Cl]$, in which a certain mobility is supposed to be conferred by the platinum atom upon the terminal chlorine. It might be possible, though unlikely, for ethylene to be displaced from such a substance by means of pyridine or potassium cyanide : it is inconceivable that the ethylene should be spontaneously replaceable by amylene or styrene.

The only compounds isolated during the present work which are comparable in stability with Zeise's ethylene compounds are the styreneplatinous chloride and potassium styrenetrichloroplatinite referred to above. The latter may be readily obtained by the action of styrene either on potassium chloroplatinite or, better, on Zeise's salt. It forms deep yellow, lustrous, apparently monoclinic prisms, which crystallise anhydrous from aqueous alcohol. The salt is extremely soluble in both water and aqueous alcohol. It undergoes some dissociation in solution, since the solution smells of styrene and invariably deposits platinous chloride on standing :

$$2K[PtCl_3,CHPh{:}CH_2] \longrightarrow K_2PtCl_4 + PtCl_2 + 2CHPh{:}CH_2.$$

The insolubility of styrene in water causes continuous decomposition of the aqueous solution, and may lead ultimately to complete conversion into potassium chloroplatinite.

Styreneplatinous chloride, $PtCl_2,CHPh{:}CH_2$, obtained from ethyleneplatinous chloride by the action of styrene, is an orange microcrystalline substance, more soluble in benzene and chloroform than the corresponding ethylene compound. It is probably to be regarded, like the latter, as possessing a doubled molecular formula in order to maintain the co-ordination number 4 of the platinum. Like the ethylene compound, it is reduced with extreme ease, reacting with hydrogen below 50°. At higher temperatures the reaction may, indeed, be accompanied by incandescence.

Although no pure compounds of the type were isolated, there is strong evidence that bisolefin compounds, *e.g.*, $PtCl_2,2CHPh{:}CH_2$, may exist. The immediate product of the action of styrene on ethyleneplatinous chloride invariably contains less platinum than corresponds to $PtCl_2,CHPh{:}CH_2$, to which constant composition it is brought by heating at 56° in a vacuum. The product so obtained is lighter in colour than the original, and dissolves in benzene to a yellow solution, which is changed to a deep orange-red colour, and takes up more styreneplatinous chloride, on addition of styrene. From this orange-red solution, reddish crystals separate, which become opaque and lose styrene, however, when washed with light petroleum, and can be obtained only with a variable composition representing the presence of 35—45% of $PtCl_2,2CHPh{:}CH_2$. Other olefins also deepen the colour of benzene solutions of styreneplatinous chloride, and an addition compound probably precedes the displacement of ethylene from $PtCl_2,C_2H_4$ by styrene, since there is a deepening of colour, but no evolution of ethylene until the pressure is reduced.

Indeneplatinous chloride, $PtCl_2,C_9H_8$, is obtained similarly to the styrene compound. Unlike the latter, it is extremely sparingly soluble in benzene or chloroform, probably owing to admixture with polymerised indene.

Δ^{β}-Amyleneplatinous chloride. Δ^{β}-Amylene reacts vigorously with ethyleneplatinous chloride to give the golden-yellow crystalline $PtCl_2,C_5H_{10}$. In this instance the colour of the solution suggests that the formation of a bisamylene compound does not occur.

Some information as to the relative co-ordinating power of the hydrocarbons examined is provided by the extent of their reaction with potassium chloroplatinite and alcoholic chloroplatinous acid. The results are summarised in Table I. A further line of evidence may be obtained from the behaviour of the olefins towards Zeise's salt and ethylene platinous chloride, as is summarised in Table II.

TABLE I.

Hydrocarbon.	Extent of reaction with K_2PtCl_4 or H_2PtCl_4.
Styrene	Very extensive : K salt may be so prepared
Amylene	Extensive : K salt may be isolated
Indene	Very incomplete : K salt may be isolated in very small amount
*cyclo*Hexene	Slight : the formation of $[PtCl_3,C_6H_{10}]$ may be proved
$CPh_2:CH_2$	Some substitution probably occurs, but no derivative could be isolated for analysis
$CPhMe:CH_2$	
Other hydrocarbons examined	No formation of complex salt

TABLE II.

Hydrocarbon.	Action on	
	$PtCl_2,C_2H_4$.	$K[PtCl_3,C_2H_4]$.
Styrene	C_2H_4 liberated vigorously	C_2H_4 liberated vigorously
Amylene	C_2H_4 liberated vigorously	C_2H_4 liberated slowly
Indene	C_2H_4 slowly displaced	No apparent action, but C_5H_{10} similarly displaced from $K[PtCl_3,C_5H_{10}]$
*cyclo*Hexene	No action, but probably displaces C_5H_{10} from $PtCl_2,C_5H_{10}$	No action
Other hydrocarbons examined	No action	No action

The above results indicate that the co-ordinating ability of the olefins decreases in the order $C_2H_4 > CHPh:CH_2 >$ indene $>$ *cyclo*hexene $> CPh_2:CH_2$ and $CPhMe:CH_2$.

The ability of amylene to co-ordinate is comparable with that of styrene, although the styrene potassium salt appears to be more stable than the corresponding amylene compound.

Progressive substitution is seen greatly to reduce the co-ordinating ability of the olefins. A steric factor is perceptible in that indene and *cyclo*hexene, in which the ring structure necessarily confers a *cis*-configuration, co-ordinate, whereas CHPh:CHMe, which is presumably *trans*, does not. On the other hand, Δ^{β}-amylene, which is presumably also *trans*, co-ordinates relatively strongly. The much more ready formation of co-ordination compounds from indene than from *cyclo*hexene suggests that dissymmetry about the double bond, and the consequent polarity of that bond, is a factor promoting co-ordination.

If the relatively high co-ordinating ability of styrene is to be attributed to the polar influence of the phenyl group, which confers on the double bond an appreciable dipole moment ($0{\cdot}37 \times 10^{-18}$ e.s.u.; Otto and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 294), a comparison with *as*-diphenylethylene provides some indication which of the unsaturated carbon atoms is concerned in the formation of the co-ordinate link. If the terminal carbon atom were active, the augmented polarity due to the introduction of the second phenyl group would be expected to increase the donor tendencies of the unsaturated group. The reverse effect is found—if *as*-diphenylethylene does form co-ordination compounds with platinous chloride, they are too unstable to be isolated. It is concluded that the augmented dissymmetry of the double bond must be outweighed by some other factor, which may well be the steric effect of two bulky phenyl groups inhibiting attachment to the α-carbon atom. On the other hand, the direction of the dipole moment of styrene is opposed to that of ethylbenzene, so that the β-carbon atom, as the seat of the permanent negative charge, might be expected to function as the donor. It cannot but be concluded from the chemical evidence, however, that in co-ordination the effect observed is opposed to that of the permanent charge distribution in the free molecule.

There remains to be considered such evidence as to the mechanism of formation of the co-ordinate linkage as is provided by the experimental material here discussed. Although the view is not universally accepted (cf. Samuel and Hunter, J., 1934, 1180; *Chem. and Ind.*, 1935, 635), since it is not altogether clear how a closed s^2 electron-pair comes to be shared with a second atom, there can be no doubt that the systematics and magnetic properties of co-ordination compounds are best explained by an electron-pair theory of the co-ordinate linkage. This, in turn, demands the presence of a "lone pair" of electrons in order that an atom may exhibit donor functions. One possible mechanism whereby such a lone pair may be produced in ethylene or an aromatic nucleus has been put forward by Bennett and Willis (J., 1929, 256).* It is supposed that the lone pair is produced by an electromeric change: $R{\cdot}CH\overset{\curvearrowright}{=}CH{\cdot}R' \longrightarrow R{\cdot}\overset{+}{C}H{-}\overset{-}{C}H{\cdot}R'$, and so is derived from an excited state of the ethylenic linkage. This, or indeed any other view of the process, involves (*a*) an opening of the double bond, (*b*) leaving one of the carbon atoms—that which bears the residual positive charge—with a sextet of electrons.

With a view to the possibility of tracing the persistence of the double bond upon co-ordination, the absorption spectra of the styrene and indene potassium salts were examined. Morton (J., 1934, 911) has shown that the chromophoric grouping CPh:C— gives rise to absorption maxima at 2700—2900 A. with both styrene and indene. The extinction curves showed, however, that general absorption sets in somewhat above these wave-lengths, leaving the question indeterminate.

If the double bond were opened by such a reversible process as co-ordination to the metal, it would be anticipated that the polymerisation of the unsaturated compound must necessarily be promoted by the reactions in which olefin complexes are formed. This expectation is not fulfilled. Indene was usually polymerised to a considerable extent by reaction with potassium chloroplatinite, Zeise's salt, and ethyleneplatinous chloride, but the other substances examined, in particular styrene, showed no such tendency. Polymerisation occurred occasionally, but quite irregularly.

The mechanism advanced by Bennett and Willis, which seems, indeed, the only means whereby a lone pair of electrons can be produced at one ethylenic carbon atom, is not altogether free from objection on physical grounds. The hypothetical polarised state of the bond concerned, supposing as it does the complete transfer of one electron, represents an excited state of the molecule, and could be represented at room temperature by only a very low probability of occurrence. Alternatively, it might be supposed that rearrangement takes place in the field of the adjacent platinum atom, which possesses a high electron affinity. In either case the reactions concerned should involve a high energy of activation. There are no data available as to the energy of activation either for reactions of the type described in the present paper, or for addition compound formation by aromatic hydrocarbons, but reactions of both kinds proceed either very rapidly or fairly rapidly at room temperature (cf. Hammick and Sixsmith, J., 1935, 580).

If the co-ordination of ethylene proceeds *via* an excitation of the ethylene, the result will be an abnormally low value for the net heat of formation of the co-ordinate linkage, as compared with the value found for the co-ordination of molecules (*e.g.*, NH_3 or CO) where rearrangement is not involved. In so far as the strength of a co-ordinate link is a measure of its heat of formation, experimental evidence shows that the linkage $Pt \leftarrow$olefin must be associated with a smaller heat of formation than the linkage $Pt \leftarrow CO$. The latter, in turn, by analogy with the values found for the co-ordination of carbon monoxide and of amines to iron (Hieber and Woerner, *Z. Elektrochem.*, 1934, **40**, 256) is probably lower than, but of the same order of magnitude as, the heat of formation of amine$\rightarrow$Pt co-ordinate linkages. It does not follow, however, that the low heat of co-ordination is evidence of internal rearrangement preceding co-ordination. Thermochemical measurements on this point, and also certain stereochemical consequences of the hypothesis discussed above, are at present under examination.

On the evidence thus far available, any attempt to formulate compounds of the type here dealt with in terms of the electron-pair bond theory possesses a certain artificiality, and

* Ref. 88 (*Ann. Reports*, 1931, **28**, 138) refers to this paper, not to Bennett and Willis (J., 1929, 2305) as quoted.

it may be that molecular-compound formation by unsaturated compounds—olefinic or aromatic—forms a crucial test of the applicability of the lone-pair bond theory.

EXPERIMENTAL.

(1) *Action of Olefins on Potassium Chloroplatinite.*—0·3—0·5 G. of the chloroplatinite, dissolved in 5 c.c. of water, was mixed with approximately 1 g. (*i.e.*, a large excess) of hydrocarbon, dissolved in 10 c.c. of alcohol. The solution was warmed to 40° with constant shaking, and left for several days or weeks. Where reaction occurred, a clear yellow solution resulted, together with more or less reduction to metallic platinum. The filtered solution was diluted with water to throw out dissolved hydrocarbon, which was extracted with ether. The yellow aqueous solution, containing potassium chloride and chloroplatinite and the olefin complex, was fractionally crystallised in a vacuum over sulphuric acid, or was treated with tetramminoplatinous chloride or bisethylenediaminodichlorocobaltic chloride to precipitate the corresponding insoluble salts. Attempts to regenerate the potassium olefin complex salts from the insoluble salts $[Pt(NH_3)_4][PtCl_3,X]_2$ and $[CoCl_2en][PtCl_3,X]$ (X = olefin) by the action of K_2PtCl_4 and $[Cr(C_2O_4)_2en]K$ respectively, in the manner described by Pfeiffer and Hoyer (*Z. anorg. Chem.*, 1933, **211**, 241), were completely unsuccessful. Styrene reacted rapidly under the above conditions, and the final solution gave on evaporation deep yellow prisms of potassium styrenetrichloroplatinite, which could not readily be obtained quite pure by this method, but was identified by conversion into the plato-salt.

Tetramminoplatinous styrenetrichloroplatinite, $[Pt(NH_3)_4][PtCl_3,CHPh\dot{:}CH_2]_2$, was precipitated as golden-yellow needles by the addition of tetramminoplatinous chloride to the solution of the potassium styrene salt (Found: Pt, 54·8, 54·4. $C_{16}H_{28}N_4Cl_6Pt_3$ requires Pt, 54·55%).

Indene with potassium chloroplatinite yielded a golden-yellow solution, which underwent much dissociation during evaporation. Potassium chloroplatinite separated first, and finally a mixture of this with a small amount of a yellow salt. The latter, separated by hand picking, proved to be *potassium indenetrichloroplatinite*, $K[PtCl_3,C_9H_8]$, which "effloresced" during desiccation owing to loss of indene, as the analytical data show (Found: Pt + KCl, 60·28. $C_9H_8Cl_3KPt$ requires Pt + KCl, 59·1%). The nature of the compound was proved by its conversion into 1 : 6-*dichlorobisethylenediaminocobaltic indenetrichloroplatinite*,

$$[CoCl_2en_2][PtCl_3,C_9H_8],$$

which was precipitated as a dull green microcrystalline powder on the addition of $[CoCl_2en_2]Cl$ to a solution of an excess of the potassium salt (Found: Pt + Co, 38·3; N, 8·6. $C_{13}H_{24}N_4Cl_5CoPt$ requires Pt + Co, 38·1; N, 8·4%).

*cyclo*Hexene gave by this method a weakly yellow solution affording definite evidence of reaction, but the amount of the complex salt formed was too small for isolation.

The other hydrocarbons examined, with the uncertain exception of *as*-diphenylethylene, afforded no evidence of complex formation. With tetraphenylethylene, complete reduction to metallic platinum occurred.

(2) *Action of Olefins on Alcoholic Chloroplatinous Acid.*—cyclo*Hexene.* 0·51 G. of platinous chloride, dissolved in 9 c.c. of absolute-alcoholic hydrogen chloride, was sealed up with 2 c.c. of *cyclo*hexene. After several days the liquid was filtered from a residue of platinous chloride and reduced metallic platinum into 70 c.c. of water. The brown *cyclo*hexene layer was separated off, and the golden-yellow aqueous solution was fractionally precipitated with 0·35 g. of 1 : 6-$[CoCl_2en_2]Cl$ in 10 c.c. of water, added in five equal portions. The first three fractions consisted of pure 1 : 6-*dichlorobisethylenediaminocobaltic* cyclo*hexenetrichloroplatinite* $[CoCl_2en_2][PtCl_3C_6H_{10}]$ (Found: Pt + Co, 39·7, 39·7; N, 8·8, 8·4. $C_{10}H_{26}N_4Cl_5CoPt$ requires Pt + Co, 39·9; N, 8·8%).

as-Diphenylethylene was similarly treated with alcoholic chloroplatinous acid. The resulting orange solution was filtered into an equal volume of aqueous potassium chloride. On filtration from potassium chloride and chloroplatinite, a pale yellow solution was obtained, too dilute to give any precipitate with $[CoCl_2en_2]Cl$. Addition of $[Pt(NH_3)_4]Cl_2$ to this solution yielded a yellow-green precipitate. Microscopic examination showed this to consist chiefly of the highly characteristic slender green needles of Magnus's salt, $[Pt(NH_3)_4]PtCl_4$, with a very small amount of a yellow substance. On standing for a few hours, however, the precipitate turned green, and was then found to consist only of Magnus's salt. There is thus evidence of the formation of a complex ion $[PtCl_3,CPh_2\dot{:}CH_2]'$, which must, however, be unstable in the absence of an excess of the olefin.

Very similar behaviour was shown by β-phenylpropylene. The other hydrocarbons examined showed no evidence of complex formation by this method.

(3) *The Action of Olefins on Zeise's Salt and Ethyleneplatinous Chloride.*—*Action of styrene on*

Zeise's salt. The reaction was carried out in a pear-shaped flask (to facilitate collection of the solid product) connected to a Toepler pump and gas burette, with a trap, maintained at − 40°, interposed in order to condense out alcohol, excess styrene, etc. 0·1488 G. of Zeise's salt was treated in a vacuum with 0·5 c.c. of styrene, dissolved in 4 c.c. of alcohol. An immediate vigorous evolution of gas occurred, which was completed on warming. 7·45 C.c. of gas (at *N.T.P.*) were pumped out, corresponding to 6·2% of ethylene (Calc. for $K[PtCl_3,C_2H_4],H_2O$: C_2H_4, 7·2%). The alcohol and excess of styrene distilled over completely, indicating that practically no polymerisation of the styrene occurred. The pale yellow solid residue, on recrystallisation from 50% aqueous alcohol, yielded deep orange, very soft, monoclinic or triclinic prisms of *potassium styrenetrichloroplatinite*, $K[PtCl_3,C_8H_8]$ (Found : Pt + KCl, 60·7; Cl, 23·9; H_2O, 0·0. $C_8H_8Cl_3KPt$ requires Pt + KCl, 60·8; Cl, 24·3%). This salt gave with $[Pt(NH_3)_4]Cl_2$ a plato-salt identical with that described above (section 1).

Action of styrene on ethyleneplatinous chloride. 0·1372 G. of $PtCl_2,C_2H_4$ was treated with 0·5 c.c. of styrene, dissolved in benzene. Vigorous exothermic action occurred, and was completed on warming; 11·25 c.c. (at *N.T.P.*) of gas were liberated, corresponding to 10·3% of ethylene (Calc. for $PtCl_2,C_2H_4$: C_2H_4, 10·5%). The residue after evaporation of the golden-red benzene solution was an orange crystalline solid containing less platinum than corresponds to $PtCl_2,CHPh{:}CH_2$ (Found : Pt, 49·95. $C_8H_8Cl_2Pt$ requires Pt, 52·7%), and which could not be completely purified by recrystallisation from benzene or chloroform, in which solvents the substance is fairly soluble (Found, after two recrystallisations : Pt, 51·2%). On heating at 56° in a vacuum some styrene was lost, constant weight being attained at a composition corresponding to $PtCl_2,C_8H_8$ (Found : Pt, 52·4%). This product was lighter in colour and distinctly less soluble in benzene than the original substance. It formed a yellow benzene solution, turned to a deep orange red on addition of styrene. From this solution were obtained reddish-orange crystals, which could not be dried without loss of styrene. As has been discussed above, these crystals as deposited from solution probably consist of *distyreneplatinous chloride*, $PtCl_2,2C_8H_8$ (Found : Pt, 47·7. $C_{16}H_{16}Cl_2Pt$ requires Pt, 41·2% ; the proportion corresponds to the presence of 43% of bis-styreneplatinous chloride).

Indene gave with Zeise's salt a very slow and incomplete evolution of ethylene : owing to the concomitant polymerisation of the indene, which led to incomplete reaction, it was not possible to prepare the indene potassium salt in this way.

With ethyleneplatinous chloride, ethylene was slowly evolved, and a yellow microcrystalline product was obtained. This differed from the styrene compound in being extremely insoluble in benzene or chloroform, thereby precluding purification by recrystallisation, and was probably contaminated with polymerised indene (Found, after heating to 56° in vacuum to constant weight : Pt, 49·7. Calc. for $PtCl_2,C_9H_8$: Pt, 51·1%).

By the addition of indene to the yellow solution of styreneplatinous chloride in benzene, the colour was deepened to a reddish-orange, and an orange microcrystalline product was deposited. As in the case of the presumed bis-styreneplatinous chloride, this addition product, which may have been an indenestyreneplatinous chloride, $PtCl_2,C_8H_8,C_9H_8$, lost olefin on removal from its solution, and no definite chemical entity could be isolated.

Δ^{β}-Amylene reacted vigorously with ethyleneplatinous chloride, and the yellow solution formed in excess of the hydrocarbon deposited golden-yellow crystals of *amyleneplatinous chloride* (Found : Pt, 57·7. $C_5H_{10}Cl_2Pt$ requires Pt, 58·0%).

With Zeise's salt Δ^{β}-amylene slowly liberated ethylene, leaving a lemon-yellow salt, presumably $K[PtCl_3,C_5H_{10}]$, which was not investigated further. From this salt, on treatment with indene, amylene was displaced in turn, giving the corresponding indene salt, as is shown by its conversion into $[CoCl_2en_2][PtCl_3,C_9H_8]$ (Found : Pt + Co, 38·9. Calc. : Pt + Co, 38·1%). The analytical figures indicate the presence of some unchanged Zeise's salt owing to the incomplete displacement of ethylene or amylene.

Anilinium Carbonyltrichloroplatinite.—Platinous chloride, dehydrated in chlorine at 270°, was heated in a stream of phosphoric oxide-dried carbon monoxide to 250°. The mixed carbonylplatinum chlorides obtained were dissolved directly in concentrated hydrochloric acid, yielding $H[PtCl_3,CO]$ with evolution of the excess of carbon monoxide. A warm solution of aniline in an excess of concentrated hydrochloric acid was added, whereupon pale, lemon-yellow, crystalline anilinium carbonyltrichloroplatinite was immediately deposited (cf. Mylius and Foerster, *loc. cit.*). This salt was dried over potassium hydroxide in a vacuum. On treatment with styrene in a vacuum, no carbon monoxide was evolved even after several hours at 40°. The unchanged condition of the carbonyltrichlorplatinite was confirmed by the immediate quantitative liberation of carbon monoxide on the addition of aqueous potassium cyanide.

Absorption Spectra of Potassium Styrene- and Indene-trichloroplatinites.—Crystalline $K[PtCl_3,CHPh{:}CH_2]$ and the solution of potassium indenetrichloroplatinite obtained by the action of indene on alcoholic chloroplatinous acid were employed. The latter salt would therefore contain an excess of potassium chloride, and also a small proportion of potassium chloroplatinite. The spectra were examined over the range 2800—4300 A. on a reflexion grating spectrograph, and were seen to conform closely to those of other platinous complexes.

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