

586. Olefin Co-ordination Compounds. Part III.* Infra-red Spectra and Structure: Attempted Preparation of Acetylene Complexes.

By J. CHATT and L. A. DUNCANSON.

The infra-red spectra of five olefin complexes with platinous chloride show that the olefin exists, with its double bond, in the complex. The $\text{C}=\text{C}$ stretching frequency is lowered by some 143 wave-numbers, about twice the lowering observed for silver-ion complexes. These facts and all data relating to olefin complexes of Pd^{II} , Pt^{II} , Cu^{I} , Ag^{I} , and Hg^{II} in the literature are consistent with a structure schematically shown in the Figures, essentially Dewar's structure (*Bull. Soc. chim.*, 1951, **18**, C 79), and with no other structure yet proposed.

From the dipole moments of compounds of the type $\text{C}_2\text{H}_4\cdot\text{am}\cdot\text{PtCl}_2$ (am = amine) we estimate that the $\text{C}_2\text{H}_4 \rightarrow \text{Pt}$ bond moment is about 2 D less (or greater) than that of the $\text{N} \rightarrow \text{Pt}$ bond. If we assume that this difference is due only to double-bond formation as required by the above structure, it indicates not more than about $\frac{1}{3}$ double-bond character in the $\text{C}_2\text{H}_4\text{-Pt}$ bond. Hel'man's evidence for the quadrivalency of platinum in olefin complexes of platinous chloride is shown to be consistent with bivalency. The chlorination of $(\text{C}_2\text{H}_4\text{PtCl}_2)_2$ yields ultimately ethylene dichloride, but not in the first stages of the chlorination. A much improved preparation of $(\text{C}_2\text{H}_4\text{PtCl}_2)_2$ has been found. Attempts to prepare platinous chloride complexes of but-2-yne and of diphenylacetylene were unsuccessful.

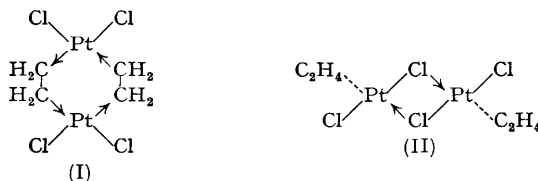
IN Parts I (*J.*, 1949, 3340) and II * the previously proposed structures of olefin complexes were reviewed and all were shown to be unsatisfactory. It was also suggested (Part I) that some sort of bond involving the participation of an electron pair from filled *d*-orbitals of the metal atom, in addition to the ordinary co-ordinate bond, was essential for olefin co-ordination. This bond was envisaged as being similar in nature to the π -bond which,

• Part II, *J.*, 1952, 2622.

as Pauling ("Nature of the Chemical Bond," Cornell Univ. Press, 1939) proposed, might exist between the carbon and nickel atoms in nickel carbonyl; however, it was difficult to formulate such a bond between a platinum atom and the two carbon atoms of an olefin.

Hel'man (*Compt. rend. Acad. Sci., U.R.S.S.*, 1939, **24**, 549) had previously proposed an apparently similar mode of binding the olefin to the platinum. Her structure is vaguely described and differs from our preliminary suggestions in two important ways. It allows only one molecule of the olefin to be attached to one platinum atom, but the carbonyl-like structure would allow more than one, and in Part II we described the preparation of $(C_2H_4)_2PtCl_2$. Her structure requires that the platinum atom in $K[C_2H_4PtCl_3]$ be formally quadrivalent, the carbonyl-like structure that it be formally bivalent. She preferred structure (I) for ethylene platinous chloride ["Complex Compounds of Platinum with Unsaturated Molecules," Soviet Acad. Sci., 1945 (in Russian); cf. Kharasch and Ashford, *J. Amer. Chem. Soc.*, 1936, **58**, 1733]. The present work shows that propylene exists, with its double bond, in propylene platinous chloride. This disposes of such structures as (I) and illustrates the essential difference between her conception of the olefin-to-platinum bond and ours. We consider ethylene platinous chloride to have a halogen-bridged structure (II) as originally suggested by Pfeiffer ("Organische Molekülverbindungen," Verlag von Ferdinand Enke, Stuttgart, 1927, p. 209), the only remaining problem being the nature of the C_2H_4 -Pt bond.

Olefins belong to the class of ligands which form only weak, if any, complexes with boron trihalides and related substances but combine fairly strongly with platinous chloride. Other such substances are CO , PF_3 , and to a lesser extent, tertiary alkyl-phosphines, -arsines, and other ligands in which the donor atom has a low electronegativity. They are all substances with a vacant orbital or a potentially vacant orbital in the valency shell of the donor atom; this orbital is available for π -bond formation by overlap with a filled d -orbital of the metal atom. It was on the basis of such considerations that we predicted the carbon monoxide-like behaviour of PF_3 , and the possible existence of volatile $Ni(PF_3)_4$ (Chatt, *Nature*, 1950, **165**, 859) which has since been confirmed (Wilkinson, *J. Amer. Chem. Soc.*, 1951, **73**, 5501; Chatt and Williams, *J.*, 1951, 3061; see also Chatt and Wilkins, *J.*, 1952, 4300).



The above class of ligands, the individual members of which readily form covalent dihalides (*e.g.*, $COCl_2$, PF_3Cl_2 , $C_2H_4Cl_2$), we consider to be bound in platinous complexes by bonds of partial double-bond character. They are characterised by their tendency to labilise substituents in the *trans*-position to themselves in platinous complexes; thus substitution occurs rapidly in that position. On the other hand, those ligands which cannot accommodate more electrons (*i.e.*, do not form covalent dihalides) direct substituents into the *cis*-positions, and substitution occurs rather slowly.

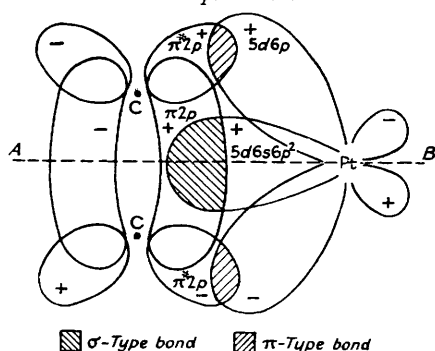
Because olefins are among the most strongly *trans*-directing ligands (Chernyaev and Hel'man, *Compt. rend. Acad. Sci., U.R.S.S.*, N.S., 1936, **4**, 181) we consider that they are bound to the metal by a σ - and a π -type of bond. To satisfy these requirements we proposed the ethylidene structure for $[C_2H_4PtCl_3]^-$ (Chatt, *Research*, 1951, **4**, 180). A second structure also satisfying these requirements, but without the objectionable feature of the migration of a hydrogen atom, was proposed at about the same time by Dewar (*Bull. Soc. chim.*, 1951, **18**, C 79). It was proposed with particular reference to the silver-ion complexes, but in its adaptation to the platinous complexes the σ -type bond would be formed by overlap of a $5d6s6p^3$ hybrid orbital of the platinum atom with the π -orbital of the olefin, and the π -type bond by overlap of a filled $5d$ -orbital of the metal atom with the antibonding π -molecular orbital of the olefin. The π -type bond would be

strengthened, however, by hybridisation of the $5d$ -orbital with the vacant $6p$ -orbital of the platinum atom to give a dp -hybrid more suitably shaped than the unhybridised $5d$ -orbital to provide a large overlap with the antibonding orbitals of the olefin (Craig, Maccoll, Nyholm, Orgel, and Sutton, personal communication). This gives us the picture of the olefin-platinum bond which is shown schematically in the Figures.

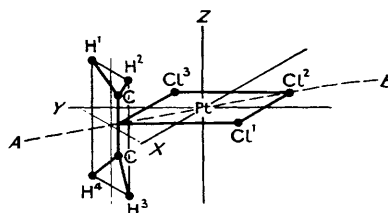
The new data which we present here show that the ethylidene structure is untenable, but accord with the above structure. A review of the properties of olefin-metal salt complexes, showing how they can all be correlated on the basis of Dewar's structure, was given at a conference in March, 1952 (Chatt, "The General Chemistry of Olefin Complexes with Metallic Salts" in "Cationic Polymerisation and Related Complexes," Ed. P. H. Plesch, Heffer, Cambridge, 1953). We shall, therefore, consider only the new data in this communication.

Infra-red Spectra.—The infra-red spectra of powdered crystalline complexes of olefins with platinous chloride have shown that the olefin retains its double bond in the complex and is symmetrically co-ordinated to the platinum. It is well established that olefinic C-H stretching modes of vibration cause absorption at frequencies greater than 3000 cm^{-1} (Fox and Martin, *Proc. Roy. Soc.*, 1938, *A*, **167**, 257; 1940, *A*, **175**, 208; Pozefsky and

Orbitals used in the combination of ethylene with platinum.



Spatial arrangement of atoms in $[\text{C}_2\text{H}_4\text{PtCl}_3]^-$.



(The plane of the hydrogen atoms is parallel to the plane Cl^1ZCl^2 but probably displaced slightly from co-planarity with the carbon atoms by the repulsion of the hydrogen atoms by the platinum atom.)

Coggershall, *Analyt. Chem.*, 1951, **23**, 1611), whereas the C-H stretching fundamentals of methyl and saturated methylene groups occur at lower frequencies. The existence of absorption bands at frequencies greater than 3000 cm^{-1} in the spectra of all the five complexes we have examined shows that the olefins are not destroyed on complex formation. For example, the spectrum of $\text{K}[\text{C}_3\text{H}_6\text{PtCl}_3]\cdot\text{H}_2\text{O}$ has absorption bands at 3068, 3034, and 3010 cm^{-1} , which can be assigned to the three olefinic C-H stretching modes of the co-ordinated olefin.

Since olefins are present in the complexes, and apparently unchanged in any essentiality, we should find absorption bands corresponding to the $\text{C}=\text{C}$ stretching frequencies, especially when the molecule of the bound olefin is not symmetrical about the double bond. The propylene complexes $\text{K}[\text{C}_3\text{H}_6\text{PtCl}_3]\cdot\text{H}_2\text{O}$ and $(\text{C}_3\text{H}_6\text{PtCl}_2)_2$ have a strong absorption band at 1504 cm^{-1} . This absorption is at higher frequencies than the C-H deformation and C-C stretching fundamentals and is very weak in the spectrum of the corresponding ethylene complexes. It is, therefore, assigned to the $\text{C}=\text{C}$ stretching frequency, lowered by some 143 cm^{-1} by co-ordination to the metal. This lowering of frequency is about twice that observed in the Raman spectra of silver-ion-olefin complexes (Taufen, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3500) and must be due to the much stronger binding of the olefin to platinum than to silver. The butadiene complex $\text{K}_2[\text{C}_4\text{H}_6(\text{PtCl}_3)_2]\cdot\text{H}_2\text{O}$ has a strong absorption band at 1475 cm^{-1} , which cannot be assigned with as much certainty as the absorption at 1504 cm^{-1} by the propylene complex, but it is possibly a $\text{C}=\text{C}$ stretching frequency lowered by both conjugation and co-ordination to the metal. In gaseous *trans*-butadiene the corresponding absorption occurs at 1592 cm^{-1} .

Ethylene platinous chloride $(\text{C}_2\text{H}_4\text{PtCl}_2)_2$ has a weak absorption at 1506 cm^{-1} , but in

the spectrum of Zeise's salt, $K[C_2H_4PtCl_3] \cdot H_2O$, any absorption in the 1500 cm^{-1} region of the spectrum was too weak to be observed. The existence of this absorption band, due to the $C\equiv C$ stretching mode, is evidence of the loss of a centre of symmetry by the olefin, but its weakness indicates that the symmetry of the olefin, in so far as it affects the infra-red activity of the $C\equiv C$ stretching frequency, has scarcely been altered by co-ordination to the metal atom. The olefin is thus symmetrically co-ordinated about the double bond as required by the structure shown in the Figures.

Anderson (*J.*, 1934, 971) showed that hydrolysis of Zeise's salt at 100° occurred as follows: $[C_2H_4PtCl_3]^- + H_2O = CH_3 \cdot CHO + 2HCl + Pt + Cl^-$. The absence of symmetrical substituted ethanes led him to suggest that the ethylene was unsymmetrically co-ordinated, but this reaction may proceed through the liberation and hydration of the ethylene to give ethanol which would be oxidised by the platinous salt in the presence of water.

Dipole Moments.—In complex compounds where the ligand is bound to the metal by a double bond, the separation of charge usually associated with the co-ordinate link (the σ -bond) will be neutralised to some degree by the drift of electrons from the d -orbitals of the metal into vacant orbitals of the ligand in the formation of the π -bond. Unfortunately, it is not possible to measure accurately the dipole moments of complex compounds in solution unless the moments are fairly large, say $>3\text{ D}$. This is because the atom polarisation of co-ordination compounds is large and its value uncertain. Jensen (*Z. anorg. Chem.*, 1936, 229, 225) found it necessary to assume an atom polarisation (${}_AP$) equal to about 20% of the electron polarisation (${}_EP$) so that a number of symmetrical *trans*-platinous complexes should have zero moment.

To obtain some idea of the polarity of the olefin-platinum bond, we have examined the electrical asymmetry of such molecules as *trans*- $C_2H_4 \cdot am \cdot PtCl_2$ (am = amine). Unfortunately, no complexes of this type are known which contain symmetrical amines (*e.g.*, pyridine) and are sufficiently soluble in benzene. It was therefore necessary to use unsymmetrical amines. Assuming that ${}_AP = 20\%$ of ${}_EP$, and disregarding its uncertainty in assessing the limits of error, we have found moments of $2.35 \pm 0.02\text{ D}$ for *trans*- $C_2H_4 \cdot p\text{-CH}_3 \cdot C_6H_4 \cdot NH_2 \cdot PtCl_2$ and $1.79 \pm 0.03\text{ D}$ for *trans*- $C_2H_4 \cdot p\text{-Cl} \cdot C_6H_4 \cdot NH_2 \cdot PtCl_2$ in benzene at 25° . These moments (μ) are much smaller than the usual values for molecules containing only one co-ordinate bond, *e.g.*, $C_2H_5 \cdot NH_2 \cdot AlCl_3$, $\mu = 6.94\text{ D}$ (Nespital, *Z. physikal. Chem.*, 1932, B, 16, 153); $(CH_3)_3N \cdot BCl_3$, $\mu = 6.23\text{ D}$; $(CH_3)_3P \cdot BCl_3$, $\mu = 7.03\text{ D}$ (Phillips, Hunter, and Sutton, *J.*, 1945, 146). Hence, if the N-Pt bond has the high polarity we expect (*ca.* 6 D units) the C_2H_4 -Pt bond is also highly polar, and it is in the main a co-ordinate rather than a double bond.

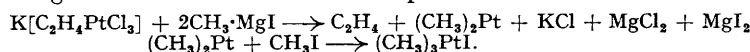
Because the moments we have measured are of the order 0—2.5 D, the actual values assumed for ${}_AP$ have a significant effect on the values of the calculated moments. Thus an estimate of the difference in bond moments, $\mu_{(N-Pt)} - \mu_{(C_2H_4-Pt)}$, and the remaining deductions given in this paragraph are somewhat speculative ($\mu_{(N-Pt)}$ = moment of the N-Pt bond, etc.). On the basis of assumptions set out in the experimental section we estimate the difference to be about 2 D, but our calculations do not determine its sign. We expect, however, on the basis of the structure in the Figures, that $\mu_{(N-Pt)} > \mu_{(C_2H_4-Pt)}$. The value $\sim 2\text{ D}$ receives some support from the moment, 2.81 D, of *trans*- $C_2H_4 \cdot NH_3 \cdot PtCl_3$ measured in dioxan (Shedlovskaya and Syrkin, *Compt. rend. Acad. Sci., U.R.S.S.*, 1947, 55, 231). Since the moment of the N-Pt bond is unknown but is perhaps of the order 6 D, then the moment of the C_2H_4 -Pt bond possibly has a value of about 4 D. The low moment thus inferred may be attributed to a weak σ -type bond, to the back-drift of electrons from the platinum to olefin in formation of the π -type bond (*cf.* Phillips, Hunter, and Sutton, *J.*, 1945, 146), or to some combination of both effects. The low moment is not proof of the existence of a partial double bond between olefin and the metal, but if the lowering is due to double-bond formation then tentatively it appears that the C_2H_4 -Pt bond has about $\frac{1}{3}$ double-bond character. This gives us an approximate upper limit to the double-bond character of the bond.

The C_2H_4 -Pt bond appears to be fairly strong in platinous chloride complexes containing only one ethylene molecule because no dissociation pressure of ethylene has

been noted over these compounds. Their thermal instability is due to autoreduction to the metal with formation of ethylene dichloride. We consider, therefore, that this, in conjunction with previous evidence for a double C_2H_4 -Pt bond, renders it highly probable that the low bond moment of about 4 D is due to partial double bonding rather than to a weak σ -type of bond.

Valency of the Platinum Atom.—The general chemistry of the olefin complexes indicates that they are square planar platinumous complexes in which the platinum atom is formally bivalent, but Hel'man's structure required that the platinum be formally quadrivalent and she presented evidence in support of such valency. We have re-examined this.

The most convincing evidence was provided by the reaction of $K[C_2H_4PtCl_3]$ or $(C_2H_4PtCl_2)_2$ with $CH_3 \cdot MgI$ to yield $(CH_3)_3PtI$, in which platinum is undoubtedly quadrivalent (Hel'man and Gorushkina, *Doklady Akad. Nauk, S.S.S.R.*, 1947, 57, 259). Since $CH_3 \cdot MgI$ is a reducing agent it appeared that the platinum in the original $K[C_2H_4PtCl_3]$ must be quadrivalent. Hel'man used a large excess of methyl iodide, however, to prepare the Grignard reagent. The reaction could thus proceed as follows:



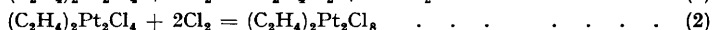
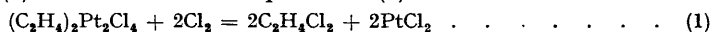
We repeated her experiment, using Na_2PtCl_4 instead of the ethylene complex, and also isolated $(CH_3)_3PtI$: thus its isolation is no evidence that the platinum was originally quadrivalent. These experiments also make it likely that dimethylplatinum exists, although it may only be as a short-lived intermediate.

The second piece of evidence appeared to be weaker. Hel'man and Ryabchikov (*Compt. rend. Acad. Sci., U.R.S.S.*, 1939, 24, 549) titrated $K[C_2H_4PtCl_3]$, $NH_4[NH_3PtCl_5]$, and $K[NH_3PtCl_3]$ electrometrically with 0.1N-permanganate. Only the last was oxidised, and the initial potentials of the three salts were 650, 660, and 520 mv, respectively. Thus $K[C_2H_4PtCl_3]$ is as resistant to oxidation as the platinic derivative. This was regarded as evidence that the platinum is quadrivalent. However, we know that the redox potentials of complex compounds are very sensitive to a change of ligand. When the co-ordination involves a drift of electrons from d -orbitals of the metal into vacant orbitals of the ligand to form a π -bond, the resultant lowering of electron density on the metal atom would reduce the tendency for electrons to be promoted from d -orbitals for principal valency formation. It is to be noted that groups of high *trans*-influence, *e.g.*, olefins, CO, PF_3 , and to a much less extent organic phosphines, arsines, etc., tend to stabilise low valency states of the later transition metals. Exceptions only occur when promotion of electrons from d -orbitals into a higher-energy orbital occurs during complex formation, as in the formation of the inner, or lower, orbital complex ion, $Ni[o-(AsMe_2)_2C_6H_4]_2^{++}$ (Burstall and Nyholm, *J.*, 1952, 3570).

It may be that the redox potentials of a series of exactly analogous inner orbital complex compounds of different ligands with a particular transition metal will serve as a measure of the relative double-bond character of the ligand-to-metal bond; always provided that oxidation occurs by the use of electrons from the d -orbitals of the reduced complex for the formation of the additional principal valencies of the oxidised complex.

We find that ethylene platinumous chloride in dry acetone is oxidised immediately by a dry acetone solution of permanganate at room temperature; the oxidation is complete when one molecule of oxygen for every molecule of ethylene has been consumed. The products were not identified.

Halogenation.—Stilbene dibromide results from the reaction of an excess of bromine with stilbene platinumous bromide $[(C_6H_5)_2C_2H_2]_2Pt_2Br_4$ (Kharasch and Ashford, *loc. cit.*), but this is one of the less stable olefin complexes and easy dissociation would account for ready halogenation. Therefore, when we were seeking proof of the ethylidene structure we thought it worth while to see if chlorination of ethylene platinumous chloride produced any ethylidene dichloride. The reaction with one molecule of chlorine might result in chlorination of the olefin (1) or oxidation of the platinum (2):



The theoretical quantity of chlorine, according to these equations, added to a chloroform solution of the ethylene complex gives no precipitate of platinous chloride; thus (2) appears to represent the course of the reaction. No crystalline product was obtained.

When twice the above quantity of chlorine was added to a nitrobenzene solution of ethylene platinous chloride and the solution boiled, ethylene dichloride was the only product derived from the ethylene of the complex.

Acetylene Complexes.—It is well known that acetylene forms indefinite brown products with potassium chloroplatinite, probably by the replacement of the active hydrogen atoms. Information as to whether simple disubstituted acetylene platinous complexes exist appears to be lacking. Hel'man, Bakhovetz, and Meilakh (*Compt. rend. Acad. Sci., U.R.S.S.*, 1945, **46**, 105) report that the acetylenic compound $\text{CMe}_2(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{CMe}_2\cdot\text{OH}$ (A) forms a complex $\text{A}\cdot\text{py}\cdot\text{PtCl}_2$ analogous to *trans*- $\text{C}_2\text{H}_4\cdot\text{py}\cdot\text{PtCl}_2$ (py = pyridine); (A) is rather complex and contains two OH groups which might be involved in complex formation. We have, therefore, attempted to obtain complexes of the simple acetylenes $\text{CH}_3\cdot\text{C}\equiv\text{C}\cdot\text{CH}_3$ and $\text{Ph}\cdot\text{C}\equiv\text{C}\cdot\text{Ph}$.

When we attempted to replace ethylene from ethylene platinous chloride in benzene solution by each of these acetylenes separately (cf. Anderson, *J.*, 1936, 1042), a change in the colour of the solution occurred on addition of the acetylene followed by rapid reduction to platinum in each case. A colour change followed by rapid reduction to the metal also occurred when diphenylacetylene was treated with a suspension of platinic chloride in acetic acid (cf. Kharasch and Ashford, *J. Amer. Chem. Soc.*, 1936, **58**, 1733). When but-2-yne (dimethylacetylene) was treated with potassium chloroplatinite in 3% hydrochloric acid (cf. Chernyaev and Hel'man, *Chem. Abs.*, 1938, **32**, 445) no reaction occurred although the substances were kept together in a sealed glass bulb for 9 months. It is evident that platinous complexes of the simple disubstituted acetylenes cannot be isolated by the methods in use for the preparation of olefin complexes. However, the colour changes noted above suggest that some complex formation preceded the reduction when Anderson's and Kharasch and Ashford's methods were tried.

EXPERIMENTAL

(Microanalyses were made by Mr. W. Brown, of these laboratories.)

None of the published methods of preparation of platinous olefin complexes (see Keller, *Chem. Reviews*, 1941, **28**, 229) is reliable or can be easily adapted to the production of large quantities of the complexes. We have, however, developed from Chernyaev and Hel'man's method of preparing the Zeise type of salts an excellent method of obtaining ethylene and propylene platinous chloride in 80–90% yields.

Ethylene Platinous Chloride ($\text{C}_2\text{H}_4\text{PtCl}_2$)₂.— K_2PtCl_4 (15 g.) in 3–4% hydrochloric acid solution (75 c.c.) is shaken continuously for 10 days in an atmosphere of ethylene. The solution, which has now changed colour from reddish-brown to golden-orange, yields crystalline potassium ethylene trichloroplatinite monohydrate (7 g.) if it is filtered and cooled in ice-water. To obtain ethylene platinous chloride, however, it is taken to dryness in an evaporating basin in a desiccator over sulphuric acid and sodium hydroxide pellets. The residual mixture of yellow, white (KCl), and a few brown (K_2PtCl_4) crystals is extracted with alcohol (200 c.c.) containing concentrated hydrochloric acid (*d* 1.180; 6.2 c.c.), to dissolve the yellow trichloroplatinite. The orange solution is filtered and then taken to dryness under reduced pressure, the temperature being kept below 60°. Almost pure ethylene platinous chloride (10 g.) separates as a rose-coloured powder, decomp. about 165°. The crude product has the same infra-red spectrum as the very pure material described by Chatt and Hart (*Chem. and Ind.*, 1949, 146).

Propylene platinous chloride was prepared as above except that the absorption of propylene by potassium chloroplatinite in 3% hydrochloric acid required 3 weeks. When the mixture of yellow, white, and brown crystals was obtained, a few of the best of the yellow variety were picked out free from the others. These were potassium propylene trichloroplatinite monohydrate, $\text{K}[\text{C}_3\text{H}_6\text{PtCl}_3]\cdot\text{H}_2\text{O}$ (Found: C, 9.2; H, 2.0. Calc. for $\text{C}_3\text{H}_6\text{OCl}_3\text{PtK}$: C, 9.0; H, 2.0%). The residue, treated as above except that the final distillation of the alcohol was carried out at under 45°, yielded *propylene platinous chloride* as a deep rose powder (decomp.

without melting at about 97°). It was purified by solution in carbon tetrachloride and precipitated with ligroin (b. p. 40—60°), m. p. 98—99.5° (decomp.) (Found: C, 11.7; H, 2.1. $C_6H_{12}Cl_4Pt_2$ requires C, 11.7; H, 2.0%).

trans-p-Toluidine-ethylenedichloroplatinum was prepared as previously (Chatt, *J.*, 1949, 3340). *trans-p*-Chloroaniline-ethylenedichloroplatinum, similarly prepared, is less stable than its *p*-toluidine analogue. It was purified by dissolving the crude product (5 g.) in boiling chloroform (50 c.c.), filtering at once, then adding carbon tetrachloride (21 c.c.) and cooling to 0°, giving a recovery of 3.6 g. (58%). It decomposed at 135—142° depending on the rate of heating (Found: C, 22.9; H, 2.5; N, 3.5. $C_8H_{10}NCl_3Pt$ requires C, 22.8; H, 2.4; N, 3.3%).

Attempts to Prepare Acetylene Complexes.—(1) *Anderson's method* (loc. cit.). But-2-yne (dimethylacetylene) (0.451 g.) was added to a clear acetone (10 c.c.) solution of $(C_2H_4PtCl_2)_2$ (0.61 g., 0.125 mol.). The solution reddened and started to darken immediately. The acetone was rapidly removed under reduced pressure, leaving a black intractable residue, with an odour reminiscent of mesityl oxide. Diphenylacetylene behaved similarly, except that darkening occurred more slowly.

(2) *Kharasch and Ashford's method* (loc. cit.). Dimethylacetylene (0.433 g.) was added to platinum chloride (1.62 g., 0.6 mol.) in glacial acetic acid (18 c.c.) suspension. On shaking, a very little of the platinum chloride dissolved to give a yellow-orange solution. The mixture was gradually warmed. The platinum chloride became orange without dissolving, and at 35° rapid blackening occurred.

(3) *Chernyaev and Hel'man's method*. K_2PtCl_4 (2.63 g.) in 3% HCl solution (70 c.c.) was sealed in a large ampoule with dimethylacetylene (0.38 g., 1.1 mol.) and shaken for 3 weeks. No change in colour or other obvious sign of reaction occurred. After 9 months' storage, the ampoule was opened, and the solution tested for a Zeise type of salt, $K[(CH_3)_2C_2PtCl_3]$. (a) The solution (5 c.c.) was treated cautiously with ammonia solution until just alkaline; no rapid

TABLE I.

$K[C_2H_4PtCl_3] \cdot H_2O$	$K[C_2H_4PtCl_3] \cdot H_2O$	$K_2[C_4H_6(PtCl_3)_2]$	$(C_2H_4PtCl_2)_2$	$(C_3H_6PtCl_2)_2$
* 3460 v.s.	* 3460 v.s.	—	—	—
* 3195 w	* 3217 w	—	—	—
3094 v.w.	3068 m	{ 3078 m	3088 m	3071 w
3081 w	3034 w	{ 3070 shoulder	3072 w	3039 w
3045 v.w.	3010 m	3010 w	3010 w	3012 w
3013 w	{ 2971 shoulder	2993 v.w.	2979 v.w.	2995 shoulder
2985 w	{ 2965 m	2959 v.w.	2956 v.w.	2988 w
—	—	—	—	2967 v.w.
—	—	—	—	2954 w
—	2911 v.w.	—	—	2901 v.w.
* 1615 s	* 1621 s	—	—	—
—	1504 s	1473 s	1506 w	1504 s
—	1449 s	—	—	1447 s
1425 s	1429 s	—	1428 s	1431 s
—	1392 m	1324 m	1416 m	1395 s
1300 v.w.	1365 s	1236 s	1236 w	1361 s
1241 m	1252 w	1202 w	1217 w	1243 v.w.
1179 w	1175 m	—	1175 w	1171 v.w.
1022 s	1049 s	1036 s	1027 v.s.	1045 s
1010 s	1010 s	1007 s	—	1021 s
975 v.w.	990 s	967 s	971 v.w.	995 s
—	932 s	—	—	929 s
—	899 s	—	—	898 s
—	800 w	850 s	—	877 w
—	—	—	—	820 w
—	809 s	809 w	818 m	807 w
720 m	—	725 m	—	—
—	—	719 m	—	—

* These bands are due to water of crystallisation: v.s. = very strong; s = strong; m = medium strength; w = weak; v.w. = very weak.

precipitation of $NH_3 \cdot (CH_3)_2C_2PtCl_2$ took place (cf. $K[C_2H_4PtCl_3] + NH_3$), but only slow separation of platinous amines (cf. $K_2PtCl_4 + NH_3$). (b) The solution (10 c.c.) was slowly treated with $Pt(NH_3)_4Cl_2$ solution until precipitation was complete, leaving a colourless supernatant liquid. The green precipitate (0.53 g.) was analysed: this would contain the acetylene derivative as $Pt(NH_3)_4[(CH_3)_2C_2PtCl_3]_2$ if it had been formed (Found: C, 0.2; H, 2.1; N, 9.5. Calc. for $H_{12}N_4Cl_4Pt$: C, 0.0; H, 2.015; N, 9.3%). The precipitate was, therefore, entirely Magnus salt, $Pt(NH_3)_4PtCl_4$.

Infra-red Spectra.—The infra-red spectra between 3500 and 700 cm^{-1} were measured with a Grubb-Parsons S3A spectrometer. The finely powdered solids were suspended in "Nujol" and, for the regions of CH stretching and deformation frequencies, in hexachlorobutadiene. A lithium fluoride prism was used over the range 3500–2800 cm^{-1} , and a rock-salt prism for the rest of the spectrum. The frequencies of the observed absorption bands are listed in Table 1.

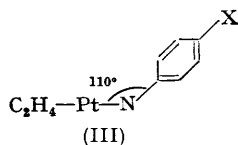
TABLE 2.*

$10^2\omega$	$10^2\Delta\epsilon$	$10^4\Delta n$	$-10^2\Delta v$	τP	ϵP	αP	μ
<i>trans</i> - $\text{C}_2\text{H}_4 \cdot p\text{-CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{PtCl}_2$							
1.021	2.09	—	—	—	—	—	—
1.509	3.08	—	—	—	—	—	—
2.704	5.42	—	1.91	—	—	—	—
2.607	—	18.7	—	—	—	—	—
4.118	—	30.4	—	—	—	—	—
4.445	—	32.7	—	204.6	76.7	112.6	2.35 ± 0.02
<i>trans</i> - $\text{C}_2\text{H}_4 \cdot p\text{-Cl} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{PtCl}_2$							
1.079	1.53	—	—	—	—	—	—
1.555	2.16	—	—	—	—	—	—
3.092	4.13	—	2.66	—	—	—	—
1.131	—	7.9	—	—	—	—	—
1.432	—	10.1	—	—	—	—	—
2.450	—	17.1	—	158.3	77.2	65.7	1.79 ± 0.03

* ω = weight fraction; $\Delta\epsilon$ = difference between the dielectric constant of the solution and that of pure benzene; Δn = difference in refractive indices; Δv = difference in specific volumes; τP = total, ϵP = electron, and αP = orientation polarisations; μ = dipole moment.

Dipole Moments.—These were determined exactly as described by Chatt and Hart (*J.*, 1953, 2363). The remarks regarding the uncertainty in the values due to unknown, but significantly large, atom polarisations apply with equal force to these compounds. The detailed results are given in Table 2. Moments were taken in benzene solution at 25°. The refractive indices are for $\lambda = 6562.8 \text{ \AA}$.

To evaluate $\mu_{\text{C-Pt}} - \mu_{\text{N-Pt}}$, the molecules are assumed to have the shape shown in (III).



X = CH_3 or Cl.

The two chlorine atoms (not shown) lie on opposite sides of the platinum atom on a line perpendicular to the plane of the paper. It is assumed that the only unbalanced moments in the molecule are $\mu_{(\text{C}_2\text{H}_4\text{-Pt})}$, $\mu_{(\text{N-Pt})}$, $\mu_{(\text{N-B})}$ and $\mu_{(\text{B-X})}$, (where B = benzene nucleus) and that $\mu_{(\text{B-X})}$ is changed by 1.95 D when Cl is replaced by CH_3 [i.e., the difference between $\mu_{(\text{B-Cl})}$ (1.55 D) and $\mu_{(\text{B-CH}_3)}$ (0.4 D) in opposite directions]. On the basis of these assumptions, we find $\mu_{(\text{C}_2\text{H}_4\text{-Pt})} - \mu_{(\text{N-Pt})} = 1.9 \text{ D}$ and $\mu_{(\text{N-B})} = 1.8 \text{ D}$ with N positive, or $\mu_{(\text{N-Pt})} - \mu_{(\text{C}_2\text{H}_4\text{-Pt})} = 1.9 \text{ D}$ and $\mu_{(\text{N-B})} = 0.5 \text{ D}$ with N positive.

Reaction of Sodium Chloroplatinite with Methylmagnesium Iodide in Presence of Methyl Iodide.—The dry, finely powdered sodium salt (5.2 g., 1 mol.) was gradually added to a well-stirred ether (25 c.c.)–benzene (50 c.c.) solution of methylmagnesium iodide containing an excess of methyl iodide (1.5 g. Mg, 4.5 mol.; 15 g. CH_3I , 7.75 mol.). The mixture was heated for 1 hr. at 30° and then hydrolysed with ice-water. Crude trimethylplatinitic iodide (1.0 g.) was isolated from the benzene layer. Recrystallised from benzene and then from chloroform, the product was obtained as orange-yellow crystals, decomp. 195–200°. It was identified as the dipyrindine derivative, m. p. 169–170°; Lile and Menzies (*J.*, 1949, 1168) give 168° (Found: C, 29.9; H, 3.5; Pt, 36.7. Calc. for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{IPt}$: C, 29.7; H, 3.6; Pt, 37.1%). The equivalent of 2.5 g. of Na_2PtCl_4 was isolated as $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$ from the aqueous solution. The poor yield of trimethylplatinitic iodide and large recovery of platinitic is attributed to the very poor solubility of the sodium salt in the ether–benzene mixture.

Chlorination of Ethylene Platinous Chloride, $(\text{C}_2\text{H}_4\text{PtCl}_2)_2$.—This chloride (1.2 g., 1 mol.) was dissolved in a minimum of chloroform, and chlorine (2.04 mols.) in carbon tetrachloride (5.7 c.c.) run in with swirling. There was immediate rise in temperature (7°) and the solution became bright reddish-orange. The solvent was now removed at 15–20 mm. pressure. There remained a fairly fluid orange oil, which could not be induced to crystallise. It was very soluble in ethanol and acetone but insoluble in ligroin, benzene, and carbon tetrachloride. It dissolved in aqueous potassium chloride, giving an odour of aldehyde resin. On slight warming, the oil darkened rapidly. On addition of ethylenediamine (2 mols.) to the chloroform solution of the orange product, there was an immediate curdy precipitate which became sticky during

filtration. It was dried at 0.1 mm. pressure, ground, redried, and analysed (Found : C, 13.6; H, 3.7%). An attempt to obtain a crystalline derivative of the orange oil by adding 2 : 2'-dipyridyl (2 mols.) instead of ethylenediamine gave an insoluble oil, stable at 0° but decomposing at room temperature to deposit dipyridyldichloroplatinum.

Chlorine (4.0 mols.) in nitrobenzene (33.5 c.c.) was gradually added to a suspension of ethylene platinous chloride (4.5 g., 1 mol.) in the same solvent (170 c.c.). When half the chlorine had been added the solution was shaken until all the suspension had dissolved to an orange solution and the smell of chlorine was no longer apparent. The remainder of the chlorine solution was now run in, giving a solution smelling strongly of chlorine. Absorption of the second molecule of chlorine was very sluggish. After $\frac{1}{2}$ hr.' standing, the smell of chlorine was still apparent and hydrogen chloride was being slowly evolved. The solution was then distilled up a short fractionating column. Much hydrogen chloride was evolved and the solution blackened. The first few c.c. of distillate were collected, washed with sodium hydrogen carbonate solution, and fractionated, yielding *ca.* 0.5 c.c. of ethylene dichloride, b. p. 82–84°, characterised by conversion into ethylenebis(phenyl sulphide), m. p. 69–70°, alone and mixed with an authentic specimen.

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