698. *Olefin Co-ordination Compounds. Part I. Discussion of Proposed Structures. The System Ethylene–Trimethylborine.*

By J. CHATT.

It is shown conclusively that in the platinous–olefinic complexes the olefin is not joined to two metal atoms and that metal–metal links are not an essential feature of their structure, so that some proposed structures may be rejected.

Ethylene–platinous chloride is diamagnetic and shows no evidence of metal alkyl character. An accurate thermal analysis of the system ethylene–trimethylborine shows a lattice compound $3C_2H_4,2BMe_3$, but no compound C_2H_4,BMe_3. In the liquid phase there is no association of ethylene with trimethylborine. The various structures which have been proposed for $(C_2H_4,PtCl_2)_2$ are discussed in the light of this result. It is considered that no direct donation of electrons from the olefin to the metal can be solely responsible for the co-ordination but that there is some additional requisite such as the formation of bonds involving *d* orbitals. This contention is further supported by analogy with the carbonyl halides.

The molar heats of fusion of ethylene and trimethylborine have been estimated as 994 and 808 cals., respectively.

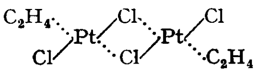
It is established that olefins can behave as ligands in complex-salt formation although the few known stable co-ordination compounds are limited almost entirely to the platinous series. Typical examples are $K[C_2H_4,PtCl_3],H_2O$ (Zeise, *Mag. Pharm.*, 1830, **35**, 105) and $(C_2H_4,PtCl_2)_2$ (Anderson, *J.*, 1934, 972). Zeise's salt is one of the most stable ethylene co-ordination compounds yet isolated and the non-ionic complexes of type $[NH_3,C_2H_4,PtCl_2]$ are sufficiently stable to show geometric isomerism (Chernyaev and Hel'man, *Compt. rend. Acad. Sci. U.R.S.S.* (*N.S.*), 1936, **4**, 181; *Ann. Secteur Platine Inst. Chim. Gen., U.S.S.R.*, 1938, **15**, 5). Solid olefinic complexes of palladous, cuprous, and silver salts have been described, although those of silver are more often obtainable only in aqueous solution. Less well-defined complexes with other metallic salts have been recorded. The subject is well reviewed by Keller (*Chem. Reviews*, 1941, **28**, 229) and the more recent work has been described by Chatt (*Ann. Reports*, **1946**, **43**, 120); detailed evidence is there given that these complexes behave as co-ordination compounds in which one olefin molecule occupies only one place in the co-ordination sphere of the metal.

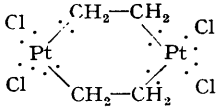
From the unstable character of olefin complexes it follows that most investigations of their chemical reactions have been carried out with the platinous complexes, and our scanty information on olefin co-ordination compounds is largely based on this one series of complex salts, the properties of which have recently been reviewed by Hel'man [" Complex Compounds of Platinum with Unsaturated Molecules," *Soviet Acad. Sci.*, 1945 (in Russian)].

Since the advent of the electronic theory of valency these substances have held great theoretical interest because they, together perhaps with the corresponding, though as yet poorly defined, complexes of the acetylenes, represent the only definite exceptions to the lone-pair theory of co-ordination. Anderson (*J.*, 1936, 1047) even suggested that their existence formed a crucial test of the theory. Clearly the theory requires some extension or modification to accommodate these substances, and the experiments recorded below are a contribution towards this end.

Numerous electronic structures have been proposed to explain the existence of olefin co-ordination complexes (Keller, *loc. cit.*), but experimental evidence to carry us far beyond Pfeiffer's formulation (I) (" Organische Molekülverbindungen," Verlag von Ferdinand Enke, Stuttgart, 1927, p. 209) is lacking; even the orientation of the ethylene molecule with respect to the metal atom is unknown.

(I.)





(II.)

First it must be established whether only one metal atom is attached to one olefin molecule, because Kharasch and Ashford (*J. Amer. Chem. Soc.*, 1936, **58**, 1735) proposed a structure (II) for ethylene–platinous chloride in which the olefin molecule acts as the bridge between the metal atoms, and so far all molecular-weight determinations have been made in order to establish that ethylene–platinous chloride and its homologues are dimeric (Anderson, *J.*, 1934, 972; Kharasch and Ashford, *loc. cit.*, p. 1737). I also have found the dimeric form to be supported by molecular-weight determinations for ethylene–platinous chloride in boiling benzene, although a moderate amount of decomposition occurred during the experiments.

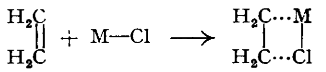
Simple non-ionic complexes $[(C_2H_4)_2,PtCl_2]$ are unknown, and previously described mixed non-ionic complexes of the type $[C_2H_4a,PtCl_2]$ ($a = NH_3$, pyridine, or quinoline) (Hel'man, *Sci. Reports Leningrad State Univ.*, 1936, **2**, No. 2, 5; *Chem. Abstr.*, 1938, **32**, 2505) are too insoluble for molecular-weight determination. However, Bokiĭ and co-workers (*Bull. Acad. sci., U.R.S.S., Classe sci. chim.*, 1942, 413), by *X*-ray structure analysis, concluded that *cis*-$[C_2H_4,NH_3,PtCl_2]$ was dimeric with a Pt–Pt bond length of 1·4 A. A stable complex of this type soluble in organic solvents has now been found in the p-*toluidine* complex $[C_6H_4Me{\cdot}NH_2,C_2H_4,PtCl_2]$, which is suitable for accurate determination of molecular weight. It is prepared by the action *p*-toluidine on an aqueous solution of $Na[C_2H_4,PtCl_3]$ and therefore probably has a *trans*-configuration (by analogy with Hel'man's work on the corresponding ammines and pyridine complexes).

The molecular weight, measured ebullioscopically and cryoscopically in benzene, showed definitely that this substance is monomeric although the ebullioscopic determination was slightly marred by the decomposition of the complex. In boiling acetone the decomposition was negligible during the time of the determination, and here too the substance was monomeric. We thus reject the structure proposed by Kharasch and Ashford, as well as Bokiĭ's contention that this type of complex necessarily contains Pt–Pt bonds (Bokiĭ *et al.*, *Doklady Akad. Nauk. S.S.S.R.*, 1943, **38**, 323; *Compt. rend. Acad. Sci. U.R.S.S.*, 1943, **38**, 307).

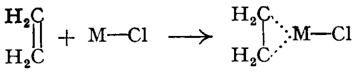
We have thus to consider only the ways in which one ethylene molecule can be linked to one metal atom, and on the grounds of the symmetry of the ethylene molecule there appear to be only four possible arrangements :

(*a*) " End-on " association, $CH_2{:}CH_2 + M{-}Cl \longrightarrow CH_2{:}CH_2{\cdots}M{-}Cl$;

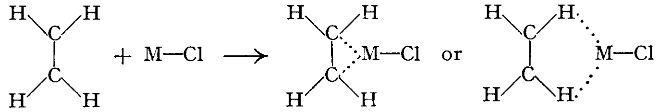
(*b*) " End-on " association in which the second carbon atom associates with the halogen atom :



(*c*) " Side-on " association in which the metal atom lies in the plane of, or originally occupied by, the π electrons :



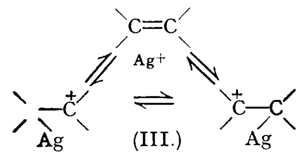
(*d*) " Side-on " association in which the metal atom lies in the plane of the carbon and hydrogen atoms :



If the ethylene is part of a planar complex and if " side-on " association occurs, then on the grounds of symmetry the carbon atoms would be expected to lie in the plane or perpendicular to it, but neither of these positions is necessarily occupied by the ethylene molecule.

Electronic structures for " (*a*) " have been proposed by Bennett and Willis (*J.*, 1929, 259) and Stiegman (Keller, *loc. cit.*, p. 253). These have the disadvantage of leaving the β-carbon atom in a reactive state as a carbonium ion and carbanion, respectively. Structures for " (*b*) " proposed by Sidgwick (footnote, Hunter and Yohe, *J. Amer. Chem. Soc.*, 1933, **55**, 1251), and Drew, Pinkard, Wardlaw, and Cox (*J.*, 1932, 997), would confer on these compounds the properties of a mixed 2-chloroethyl metallic alkyl. However, an attempt to obtain 2-benzoylethyl chloride by heating ethylene–platinous chloride with excess of benzoyl chloride on a steam-bath for two hours led only to slight blackening, and 85% of the complex salt was recovered unchanged (to be compared with an 82% recovery from benzene solution after similar treatment). This behaviour is very strong evidence against a metal alkyl type of structure, although the conclusion must be accepted with reserve because we know nothing of platinous alkyls (however, they are probably unstable as they have never been prepared).

Another serious objection to an alkyl type of structure is the ready replacement of one olefin by another, which is a reaction characteristic of co-ordination compounds but not of substituted alkyls (Anderson, *J.*, 1936, 1044).


(III.)

" (*c*) " is the most favoured orientation at present and various structures have been proposed. Winstein and Lucas (*J. Amer. Chem. Soc.*, 1938, **60**, 841) suggest a resonance of type (III) for the silver ion complex. Pitzer (*J. Amer. Chem. Soc.*, 1945, **67**, 1127) has applied his idea of a " protonated double bond " to olefin complexes such as the silver ion complexes in which the silver ions, or any other atoms with vacant *s* orbitals, are embedded in the antinodes of the π bond.

Walsh (*J.*, 1947, 89) suggested that bonding electrons may be donated in a similar manner to a lone pair provided that their ionisation potential is sufficiently low and pointed out that the π electrons of ethylene lie in an orbital of ionisation potential 10·45 v., almost equal to that (10·8 v.) of the ammonia lone pair. He predicted that compounds such as C_2H_4,BF_3 should be expected (*Nature*, 1947, **159**, 165, 712). Hel'man (*Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 549) proposed a unique structure, the idea of which may deserve more credence than it has received (Keller, *loc. cit.*, p. 255). She suggests that a four-electron bond is formed by donation of the electrons at whose expense platinum shows its quadrivalency, to the olefin, followed by donation of the electrons now released from the double bond to the platinum—a structure recalling the double-bonded metal–carbon monoxide links suggested for the metal carbonyls (Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, 1948, p. 250 *et seq.*; but see Wells, this vol., p. 55). Hel'man is not explicit how the binding occurs and suggests some sort of resonance.

No electronic structure corresponding to the orientation " (*d*) " has been suggested unless Hel'man's is of this type (*loc. cit.*, p. 550).

It seems improbable that ethylene–platinous chloride contains unpaired electrons, and this view was confirmed by magnetic measurements. By the Gouy method a susceptibility of $\chi = -0{\cdot}31 \times 10^{-6}$ per g. has been found for the solid complex.

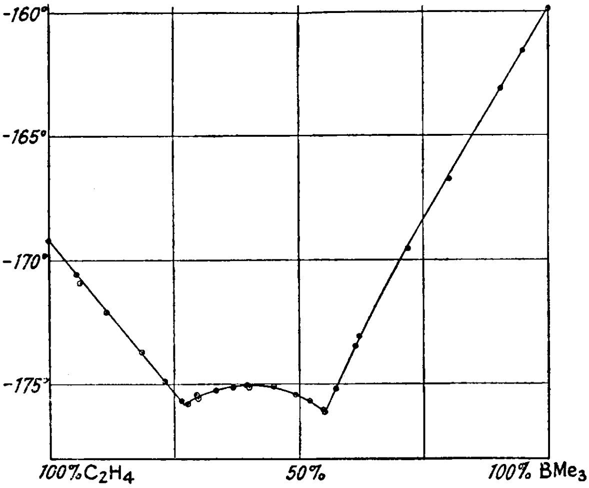
The only experimental evidence regarding the orientation of the olefin molecule is provided by Anderson (*J*, 1934, 973), who showed that Zeise's salt was decomposed in boiling aqueous solution to produce acetaldehyde, which he considered evidence for an unsymmetrical linkage. Neither ethylene glycol nor 2-chloroethyl alcohol which might be expected from a symmetrical linkage was detected. Kharasch and Ashford (*loc. cit.*, p. 1737) obtained stilbene dibromide by bromination of stilbene–platinous chloride with an excess of bromine, but as this complex probably dissociated in solution the result is of doubtful significance.

Against this background of scant information it was decided to try to obtain olefin compounds of the lighter elements, which, if solid, might be suitable for *X*-ray structure analysis or, if readily dissociable, for precise thermodynamic measurements.

Of all elements, the lighter elements of Group III in their tercovalent state form co-ordination complexes with the greatest variety of ligands. The complexes with the fluoride and the alkyls of boron are usually formed almost instantaneously from their components at suitably low temperatures and may dissociate easily at and above room temperature according to the ligand; nevertheless such substances as ethers and tertiary amines which do not usually form stable complexes with metallic salts do form complexes with such substances as trimethylborine and boron trifluoride.

FIG. 1.

Freezing-point curve: ethylene–trimethylborine.



They also have the advantage of being amenable to study in the gaseous or the liquid phase. Ethylene is known to react destructively with boron trifluoride in sunlight (Landolph, *Ber.*, 1879, **12**, 1586) and with diborane, B_2H_6 (Hurd, *J. Amer. Chem. Soc.*, 1948, **70**, 2053) at 100° to produce triethylborine. The system ethylene–trimethylborine has therefore been investigated by thermal analysis. The freezing-point curve (Fig. 1) shows definitely that there is no one-to-one association between these two substances at temperatures down to the freezing point of the mixed gases. When the log of the mol. fraction (N) of each substance is plotted against the reciprocal of the absolute temperature of freezing, the plots (Fig. 2) are, within 0·1°, straight lines from the eutectic points to the melting points of the pure substances. The compound $3C_2H_4,2BMe_3$ can only be a lattice compound. If it were not, and any type of chemical association occurred, the log N–$1/T$ plots would deviate markedly from linearity. Also the freezing-point curve at the point $3C_2H_4,2BMe_3$ is horizontal, and no discontinuity occurs (Kendal, Davidson, and Adler, *ibid.*, 1921, **43**, 1485).

I am indebted to Mrs. Moore of these laboratories for a statistical examination of the log N and $1/T$ values; she reported that the curvature is just significant and the best straight lines are: (*a*) for the solution of ethylene in trimethylborine, $\log N_B = 1{\cdot}560 - 176{\cdot}5/T$; and (*b*) for the solution of trimethylborine in ethylene, $\log N_E = 2{\cdot}09 - 217/T$; where N_B is the mol. fraction of trimethylborine, and N_E is that of ethylene.

The constants in these equations give values of 808 cals. for the molar heat of fusion of trimethylborine and 994 cals. for that of ethylene. Except for evidence based on the constancy of the melting point of ethylene, which serves as an indication that the latent heat of fusion of ethylene is larger than for liquids used in low-temperature work (Malisoff and Egloff, *J. Physical Chem.*, 1919, **23**, 69), neither of these appears to have been measured directly or estimated previously, but because these substances obey the ideal-solution law so closely these values are probably very near to the true values.

The significance of this result lies in the demonstration that no association—not even weak interaction—occurs between the π electrons of ethylene and the vacant orbital in trimethylborine. Also if co-ordination occurred by any donation of electrons in " end-on " association [" (*a*) "], then there is every reason to suppose that it would have occurred in this system because the ionisation potential (10·45 v.) of the π electrons is sufficiently low and steric hindrance would be negligible. Its complete absence is positive evidence that such association cannot lead to stable complex formation.

The possibility of the " (*b*) " type of association does not arise, but " (*c*) " merits a close examination in the light of the above result. It may be considered that if " side-on " association occurred the boron atom would become quinquecovalent; this is not so; only two electrons would be involved in the ethylene–boron link, the octet rule would be obeyed, and the covalency maximum for boron would not be exceeded.

It may also be considered that the ethylene is hindered sterically from approaching sufficiently close in " side-on " association to the boron atom; this, however, does not seem probable. If we allow a radius of 1·08 A. for the methyl group and 0·88 A. for the tetrahedrally co-ordinated boron atom, the radius ratio 0·815 is sufficiently great to allow even 9-fold co-ordination and is almost twice the minimum ratio 0·414 for octahedral co-ordination. Further, if we maintain without strain a tetrahedral distribution of three of the valencies from the boron atom and bring in a flat ethylene molecule in the best possible orientation so that the carbon atoms are at a distance of 0·88 A. from the boron atom, then the van der Waals radii of only one of the hydrogen atoms attached to a methyl group and two attached to the ethylene molecule just overlap. If combination occurred we would expect the carbon atoms of the ethylene molecule to approach as near as possible to a tetrahedral configuration, which would cause the hydrogen atoms to move out of the plane of the original ethylene molecule away from the trimethylborine molecule. Thus there is no doubt about the ability of the trimethylborine molecule to accommodate an ethylene molecule within combining distance of the boron atom. This contention is further supported by the fact that such highly hindered molecules as tri-α-naphthylborine and tri-*tert.*-butylborine form complexes with simple aliphatic amines (Brown and Sujishi, *J. Amer. Chem. Soc.*, 1948, **70**, 2793; Brown, *ibid.*, 1945, **67**, 1454).

It seems highly probable, therefore, that donation of electrons in any manner from the ethylene molecule to the metal cannot, of itself, be responsible for the co-ordination of ethylene. There is some other mechanism or additional condition, which can be satisfied by platinous chloride and not by trimethylborine.

The structures proposed by Winstein and Lucas, and by Walsh, are essentially electron-pair bonds and in the light of the above result appear highly improbable. Pitzer's does not enter into the argument as neither the platinum nor the boron atoms have vacant unhybridised *s* orbitals in their valency shells; it may apply to the silver ion complexes.

The fact that platinum can form ethylene compounds, whereas boron cannot, indicates that there is probably some truth in Hel'man's suggestion that filled *d* orbitals take part in valency formation. It is significant that with the possible exception of aluminium all those metals which are known to form complex salts with ethylene are towards the end of the transition series of elements, thus having filled *d* orbitals at almost the same energy level as the orbitals of the valency shell. Regarding aluminium, Gangloff and Henderson (*J. Amer. Chem. Soc.*, 1916, **38**, 1382; 1917, **39**, 1420) produced a number of crystalline substances, *e.g.*, $AlCl_3,3C_2H_4,H_2O$ and $AlCl_3,C_2H_4,2C_2H_5{\cdot}OH$. These were difficult to prepare and analyse, they dissociated and decomposed readily, and there is no evidence that they were in fact co-ordination compounds.

Hel'man is not very explicit regarding her structure beyond saying: " In all we have a four-electron covalent bond." She considers, however, that only the two electrons involved in raising the valency of the platinum from two to four can be used, so that the addition of one molecule of the olefin to one platinum atom is the absolute theoretical limit. She also considers the platinum in these compounds to be platinic and shows that the oxidation–reduction potential of $K[Pt,C_2H_4,Cl_3]$ is 650 mv., compared with 520 for $NH_4[Pt,NH_3,Cl_3]$ and 660 for $NH_4[Pt,NH_3,Cl_5]$ (Hel'man and Ryabchikov, *Compt. rend. Acad. Sci. U.R.S.S.*, 1941, **33**, 462).

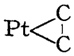
She points out the analogy between ethylene and carbon monoxide in its complexes and explains the greater stability of carbonyl–platinum halides by correlating it with the fact that the carbon atom is already an acceptor of electrons from the oxygen atom $C \overset{\leftarrow}{\equiv} O$ and thus may become a more ready acceptor from the platinum atom than is ethylene.

The correspondence between the properties of ethylene–platinous chloride and the carbonyls has been emphasised a number of times (Anderson, *J.*, 1934, 972; Hel'man, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 549), and the present work has further emphasised the resemblance.

Carbon monoxide can co-ordinate by donation of electrons according to classical theory and must do so in its combination with boron so as not to exceed the covalency maximum for boron. CO,BMe_3 is unknown, but CO,BH_3 is an unstable gas dissociating rapidly at room temperature (Bury and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780) and the B–C bond length corresponds to a single bond (Bauer, *Chem. Reviews*, 1942, **31**, 57). On the other hand, platinous carbonyl halides are formed at 240—250°, and $CO,PtCl_2$ is stable to $>300°$. This difference in stability contrasts strongly with the well-known high stability of the ammines in both the boron and the platinum series of complexes, where again only a two-electron bond can be involved so as not to exceed the covalency maximum for nitrogen. We must thus conclude that, as in the case of ethylene, there is some essential and very great difference between complex formation between carbon monoxide and platinous chloride on the one hand and carbon monoxide and boron compounds on the other.

It is becoming evident that the simple co-ordinate link of classical electronic-valency theory is not adequate to explain these differences in stability and many others equally striking, so that a large measure of support is accumulating for the idea that, except when precluded by the rule of covalency maximum, the co-ordinate link has considerable double-bond character probably arising from interaction with *d* orbitals of the central atom (Phillips, Hunter, and Sutton, *J.*, 1945, 146; Pauling, " Contribution à l'Etude de la Structure Moléculaire," Desoer, Liège, 1948, p. 1).

It must be admitted that Hel'man's structure is difficult to visualise in terms of modern theory, as π bonding from the two carbon atoms of an olefin to *d* orbitals of the metal appears impossible except by a structure closely related to that suggested by Walsh for *cyclo*propane and ethylene oxide (*loc. cit.*; *Trans. Faraday Soc.*, 1949, **45**, 179), and serious objections have been brought against this structure (Coulson, *Phil. Mag.*, 1949, **40**, 29), whereas π bonding to a single atom as in the carbonyls is feasible (Hieber, *Die Chemie*, 1942, **55**, 25).

Alternatively, one carbon atom may be linked by a strong $Pt(dsp^2)–C(sp^3)$ bond and the second by a weaker $Pt(d)–C(sp^3)$ bond. In this connection it is interesting that the bond lengths Pt–C = 2·08 and C–C = 1·54 would lead to an angle of 43° at the platinum atom in a  triangle; this is very close to the angle 45° one would expect between a dsp^2 hybridised orbital and a *d* orbital. This structure also satisfies Anderson's contention that the ethylene is unsymmetrically bound.

Neither of these speculative suggestions, however, imposes an absolute theoretical limit of one olefin molecule to one platinum atom, and also, although the platinum atom is using four of its valency electrons in bond formation, these are not in d^2sp^3 octahedral orbitals. Thus it would be wrong to label the platinum " platinic " as suggested by Hel'man, for the olefin is still essentially bound by dsp^2 square orbitals as demonstrated by the geometric isomerism exhibited by $[C_2H_4,NH_3,PtCl_2]$. The greatly increased resistance to oxidation of the platinum atom in olefin–platinous complexes as compared with the ammines is perhaps a manifestation of interference with the *d* orbitals, although not of actual conversion into the platinic state.

In the light of present knowledge it appears probable that electrons from 5*d* orbitals in the platinum atom take part in complex formation with olefins, and these complexes may turn out to be the apparent exceptions to the lone-pair theory which will prove the rule with respect to co-ordination to the transition-metal ions. Work is continuing to find the magnitude of the electron drift to the metal atom in olefin and carbonyl complex formation and to determine the orientation of the olefin with respect to the plane of the platinous complex.

EXPERIMENTAL.

* indicates microanalyses by Drs. Weiler and Strauss, Oxford, † those by Dr. Weiser, Basle.

Ethylene–platinous chloride, $(C_2H_4,PtCl_2)_2$, prepared by the method of Anderson (*J.*, 1934, 973) and recrystallised from toluene, was used as raw material, decomp. 190—200° [Found : Pt,* 66·7%; *M*, (ebullioscopically in 1·588% benzene solution) 520, (in 2·390% solution) 573. Calc. for $C_4H_8Cl_4Pt_2$: Pt, 66·4%; *M*, 588]. Anderson records 125—130°, Kharasch and Ashford (*loc. cit.*, p. 1738) 170—180°. The lower values may be due to the use of older and therefore probably less pure platinum (Chatt and Hart, *Chem. and Ind.*, 1949, 146). Some decomposition occurred during the molecular-weight determinations, as indicated by darkening of the solution and a brown deposit, but unchanged material separated as orange crystals as the benzene solution cooled.

p-*Toluidine–ethylene–dichloroplatinum.*—Ethylene–platinous chloride (7·0 g.) was dissolved at room temperature in 45 c.c. of water containing 1·4 g. of sodium chloride. A slight insoluble suspension was filtered off, and to the clear filtrate, cooled in ice-water, an ice-cold solution of resublimed *p*-toluidine (2·6 g.) in 50 c.c. of water and a minimum quantity of hydrochloric acid was added, slowly with shaking. A yellow precipitate formed immediately but the supernatant liquid was yellow. The cold suspension was neutralised by cautious addition of 3% sodium hydroxide solution, and the supernatant liquid became colourless. The bright yellow precipitate was recrystallised from carbon tetrachloride, an operation which must be carried out quickly as a complex decomposition occurs in the boiling solvent.

The *product* was obtained in beautiful lemon-yellow crystals, decomp. 125° to 135° (with effervescence) depending on the rate of heating [Found : C*, 27·0; H*, 3·35; Pt†, 48·4; Cl†, 18·1%; *M* (ebullioscopically in 2·387% benzene solution) 466, (in 4·441% solution) 489, (some decomposition occurred), (in 3·095% acetone solution) 394, (in 4·094% solution) 406, (in 2·012% solution) 401, (in 2·720% solution) 400, (cryoscopically in 0·4783% benzene solution) 357, (in 0·8635% solution) 377, (in 0·8428% solution) 409. $C_9H_{13}NCl_2Pt$ requires C, 26·9; H, 3·3; Pt, 48·6; Cl, 17·7%; *M*, 401]. This substance is probably the most readily soluble in organic solvents of all known ethylene complexes. It is very soluble in methanol, acetone, ether, benzene, and chloroform, moderately soluble in carbon tetrachloride, slightly soluble in *cyclo*hexane, insoluble in light petroleum (b. p. 60—80°) and in water.

Fig. 2.

Log N–1/T *plots for trimethylborine and ethylene as solvents.*

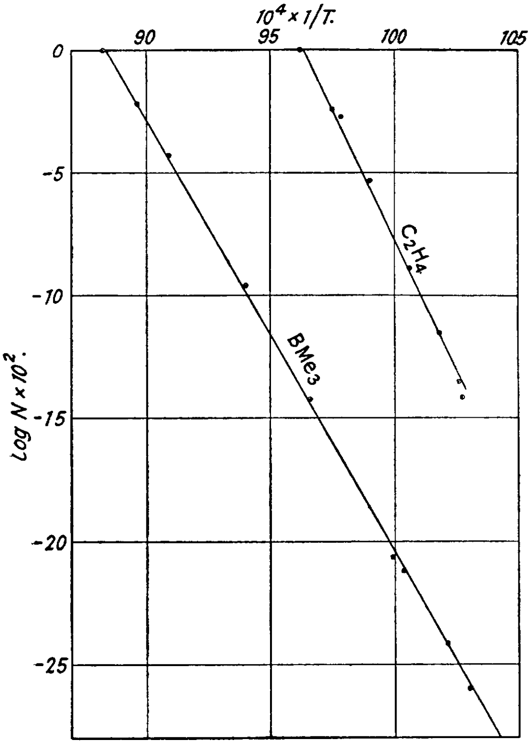
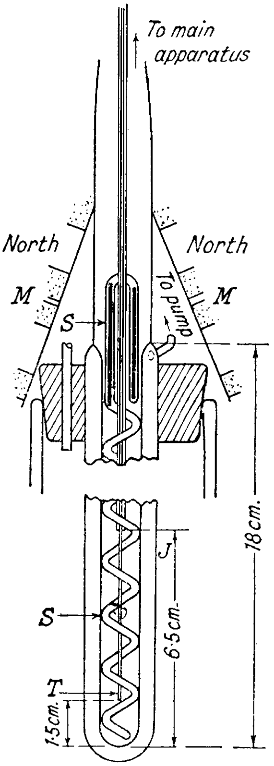


Fig. 3.

Freezing-point cell.



Attempt to cause Ethylene-platinous Chloride to react with Benzoyl Chloride.—Ethylene-platinous chloride (1 g.) was dissolved in warm benzoyl chloride (26 c.c.) and kept on a steam-bath for 2 hours. Some blackening took place, but 0·75 g. of unchanged ethylene complex, decomp. 170—180°, separated on cooling. A further 0·1 g. was obtained by evaporation of the mother-liquor at 15 mm., giving 85% total recovery. A solution of the same strength in dry benzene similarly treated showed more evidence of decomposition and gave an 82% recovery of material, decomp. 185—195°.

Freezing-point Measurements, Ethylene–Trimethylborine.

Apparatus.—This was essentially that described by Germann and Booth (*J. Physical Chem.*, 1926, **30**, 371) except that the manometer was of the conventional type (Farkas and Melville, " Experimental Methods in Gas Reactions," Macmillan, 1939, p. 72, Fig. 40) with limbs of 11-mm. bore and the freezing-point cell was modified slightly. The pressures were measured with a cathetometer, to an accuracy of at least 1 : 500 and generally better. The freezing-point cell Fig. 3 contained a spiral glass stirrer *S* automatically operated by two electro-magnets *M*. A solenoid sufficiently powerful to work the stirrer generated too much heat and caused leaks into the apparatus by melting the grease in the top cone. The outer vacuum jacket *J* was connected directly to the pumping system, independently of the main part of the apparatus. The copper–constantan thermocouple *T* was in direct contact with the liquid and was calibrated accurately by comparison with oxygen and methane vapour-pressure thermometers in baths of liquid nitrogen, oxygen, and methane. The calibration was repeatable to within the accuracy of the potentiometer (0·05°), a Tinsley three-dial precision potentiometer reading in steps of one μv.

The volumes of gases used to prepare the mixtures were measured in two bulbs of accurately-known volumes (1083 and 1074 c.c. at 0°), and surrounded by ice. These bulbs were not reserved one for ethylene and the other for trimethylborine, but were generally filled together to the same pressure and their contents admitted to the freezing-point cell separately.

Experimental Procedure.—Preliminary experiments with the pure gases showed that immersion of the thermocouple junction to a depth of 1 cm. sufficed to give accurate values of the freezing point provided that efficient stirring was maintained, although the reading drifted rapidly when the stirring was stopped, and in the following experiments an immersion of at least 1·5 cm. was used. The whole apparatus was sufficiently stable to repeat, during 3 months, the melting point of a pure substance within ±0·05° of the mean value, and the probable absolute accuracy is ±0·1°.

The freezing was observed between crossed polaroids, and liquid nitrogen used as refrigerant. The rate of heating and cooling was conveniently regulated by adjusting the air pressure in *J*. Only very slight pressure was necessary to maintain an almost steady temperature, and a rate of rise in temperature of 0·1° in 15 minutes was easily obtained.

To plot the freezing-point curve a known quantity of one gas was condensed in the freezing-point cell, followed by a measured quantity of the second gas to cover the thermocouple junction by about 1·5 cm. and produce a mixture of the appropriate approximate composition. After measurement of the freezing point of this mixture a further quantity of one of the gases was added and the determination repeated. This was repeated usually twice or three times more, and then a new primary mixture made up to obtain further points.

The m. p. was determined by cooling the mixture, with good stirring throughout, until solid appeared in the supercooled liquid, and then opening the jacket *J* to the pumps for a short time, the duration of which was easily guessed with practice. A slow rise in temperature, about 0·05° in 5 minutes, was thus obtained and the temperature at which the fine suspended solid disappeared leaving a few flakes of larger crystals was taken as the m. p. This was found to be the best procedure by observations with the pure substances, and with the mixture was repeatable within ±0·05° and was certainly within 0·1° of the true m. p., so that an absolute accuracy of ±0·15° was probably attained. The freezing-point curve Fig. 1 indicates a much higher relative accuracy. The usual trouble of solid collecting on the walls of the cell above the level of the liquid was experienced with this apparatus, particularly in the region N_B = 0·50—0·65, but could usually be eliminated by adjusting the level of liquid-nitrogen refrigerant.

Ethylene.—Cylinder ethylene (about 25 l.) was purified by distillation between bulbs through a U trap cooled in solid acetone (−95°) and retention only of middle fractions. In this way material of m. p. —169·3° was obtained. Finally the ethylene was distilled from a bulb cooled in liquid methane, through a trap cooled in liquid methane (−161°), into a bulb cooled in liquid nitrogen. A small middle fraction was collected. The gas (13 l.) thus obtained had m. p. −169·2° and was used. Recorded values in the literature vary widely, but generally lie between −169·0° and −169·5°. The accepted value is −169·15° [" Selected Values of Properties of Hydrocarbons," Internat. Bureau Standards, Circular C461, p. 46, (1947)].

C_2H_4, c.c.	BMe_3, c.c.	$N_B \times 10^2$.	Temp. (T) (° K.).	log $N_E \times 10^2$.	$1/T \times 10^4$.
1889	0	0	103·95°	0	96·2
1889	110·0	5·52	102·55	− 2·47	97·5
1617	106·4	6·17	102·2	− 2·77	97·85
1617	211·9	11·59	101·0	− 5·35	99·0
1196	272·7	18·57	99·4	− 8·92	100·6
1196	363·2	23·29	98·25	−11·51	101·8
1196	436·3	26·72	97·45	−13·50	102·6
1323	508·7	27·78	97·35	−14·13	102·7
1296	545·5	29·62	97·7	—	102·35
1196	508·7	29·84	97·6	—	102·5
1296	652·6	33·49	97·9	—	102·15
1296	758·7	36·93	98·0	—	102·0
822·2	545·5	39·88	98·05	—	102·0
611·5	406·6	39·93	98·1	—	101·9
611·5	500·1	44·99	98·05	—	102·0
611·5	592·9	49·21	97·7	—	102·35
605·6	664·4	52·32	97·45	log N_B	102·7
718·5	873·1	54·85	97·1	$\times 10^2$	103·0
611·5	747·5	55·00	97·1	−25·96	103·0
605·6	816·1	57·40	97·95	−24·11	102·1
605·6	966·6	61·48	99·65	−21·13	100·35
529·8	873·1	62·23	100·05	−20·60	99·95
339·5	873·1	72·00	103·6	−14·27	96·52
216·3	873·1	80·14	106·4	− 9·61	93·99
92·1	873·1	90·46	110·05	− 4·35	90·87
46·25	873·1	94·97	111·6	− 2·24	89·61
0	873·1	100·00	113·3	0	88·26

Eutectic, 27·1% BMe_3 at −175·8°; eutectic, 54·9% BMe_3 at −176·05°; maximum, 40·0% BMe_3 at −175·05°.

Trimethylborine.—This was prepared by the action of methylmagnesium bromide on boron fluoride in *n*-butyl ether and purified through its triethylamine complex (Brown, *J. Amer. Chem. Soc.*, 1945, **67**, 375). It was then fractionated with a modified Podbielniak still with a 90-cm. fractionating column and liquid ammonia in the still-head. It distilled at about 55 cm. of Hg pressure, and small first and last fractions were rejected. After 2 fractionations the mixed first runnings and tailings had the same m. p. as a narrow middle fraction. The m. p. was now −159·9°. Stock and Zeidler (*Ber.*, 1921, **54**, *B*, 531) record −161·5°, and Bamford, Levi, and Newitt (*J.*, 1946, 469) −153°. In view of the discrepancy which might have been due to the separation of an azeotropic mixture, the material was redistilled at 4·7 cm. of Hg pressure with solid carbon dioxide–acetone in the still-head, but no separation could be effected. Only two l. of trimethylborine, repeatedly separated from ethylene, were used in these experiments, and the m. p. after each separation lay in the range −159·8° to 159·9°, which is within experimental error over so long a period. Bamford *et al.* give no details of the purification used, but were not altogether satisfied with the behaviour of their product and attributed discrepancies to dissolved gas. However, there can be no doubt about the purity of our repeatedly distilled sample, and the true m. p. of trimethylborine is −159·85° ±0·1°.

Results.—Results are listed in the attached Table. The mol. fraction of trimethylborine (N_B) is calculated on the assumption that both gases have the same molar volume. Volumes are corrected to N.T.P. The measured pressures were generally of the order of only a few cm. of Hg, except in the making up of primary mixtures. $N_E = 1 - N_B =$ mol. fraction of ethylene. Log N_E and log N_B are listed from the eutectic points to $N_E = 1$ and $N_B = 1$ respectively.

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