141. *Alkyls and Aryls of Transition Metals. Part I. Complex Methylplatinum*(II) *Derivatives.**

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A reason for the instability of the alkyl and aryl derivatives of transition metals is suggested. This leads to the conclusion that ligands causing large splittings of the *d*-energy levels should stabilise planar and octahedral complexes of d^3 to d^8 types. This has been explored for the d^8 planar complexes of the nickel Group, and this paper records the preparation and properties of a series of methylplatinum(II) derivatives stabilised by tertiary phosphines and a chelating organic disulphide as ligands. The types *trans*-$[(PR_3)_2PtMeX]$ and *cis*-$[(PR_3)_2PtMe_2]$ (X = halogen) are most stable and both are prepared by the action of methyl-lithium or methylmagnesium halide on *cis*- or *trans*-$[(PR_3)_2PtX_2]$. The less stable *cis*-$[(PEt_3)_2PtMeCl]$ was prepared by action of hydrogen chloride on the *cis*-dimethyl compound, but *trans*-$[(PR_3)_2PtMe_2]$ was not obtained pure. The isomerisation, cleavage, and addition reactions of the stable methylplatinous compounds are described. The addition of methyl iodide to *trans*-$[(PR_3)_2PtMeI]$ gives a platinum(IV) derivative $[(PR_3)_2PtMe_2I_2]$. Dipole moments are also recorded.

Transition metals do not form organometallic compounds in the same way as most other metals; instead their alkyl and aryl derivatives appear to be very unstable at room temperature.[1] Transition metals differ from the others in that the *d*-orbitals in their penultimate shells are on an energy level close to that of their valency *s*- and *p*-orbitals. In some way this must account for the instability of their organic derivatives. Perhaps it is because electrons can easily be promoted from the relatively high-energy filled *d*-orbitals into antibonding σ-orbitals of the metal-to-carbon bond, or, if the *d*-orbitals are empty, from the carbon-to-metal bonding orbitals into a *d*-orbital, in either case weakening the metal-to-carbon bond. At any rate it appears (*a*) that for the formation of stable organometallic compounds it is essential to have more than a certain minimum difference in energy (ΔE) (Fig. 1) between the highest-energy orbital which contains electrons and the lowest-energy orbital which is vacant, and (*b*) that in most transition-metal compounds with their rather close *d*-energy levels this minimum is not attained.

Starting from this premise we have been able to isolate a number of very stable complex alkyl and aryl derivatives of Group VIII metals by adjusting the energy levels of the *d*-orbitals by co-ordination. These have the general formula $L_lMX_mR_n$, where L is an uncharged ligand, M the transition metal, X a halogen atom, and R an alkyl or aryl group. To the present we have concerned ourselves only with complexes where the *d*-orbitals not used in σ-bonding are at least singly occupied, *i.e.*, metals in the second half of the transition series Fe(II), Co(II), Ni(II), Cu(I), and their analogues. The energy levels of these non-σ-bonding *d*-orbitals in the penultimate shells of the metal atoms lie below those of the anti-bonding σ-levels. They constitute the highest occupied energy level in the complex. The lowest vacant level is an antibonding σ-orbital (or, according to crystal-field theory, a vacant *d*-orbital directed towards the ligands). It appeared to us that the best way to increase the energy difference between these levels would be to lower still further the energy of the non-σ-bonding *d*-orbitals by combining them with π-type orbitals of low energy in suitable ligands. In terms of molecular-orbital theory, to form stable organo-transition-metal complexes, with all the *d*-orbitals either occupied or used in bond formation, we need to combine the metal with ligands, L, capable of forming strong dative π-bonds with the metal. In terms of ligand-field theory, in those complexes where one or more

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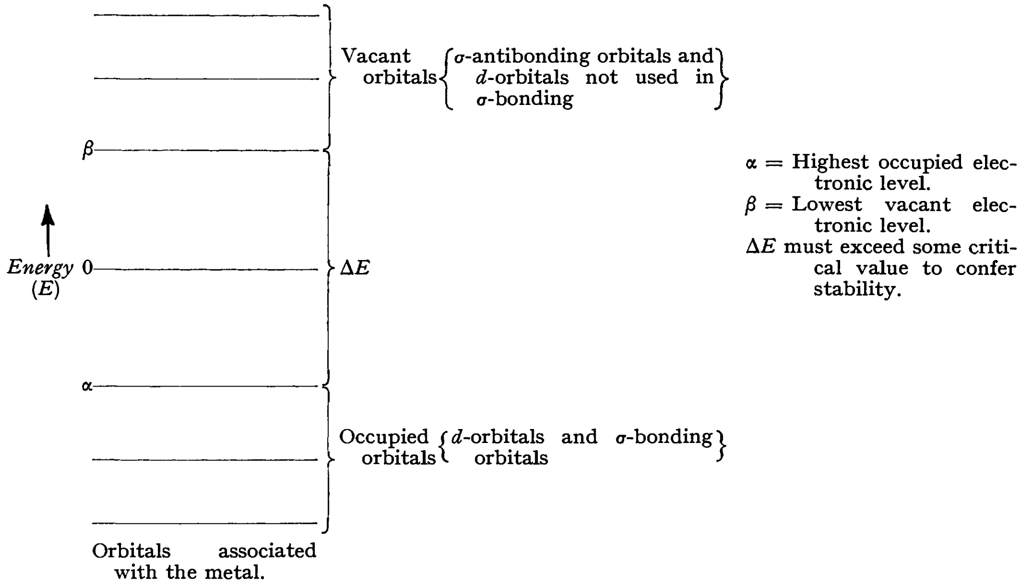
* A brief account of this work formed part of a paper read before the American Chemical Society at its April, 1958, Meeting in San Francisco.

[1] Cotton, *Chem. Rev.*, 1955, **55**, 551.

d-orbitals are used in hybridisation to form σ-bonds we need ligands with a strong field causing sufficiently large ligand field splittings in the energy levels of the *d*-shell.*

If these views are correct the stability of organo-transition-metal complexes with their *d*-orbitals either occupied or used in σ-bond formation will be greater when the ligands are in square planar and octahedral than when they are in tetrahedral configurations. This follows because ligands in orthogonal relationship form stronger dative π-bonds than when they are in tetrahedral positions. Also, since double-bonding and ligand field splittings are greater in the heavier transition-metal complexes than in the corresponding light transition-metal complexes, the heavier transition metals should form the more stable organometallic compounds, having *occupied* non-σ-bonding *d*-orbitals (Fig. 1).[3]

FIG. 1. *Suggested condition for stability of organo-transition-metal complexes.*



This is the reverse of what is found in the rest of the Periodic Table, where the heaviest element in each Sub-group forms the least stable alkyl and aryl derivatives. The only exception is the zinc Group where there is a mixed sequence of thermal stabilities $ZnR_2 > CdR_2 < HgR_2$,[4] and a completely reversed sequence of chemical reactivities. Presumably there is sufficient transition-metal character in this Group to cause the irregularity in these sequences.

To test these views we have examined the organometallic derivatives of the nickel Group of elements in their bivalent state, using tertiary organic phosphines to adjust the energy levels of the *d*-orbitals. Phosphines were chosen because they appear to be the most strongly double-bonding to the metal of all ligands except those containing carbon as ligand atoms, *e.g.*, CO and C_2H_4;[5] also they form very stable complexes of the type

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* At the beginning of the transition-metal series (*e.g.*, Ti, V) where the non-σ-bonding *d*-orbitals are empty, we need to increase the energy difference between them and the σ-bonding orbitals. This requires electronegative ligands with small ligand field strengths. Therefore a compromise must be struck between electronegativity and ligand field strengths as in the organotitanium compounds, *e.g.*, $TiPh(OPr^i)_3$.[2]

[2] Herman and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 3877, 3882.

[3] Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 381; Jörgensen, Tenth Solvay Conference in Chemistry, R. Stoops, Brussels, 1956, p. 355; Chatt, Gamlen, and Orgel, *J.*, 1958, 486.

[4] Rochow, Hurd, and Lewis, " The Chemistry of Organo-metallic Compounds," Wiley, New York, 1957, p. 105.

[5] Chatt, Duncanson, and Venanzi, *J.*, 1958, 3203, and previous references therein.

$[(PR_3)_2MX_2]$ (M = Ni, Pd, and Pt; X = halogen) of square planar configuration and suitable for this study.

On treating the above complexes in ether at room temperature with alkyl- and aryl-lithium or similar Grignard reagents we isolated stable organometallic derivatives of the three metals. Their stabilities fall rapidly in the order Pt > Pd > Ni in analogous compounds, in accordance with the views expressed above. Only the platinum(II) and nickel(II) compounds have been examined in detail because we learnt during the progress of this work that Professor G. E. Coates [6] had independently prepared similar compounds and was making a detailed study of those of palladium(II).

Whilst this work was in progress a number of alkyl and aryl derivatives of transition metals, stabilised by co-ordination to the *cyclo*pentadienyl anion or carbon monoxide, or both, have been reported, *e.g.*, $[Ti(C_5H_5)_2Ph_2]$,[7] $[(CO)_5MnMe]$,[8] $[C_5H_5Mo(CO)_3Me]$,[9] and with nitric oxide, $[C_5H_5Cr(NO)_2Me]$.[9] There is also the very unstable compound $[Co(CO)_4Me]$.[10] Similarly the olefinic double bond has been shown to stabilise a metal–alkyl bond in some complex chelate derivatives of platinum(II) and palladium(II).[11] These all have filled *d*-orbitals and fit into the above scheme. The recently discovered chromium(III) organic derivatives $[Cr(H_2O)_5{\cdot}CH_2Ph]$ [12] and $[Cr(Thf)_3Ph_3]$ [13] (Thf = tetrahydrofuran) are not exactly in this category because the ligands are not strongly double-bonding. However, with their singly occupied non-σ-bonding *d*-orbitals the tendency for electrons to be promoted into anti-bonding σ-orbitals must be very small, and so they accord with our original premise.

It should be noted that those electronic configurations which occur in stable organo-transition-metal complexes are just those which Taube [14] has pointed out as occurring in non-labile complexes with the common ligands.

In this paper we shall describe in detail only methylplatinum(II) compounds. Their study was started in 1952 in collaboration with Dr. M. E. Foss at Gloucester Technical College. He prepared the first well-defined methyl derivative, *trans*-$[(PPr^n_3)_2PtMeI]$, and studied its reaction to give $[(PPr^n_3)_2PtMe_2I_2]$, but then had to abandon the work. Methylplatinum(II) compounds were previously unknown, unless some of the ill-defined substances described by Gilman and Lichtenwalter [15] are eventually found to be of this type. Here we describe new compounds of the types *trans*-$[(PR_3)_2PtMeX]$ and *cis*-$[(PR_3)_2PtMe_2]$ (where R = Et, Pr^n, and Ph, and X = Cl, Br, I, SCN, and NO_3), and the less stable *cis*-$[(PEt_3)_2PtMeCl]$. Pure *trans*-$[(PEt_3)_2PtMe_2]$ is difficult to obtain. The stable chelate compounds $[(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)PtMe_2]$ and $[(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)PtMe_2]$ are also described.

Methylplatinum(II) compounds, stabilised by combination with tertiary phosphines, are remarkably inert, colourless, and crystalline. They are not hydrolysed by dilute acids or oxidised in moist air, and appear stable indefinitely (no deposition of metallic platinum). A sample of *trans*-$[(PEt_3)_2PtMeI]$ is unchanged after a year and one of *trans*-$[(PPr^n_3)_2PtMeI]$ has not deposited platinum during six years. They are soluble in organic solvents and insoluble in water. *cis*$[(PEt_3)_2PtMe_2]$ distils without decomposition at 85°/10^{-4} mm., but not at higher temperatures (100—130°) and pressures (0·05—12 mm.). The derivatives *trans*-$[(PEt_3)_2PtMeX]$ (where X = Cl, Br, I) and *cis*-$[(PEt_3)_2PtMeCl]$ can be purified by chromatography on alumina (Spence Grade "H") with some loss, but *cis*-$[(PEt_3)_2PtMe_2]$ is recoverable from the column only in poor yield.

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[6] Calvin and Coates, *Chem. and Ind.*, 1958, 160.

[7] Summers and Uloth, *J. Amer. Chem. Soc.*, 1954, **76**, 2278.

[8] Coffield, Kozikowski, and Closson, *J. Org. Chem.*, 1957, **22**, 598.

[9] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[10] Hieber, Vohler, and Braun, *Z. Naturforsch.*, 1958, **13**b, 192.

[11] Chatt, Vallarino, and Venanzi, *J.*, 1957, 2496, 3413.

[12] Anet and Leblanc, *J. Amer. Chem. Soc.*, 1957, **79**, 2649.

[13] Herwig and Zeiss, *ibid.*, p. 6561.

[14] Taube, *Chem. Rev.*, 1952, **50**, 69.

[15] Gilman and Lichtenwalter, *J. Amer. Chem. Soc.*, 1938, **60**, 3085; 1939, **61**, 957; Lichtenwalter, *Iowa State Coll. J. Sci.*, 1939, 1457; cf. Gilman, Lichtenwalter, and Benkeser, *J. Amer. Chem. Soc.*, 1953, **75**, 2063.

Preparations.—In general, a mixture of the mono- and di-methyl derivative is obtained by the reaction of either *cis*- or *trans*-$[(PR_3)_2PtX_2]$ with methylmagnesium halide. These are not easily separable and, since the use of the theoretical quantity of Grignard reagent leaves some of the starting material in the mixture, a large excess of Grignard reagent was usually used. The ratio of products *trans*-$[(PR_3)_2PtMeX]$, *cis*-$[(PR_3)_2PtMe_2]$, and *cis*-$[(PR_3)_2PtMeX]$ depends upon the halogen X and the configuration of the starting material. Attempts to isolate *trans*-$[(PR_3)_2PtMe_2]$ failed.

The highest proportion of the *trans*-monomethyl compound is produced by the use of *trans*-starting material and the Grignard iodide. Thus *trans*-$[(PEt_3)_2PtMeI]$ is obtained in 90% yield by use of a large excess of iodide at 20°. Even use of a higher reaction temperature (80°) still gives *trans*-$[(PEt_3)_2MeI]$ in good yield and no isolatable quantity of the dimethyl derivative, suggesting that the proportions of the two products depend in this case on thermodynamic rather than kinetic factors. The use of *cis*-starting material or of the lighter halogens increases the proportion of dimethyl derivative, but even the reaction of *cis*-$[(PR_3)_2PtCl_2]$ with a large excess of methylmagnesium chloride will not give the latter pure. It is best prepared by the use of methyl-lithium (prepared from methyl chloride). *cis*-$[(PEt_3)_2PtMe_2]$ is obtained in 88% yield by reaction of the *cis*-dichloride with a 10% excess of methyl-lithium, and the analogues $C_2H_4(PEt_2)_2PtMe_2$ and $C_2H_4(SEt)_2PtMe_2$ are prepared similarly.

The monomethyl derivatives, when present in large proportion, are best removed from *cis*-$(PEt_3)_2PtMe_2$ by treating the mixture in ethanol with thiourea. This forms easily separable complexes with the mono-, leaving the di-methyl derivative.

The compound *cis*-$[(PEt_3)_2PtMeCl]$ is probably an intermediate in the formation of *cis*-$[(PEt_3)_2PtMe_2]$ from *cis*-$[(PEt_3)_2PtCl_2]$ by the Grignard or methyl-lithium procedure, but was isolated only in very small quantity; it was obtained also in similar quantity from some preparations of *trans*-$[(PEt_3)_2PtMeCl]$ from *trans*-$[(PEt_3)_2PtCl_2]$.

Many possible methods of preparation were tried but only the cleavage of *cis*-$[(PEt_3)_2PtMe_2]$ by dry hydrogen chloride was satisfactory. Stoicheiometric quantities of the reagents in ether gave a quantitative yield at room temperature.

cis-$[(PEt_3)_2PtMeCl]$ is stable in benzene solution, but a trace of triethylphosphine causes rapid and almost complete isomerisation. In contrast, *trans*-$[(PEt_3)_2PtMeCl]$ was almost unchanged after 2 weeks in the presence of free triethylphosphine, and no *cis*-$[(PEt_3)_2PtMeCl]$ was isolated from the solution.[16]

trans-$[(PEt_3)_2PtX_2]$ ($X = Cl$ or Br) reacts with the corresponding methylmagnesium halide at 20° much more slowly than does the *cis*-isomer, to give the monomethyl compound as the major product. At 80° the second halogen atom is partially replaced, but only the *cis*-dimethyl derivative can be isolated. Similarly from the reaction of methyl-lithium (2·2 mol. at 20°) the only dimethyl derivative isolated has a *cis*-configuration.

Repeated distillation of *cis*-$[(PEt_3)_2PtMe_2]$ (m. p. 81—82°) at 130°/12 mm. gave a product of low m. p. (almost completely molten at 57°) but identical analysis. This product also had a low dipole moment and was probably a mixture of *cis*- and *trans*-$[(PEt_3)_2PtMe_2]$. A very small quantity of the substantially pure *trans*-isomer (m. p. 76—79°) was isolated by chromatography.

Methylplatinum(II) derivatives stabilised by tri-*n*-propylphosphine and by triphenylphosphine were also prepared. The monomethyl compound, *trans*-$[(PPh_3)_2PtMeI]$, is difficult to separate from the dimethyl analogue and so is more readily obtained by reaction of methyl iodide with tris(triphenylphosphine)platinum(0):[17]

$$[Pt(PPh_3)_3] + 2MeI \longrightarrow trans\text{-}[(PPh_3)_2PtMeI] + [PPh_3Me]I$$

This is an interesting reaction since it produces the methylplatinum compound without intervention of any other organometallic substance.

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[16] Cf. Chatt and Wilkins, *J.*, 1951, 2532.

[17] Malatesta and Cariello, Internat. Conf. on Co-ordination Compounds, Rome, 1957; *J.*, 1958, 2323.

The methyl derivatives prepared during this work are listed in Table 1. The dipole moments were used to determine their configurations. The reactions of *trans*-$[(PEt_3)_2PtMeCl]$, *trans*-$[(PEt_3)_2PtMeI]$, and *cis*-$[(PEt_3)_2PtMe_2]$ were studied as typical of the commoner derivatives.

TABLE 1.

Substance	M. p.	Dipole moment (±0·1; D)	Substance	M. p.	Dipole moment (±0·1; D)
		A. Methylplatinum(II) *complexes.*			
cis-$[(PEt_3)_2PtMe_2]$	81—82°	5·65	*trans*-$[(PPr^n{}_3)_2PtMeI]$	47—48°	(3·9)
trans-$[(PEt_3)_2PtMeI]$	71—71·5	4·1	*cis*-$[(PPh_3)_2PtMe_2]$	235—237 †	5·45
trans-$[(PEt_3)_2PtMeBr]$	87—90	(3·7) *	$[(PPh_3)_2PtMeI]$	270—274	‡
trans-$[(PEt_3)_2PtMeCl]$	99—100	3·4	*trans*-$[(PPh_3)_2Pt(Me)SCN]$	247—249	(6·5)
cis-$[(PEt_3)_2PtMeCl]$	113—116 †	(8·4)	$[(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)PtMe_2]$	74·5—75·5	(6·7)
trans-$[(PEt_3)_2Pt(Me)SCN]$	93—95	6·65	$[(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)PtMe_2]$	50—51	—
trans-$[(PEt_3)_2Pt(Me)NO_3]$	56—58	(6·0)			
		B. New methylplatinum(IV) *complexes.*			
$[(PEt_3)_2PtMe_2I_2]$	101—103° †	5·85	$[(PPr^n{}_3)_2PtMe_2I_2]$	128° †	(5·8)
$[(PEt_3)_2PtMe_2Cl_2]$	114—117	(5·3)			

* Values in parentheses were calculated by using estimated refractivities and densities. Since the moments are high this introduces only an insignificant error. The margin of error (0·1 D) is determined by the uncertainty in the atom polarisation which may be up to 20% of the electron polarisation in complex compounds. † Decomp. ‡ Insol. in benzene.

Replacement of Halogens.—The halogen atoms of the monomethyl derivatives are readily replaced by treatment with an appropriate salt. Thus $[(PEt_3)_2PtMeCl]$ is converted almost quantitatively into the corresponding bromide and iodide by treatment with the corresponding alkali-metal salts in acetone, *e.g.*:

$$\textit{trans}\text{-}[(PEt_3)_2PtMeCl] + LiBr \longrightarrow \textit{trans}\text{-}[(PEt_3)_2PtMeBr + LiCl$$

Similarly, *trans*-$[(PEt_3)_2PtMeI]$ is converted into the thiocyanate by treatment with potassium thiocyanate and, in smaller yield, into the nitrate by treatment with silver nitrate in aqueous methanol.

Cleavage of the Methyl Group from the Metal.—This was investigated in attempts to find a route to *cis*-$[(PR_3)_2PtMeX]$. The methyl groups are rapidly removed from the metal at room temperature by reaction with iodine, magnesium iodide, or hydrogen chloride in ether, and one methyl group from the dimethyl complex by *cis*-$[(PEt_3)_2PtCl_2]$ in boiling benzene. Methyl iodide also causes cleavage (see addition reactions), *e.g.*:

$$\textit{cis}\text{-}[(PEt_3)_2PtMe_2] \xrightarrow{I_2} \textit{trans}\text{-}[(PEt_3)_2PtMeI] + MeI$$

$$\textit{trans}\text{-}[(PEt_3)_2PtMeI] \xrightarrow{I_2} \textit{trans}\text{-}[(PEt_3)_2PtI_2] + MeI$$

$$\textit{cis}\text{-}[(PEt_3)_2PtMe_2] \xrightarrow{MgI_2} \textit{trans}\text{-}[(PEt_3)_2PtI_2] + \textit{trans}\text{-}[(PEt_3)_2PtMeI] + MeMgI$$

$$\textit{cis}\text{-}[(PPh_3)_2PtMe_2] \xrightarrow{MgI_2} \textit{trans}\text{-}[(PPh_3)_2PtMeI] + MeMgI$$

$$\textit{cis}\text{-}[(PEt_3)_2PtMe_2] \xrightarrow{HCl} \textit{cis}\text{-}[(PEt_3)_2PtMeCl] + CH_4$$

$$\textit{cis}\text{-}[(PEt_3)_2PtMe_2] \xrightarrow{2HCl} \textit{cis}\text{-}[(PEt_3)_2PtCl_2] + 2CH_4$$

In the first two of these reactions there is no evidence for the formation of a platinic compound $[(PEt_3)_2PtMe_nI_{4-n}]$ stable at room temperature, but in the third reaction (with magnesium iodide in ether) there is an immediate precipitate when the components are mixed, which is evidence for the formation of an intermediate complex since both the reactants and the final products are soluble in ether.

Reaction of *cis*-$[(PEt_3)_2PtCl_2]$ with *cis*-$[(PEt_3)_2PtMe_2]$ (1·1 mol.) in hot benzene rapidly gives a mixture containing *cis*- and *trans*-$[(PEt_3)_2PtCl_2]$, *cis*-$[(PEt_3)_2PtMe_2]$, and *trans*-$[(PEt_3)_2PtMeCl]$. This variety of products suggests that some free triethylphosphine is formed and causes isomerisation of the *cis*-$[(PEt_3)_2PtCl_2]$.[16] Reaction in the presence of a small quantity of the bridged complex $[(PEt_3)_2Pt_2Cl_4]$, which reacts immediately with any free phosphine, is much slower, no *trans*-$[(PEt_3)_2PtCl_2]$ is found and in addition to unchanged starting material and *trans*-$[(PEt_3)_2PtMeCl]$ a small quantity of *cis*-$[(PEt_3)_2PtMeCl]$ is isolable.

Addition Reactions.—(a) *Methyl iodide.* The monomethyl derivatives add methyl iodide at 100°, producing platinic compounds, *e.g.*, $[(PEt_3)_2PtMe_2I_2]$, m. p. 101—103° and $[(PPr^n{}_3)_2PtMe_2I_2]$, m. p. 128°. This is analogous to the reaction which, it has been suggested, is responsible for the production of $(Me_3PtI)_4$ from platinous salts by reaction with methylmagnesium iodide in presence of an excess of methyl iodide.[18] The methyl iodide in $[(PEt_3)_2PtMe_2I_2]$ is rather loosely held and is removed in 3 hours at 80°/0·01 mm., or slowly in boiling solvents. It is not held as solvent of crystallisation because this product cannot be obtained from a solution of the monomethyl derivative in methyl iodide at room temperature, or even, except in very poor yield, at the boiling point of methyl iodide. When the components are heated in a sealed tube at 100° for a prolonged time (20 hours) cleavage of the methyl groups occurs:

$$[(PEt_3)_2PtMe_2I_2] \longrightarrow [(PEt_3)_2PtI_2] + C_2H_6$$

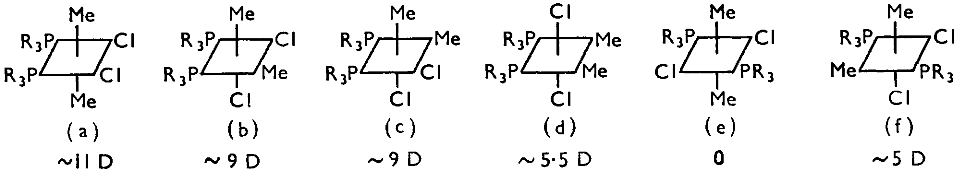
Iodine does not react with $[(PEt_3)_2PtMe_2I_2]$ in cold benzene, but on 15 minutes' boiling the methyl groups are eliminated. This reaction may occur through dissociation of the platinum(IV) complex, $[(PEt_3)_2PtMe_2I_2] \longrightarrow$ *trans*-$[(PEt_3)_2PtMeI]$ + MeI, followed by fission with iodine as above.

Methyl iodide did not react with *trans*-$[(PEt_3)_2PtI_2]$, whence we expected to obtain $[(PEt_3)_2PtMeI_3]$, and with *cis*-$[(PEt_3)_2PtMe_2]$ it gave a mixture which was not separated.

(b) *Chlorine.* *cis*-$[(PEt_3)_2PtMe_2]$ reacts with two equivalents of chlorine to give $[(PEt_3)_2PtMe_2Cl_2]$.

(c) *Iodine.* In contrast, iodine causes cleavage of *cis*-$[(PEt_3)_2PtMe_2]$ (see above). This failure to give a stable platinic derivative must mean that the addition gives an isomeric form of $[(PEt_3)_2PtMe_2I_2]$ which is unstable and rapidly decomposes at room temperature.

FIG. 2.



The Configuration of the Dimethylplatinum(IV) *Complexes.*—Six stereoisomers of $[(PEt_3)_2PtMe_2Cl_2]$ are possible and estimates of their dipole moments are given in Fig. 2; two of these isomers (b and c) are mirror images. The dipole moments were estimated by assuming that the bond moments in the octahedral platinum(IV) complexes are approximately the same as in planar platinum(II) complexes. Thus, (a) would have a moment almost identical with that of *cis*-$[(PEt_3)_2PtCl_2]$ (10·9 D),[19] and (d) with *cis*-$[(PEt_3)_2PtMe_2]$ (5·55 D). The dipole moments of (b) and (c) would be the vector sum of the moments of *cis*-$[(PEt_3)_2PtMeCl]$ (8·4 D) and the system Me–Pt–Cl acting at right angles. The latter is the moment of *trans*-$[(PEt_3)_2PtMeCl]$ (3·4 D), and so the estimated moment of (b) and (c) is approximately $[(8{\cdot}4)^2 + (3{\cdot}4)^2]^{\frac{1}{2}} = 9{\cdot}1$ D. Form (f) would similarly have a moment compounded from the vector sum of two Me–Pt–Cl systems at right angles, *i.e.*, $[(3{\cdot}4)^2 + (3{\cdot}4)^2]^{\frac{1}{2}} = 4{\cdot}8$ D.

We expect that the dipole moments of the iodides $[(PEt_3)_2PtMe_2I_2]$ corresponding to

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[18] Chatt and Duncanson, *J.*, 1953, 2939.

[19] Chatt and Wilkins, *J.*, 1952, 4300.

(d) and (e) would be similar to those of the chlorides; the others, where the iodine atoms are in *cis*-relation, might have dipole moments up to 1 D greater {compare *trans*-[$(PEt_3)_2PtMeCl$] and the corresponding iodide in Table 1*B*}.

The complex methylplatinic chloride and iodide listed in Table 1*B* have dipole moments of 5·3 and 5·8 D, respectively, and so must have configurations as (d) or (f).

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

The complex platinous halides were prepared by established methods,[16, 20] and 1 : 2-bis-(diethylphosphino)ethane as described by Wymore.[21] M. p.s were determined on a Kofler hot-stage and are corrected. Spence alumina (grade " H ") was used for chromatography.

trans-*Bis(triethylphosphine)iodo(methyl)platinum* [$(PEt_3)_2PtMeI$].—A solution of methylmagnesium iodide was prepared from methyl iodide (10·0 g.), magnesium (1·52 g.), and ether (60 c.c.). Benzene (20 c.c.) was added, followed by a solution of *trans*-bis(triethylphosphine)-dichloroplatinum (8·00 g.) in benzene (50 c.c.). After 1 hour's stirring at 20° dilute hydrochloric acid was added slowly with ice-cooling. The organic layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the solvent and crystallisation of the residue from methyl alcohol containing a little water afforded trans-*bis(triethylphosphine)iodo(methyl)platinum* (8·28 g., 90%) as colourless plates (Found: C, 27·2; H, 5·8%; *M*, ebullioscopically in 1·44% benzene solution, 568; *M*, in 2·28% benzene solution, 537. $C_{13}H_{33}IP_2Pt$ requires C, 27·2; H, 5·8%; *M*, 573). The compound was non-conducting in nitrobenzene solution. It was also prepared, in 40% yield, from *cis*-bis(triethylphosphine)dichloroplatinum and methylmagnesium iodide under similar conditions.

trans-*Bis(tri*-n-*propylphosphine)iodo(methyl)platinum* [$(PPr^n{}_3)_2PtMeI$].—This *compound* was similarly prepared from *cis*- or *trans*-bis(tri-*n*-propylphosphine)dichloroplatinum and formed plates (Found: C, 34·9; H, 6·5%; *M*, ebullioscopically in 1·8% benzene solution, 630; *M*, in 2·58% benzene solution, 626. $C_{19}H_{45}IP_2Pt$ requires C, 34·7; H, 6·9%; *M*, 657).

trans-*Bis(triethylphosphine)bromo(methyl)platinum* [$(PEt_3)_2PtMeBr$] was similarly prepared from methylmagnesium bromide (magnesium, 0·65 g.; ether, 25 c.c.) and *cis*-bis(triethylphosphine)dibromoplatinum (2·00 g.). Crystallisation, once from light petroleum (b. p. 60—80°), and several times from methyl alcohol, gave the pure complex as elongated prisms (Found: C, 29·7; H, 6·3. $C_{13}H_{33}BrP_2Pt$ requires C, 29·7; H, 6·3%).

trans-*Bis(triethylphosphine)chloro(methyl)platinum* [$(PEt_3)_2PtMeCl$].—Methylmagnesium chloride was prepared from magnesium (0·96 g.), ether (80 c.c.; plus iodine) and dry methyl chloride. *trans*-Bis(triethylphosphine)dichloroplatinum (2·0 g.) was added, and, after 1 hour's stirring at 20° the colourless mixture was hydrolysed with ice and hydrochloric acid. The residue from evaporation of the dried (magnesium sulphate) ether layer was chromatographed in light petroleum (b. p. 40—60°; 15 c.c.) containing ether (3 c.c.) on alumina (100 g.). Elution with light petroleum (b. p. 40—60°) containing ether (20% v/v) afforded trans-*bis(triethylphosphine)chloro(methyl)platinum* (1·1 g., 61%) as needles from light petroleum (b. p. 60—80°) (Found: C, 32·4; H, 6·9. $C_{13}H_{33}ClP_2Pt$ requires C, 32·4; H, 6·9%). Elution with ether gave needles (0·12 g.), m. p. 109—114° (decomp.), which, after two crystallisations from light petroleum (b. p. 60—80°), afforded long, very thin needles of cis-*bis(triethylphosphine)chloro(methyl)platinum* (Found: C, 32·7; H, 6·9%).

cis-*Bis(triethylphosphine)dimethylplatinum* [$(PEt_3)_2PtMe_2$] (*Grignard Method*).—Methylmagnesium chloride was prepared from magnesium (0·96 g.), ether (75 c.c.), iodine, and gaseous methyl chloride. *cis*-Bis(triethylphosphine)dichloroplatinum (3·00 g.) was added, and the mixture stirred for 1 hr. and hydrolysed by pouring it on ice and dilute hydrochloric acid. The ether layer was dried ($MgSO_4$) and evaporated under reduced pressure. Two crystallisations from light petroleum (cooling to −10°) and one from methyl alcohol gave colourless prisms (1·05 g.). These were warmed to 80° with a solution of thiourea (2 g.) in aqueous methanol (7 c.c. of H_2O, 3 c.c. of MeOH), and, after cooling, the solid was filtered off and dissolved in ether. After drying ($MgSO_4$), the ether was removed under reduced pressure and the residue recrystallised from light petroleum (b. p. 60—80°), to give cis-*bis(triethylphosphine)dimethylplatinum* (0·55 g.)

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[20] Jensen, *Z. anorg. Chem.*, 1936, **229**, 237; Chatt and Venanzi, *J.*, 1955, 2787.

[21] Wymore, Ph.D. Thesis, 1957, Univ. Illinois; *Diss. Abs.*, 1957, **17**, 1208.

as colourless prisms (Found: C, 36·7; H, 7·9%; *M*, ebullioscopically in 1·52% benzene solution, 485; *M*, in 2·25% benzene solution, 473. $C_{14}H_{36}P_2Pt$ requires C, 36·45; H, 7·85%; *M*, 461).

cis-*Bis*(*triphenylphosphine*)*dimethylplatinum* $[(PPh_3)_2PtMe_2]$.—Methylmagnesium bromide was prepared from gaseous methyl bromide, ether (50 c.c.), and magnesium (1·2 g.). Benzene (50 c.c.) was added, followed by *cis*-bis(triphenylphosphine)dichloroplatinum (3·00 g.), and the mixture was heated under reflux for 2 hr. After cooling to −10° the mixture was cautiously hydrolysed with dilute hydrobromic acid, and the white precipitate was filtered off. A further quantity was obtained from the organic layer on evaporation. The combined product was heated under reflux for 1 hr. with thiourea (1·0 g.) in ethyl alcohol (50 c.c.) and benzene (10 c.c.), and the whole was filtered hot. The residue, on crystallisation from benzene, afforded cis-*bis*(*triphenylphosphine*)*dimethylplatinum* as colourless prisms (1·64 g.) (Found: C, 60·9; H, 4·9. $C_{38}H_{36}P_2Pt$ requires C, 60·9; H, 4·85%).

1 : 2-*Bis*(*diethylphosphino*)*ethanedichloroplatinum* $[C_2H_4(PEt_2)_2PtCl_2]$.—*trans*-Bis(dimethyl sulphide)dichloroplatinum (3·42 g.) in chloroform (30 c.c.) was treated with 1 : 2-bis(diethylphosphino)ethane (1·88 g.) in an atmosphere of nitrogen. After 2 minutes' boiling the solution was cooled and light petroleum (b. p. 80—100°) was added. The precipitate was collected and dissolved in hot dilute ammonia, the mixture filtered, and the solution acidified at 0° with concentrated hydrochloric acid. The resultant precipitate was washed with water and crystallised from methyl alcohol, to give 1 : 2-*bis*(*diethylphosphino*)*ethanedichloroplatinum* (1·06 g.) as colourless prisms, m. p. 291—295° (with sublimation) (Found: C, 25·25; H, 5·15. $C_{10}H_{24}Cl_2P_2Pt$ requires C, 25·45; H, 5·15%).

Preparation of Methyl-lithium Solution.—This was prepared, in a typical case, from lithium (3 g.), ether (150 c.c.), and methyl chloride (about 50% of the theoretical quantity). To ensure that no unchanged methyl chloride remained the solution was stirred for at least 1 hr. after the addition. It was then filtered through asbestos and estimated by titration against 0·1N-hydrochloric acid.

Preparation of Dimethylplatinum(II) *Derivatives by Methyl-lithium. General Method.*—The finely divided platinous chloride complex (*cis*-isomer), suspended in dry benzene, was treated with ethereal methyl-lithium (10% excess) at 20°. After 15 min., light petroleum (10 c.c.; b. p. 60—80°) was added, the precipitated lithium chloride filtered off, and the product isolated by evaporating the solvent at 15 mm. and recrystallising the residue from light petroleum (b. p. 40—60°). Alternatively the lithium salts were removed by water, and the product was isolated from the organic layer. Prepared by the general method were: *cis*-bis(triethylphosphine)dimethylplatinum (yield 88%); 1 : 2-*bis*(*diethylphosphino*)*ethanedimethylplatinum*, colourless prisms (80%) (Found: C, 33·65; H, 7·1. $C_{12}H_{30}P_2Pt$ requires C, 33·4; H, 7·0%); and 1 : 2-*di*(*ethylthio*)*ethanedimethylplatinum*, colourless needles (66%) (Found: C, 25·6; H, 5·3. $C_8H_{20}S_2Pt$ requires C, 25·6; H, 5·35%).

cis-*Bis*(*triethylphosphine*)*chloro*(*methyl*)*platinum* $[(PEt_3)_2PtMeCl]$.—A solution of *cis*-bis(triethylphosphine)dimethylplatinum (0·42 g.) in dry ether (8 c.c.) was treated with hydrogen chloride in dry ether (2·00 c.c.; 0·461N; 1 mol.). Almost immediately, colourless crystals separated. The mixture was evaporated to dryness, and the residue digested with light petroleum (b. p. <40°), leaving *cis*-bis(triethylphosphine)chloro(methyl)platinum (0·43 g.), m. p. 112—120° (decomp.). On recrystallisation from light petroleum (b. p. 60—100°) it formed long colourless needles, m. p. 114—119° (decomp.).

Attempts to prepare cis-*Bis*(*triethylphosphine*)*chloro*(*methyl*)*platinum* $[(PEt_3)_2PtMeCl]$.—(1) *By action of methyl-lithium* (1 *mol.*) *on* cis-*bis*(*triethylphosphine*)*dichloroplatinum*. *cis*-Bis(triethylphosphine)dichloroplatinum (1·50 g.) in boiling benzene (175 c.c.) under nitrogen was treated with methyl-lithium in ether (10·0 c.c.; 0·33N). Lithium chloride was filtered off and the filtrate, on cooling, deposited unchanged *cis*-bis(triethylphosphine)dichloroplatinum (0·25 g.). The colourless mother-liquor was evaporated and the residue dissolved in hot light petroleum (b. p. 80—100°). On cooling, *cis*-bis(triethylphosphine)chloro(methyl)platinum (0·03 g.) separated which recrystallised from light petroleum (b. p. 80—100°) in needles, m. p. and mixed m. p. 110—113° (decomp.). The original petroleum mother-liquors, on evaporation, yielded *cis*-bis(triethylphosphine)dimethylplatinum (0·49 g.), m. p. 78—81°.

(2) *By fission of* cis-*bis*(*triethylphosphine*)*dimethylplatinum with excess of hydrogen chloride.* A solution of *cis*-bis(triethylphosphine)dimethylplatinum (0·40 g.) in light petroleum (15 c.c.; b. p. <40°) was treated with an excess of dry hydrogen chloride at 0° for 30 seconds. Almost immediately a colourless precipitate was formed. The suspension was extracted repeatedly

with light petroleum (b. p. 60—100°). This extract, on cooling to 0°, deposited *cis*-bis(triethylphosphine)chloro(methyl)platinum (0·11 g.) as long colourless needles, m. p. 116—119° (decomp.) (Found: C, 32·5; H, 7·0%). The petroleum-insoluble residue, on crystallisation from chloroform–light petroleum, gave *cis*-bis(triethylphosphine)dichloroplatinum (0·09 g.), m. p. 187—190°.

(3) *By isomerisation of* trans-*bis(triethylphosphine)chloro(methyl)platinum to the* cis-*isomer.* The *trans*-compound (0·24 g.) in light petroleum (b. p. 60—80°; 4 c.c.) and triethylphosphine (0·03 g.) were kept for 1 hr. at 25°. By this time colourless prisms, m. p. 96—99°, of the unchanged starting material had separated. After 2 weeks at 20° evaporation under reduced pressure gave a quantitative recovery of material, m. p. 93—99°, undepressed on admixture with the pure starting material, m. p. 99—100°. Very little *cis*-bis(triethylphosphine)chloro(methyl)platinum could have been formed.

Isomerisation of cis-*Bis(triethylphosphine)chloro(methyl)platinum to the* trans-*Isomer.*—The *cis*-compound (0·15 g.), suspended in light petroleum (b. p. 60—80°; 4 c.c.), was heated with triethylphosphine (0·01 g.), giving a homogeneous solution. This was cooled and evaporated to dryness, giving a colourless crystalline residue (0·15 g.), m. p. 95—100°, of *trans*-bis(triethylphosphine)chloro(methyl)platinum. Recrystallisation from methyl alcohol containing a little water gave the pure *trans*-isomer, m. p. 98—100°.

Attempts to prepare trans-*Bis(triethylphosphine)dimethylplatinum.*—(1) *From* cis-*bis(triethylphosphine)dimethylplatinum.* The *cis*-compound (0·1 g.) was heated at 130°/12 mm. and the distillate condensed on a cold finger placed *ca.* 1 cm. away. The solid distillate was collected at intervals, and heating was continued until no more distilled (a black residue remained) (yield 0·04 g.; m. p. 50—78°). This distillate was chromatographed on alumina (10 g.); elution with light petroleum (b. p. <40°) containing 20% of ether gave substantially pure trans-*bis(triethylphosphine)dimethylplatinum,* as colourless needles, m. p. 76—79° (0·012 g.) (Found: C, 36·75; H, 7·9. $C_{14}H_{36}P_2Pt$ requires C, 36·45; H, 7·85%). The mixed m. p. with the *cis*-isomer was 55—81°.

(2) *From* trans-*bis(triethylphosphine)dibromoplatinum.* Methylmagnesium bromide was prepared from magnesium (0·48 g.), ether (20 c.c.), and methyl bromide. Benzene (30 c.c.) was added and most of the ether was distilled off (temperature of vapour 65°). *trans*-Bis(triethylphosphine)dibromoplatinum (1·2 g.) was added, and the mixture heated under reflux for 1½ hr. After hydrolysis with ice and hydrochloric acid isolation in the usual way gave a product which, after four crystallisations from methyl alcohol, afforded *cis*-bis(triethylphosphine)dimethylplatinum as colourless prisms (0·42 g.), m. p. 80—81° (Found: C, 36·5; H, 7·85%).

(3) *By action of methyl-lithium* (2·2 *mol.*) *on* trans-*bis(triethylphosphine)dichloroplatinum.* *trans*-Bis(triethylphosphine)dichloroplatinum (1·00 g.) in dry ether (15 c.c.) and benzene (15 c.c.) was treated with a solution of methyl-lithium (10 c.c.; 0·445N; 2·2 mol.). The solution became colourless at once and lithium chloride was precipitated. After evaporation to dryness the residue was extracted with hot light petroleum (b. p. 60—80°), and the filtrate evaporated to dryness. After one crystallisation from methyl alcohol and one from light petroleum (b. p. 60—80°) this last residue gave *cis*-bis(triethylphosphine)dimethylplatinum (0·32 g.) as colourless prisms, m. p. 78—81°.

Bis(triphenylphosphine)iodo(methyl)platinum [$(PPh_3)_2PtMeI$].—Tris(triphenylphosphine)platinum [17] was prepared by reduction of *cis*-[$(PPh_3)_2PtCl_2$] in alcoholic suspension in the presence of triphenylphosphine (1 mol.) with hydrazine hydrate (Found: C, 65·7; H, 4·7. Calc. for $C_{54}H_{45}P_3Pt$: C, 66·05; H, 4·6%). This (2·00 g.) in methyl iodide (18 c.c.) was kept for 1 hr. The solution gradually lightened and methyl(triphenyl)phosphonium iodide separated. The mixture was evaporated to dryness, and the residue boiled with methyl alcohol and filtered off. The insoluble portion, recrystallised from benzene, formed colourless prisms (1·2 g.) of *bis(triphenylphosphine)iodo(methyl)platinum* (Found: C, 51·4; H, 3·9. $C_{37}H_{33}IP_2Pt$ requires C, 51·6; H, 3·85%). With potassium thiocyanate in boiling acetone this iodide was converted into the *thiocyanate, trans*-[$(PPh_3)_2PtMe(SCN)$], which formed colourless prisms from benzene–methyl alcohol (Found: C, 57·55; H, 4·35. $C_{38}H_{33}NSP_2Pt$ requires C, 57·55; H, 4·2%).

Metathetical Replacements.—(1) trans-*Bis(triethylphosphine)bromo(methyl)platinum from the chloride.* *trans*-Bis(triethylphosphine)chloro(methyl)platinum (0·13 g.) in acetone (12 c.c.) was heated under reflux with lithium bromide (1·0 g.) for ½ hr. The acetone was removed under reduced pressure and the water-insoluble residue crystallised twice from methyl alcohol, to give *trans*-bis(triethylphosphine)bromo(methyl)platinum (0·085 g.) (Found: C, 29·7; H, 6·3%).

(2) trans-*Bis*(*triethylphosphine*)*iodo*(*methyl*)*platinum from the chloride.* A solution of the chloride (0·12 g.) and sodium iodide (0·250 g.) in acetone (5 c.c.) was put aside for 1 hr. After evaporation the residue was washed with water, to give *trans*-bis(triethylphosphine)iodo(methyl)platinum (0·135 g.), m. p. 70—70·5° without recrystallisation.

(3) trans-*Bis*(*triethylphosphine*)*methyl*(*thiocyanato*)*platinum* [$(PEt_3)_2PtMe(SCN)$] *from the iodide.* The iodo-complex (0·350 g.) in acetone (20 c.c.) was heated with potassium thiocyanate (1·0 g.) under reflux for 90 min. Evaporation and isolation of the water-insoluble portion afforded the trans-(*thiocyanato-compound* (0·210 g.) as needles [from light petroleum (b. p. 80—100°)] (Found: C, 33·2; H, 6·5; N, 3·1. $C_{14}H_{33}NSP_2Pt$ requires C, 33·3; H, 6·6; N, 2·8%).

(4) trans-*Bis*(*triethylphosphine*)*methyl*(*nitrato*)*platinum* [$(PEt_3)_2PtMe(NO_3)$] *from the iodide.* A solution of the *trans*-iodide (0·530 g.) in methyl alcohol (25 c.c.) was treated with silver nitrate (0·170 g.) in aqueous methyl alcohol [methyl alcohol (10 c.c.), water (5 c.c.)]. Silver iodide was precipitated at once but there was also some reduction to metallic silver. The precipitate was filtered off and the solution evaporated to dryness, giving a solid residue which on crystallisation from light petroleum (b. p. 60—80°) yielded trans-*bis*(*triethylphosphine*)*methyl*(*nitrato*)*platinum* (0·33 g.) as colourless needles (Found: C, 31·0; H, 6·7; N, 2·7. $C_{13}H_{33}O_3NP_2Pt$ requires C, 30·7; H, 6·5; N, 2·8%). In 0·137% w/v nitrobenzene solution at 19° the nitrate had a molar conductivity of 1·41 mho.

Fission Reactions.—(1) *Iodine and* cis-*bis*(*triethylphosphine*)*dimethylplatinum.* To a solution of bis(triethylphosphine)dimethylplatinum (0·273 g.) in benzene (10 c.c.) was added iodine (0·127 g.) in benzene (10 c.c.) with vigorous shaking. The iodine colour was discharged rapidly, the solution becoming pale orange. Removal of the benzene under reduced pressure and crystallisation of the residue from methyl alcohol afforded *trans*-bis(triethylphosphine)iodo(methyl)platinum (0·260 g.), m. p. and mixed m. p. 71—71·5° (Found: C, 27·5; H, 5·7%).

(2) *Iodine and* trans-*bis*(*triethylphosphine*)*iodo*(*methyl*)*platinum.* The complex (0·563 g.) was treated in benzene (10 c.c.) with iodine (0·254 g.) in benzene (10 c.c.), with shaking. The colour of the iodine was discharged rapidly. Evaporation of the solution and crystallisation of the residue from methyl alcohol afforded *trans*-bis(triethylphosphine)di-iodoplatinum (0·510 g.), m. p. 136·5—137·5°.

(3) *Magnesium iodide and bis*(*triphenylphosphine*)*dimethylplatinum.* A solution of magnesium iodide in ether was prepared from magnesium (excess), iodine (3·0 g.), and ether (40 c.c.). This was added to the dimethylplatinum complex (0·30 g.) in benzene (15 c.c.), and the mixture heated under reflux for 3 hr., then kept at 20° for 16 hr. Bis(triphenylphosphine)iodo(methyl)platinum separated (0·29 g.), having m. p. 267—270° (decomp.). This iodide is identical with that prepared from tris(triphenylphosphine)platinum(0) (mixed m. p., infrared spectra, and identical thiocyanate produced on treatment with potassium thiocyanate).

(4) *Magnesium iodide and* cis-*bis*(*triethylphosphine*)*dimethylplatinum.* A solution of magnesium iodide, from iodine (0·40 g.), ether (25 c.c.), and excess of magnesium, was decanted from excess of magnesium, and *cis*-bis(triethylphosphine)dimethylplatinum (0·15 g.) was added. A white precipitate was formed rapidly. After 1 hr. at 20° the mixture was poured on ice and dilute hydrochloric acid. The ether layer was dried and evaporated. The residue recrystallised from methyl alcohol, giving *trans*-bis(triethylphosphine)di-iodoplatinum (0·11 g.), m. p. 135—136°. Dilution of the mother-liquors with water gave a cream precipitate which, recrystallised from aqueous methyl alcohol, gave *trans*-bis(triethylphosphine)iodo(methyl)platinum, m. p. 70—71°.

Reaction between cis-*Bis*(*triethylphosphine*)*dimethylplatinum and* cis-*Bis*(*triethylphosphine*)*dichloroplatinum.*—A mixture of *cis*-bis(triethylphosphine)dimethylplatinum (0·461 g., 0·001 mole) and *cis*-bis(triethylphosphine)dichloroplatinum (0·502 g., 0·001 mole) was heated under reflux in benzene (10 c.c.) for 12 min. The pale yellow solution was evaporated to dryness and the residue extracted with hot light petroleum (b. p. 80—100°). The undissolved residue (small) was unchanged *cis*-bis(triethylphosphine)dichloroplatinum. The petroleum extract, on cooling to 0°, deposited *trans*-bis(triethylphosphine)dichloroplatinum (0·22 g.). The mother-liquors on evaporation under reduced pressure gave a mixture of colourless needles and colourless prisms which were separated by hand-picking and shown to be *trans*-bis(triethylphosphine)chloro(methyl)platinum, m. p. 93—98°, and *cis*-bis(triethylphosphine)dimethylplatinum, m. p. 78—81°, respectively.

TABLE 2. *Dipole moments of methylplatinum complexes in benzene at 25°*

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$_{T}P$	$_{E}P$	$_{O}P$	$\mu(\pm 0{\cdot}1\,D)$
cis-$(PEt_3)_2PtMe_2$							
5·422	7·562	—	—	—	—	—	—
6·133	7·558	—	—	—	—	—	—
6·461	7·521	—	—	—	—	—	—
25·10	—	—	0·466	—	—	—	—
33·96	—	—	0·477	—	—	—	—
42·00	—	4·143	—	—	—	—	—
63·39	—	4·297	—	741·10	93·71	633·33	5·55
trans-$(PEt_3)_2PtMeI$							
2·851	3·521	—	—	—	—	—	—
3·462	3·509	—	—	—	—	—	—
4·085	3·551	—	—	—	—	—	—
24·63	—	—	0·601	—	—	—	—
34·92	—	—	0·624	—	—	—	—
24·92	—	5·899	—	—	—	—	—
38·95	—	5·912	—	—	—	—	—
55·51	—	5·912	—	—	—	—	—
73·73	—	5·934	—	472·28	109·36	346·52	4·1
trans-$(PEt_3)_2PtMeBr$							
2·525	3·103	—	—	—	—	—	—
—	—	—	(0·57)	398 *	(101)	282 *	3·7 *
trans-$(PEt_3)_2PtMeCl$							
5·610	2·947	—	—	—	—	—	—
5·352	2·865	—	—	—	—	—	—
1·673	2·904	—	—	—	—	—	—
16·79	—	—	0·524	—	—	—	—
15·78	—	—	0·532	—	—	—	—
21·92	—	3·963	—	—	—	—	—
52·83	—	4·154	—	—	—	—	—
61·66	—	4·002	—	352·50	98·46	239·06	3·4
cis-$(PEt_3)_2PtMeCl$							
3·792	16·264	—	—	—	—	—	—
4·513	16·157	—	—	—	—	—	—
5·621	16·233	—	(0·53)	1561 *	(98)	1447 *	8·4 *
trans-$(PEt_3)_2Pt(Me)SCN$							
2·660	9·941	—	—	—	—	—	—
6·745	—	—	0·474	—	—	—	—
14·77	—	6·107	—	—	—	—	—
29·61	—	6·220	—	1045·86	117·24	911·03	6·65
trans-$(PEt_3)_2Pt(Me)NO_3$							
6·926	7·940	—	(0·48)	862 *	(101)	745 *	6·05 *
trans-$(PPr^n_3)_2PtMeI$							
3·657	2·993	—	(0·650)	468 *	(137)	310 *	3·9 *
cis-$(PPh_3)_2PtMe_2$							
2·919	4·770	—	—	—	—	—	—
4·321	4·877	—	—	—	—	—	—
5·252	4·832	—	—	—	—	—	—
7·866	—	—	0·509	—	—	—	—
8·743	—	—	0·515	—	—	—	—
12·88	—	11·89	—	—	—	—	—
13·00	—	12·03	—	823·45	190·88	603·94	5·45
trans-$(PPh_3)_2Pt(Me)SCN$							
2·141	6·420	—	(0·52)	1108 *	(208)	869 *	6·5 *
$(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)PtMe_2$							
7·979	11·316	—	—	—	—	—	—
8·491	11·377	—	—	—	—	—	—
8·955	11·410	—	(0·47)	1011 *	(82)	916 *	6·7 *
$(PEt_3)_2PtMe_2I_2$							
5·964	5·643	—	—	—	—	—	—
6·016	5·619	—	—	—	—	—	—
6·629	5·570	—	—	—	—	—	—
7·766	5·651	—	—	—	—	—	—
12·14	—	—	0·675	—	—	—	—
38·49	—	—	0·665	—	—	—	—
24·62	—	9·037	—	—	—	—	—
30·74	—	9·007	—	858·92	136·76	701·65	5·85
$(PEt_3)_2PtMe_2Cl_2$							
5·399	6·040	—	(0·58)	696 *	(110)	569 *	5·3 *
$(PPr^n_3)_2PtMe_2I_2$							
3·909	4·928	—	(0·69)	851 *	(165)	686 *	5·8 *
$(EtS{\cdot}CH_2{\cdot}CH_2{\cdot}SEt)PtMe_2$							
4·568	14·739	—	(0·57)	1107 *	(61)	1037 *	7·1 *

* Calculated by using estimated values of densities and refractivities. Estimated values are given in parentheses. Those of $-\Delta v/\omega$ are needed only approximately and were estimated from experience of measurements on similar compounds. Those of $_{E}P$ were estimated by using group refractivities (Vogel, *J.*, 1948, 1833 and references therein) and from our measured values for other similar compounds.

Reaction between cis-*Bis(triethylphosphine)dimethylplatinum and* cis-*Bis(triethylphosphine)-dichloroplatinum in the Presence of Dichlorobis(triethylphosphine)-μμ′-dichlorodiplatinum.*—A mixture of *cis*-bis(triethylphosphine)dichloroplatinum (0·460 g.), *cis*-bis(triethylphosphine)-dimethylplatinum (0·461 g.) and dichlorobis(triethylphosphine)-μμ′-dichlorodiplatinum (0·020 g.) was heated under reflux in benzene (15 c.c.) for 30 min. A pale brown solution was formed which, on cooling, deposited unchanged *cis*-bis(triethylphosphine)dichloroplatinum (0·35 g.), m. p. 185—191°. The mother-liquors were evaporated to dryness and the residue was extracted with boiling light petroleum (b. p. $<40°$). This extract on evaporation gave a mixture of needles and prisms (0·35 g.), m. p. 60—78°, from which *cis*-bis(triethylphosphine)-dimethylplatinum was isolated by repeated recrystallisation from light petroleum (b. p. 40—60°) [*trans*-bis(triethylphosphine)chloro(methyl)platinum was also probably present]. The residue from the light petroleum (b. p. $<40°$) extraction was re-extracted with light petroleum (b. p. 60—100°), leaving a small residue of *cis*-bis(triethylphosphine)dichloroplatinum. The petroleum (b. p. 60—100°) extract, on cooling to 0°, deposited *cis*-bis(triethylphosphine)chloro(methyl)-platinum (0·008 g.), m. p. and mixed m. p. 110—113° (decomp.).

Addition Reactions.—(1) *Methyl iodide to bis(trialkylphosphine)iodo(methyl)platinum. trans-*Bis(triethylphosphine)iodo(methyl)platinum (2·00 g.) was heated with methyl iodide (10 c.c.) in a sealed tube at 100° for 1 hr. Evaporation of the methyl iodide and recrystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave bis(triethylphosphine)di-iodo-(dimethyl)platinum [$(PEt_3)_2PtMe_2I_2$] (1·65 g.) as colourless needles (Found: C, 23·65; H, 5·1. $C_{14}H_{36}I_2Pt$ requires C, 23·5; H, 5·05%). After this compound had been heated for 3 hr. at 80°/0·01 mm., *trans*-bis(triethylphosphine)iodo(methyl)platinum, m. p. 70—71° was recovered quantitatively.

*Bis(tri-*n*-propylphosphine)di-iodo(dimethyl)platinum* [$(PPr_3)_2PtMe_2I_2$] was similarly prepared from *trans*-bis(tripropylphosphine)iodo(methyl)platinum in 69% yield as colourless needles from light petroleum (b. p. 80—100°) (Found: C, 30·4, 30·4; H, 6·0, 5·7. $C_{20}H_{48}I_2P_2Pt$ requires C 30·0; H, 6·1%).

(2) *Chlorine to* cis-*bis(triethylphosphine)dimethylplatinum* The complex (0·461 g., 0·001 mole) in benzene (5 c.c.) was treated with a solution of chlorine (0·071 g., 0·001 mole) in carbon tetrachloride (2·3 c.c.). The solution was evaporated to dryness and the residue recrystallised from methyl alcohol and then light petroleum (b. p. 80—100°), giving *bis(triethylphosphine)-dichloro(dimethyl)platinum* [$(PEt_3)_2PtMe_2Cl_2$] (0·32 g.) as colourless plates (Found: C, 31·7; H, 6·8; Cl, 12·8. $C_{14}H_{36}Cl_2P_2Pt$ requires C, 31·6; H, 6·8; Cl, 13·3%).

Action of Iodine on Bis(triethylphosphine)di-iodo(dimethyl)platinum.—The di-iodo-complex (0·238 g.) was treated in benzene (15 c.c.) with iodine (0·086 g.) in benzene (10 c.c.). The colour persisted for 1 hr. but disappeared after 15 min. under reflux. Removal of the benzene under reduced pressure and crystallisation of the residue from methyl alcohol gave bis(triethyl-phosphine)di-iodoplatinum (0·23 g.), m. p. 135—137°.

Determination of Dipole Moments.—Dielectric constants (ε) were measured with a heterodyne beat capacity meter based on that of Hill and Sutton,[22] and a glass cell, of about 9 c.c. liquid capacity and 33·52 μμF electrical capacity, based on that manufactured by Kipp of Delft. The refractive indices (n) were determined with a Pulfrich refractometer and specific volumes (v) with the usual U -shaped pyknometer. The dipole moments were evaluated by the method of Everard, Hill, and Sutton.[23] It was assumed, however, that the atom polarisation (${}_{\mathrm{A}}P$) is equal to 15% of the electron polarisation (${}_{\mathrm{E}}P$) and that ${}_{\mathrm{E}}P$ is equal to the molar refractivity for the red helium line (6678·1 Å). The measurements are recorded in Table 2. ω is the weight fraction of solute, $\Delta\varepsilon = \varepsilon_S - \varepsilon_B$, where ε_S = dielectric constant of solution, ε_B = dielectric constant of benzene, and similarly for Δn and Δv. Measurements refer to benzene solution at 25°. The value ε_B 2·2727 was used to calibrate the capacity meter.[24]

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[22] Cf. Everard and Sutton, *J.*, 1949, 2313.

[23] Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417.

[24] Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, *A*, **123**, 683.