

808. Alkyls and Aryls of Transition Metals. Part II.¹ Platinum(II) Derivatives.*

By J. CHATT and B. L. SHAW.

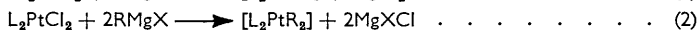
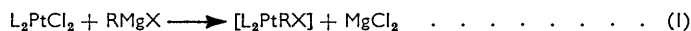
Series of organoplatinum derivatives of the types $[L_2PtRX]$ and $[L_2PtR_2]$ have been prepared, where L is a tertiary phosphine or arsine, and R an aliphatic, aromatic, ethynyl, or substituted ethynyl group. They are stable to moist air and dilute acids, and generally their stabilities increase in the order of $R = C\equiv CH < \text{alkyl} < \text{phenyl} \sim p\text{-substituted phenyl} < C\equiv CPh < o\text{-substituted phenyl}$. The longer-chain alkyl groups and benzyl form less stable complexes than methyl, as is usual in organometallic compounds. The only dialkyl derivatives, $[L_2PtR_2]$, obtained have a *cis*-configuration, whatever the configuration of the starting material. Aryl radicals form both *cis*- and *trans*-compounds, and the acetylides only *trans*- $[L_2Pt(C\equiv CR)_2]$. Cleavage of the organic radicals by dry hydrogen chloride occurs one at a time from the dialkyl- and diaryl-platinum derivatives.

Other reactions of these compounds are described, and also the preparation of the first recorded aryl derivatives of platinum(IV), *viz.*, $(PEt_3)_2PtPh_2Cl_2$ and $(PEt_3)_2PtPh_2I_2$.

The dipole moments of the organoplatinum complexes are determined and a few anomalies discussed in terms of π -bonding between the platinum atom and the aryl groups.

TRIMETHYLPLATINUM IODIDE, $(Me_3PtI)_4$, was one of the first of the very few alkyl derivatives of the transition metals to be described, and it is also one of the most stable.^{2,3} It is therefore surprising that no ethyl or phenyl derivative is known, and that attempts to isolate them have failed.^{4,5} In Part I¹ we described the preparation and properties of a new series of very stable complex compounds derived from the unknown dimethylplatinum(II), Me_2Pt , and methylplatinum(II) halides, $MePtX$ ($X = \text{halogen}$). These are of the types *cis*- $[(PR'_3)_2PtMe_2]$ and *cis*- and *trans*- $[(PR'_3)_2PtMeX]$ ($R = \text{organic radical}$). *trans*- $[(PR'_3)_2PtMe_2]$ was much less stable. In view of the unique stability of the platinum(IV) methyl derivative mentioned above, it was of interest to see whether other organic groups could be introduced in place of the methyl groups in this series of organoplatinum(II) complexes, and our investigation of this is now reported.

We successfully introduced a range of hydrocarbon radicals, R, by the general reactions (1) and (2):



In these equations, L is a tertiary phosphine or arsine; lithio- or sodio-derivatives of the hydrocarbon radical, R, might be used instead of the Grignard reagent. The reactions were performed in ether, ether-benzene, or other appropriate solvent, the product was hydrolysed with dilute hydrochloric acid, and the organometallic complex isolated from the organic layer. Triphenylmethylsodium, cyclohexylmagnesium bromide, and cyclopentadienylsodium failed to give stable organoplatinum complexes. All other radicals, R, which we tried, gave organoplatinum(II) complexes, which are colourless, stable in the

* 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 Part I, Chatt and Shaw, *J.*, 1959, 705.

² Pope and Peachy, *Proc. Chem. Soc.*, 1907, **23**, 86; *J.*, 1909, **95**, 571.

³ Cotton, *Chem. Reviews*, 1955, **55**, 551.

⁴ Foss, personal communication.

⁵ Gilman and Lichtenwalter, *J. Amer. Chem. Soc.*, 1939, **61**, 957.

presence of air, moisture, and cold dilute acids, soluble to varying degrees in organic solvents, and non-electrolytes in nitrobenzene solution.

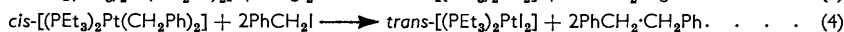
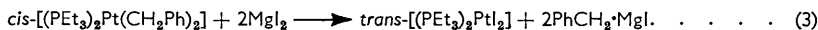
Since the courses of the above reactions depend to some extent on the nature of the radicals, R, *i.e.*, whether they be alkyl, aryl, or ethynyl, it is convenient to describe these three types of organoplatinum(II) complex separately.

Alkyl and Benzyl Derivatives, $cis\text{-}[L_2PtAlk_2]$, $trans\text{-}[L_2Pt(Alk)X]$, and their Benzyl Analogues.—Since the methylplatinum complexes have been extensively investigated,¹ complexes of the other alkyls were investigated only cursorily. As in the preparation of the corresponding methyl derivatives, the product of reaction (1) has a *trans*-configuration and that of reaction (2) a *cis*-configuration, whatever the configuration of the starting material. Nevertheless, it is best to prepare $cis\text{-}[L_2Pt(Alk)_2]$ from $cis\text{-}[L_2PtCl_2]$ and alkyl-lithium, prepared from the alkyl chloride. $trans\text{-}[L_2PtCl_2]$ is much less reactive, and Grignard reagents tend to give mixtures which are difficult to separate. Complexes were prepared with L = PMe_3 , PEt_3 , and $AsEt_3$ and R = Me, Et, Pr^n , Bu^n , and benzyl. Trimethylphosphine was used in order to promote crystallisability of the higher alkylplatinum complexes. The lowest homologue, $cis\text{-}[(PMe_3)_2PtMe_2]$, is remarkably stable and volatile; it sublimates slowly in air at 110° and atmospheric pressure. The higher homologues and benzyl derivatives of types $cis\text{-}[(PR'_3)_2PtR_2]$ and $trans\text{-}[(PR'_3)_2PtRCl]$, are less stable than the corresponding methyl derivatives.

Cyclohexylmagnesium bromide reacts anomalously with $cis\text{-}[(PEt_3)_2PtCl_2]$ in ether to form $trans\text{-}[(PEt_3)_2PtHBr]$ ⁶ and presumably cyclohexene.

$trans\text{-}[(PPh_3)_2PtMeI]$ was prepared by reaction of methyl iodide on $[(PPh_3)_3Pt]$,¹ but the corresponding reaction with ethyl iodide gave only a poor yield of $trans\text{-}[(PPh_3)_2PtEtI]$, and with benzyl iodide a complex mixture of products was obtained.

The benzyl complexes, $trans\text{-}[(PEt_3)_2Pt(CH_2Ph)Cl]$ and $cis\text{-}[(PEt_3)_2Pt(CH_2Ph)_2]$, differ from their methylplatinum analogues in some of their main reactions. They are more easily formed and more readily destroyed. Thus benzylmagnesium chloride undergoes reaction (2) under conditions where the purely aliphatic Grignard reagents undergo reaction (1), and both benzyl groups are more readily cleaved from the metal by reaction with magnesium iodide in ether [reaction (3)]. Benzyl iodide also cleaves both benzyl groups [reaction (4)]:



The reaction analogous to (4) in the methylplatinum series gives a white mixture, probably of isomeric addition products, $[(PEt_3)_2PtMe_3I]$, but certainly not containing any of the deep yellow di-iodide, $trans\text{-}[(PEt_3)_2PtI_2]$.

In the methyl series, $cis\text{-}[(PEt_3)_2PtMeCl]$ is readily obtained by the reaction of $cis\text{-}[(PEt_3)_2PtMe_2]$ with dry hydrogen chloride in ether. The corresponding reaction in the benzyl series gives a mixture consisting mainly of $trans\text{-}[(PEt_3)_2Pt(CH_2Ph)Cl]$, but containing some *cis*-isomer as indicated by the apparent dipole moment of 4.35 D. However, only the pure *trans*-isomer could be isolated by chromatography.

$trans\text{-}[(AsEt_3)_2Pt(CH_2Ph)Cl]$ is obtained from $cis\text{-}[(AsEt_3)_2PtCl_2]$ under exactly the same conditions as when $cis\text{-}[(PEt_3)_2Pt(CH_2Ph)_2]$ is formed from $cis\text{-}[(PEt_3)_2PtCl_2]$. This may be caused by the greater lability of arsine complexes; the $cis\text{-}[(AsEt_3)_2Pt(CH_2Ph)Cl]$ initially formed might thus isomerise to the less reactive *trans*-isomer before the second chlorine atom can be replaced.

Aryl Derivatives, $cis\text{-}$ and $trans\text{-}[L_2PtAr_2]$, and $cis\text{-}$ and $trans\text{-}[L_2PtArX]$.—The complexes derived from phenyl and *p*-substituted phenyl groups appear to be similar in their properties and only the phenyl derivatives were investigated in any detail. *m*-Substituted phenyl derivatives were not investigated. *o*-Substituted phenyls gave especially stable

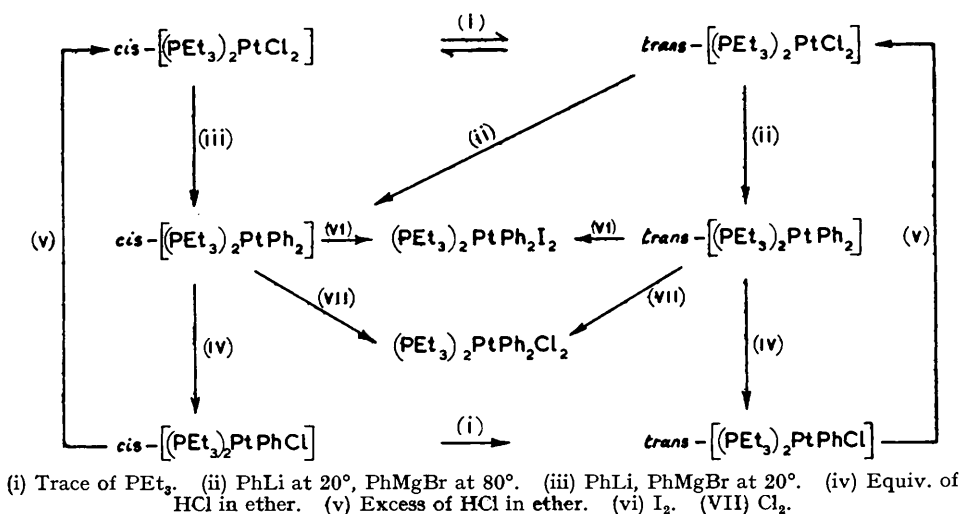
⁶ Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343; *Chem. and Ind.*, 1958, 859.

complexes and were therefore examined more closely than other substituted aromatic derivatives.

In general, the arylplatinum derivatives are more easily prepared and purified, and are more stable than the aliphatic compounds. We would expect the aryl groups to form bonds of partial double-bond character to a platinum(II) atom, and indeed the dipole moments on p. 4026 support the view that there is some double bonding. Such double bonding might account for the greater stability of the arylplatinum complexes and could be due to two causes: (a) increased M-C bond strength due to the addition of a certain amount of π -bonding between the metal and carbon atoms, and (b) increased splitting of the $5d$ -energy levels leading to stabilisation as discussed in Part I.

It is easier to obtain the diarylplatinum derivatives by reaction (2) than the monoaryl platinum derivatives by reaction (1). Reaction (2) occurs most readily with *cis*-[L₂PtCl₂] (at 20°) to give a product of *cis*-configuration. With *trans*-[L₂PtCl₂] the reaction is more sluggish, needing a higher temperature (80°), and the product is a mixture of *cis*- and

FIG. 1. Preparation and reactions of phenylplatinum(II) derivatives.



trans-isomers. Aryl-lithiums react similarly but much more readily than Grignard reagents, and give better yields of the *cis*-isomers from both *cis*- and *trans*-[L₂PtCl₂].

cis- and *trans*-[L₂PtAr₂] are cleaved to the corresponding monoaryl complexes, [L₂PtArCl], by dry hydrogen chloride in ether. This is the best method of preparing the *cis*-monoaryl derivatives, e.g., *cis*-[(PEt₃)₂PtPhCl], from which the *trans*-isomers are best prepared by isomerisation using a trace of the free phosphine.⁷ The *trans*-diaryl complexes are not readily obtained in sufficient quantity to serve as raw materials for the preparation of the *trans*-monoaryl complexes.

Only the complexes having at least one anionic ligand such as [(PR₃)₂PtCl₂] and [(PR₃)₂PtRCl] are isomerised rapidly to the equilibrium mixture of *cis*- and *trans*-isomers by a trace of the free phosphine. The diaryls [(PEt₃)₂PtPh₂] are not isomerised. This points to isomerisation through an ionic intermediate, e.g., [(PR₃)₃PtR]Cl, rather than by the intramolecular rearrangement of a 5- or 6-co-ordinated intermediate, e.g., [(PR₃)₃PtRCl].

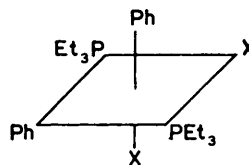
The reactions of the platinum(II) aryls exemplified by the phenyls are summarised in Fig. 1.

In contrast to *cis*-(PEt₃)₂PtMe₂, which loses a methyl group by reaction with one

⁷ Cf. Chatt and Wilkins, *J.*, 1951, 2532.

molecule of iodine, both the *cis*- and the *trans*- $[(\text{PEt}_3)_2\text{PtPh}_2]$ add iodine to give the same stable Pt(IV) derivative $[(\text{PEt}_3)_2\text{PtPh}_2\text{I}_2]$. Chlorine behaves similarly. Thus are formed the first isolable arylplatinum(IV) derivatives. Their configuration, as determined from their dipole moments of 4.95 and 4.25 D, respectively, is shown in Fig. 2. The moments of the possible isomers of $[(\text{PEt}_3)_2\text{Ph}_2\text{Cl}_2]$, estimated as described for the corresponding methyl compounds in Part I, are: (a) 10.7, (b) 9.4, (c) 9.4, (d) 7.2, (e) 0.0, and (f) 3.7 D, where (a), (b), etc., are the configurations shown in Fig. 2 of Part I.¹ The phenylplatinic chloro-complex can only have the configuration (f) (*i.e.*, as in Fig. 2) because no other

FIG. 2. Configuration of the isomer $[(\text{PEt}_3)_2\text{PtPh}_2\text{X}_2]$ (X = Cl, I), obtained by the reaction of the halogen X_2 with either *cis*- or *trans*- $[(\text{PEt}_3)_2\text{PtPh}_2]$



isomer has an estimated moment anywhere near the observed 4.25 D. The correspondence between this and the estimated moment of 3.7 D is reasonable, and the discrepancy is consistent with the expectation that dative π -bonding from the metal to the phenyl groups, which would render the latter more negative, is greater in the platinum than in the platinum series of complexes. The discrepancy might also be caused by different degrees of distortion from the ideally rectilinear arrangement of groups around the platinum atom, in the planar and octahedral complexes, and probably both effects contribute.

The complex iodides have rather higher moments than the corresponding chlorides, except where the halogen atoms are in *trans*-positions, and its moment of 4.95 D leaves little doubt that the $[(\text{PEt}_3)_2\text{PtPh}_2\text{I}_2]$ formed by the addition reaction has the same configuration as the chloride.

Methyl iodide reacts with both *cis*- and *trans*- $[(\text{PEt}_3)_2\text{PtPh}_2]$ to form a mixture of products.

ortho-Substituted Phenyl Derivatives.—The *o*-substituted phenylplatinum derivatives are especially stable, probably because the *ortho*-group hinders the attack of reagents at the platinum atom, and so the reactions of cleavage and decomposition are considerably slower than those of the phenyl and *para*-substituted phenyl complexes. *trans*- $[(\text{PEt}_3)_2\text{Pt}(o\text{-tolyl})_2]$ is also interesting stereochemically. Models show that there is not room for the *o*-tolyl groups to rotate about the Pt-C bonds, but that they are fixed by the bulky phosphine ligands so that the plane of the benzene rings is perpendicular to that containing the platinum atom and its four surrounding ligand atoms. Thus two isomers are possible as in Fig. 3, where the phosphine ligands, which would lie in front of and behind the plane of the paper, have been omitted for clarity. A model also shows that

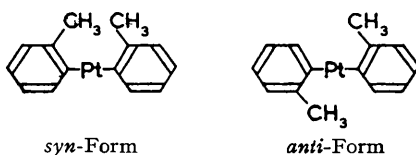


FIG. 3. *syn*- and *anti*-forms of *trans*- $[(\text{PEt}_3)_2\text{Pt}(o\text{-tolyl})_2]$ (the PEt_3 groups have been omitted for clarity and lie above and below the plane of the paper).

there is room for the methyl groups in the *syn*-form. Nevertheless, only one form was obtained, and this is probably the *anti*-form. The dipole moment is not diagnostic in this case, because it is so small that the uncertainty in the atom polarisation introduces a significant error.

Attempts to prepare a dimesityl complex $[(\text{PEt}_3)_2\text{Pt}(\text{mesityl})_2]$ failed, but the monomesityl complex, *cis*- $[(\text{PEt}_3)_2\text{Pt}(\text{mesityl})\text{Br}]$, was easily obtained. A model shows that there is room for the two mesityl groups, and the fact that both *trans*- $[(\text{PEt}_3)_2\text{Ni}(\text{mesityl})_2]$

and *trans*-[(PEt₃)₂Co(mesityl)₂] are stable crystalline substances of planar configuration⁸ is in agreement with this. The kinetic difficulty of introducing the second mesityl group was probably responsible for our not obtaining [(PEt₃)₂Pt(mesityl)₂]. A similar kinetic difficulty may be responsible for our failure to find two forms of *trans*-[(PEt₃)₂Pt(*o*-tolyl)₂], but in this case we have also been unable to obtain two forms of the palladium or nickel analogues.

Ethynyl Derivatives, *trans*-[L₂Pt(C≡CR)₂].—These can be obtained by reaction (2) from the ethynylmagnesium halide in ether but they are most readily prepared by the reaction of the sodium acetylide (RC≡CNa) with [L₂PtCl₂] in liquid ammonia.

They are stable, beautifully crystalline compounds, whose stabilities increase in the order R = H < Me < Ph. The substituted ethynyls have very strong bands in the infrared spectrum at *ca.* 2100 cm.⁻¹, and in [(PEt₃)₂Pt(C≡CH)₂] at 1958 cm.⁻¹, indicating that these organic radicals have retained their triple bonds in the complex.

Styryl and Cyclopentadienyl Derivatives of Platinum(II).—Attempts to prepare styryl derivatives [(PEt₃)₂Pt(CH:CHPh)Br] or [(PEt₃)₂Pt(CH:CHPh)₂] by reactions (1) and (2) respectively led to the formation of *trans,trans*-1,4-diphenylbuta-1,3-diene, *trans*-[(PEt₃)₂PtHBr], and *trans*-[(PEt₃)₂PtBr₂], but no styrylplatinum compounds were found.

The reactions of cyclopentadienylsodium in tetrahydrofuran with *cis*-[(PEt₃)₂PtCl₂] and with the bridged complex [(PEt₃)₂Pt₂Cl₄] caused development of a dark red colour and precipitation of sodium chloride as though a coloured organoplatinum derivative had been formed, but attempts to isolate it led to general decomposition and blackening of the solution. This is surprising in view of the very wide occurrence of stable cyclopentadienyl-metal derivatives and the relatively high stability of complex alkyl and aryl derivatives of platinum(II).

The new organometallic complexes prepared during this investigation are listed in the Table, together with their melting points and electric dipole moments which were used to determine their configurations.

Electric Dipole Moments.—These, together with the moments of the methyl complexes recorded in Part I, show a number of interesting features, some of which must await further experiment for their explanation. Large dipole moments, measured in solution, may be appreciably in error owing to uncertainty in the effects of solvation or in the magnitude of atom polarisation, and to the assumptions made in deriving the equations by which they were calculated. Nevertheless, the differences between the moments of similar compounds appear to be reasonably accurate and here we are concerned only with differences.

Phenyl and Toly Complexes.—The organoplatinum groups lie at the negative end of the dipole as would be expected. This is shown by comparing the moments of the *cis*-ditolyl and *cis*-diphenyl complexes. Thus when the ⁺C_{ar}-CH₃⁻ bond moment opposes the molecular moment expected from this assignment of polarity, as in *cis*-[(PEt₃)₂Pt(*p*-tolyl)₂], the molecular moment (6.75 D) is less than that of the analogous diphenyl complex (7.2 D), and when it reinforces the molecular moment as in *cis*-[(PEt₃)₂Pt(*o*-tolyl)₂], the molecular moment is greater (7.5 D). Quantitatively, if we assume that the Pt-C bonds are at an angle of 90° and that the moment⁹ of toluene is 0.35 D, we can estimate the difference between the moments of *cis*-[(PEt₃)₂PtPh₂] and its *p*-tolyl analogue to be 2 × 0.35 cos 45° = 0.49 D as compared with the observed difference of 0.45 D. Also, on the assumption, in addition, that *cis*-*o*-tolyl groups do not rotate but are fixed in *anti*-configuration, an assumption not altogether justified, the difference between the moments of *cis*-[(PEt₃)₂PtPh₂] and its *o*-tolyl analogue should be 2 × 0.35 cos 60° cos 45° = 0.25 D (observed 0.3 D). These agreements are surprisingly satisfactory in view of the uncertainty in absolute values of the dipole moments involved in the calculations.

⁸ Chatt and Shaw, *Chem. and Ind.*, 1959, 675.

⁹ Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, 1948, p. 36.

Chelate and "Free" Complexes.—The chelate complexes $[\text{C}_2\text{H}_4(\text{PEt}_2)_2\text{PtPh}_2]$ and $[\text{C}_2\text{H}_4(\text{PEt}_2)_2\text{PtMe}_2]$ have moments which are about 1.2 D greater than those of the corresponding complexes of monophosphines, e.g., $[(\text{PEt}_3)_2\text{PtPh}_2]$. This difference is undoubtedly due to the rather smaller P–Pt–P bond angles which must occur in the chelate complex. The dipole moments of complexes containing the strongly dipolar P–Pt bonds must be very sensitive to slight changes in the angles between these bonds.

Phenyl and Methyl Complexes.—It might be expected that the difference between the moments of the Pt–CH₃ and Pt–Ph bonds would be about 0.35 D, the dipole moment of toluene. The observed differences are all greater than this, and the phenyl group appears to carry an appreciably greater negative charge, relative to the methyl group, than would be expected on the basis of their difference in electronegativity.

This is shown most markedly in the comparison of the moments of *cis*- $[(\text{PEt}_3)_2\text{PtPh}_2]$ (7.2 D) and $[\text{C}_2\text{H}_4(\text{PEt}_2)_2\text{PtPh}_2]$ (8.4 D) with those of their dimethylplatinum analogues (5.55 D and 6.7 D, respectively). The differences are about 1.7 D in each case instead of the 0.5 D which would be expected on the basis of the moment of toluene. The unexpectedly large difference between the moments of the corresponding *cis*-diaryl and *cis*-dialkyl complexes such as the phenyl and methyl discussed above might be due to the distortion of the P–Pt–P bond angle and would require the angle to be smaller in the diaryl than in the dialkyl complexes. It would then be a steric effect of the more bulky aryl groups. We do not consider this to be the sole reason for the large difference, even if it contributes to it, because the difference is the same whether we consider the "free" triethylphosphine complexes or the more strained chelate complexes. In our opinion it is more likely that dative π -bonding ($d\pi-p\pi$) from the platinum to the aryl groups is sufficiently strong to account for the greater negative charge they appear to carry. In other words, there is a significant mesomeric drift of *d*-electrons from the platinum atom into the antibonding orbitals of the aromatic system. This explanation would also accord with the discrepancy, noted earlier in this paper, between the observed moments of the diphenyldichloroplatinic complex and that estimated from the observed moments of the pertinent platinumous complexes.

When the moments of the complexes of the type $[\text{L}_2\text{PtRX}]$ are compared, it is again found that arylplatinum groups are rather more negatively charged than would be expected on the basis of the moments of the analogous methylplatinum complexes, but rather less so than would be expected on the basis of the moments of the above diarylplatinum complexes. Thus *trans*- $[(\text{PEt}_3)_2\text{PtPhCl}]$ and its bromo-analogue have moments which are about 0.8 D less than those of their methyl analogues, and *cis*- $[(\text{PEt}_3)_2\text{PtPhCl}]$ and its *o*- and *p*-tolyl analogues have moments 0.65, 0.75, and 0.55 D greater, roughly twice the expected values.

Halide Complexes.—It is apparent from the Table and from the moments of the methylplatinum complexes described in Part I that in an analogous series of halides, where the metal to halogen bonds contribute to the dipole moment, the moment increases along the series $\text{Cl} < \text{Br} < \text{I}$. This is the reverse of the normal sequence which is found in the gaseous hydrogen halides and in carbon-halogen compounds.⁹

This effect might be attributed to (a) increasing dative π -bonding from metal to halogen along the series $\text{Cl} < \text{Br} < \text{I}$, sufficiently strong to overcome and reverse the normal electrostatic effects of decreasing electronegativity, or to (b) increasing steric repulsion of the phosphine groups by the halogen atoms as they increase in size. This repulsion would tend to close the P–Pt–P bond angle slightly, so introducing a strong dipole moment from that atomic grouping. This moment would have its negative end pointing towards the halogen which caused it. Thus the larger halogen atom would appear to be the more negatively charged, provided that the increased polarity caused by the greater distortion of the P–Pt–P bond angle is sufficient to counteract and overcome the electrostatic effect of the lower electronegativity of the larger halogen atom.

At present there is conflicting evidence from infrared data as to whether the heavier

Melting points and dipole moments of complex organometallic compounds of platinum in benzene at 25°.

	$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τP	εP	oP	$\mu \dagger$
<i>cis</i> -[(PMe ₃) ₂ PtMe ₂], m. p. 130—131° (with sublimation)								
	9.122	9.34						
	6.809	9.35						
				(0.47)	740 *	(65)	665 *	5.7 *
<i>cis</i> -[(PMe ₃) ₂ PtEt ₂], m. p. 89—91°								
	5.807	8.534						
	8.641	8.543						
				(0.47)	780 *	(75)	693 *	5.8 *
<i>cis</i> -[(PEt ₃) ₂ PtEt ₂], m. p. 35—36°								
	8.463	6.890						
	7.178	6.853						
				(0.47)	732 *	(103)	614 *	5.5 *
<i>trans</i> -[(PEt ₃) ₂ PtEtCl], m. p. 53—55°								
	7.07	2.798						
	4.91	2.795						
				(0.53)	399 *	(105)	278 *	3.7 *
<i>trans</i> -[(PEt ₃) ₂ PtEtI], m. p. 75—77°								
	4.72	3.533						
	7.48	3.519						
				(0.61)	484 *	(114)	353 *	4.15 *
<i>trans</i> -[(PPh ₃) ₂ PtEtI], m. p. 257—262° (d.) §								
	4.653	2.839						
				(0.58)	615 *	(211)	372 *	4.25 *
<i>trans</i> -[(PPh ₃) ₂ PtEt(SCN)], m. p. 235—243 (d.)								
								(μ not measured)
<i>cis</i> -[(PMe ₃) ₂ PtPr ⁿ ₂], m. p. 95—97°								
	7.002	8.231						
	5.157	8.166						
				(0.47)	757 *	(85)	659 *	5.7 *
<i>cis</i> -[(PMe ₃) ₂ PtBu ⁿ ₂], m. p. 37—39°								
	4.829	7.68						
				(0.47)	761 *	(95)	652 *	5.65 *
<i>cis</i> -[(PEt ₃) ₂ Pt(CH ₂ Ph) ₂], m. p. 103—104°								
	5.406	8.374						
	5.447	8.270						
	5.183	8.200						
				(0.46)	1083 *	(143)	919 *	6.7 *
<i>trans</i> -[(PEt ₃) ₂ Pt(CH ₂ Ph)Cl], m. p. 81—83°								
	5.498	1.984						
				(0.56)	306 *	(123)	164 *	2.8 *
<i>trans</i> -(AsEt ₃) ₂ Pt(CH ₂ Ph)Cl], m. p. 72—73.5°								
	4.59	1.768						
	5.49	1.749						
				(0.56)	327 *	(143)	162 *	2.8 *
<i>cis</i> -[(PEt ₃) ₂ PtPh ₂], m. p. 151—154° (d.)								
	6.863	9.975						
	7.962	10.05						
	2.83	10.12						
	18.53							0.464
	20.18							0.456
	29.89		6.88					
	15.22		6.66		1229	139.7	1070	7.2
<i>trans</i> -[(PEt ₃) ₂ PtPh ₂], m. p. 176—180°								
	10.08	0.341						
	8.288	0.305						
	8.233	0.342						
	25.73							0.433
	16.95							0.431
	56.22		6.41					
	28.55		6.41		160.1	142.0	—3	~0

TABLE. (Continued.)

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^3\Delta n/\omega$	$-\Delta\nu/\omega$	τP	εP	σP	$\mu \dagger$
<i>cis</i> -[(PEt ₃) ₂ PtPhCl], m. p. 133—136° (d.)							
2·279	16·57						
2·392	16·78						
			(0·56)	1804 *	(106)	1682 *	9·05 *
<i>trans</i> -[(PEt ₃) ₂ PtPhCl], m. p. 105—107°							
5·020	1·532						
8·272	1·592						
5·285			0·568				
5·402			0·555				
22·34		3·66 ‡					
31·21		4·07 ‡		258·4	106	137·1	2·6
<i>cis</i> -[(PPh ₃) ₂ PtPh ₂], m. p. 144—160° (d.)							
3·581	6·55						
2·689	6·60						
			(0·43)	1270 *	(237)	997 *	7·0 *
<i>cis</i> -[(AsEt ₃) ₂ PtPh ₂], m. p. 110—111°							
11·48	8·29						
22·13		7·07					
29·48		7·63		(0·46)	1272 *	163 *	1084 *
							7·25 *
<i>trans</i> -[(AsEt ₃) ₂ PtPh ₂], m. p. 138—141°							
8·69	0·331						
			(0·46)	180 *	(163)	—9 *	~0 *
<i>trans</i> -[(AsEt ₃) ₂ PtPhBr], m. p. 91—94°							
5·317	1·723						
			(0·60)	330 *	(134)	176 *	2·9 *
<i>trans</i> -[(AsPr ⁿ) ₂ PtPh ₂], m. p. 130—133°							
6·366	0·273						
5·594	0·275						
			(0·46)	194 *	(163)	6 *	~0 *
<i>cis</i> -[(Et ₂ P·CH ₂ ·CH ₂ ·PEt ₂)PtPh ₂], m. p. 210—215° (d.)							
5·013	14·075						
5·228	14·128						
5·642	14·077						
			(0·46)	1587 *	(129)	1439 *	8·4 *
<i>cis</i> -[(PEt ₃) ₂ Pt(<i>o</i> -tolyl) ₂], m. p. 176—180° (d.)							
2·923	10·273						
2·633	10·251						
			(0·45)	1314 *	(147)	1145 *	7·5 *
<i>trans</i> -[(PEt ₃) ₂ Pt(<i>o</i> -tolyl) ₂], m. p. 192—196°							
4·340	0·342						
10·81	0·319						
7·007			0·442				
4·847			0·448				
24·75		6·18 ‡					
15·09		5·61 ‡		165·8	146·7	0	~0
<i>cis</i> -[(PEt ₃) ₂ Pt(<i>o</i> -tolyl)Cl], m. p. 153—157°							
4·865	16·643						
4·754	16·693						
			(0·55)	1852 *	(111)	1724 *	9·15 *
<i>cis</i> -[(PEt ₃) ₂ Pt(<i>p</i> -tolyl) ₂], m. p. 149—153° (d.)							
6·384	8·410						
6·861	8·385						
			(0·45)	1098 *	(147)	929 *	6·75 *
<i>cis</i> -[(PEt ₃) ₂ Pt(<i>p</i> -tolyl)Cl], m. p. 130—138 (d.)							
5·613	15·797						
5·660	15·765						
			(0·55)	1758 *	(111)	1630 *	8·95 *

TABLE. (Continued.)

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τ^P	ϵ^P	σ^P	$\mu \dagger$
<i>cis</i> -[(PEt ₃) ₂ Pt(mesityl)Br], m. p. 182—185°							
5.435	14.90						
6.526	14.92		(0.60)	1872 *	(128)	1725 *	9.15 *
<i>trans</i> -[(PEt ₃) ₂ Pt(<i>p</i> -chlorophenyl) ₂], m. p. 228—230°							
7.031	0.461						
6.318	0.450		(0.52)	178 *	(149)	6 *	~0 *
<i>trans</i> -[(PEt ₃) ₂ Pt(C≡CH) ₂], m. p. 62—63°							
4.175	0.596		(0.47)	151 *	(121)	11 *	0.7 *
<i>trans</i> -[(PEt ₃) ₂ Pt(C≡CMe) ₂], m. p. 93—95.5°							
(μ not measured)							
<i>trans</i> -[(PEt ₃) ₂ Pt(C≡CPh) ₂], m. p. 186—187° (d.)							
7.442	0.613						
7.374	0.677						
28.4		11.2					
26.8		10.4	(0.45)	209 *	169 *	15 *	0.9 *
<i>trans</i> -[(AsEt ₃) ₂ Pt(C≡CPh) ₂], m. p. 178—181° (d.)							
4.396	0.758		(0.45)	252 *	(190)	34 *	1.3 *
[(PEt ₃) ₂ PtPh ₂ Cl ₂], m. p. 153—155°							
5.840	3.467						
7.158	3.462						
4.500			0.456				
6.316			0.523				
17.85		9.46					
14.41		9.72		557	161	372	4.25
[(PEt ₃) ₂ PtPh ₂ I ₂], m. p. 149—152°							
8.978	3.676						
5.849	3.645						
5.927	3.705						
4.865			0.583				
13.81		11.8					
14.19		11.7		722	194	499	4.95

* 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 ϵ^P were estimated by using group refractivities (Vogel, *J.*, 1948, 1833, and references therein) and from our measured values for other similar compounds.

† For moments greater than *ca.* 4 D the margin of error is probably <0.1 D and is partly determined by the uncertainty in the atom polarisation, which may be up to 20% of the electron polarisation in complex compounds (the above values were calculated assuming it to be 15%). Similarly, the moments between 2.5 and 4 D will be in error by <0.2 D. The three complex acetylides appear to have small moments but, because the atom polarisation is difficult to estimate, the values of such moments are uncertain. It appears that either the atom polarisation is larger than usual in these compounds, or that a small amount of the *cis*- exists in equilibrium with the *trans*-isomer in solution.

‡ Molar refractivity for the yellow helium line (λ 5876.6 Å); the remainder are for the red helium line (λ 6678.1 Å).

§ (d.) = With decomposition.

halogens in platinous complexes carry a greater or lesser negative charge than chlorine,¹⁰ and it is useless to speculate at this stage which of the above effects is mainly responsible for the anomalous sequence of increasing dipole moment with decreasing electronegativity of the halogen in complex organoplatinum halides.

¹⁰ Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

EXPERIMENTAL

(Microanalyses are by Messrs. W. Brown and A. G. Olney, and Miss S. J. Lathwell, of these laboratories.)

The complexes $[(PR_3)_2PtCl_2]$ and $[(AsEt_3)_2PtCl_2]$ were prepared by reaction of the phosphine or arsine with K_2PtCl_4 ,^{7,11} and are described in Gmelin's "Handbuch."¹² Spence Grade "H" alumina was used for chromatography. The m. p.s were determined on a Kofler hot-stage and are corrected. Reactions involving organo-lithium and -magnesium compounds were carried out in an atmosphere of nitrogen.

Preparation of Platinous Alkyls.—(1) *Platinous dialkyls: General method.* The finely divided platinous chloride complex, $[L_2PtCl_2]$ (ca. 2 g.; *cis*-isomer), suspended in dry benzene, was treated with an ether solution of the alkyl-lithium (10% excess; prepared from the alkyl chloride) at 20°. After 15 min., light petroleum (10 c.c.; b. p. 60–80°) was added, followed by water. The crude product isolated from the organic layer was purified by crystallisation. Prepared in this manner were: *cis-bis(trimethylphosphine)dimethylplatinum*, plates from light petroleum (b. p. 60–80°) (yield 62%) (Found: C, 25.65; H, 6.3. $C_6H_{14}P_2Pt$ requires C, 25.45; H, 6.4%); *cis-bis(trimethylphosphine)diethylplatinum*, prisms from light petroleum (b. p. 40–60°) (yield 41%) (Found: C, 29.95; H, 7.0. $C_{10}H_{28}P_2Pt$ requires C, 29.65; H, 6.95%); *cis-bis(triethylphosphine)diethylplatinum*, plates from methyl alcohol (yield 73%) (Found: C, 39.75; H, 8.25. $C_{16}H_{40}P_2Pt$ requires C, 39.25; H, 8.25%); *cis-bis(trimethylphosphine)di-n-propylplatinum*, prisms from light petroleum (b. p. 40–60°) (yield 75%) (Found: C, 33.3; H, 7.55. $C_{12}H_{32}P_2Pt$ requires C, 33.25; H, 7.45%); *cis-bis(trimethylphosphine)di-n-butylplatinum*, large prisms from light petroleum (b. p. 30–40°) on cooling the solution to –10° (yield 40%) (Found: C, 36.3; H, 8.0. $C_{14}H_{36}P_2Pt$ requires C, 36.45; H, 7.85%).

(2) *trans-Bis(triethylphosphine)chloro(ethyl)platinum*, *trans*- $[(PEt_3)_2PtEtCl]$. Ethylmagnesium chloride was prepared from magnesium (0.24 g.), ether (30 c.c.), a crystal of iodine, and ethyl chloride. A solution of *trans*-bis(triethylphosphine)dichloroplatinum (1.5 g.) in benzene (25 c.c.) was added and, after 45 minutes' stirring at 20°, the reaction mixture was cooled to –10° and hydrolysed with dilute hydrochloric acid. The organic layer was separated and dried ($MgSO_4$), and the crude product obtained on evaporation was chromatographed, elution with ether then giving *trans-bis(triethylphosphine)chloro(ethyl)platinum* (0.23 g.). After one crystallisation from aqueous methyl alcohol and two from light petroleum (b. p. 30–40°) it formed prisms (Found: C, 33.95; H, 7.15. $C_{14}H_{35}ClP_2Pt$ requires C, 33.9; H, 7.1%).

(3) *trans-Bis(triethylphosphine)iido(ethyl)platinum*, *trans*- $[(PEt_3)_2PtEtI]$. Ethylmagnesium iodide was prepared from magnesium (0.48 g.), ether (15 c.c.), and ethyl iodide (3.5 g.). *cis*-Bis(triethylphosphine)dichloroplatinum (1.5 g.) was added and, after 1½ hours' stirring, hydrolysis with ice and hydrochloric acid gave *trans-bis(triethylphosphine)iido(ethyl)platinum* (0.65 g.) as prisms from methyl alcohol (Found: C, 28.8; H, 6.1. $C_{14}H_{35}IP_2Pt$ requires C, 28.6; H, 6.0%).

(4) *trans-Bis(triphenylphosphine)iido(ethyl)platinum*, *trans*- $[(PPh_3)_2PtEtI]$. Tris(triphenylphosphine)platinum (0.70 g., see Malatesta and Cariello¹³) was dissolved in ethyl iodide (10 c.c.). After 1 hr. the product was isolated by evaporation, digestion with methyl alcohol, and crystallisation from benzene, giving slightly impure *trans-bis(triphenylphosphine)iido(ethyl)platinum* (0.31 g.) as needles (Found: C, 51.4; H, 3.85. $C_{38}H_{35}IP_2Pt$ requires C, 52.1; H, 4.05%). This iodide on treatment with potassium thiocyanate in acetone gave the corresponding thiocyanate as prisms (Found: C, 57.5; H, 4.35; N, 1.85. $C_{39}H_{35}NSP_2Pt$ requires C, 58.05; H, 4.35; N, 1.75%).

(5) *cis-Bis(triethylphosphine)dibenzylplatinum*, *cis*- $[(PEt_3)_2Pt(CH_2Ph)_2]$. Benzylmagnesium chloride was prepared from magnesium (0.96 g.), ether (20 c.c.), and benzyl chloride (5.56 g.). *cis*-Bis(triethylphosphine)dichloroplatinum (2.0 g.) and benzene (10 c.c.) were added and, after 1 hour's stirring, hydrolysis with hydrochloric acid and isolation gave *cis-bis(triethylphosphine)dibenzylplatinum* (1.27 g.) as plates from methyl alcohol (Found: C, 50.95; H, 7.35. $C_{26}H_{44}P_2Pt$ requires C, 50.9; H, 7.25%). Treatment of *trans*-bis(triethylphosphine)dichloroplatinum with benzylmagnesium chloride in benzene at 80° gave the same *cis*-dibenzylplatinum complex together with bibenzyl; even chromatography failed to disclose the presence of the *trans*-isomer.

(6) *trans-Bis(triethylphosphine)chloro(benzyl)platinum*, *trans*- $[(PEt_3)_2Pt(CH_2Ph)Cl]$. To a

¹¹ Jensen, *Z. anorg. Chem.*, 1936, **229**, 237.

¹² Gmelin's "Handbuch," Vol. 68, Part D, pp. 343–350 (1957).

¹³ Malatesta and Cariello, *J.*, 1958, **2323**.

solution of *cis*-bis(triethylphosphine)dibenzylplatinum (2.00 g.) in dry ether (20 c.c.) was added an ethereal solution of hydrogen chloride (22.0 c.c., 0.154N). Almost immediately a precipitate formed, which was collected and recrystallised from benzene–light petroleum (b. p. 60–80°) to give bis(triethylphosphine)chloro(benzyl)platinum (1.52 g., *cis*- and *trans*-mixture). This was chromatographed on alumina (100 g.) and elution with benzene then gave the pure *trans*-isomer as prisms (1.02 g.), m. p. 81–83°, from light petroleum (b. p. 40–60°) (Found: C, 41.1; H, 6.9. $C_{18}H_{37}ClPt$ requires C, 40.9; H, 6.7%).

(7) *trans*-Bis(triethylarsine)chloro(benzyl)platinum, *trans*-[(AsEt₃)₂Pt(CH₂Ph)Cl]. Benzylmagnesium chloride was prepared from magnesium (0.24 g.), ether (20 c.c.), and benzyl chloride (1.39 g.). Benzene (10 c.c.) and *cis*-bis(triethylarsine)dichloroplatinum (1.0 g.) were added and, after 1 hour's stirring at 20°, hydrolysis with dilute hydrochloric acid and isolation gave a crude product. The latter was chromatographed on alumina; elution with light petroleum (b. p. 40–60°) then gave bibenzyl and elution with ether gave *trans*-bis(triethylarsine)chloro(benzyl)platinum as cream plates (0.38 g.) from light petroleum (b. p. 60–80°) (Found: C, 35.45; H, 5.8. $C_{18}H_{37}ClAs_2Pt$ requires C, 35.35; H, 5.8%).

Fission of cis-Bis(triethylphosphine)dibenzylplatinum by Magnesium Iodide.—To a solution of magnesium iodide, prepared from iodine (0.60 g.), ether (15 c.c.), and excess of magnesium, was added *cis*-bis(triethylphosphine)dibenzylplatinum (0.20 g.); the mixture was then put aside for 1 hr. Hydrolysis with ice and hydrochloric acid and isolation gave *trans*-bis(triethylphosphine)di-iodoplatinum (0.18 g.) as yellow needles, m. p. 136–137°, from ethyl alcohol (Found: C, 20.7; H, 4.25. Calc. for $C_{12}H_{30}I_2Pt$: C, 21.0; H, 4.4%).

Reaction between cis-Bis(triethylphosphine)dibenzylplatinum and Benzyl Iodide.—A mixture of benzyl iodide (0.34 g.) and *cis*-bis(triethylphosphine)dibenzylplatinum (0.55 g.) was heated at 100–120° for 15 min., cooled, and extracted with hot methyl alcohol. The extract was evaporated, and the residue distilled in a short-path still at 20 mm. (heating with a free flame). Bibenzyl, m. p. 49–52°, distilled first, followed by *trans*-bis(triethylphosphine)di-iodo-platinum; the latter formed yellow needles, m. p. 134–136°, from ethyl alcohol.

Reaction between Cyclohexylmagnesium Bromide and cis-Bis(triethylphosphine)dibromoplatinum.—Cyclohexylmagnesium bromide was prepared from magnesium (0.38 g.), cyclohexyl bromide (2.61 g.), and ether (30 c.c.). *cis*-Bis(triethylphosphine)dibromoplatinum (1.18 g.) was added and, after being stirred for 1 hr. at 20°, the mixture was hydrolysed with dilute hydrochloric acid. The residue obtained by evaporation of the organic layer, on crystallisation from methyl alcohol, gave *trans*-bis(triethylphosphine)bromohydroplatinum (0.23 g.), m. p. 89–91°, identical with an authentic sample.⁶

Preparation of cis-Diaryplatinum Derivatives by using Arylmagnesium Bromides; General Method.—The platinous chloride complex (*cis*-isomer) was added to a solution of the arylmagnesium bromide (100% excess) in ether–benzene. After being stirred for 1–1½ hr. at 20° the reaction mixture was cooled to 0° and hydrolysed with dilute hydrochloric acid. The organic layer was separated, dried (MgSO₄), and evaporated to dryness, and the residue purified by chromatography and/or crystallisation. Prepared in this manner were: *cis*-bis(triethylphosphine)diphenylplatinum, which was eluted from alumina by light petroleum (b. p. 40–60°) containing ether (5%) and formed needles from light petroleum (b. p. 80–100°) (yield 56%) (Found: C, 49.3; H, 6.85%; *M*, ebullioscopically in 1.5% benzene solution, 536; in 2.29% benzene solution, 570. $C_{24}H_{40}P_2Pt$ requires C, 49.2; H, 6.9%; *M*, 585); *cis*-bis(triphenylphosphine)diphenylplatinum, rhombs from benzene–light petroleum (b. p. 60–80°) (yield 61%) (Found: C, 66.3; H, 4.8. $C_{48}H_{40}P_2Pt$ requires C, 66.0; H, 4.6%).

trans-Bis(triethylphosphine)diphenylplatinum.—Phenylmagnesium bromide was prepared from magnesium (1.3 g.), bromobenzene (8.37 g.), and ether (40 c.c.); benzene (150 c.c.) was added, and most of the ether removed by distillation. After cooling, *trans*-bis(triethylphosphine)dichloroplatinum (3.5 g.) was added, and the mixture heated under reflux for 1 hr., cooled and, after hydrolysis with dilute hydrochloric acid, the crude product was isolated and chromatographed on alumina. Elution with light petroleum (b. p. 60–80°) afforded *trans*-bis(triethylphosphine)diphenylplatinum, which formed prisms (2.30 g.) from ethyl alcohol (Found: C, 49.3; H, 6.9%; *M*, ebullioscopically in 1.51% benzene solution, 538; in 2.54% solution, 566). Elution with ether gave *cis*-bis(triethylphosphine)diphenylplatinum which formed needles (0.23 g.) from methyl alcohol.

Action of Phenyl-lithium on trans-Bis(triethylphosphine)dichloroplatinum.—The *trans*-dichloride [(PEt₃)₂PtCl₂] (3.4 g.), dissolved in benzene (30 c.c.), was treated under nitrogen with

an ethereal solution of phenyl-lithium (20 c.c., 0.756N). After 15 min. water was added, and the crude product isolated and chromatographed on alumina, as described above for the corresponding Grignard reaction. In this way *trans* (0.55 g.)- and *cis* (1.29 g.)-bis(triethylphosphine)-diphenylplatinum were isolated.

cis-Bis(triethylphosphine)chloro(phenyl)platinum, *cis*-[(PEt₃)₂PtPhCl].—*cis*-Bis(triethylphosphine)diphenylplatinum (1.11 g.) in benzene (15 c.c.) was treated with an ethereal solution of dry hydrogen chloride (5 c.c., 0.41N). After 15 min. the solution was evaporated to dryness, and the residue recrystallised from light petroleum (b. p. 80—100°) to give *cis*-bis(triethylphosphine)chloro(phenyl)platinum (0.76 g.) as glistening needles (Found: C, 39.95; H, 6.45. C₁₈H₃₅ClP₂Pt requires C, 39.75; H, 6.5%). With an excess of dry hydrogen chloride under similar conditions *cis*-bis(triethylphosphine)diphenylplatinum gave an almost quantitative yield of *cis*-bis(triethylphosphine)dichloro(phenyl)platinum.

trans-Bis(triethylphosphine)chloro(phenyl)platinum.—Dry hydrogen chloride was passed into a solution of *trans*-bis(triethylphosphine)diphenylplatinum (0.50 g.) in benzene (10 c.c.) for 1 min. The residue obtained on evaporation was recrystallised from light petroleum (b. p. 60—80°) to give *trans*-bis(triethylphosphine)chloro(phenyl)platinum as prisms (0.38 g.) (Found: C, 39.7; H, 6.5. C₁₈H₃₅ClP₂Pt requires C, 39.75; H, 6.5%).

Isomerisation of cis- to trans-Bis(triethylphosphine)chloro(phenyl)platinum.—The *cis*-isomer (0.202 g.) was suspended in light petroleum (5 c.c., b. p. 60—80°) and triethylphosphine (0.05 c.c.) was added. After being heated to boiling, the solution was evaporated under reduced pressure, and the excess of triethylphosphine allowed to oxidise in air. Crystallisation of the residue from methyl alcohol afforded the *trans*-isomer as prisms (0.171 g.), m. p. 105—107°.

Addition Reactions.—(1) *Chlorine to cis-bis(triethylphosphine)diphenylplatinum.* The *cis*-platinum diphenyl complex (1.17 g.) in carbon tetrachloride was treated with a solution of chlorine in carbon tetrachloride (4 c.c., 0.50M). After 15 min. at 20° the solution was evaporated to dryness, and the residue recrystallised from light petroleum (b. p. 60—80°)—benzene, giving *bis*(triethylphosphine)dichloro(diphenyl)platinum (0.87 g.) as prisms (Found: C, 43.95; H, 6.15. C₂₄H₄₀Cl₂P₂Pt requires C, 43.9; H, 6.15%).

(2) *Chlorine to trans-bis(triethylphosphine)diphenylplatinum.* The *trans*-platinum diphenyl complex on similar treatment with chlorine (1 mol.) in carbon tetrachloride gave the same *bis*(triethylphosphine)dichloro(diphenyl)platinum as above (Found: C, 44.1; H, 6.2%).

(3) *Iodine to cis-bis(triethylphosphine)diphenylplatinum.* The latter (0.264 g.) in benzene (15 c.c.) was treated with a solution of iodine (0.113 g.) in benzene (10 c.c.). The colour of the iodine disappeared very rapidly. Evaporation and crystallisation of the residue from light petroleum (b. p. 80—100°) and then ethyl alcohol gave *bis*(triethylphosphine)di-iodo(diphenyl)platinum (0.29 g.) as yellow prisms (Found: C, 34.4; H, 4.8%; *M*, ebullioscopically in 2% benzene solution, 816; in 3% benzene solution, 808. C₂₄H₄₀I₂P₂Pt requires C, 34.35; H, 4.8%; *M*, 839). Treatment of *trans*-bis(triethylphosphine)diphenylplatinum with iodine under similar conditions gave an identical product to the above.

The Reaction between Phenylmagnesium Bromide and cis-Bis(triethylarsine)dichloro(phenyl)platinum.—*cis*-Bis(triethylarsine)dichloro(phenyl)platinum (1.18 g.) was added to a solution of phenylmagnesium bromide (0.015 mole) in ether (20 c.c.) and benzene (20 c.c.). After 1½ hours' stirring at 20°, hydrolysis with ice and hydrochloric acid and isolation gave a crude product, which was chromatographed on alumina (150 g.). Elution with light petroleum (b. p. 40—60°) gave *trans*-bis(triethylarsine)diphenylplatinum as needles (0.24 g.) from methyl alcohol (Found: C, 42.7; H, 6.0. C₂₄H₄₀As₂Pt requires C, 42.8; H, 6.0%). Elution with light petroleum (b. p. 40—60°) containing ether (2%) afforded *cis*-bis(triethylarsine)diphenylplatinum as prisms (0.42 g.), from light petroleum (b. p. 60—80°) (Found: C, 42.8; H, 6.05%). Elution with ether gave *trans*-bis(triethylarsine)bromo(phenyl)platinum as prisms (0.16 g.) from methyl alcohol (Found: C, 31.85; H, 5.2. C₁₈H₃₅BrAs₂Pt requires C, 31.95; H, 5.2%). Treatment of *trans*-bis(triethylarsine)dichloro(phenyl)platinum (1.00 g.) under similar conditions to the above gave *trans*- (0.20 g.)- and *cis*- (0.60 g.)-bis(triethylarsine)diphenylplatinum and *trans*-bis(triethylarsine)-bromo(phenyl)platinum (0.15 g.).

Bis(tri-n-propylarsine)diphenylplatinum [(AsPr₃)₂PtPh₂].—This was prepared from *trans*-bis(tri-n-propylarsine)dichloro(phenyl)platinum (1.18 g.) and phenylmagnesium bromide, and formed prisms (0.76 g.) from ethyl alcohol (Found: C, 47.3; H, 7.0. C₃₀H₅₂As₂Pt requires C, 47.55; H, 6.9%).

Preparation of cis-Diarylplatinum Derivatives by use of Aryl-lithiums: General Method.—The

finely divided *cis*-platinous chloride complex, suspended in dry benzene, was treated with an ether solution of the aryl-lithium (10% excess) at 20°. After intermittent agitation for 15 min., benzene and water were added and the product was isolated from the organic phase and purified by chromatography and/or crystallisation. Prepared in this manner were: *cis*-bis(triethylphosphine)diphenylplatinum (yield 81%); *cis*-bis(triethylphosphine)*di*-*o*-tolylplatinum, needles from light petroleum (b. p. 80—100°) (yield 72%) (Found: C, 51.1; H, 7.35. $C_{26}H_{44}P_2Pt$ requires C, 50.9; H, 7.25%); *cis*-bis(triethylphosphine)*di*-*p*-tolylplatinum, prisms from methyl alcohol (yield 47%) (Found: C, 50.9; H, 7.35%); and 1,2-bis(diethylphosphino)ethanediphenylplatinum, needles from ethyl alcohol (yield 73%) (Found: C, 47.65; H, 6.35. $C_{22}H_{34}P_2Pt$ requires C, 47.55; H, 6.15%).

cis-Bis(triethylphosphine)chloro-(*o*-tolyl)platinum, *cis*-[(PEt_3)₂Pt(*o*-tolyl)Cl].—Treatment of *cis*-bis(triethylphosphine)*di*-*o*-tolylplatinum with hydrogen chloride (1.2 mol.) in ether–benzene for 1 hr. gave *cis*-bis(triethylphosphine)chloro-(*o*-tolyl)platinum as needles from benzene–light petroleum (b. p. 80—100°) (Found: C, 40.8; H, 6.75. $C_{19}H_{37}ClP_2Pt$ requires C, 40.9; H, 6.7%); yield 66%.

cis-Bis(triethylphosphine)chloro-(*p*-tolyl)platinum, *cis*-[(PEt_3)₂Pt(*p*-tolyl)Cl].—Similarly, fission of *cis*-bis(triethylphosphine)*di*-*p*-tolylplatinum with hydrogen chloride (1.05 mol.) in ether–benzene for ½ hr. afforded *cis*-bis(triethylphosphine)chloro-(*p*-tolyl)platinum as rhombs from benzene–light petroleum (b. p. 80—100°) (Found: C, 41.0; H, 6.75%); yield 67%.

cis-Bis(triethylphosphine)bromo(mesityl)platinum.—Mesitylmagnesium bromide was prepared from magnesium (0.77 g.), 2-bromomesitylene (6.38 g.), and tetrahydrofuran (30 c.c.). *cis*-Bis(triethylphosphine)dichloroplatinum (4.0 g.) and benzene (20 c.c.) were added, and after being stirred for 1 hr. at 20° and heated under reflux for 15 min., the mixture was cooled and hydrolysed with dilute hydrochloric acid. Isolation then gave *cis*-bis(triethylphosphine)bromo(mesityl)platinum (3.7 g.) as matted needles from benzene–light petroleum (b. p. 60—80°) (Found: C, 40.15; H, 6.65. $C_{21}H_{41}BrP_2Pt$ requires C, 40.05; H, 6.55%).

trans-Bis(triethylphosphine)*di*-*p*-chlorophenylplatinum.—This was prepared from *cis*-bis(triethylphosphine)dichloroplatinum and *p*-chlorophenylmagnesium bromide (4 mol.; reaction time 1 hr. at 20° + 15 min. at 80°) and formed prisms from benzene (yield 46%) (Found: C, 44.35; H, 5.9. $C_{24}H_{38}Cl_2P_2Pt$ requires C, 44.05; H, 5.85%).

trans-Bis(triethylphosphine)*di*(phenylethynyl)platinum, *trans*-[(PEt_3)₂Pt(C≡CPh)₂]: *Grignard Method*.—Ethylmagnesium bromide was prepared from ethyl bromide (1.63 g.), magnesium (0.33 g.), and ether (30 c.c.). Phenylacetylene (1.39 g.) and benzene (25 c.c.) were added and the mixture was heated under reflux for 15 min., cooled to 20°, and *cis*-bis(triethylphosphine)*di*-bromoplatinum (2.00 g.) added. After 17 hr. at 20° hydrolysis with ice and hydrochloric acid and isolation afforded *trans*-bis(triethylphosphine)*di*(phenylethynyl)platinum (1.67 g.) as needles, m. p. 186—187°, from light petroleum (b. p. 100—120°) (Found: C, 52.95; H, 6.35. $C_{28}H_{40}P_2Pt$ requires C, 53.05; H, 6.35%). The infrared spectrum (in a Nujol mull) had a strong band at 2100 cm^{-1} (C≡C stretching).

trans-Bis(triethylphosphine)*di*ethynylplatinum, *trans*-[(PEt_3)₂Pt(C≡CH)₂].—A suspension of sodamide was prepared in a small Dewar vessel from sodium (0.46 g.) and liquid ammonia (100 c.c.). An excess of dry acetylene was passed in and then *cis*-bis(triethylphosphine)*di*-chloroplatinum (1.0 g.) was added to the resultant solution of sodium acetylide. After 20 minutes' intermittent stirring, dry ammonium chloride (1.5 g.) was added, the mixture was poured into a beaker, and the ammonia allowed to evaporate. Isolation with ether then gave *trans*-bis(triethylphosphine)*di*ethynylplatinum as needles (0.52 g.) from aqueous methyl alcohol (Found: C, 40.2; H, 6.85. $C_{18}H_{32}P_2Pt$ requires C, 39.9; H, 6.7%). The infrared spectrum in a Nujol mull included strong bands at 3275 (C≡C↔H) and 1958 cm^{-1} (C≡C stretching). Similarly was prepared *trans*-bis(triethylphosphine)*di*propynylplatinum, *trans*-[(PEt_3)₂Pt(C≡CMe)₂], as prisms (Found: C, 42.3; H, 7.1. $C_{18}H_{36}P_2Pt$ requires C, 42.4; H, 7.1%). The infrared spectrum (in Nujol mull) included a strong band at 2124 cm^{-1} (C≡C stretching). *trans*-Bis(triethylphosphine)*di*(phenylethynyl)platinum was also prepared in this way from *trans*-bis(triethylphosphine)*di*-iodoplatinum (88% yield) and from *cis*-bis(triethylphosphine)dichloroplatinum (79% yield).

trans-Bis(triethylarsine)*di*(phenylethynyl)platinum, *trans*-[($AsEt_3$)₂Pt(C≡CPh)₂].—*trans*-Bis(triethylarsine)dichloroplatinum (1.0 g.) in ether (25 c.c.) was added to a solution of sodium phenylacetylide, prepared from sodium (0.46 g.), ammonia (50 c.c.), and phenylacetylene (2.04 g.). The mixture was kept for 10 min., then ammonium chloride (1.5 g.) was added, and

the ammonia allowed to evaporate. Addition of water and benzene to the residue gave a pale, insoluble precipitate which in hot water decomposed to give ammonia, platinum, and phenylacetylene and may have been a salt-like acetylide similar to those prepared by Nast and his co-workers.¹⁴ The benzene-soluble portion, after repeated recrystallisation from light petroleum (b. p. 80—100°) and ethyl alcohol, formed yellow needles (Found: C, 47.35; H, 5.8. $C_{28}H_{40}As_2Pt$ requires C, 46.6; H, 5.6%).

Reaction of β -Styrylmagnesium Bromide with cis-Bis(triethylphosphine)dichloroplatinum.— β -Styrylmagnesium bromide was prepared from magnesium (0.48 g.), β -bromostyrene (3.66 g.), a crystal of iodine, and ether (30 c.c.). Benzene (20 c.c.) and *cis*-bis(triethylphosphine)dichloroplatinum (2.0 g.) were added, and after being stirred for 1 hr. the mixture was hydrolysed with dilute hydrobromic acid, and the crude product isolated in the usual way and chromatographed on alumina. Elution with light petroleum (b. p. 40—60°) gave *trans,trans*-1,4-diphenylbuta-1,3-diene (0.28 g.) as plates, m. p. 150—155°, from methyl alcohol. Elution with light petroleum (b. p. 40—60°) containing ether (20%) gave *trans*-bis(triethylphosphine)bromohydroplatinum which formed prisms (0.24 g.), m. p. 95—97°, from light petroleum (b. p. 40—60°). Styrene and *trans*-bis(triethylphosphine)dibromoplatinum were also isolated from the chromatogram.

Determination of Dipole Moments.—These were determined as described in Part I¹ and are recorded in the Table. The margin of error is discussed in a footnote.

The authors thank Mr. T. Remington and Miss I. Bates for assistance in measuring the dipole moments and Messrs. A. E. Field, C. J. Pembroke, and M. L. Searle for other experimental assistance.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
AKERS RESEARCH LABORATORIES,
THE FRYTHE, WELWYN, HERTS.

[Received, March 16th, 1959.]

¹⁴ Nast, Vester, and Griesshammer, *Chem. Ber.*, 1957, **90**, 2678.
