

### 980. *Hydrido-complexes of Platinum(II).*

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The preparation, properties, and some reactions of a series of hydrido-complexes of the general formula *trans*-[PtHX(PR<sub>3</sub>)<sub>2</sub>] (where X = a univalent anionic ligand, R = alkyl or aryl) are described. These complexes are obtained by reduction of the corresponding *cis*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] complexes by reagents ranging from aqueous hydrazine, through alcoholic potassium hydroxide to lithium aluminium hydride in tetrahydrofuran. An arsenic analogue *trans*-[PtHCl(AsEt<sub>3</sub>)<sub>2</sub>] is also described. Many of these compounds show surprising resistance to thermal decomposition, oxidation, and hydrolysis. Ethylene reacts reversibly with *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] to form *trans*-[PtCl(C<sub>2</sub>H<sub>5</sub>)(PEt<sub>3</sub>)<sub>2</sub>].

IN 1957 we announced the discovery of a stable hydrido-complex of platinum of the formula *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>].<sup>1</sup> This compound was remarkable because, although it contained a transition-metal-hydrogen bond, it was not oxidised by air and was sufficiently stable to be distilled at 130° (bath-temperature)/0.01 mm. Since that time a considerable number

<sup>1</sup> Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343.

of similar hydrido-complexes of Group VIII metals and rhenium, stabilised by tertiary phosphines and arsines, has been reported in a series of short notes,<sup>2-18</sup> but little is known except the compositions of the compounds, the stretching frequencies of the metal-hydrogen bonds as found from the infrared spectra, and the chemical shifts (always large) of the proton magnetic resonances.

Apart from these routinely determined properties it has been shown that the hydrogen atom has a high *trans*-effect in platinum complexes<sup>19</sup> and that the stretching frequency of the Pt-H bond,  $\nu(\text{Pt-H})$  is very sensitive to the nature of the group in *trans*-position to the hydrogen, decreasing with increasing *trans*-effect of that group.<sup>2</sup> The hydrogen has also a very large ligand field strength, as has been demonstrated in certain hydrido-ruthenium complexes.<sup>20</sup> The exact structure of *trans*-[PtHBr(PEt<sub>3</sub>)<sub>2</sub>] has been determined by X-rays:<sup>21</sup> it has an essentially square-planar arrangement of the three heavy ligands about the metal atom, and the hydrogen is assumed to occupy the fourth position. Thus the hydrogen takes the place of any other anionic ligand such as a halogen, but differs from all other monatomic ligands in having a very high *trans*-effect and high ligand field strength.

These hydrides have dipole moments which are large for *trans*-complexes. This charge separation is most reasonably explained by supposing that the halogen in *trans*-position to the hydrogen is more ionic than is usual in platinum(II) complexes and so carries a greater negative charge. This explanation is more reasonable than one which assumes that the hydrogen carries a slight positive charge, since the hydrogen is more hydridic than acidic in character.<sup>22</sup>

In the present paper we present the detailed chemistry of the hydrido-complexes of general formula *trans*-[PtHX(PRR'R'')<sub>2</sub>] (X = univalent acid radical; R, R', R'' = alkyl or aryl radicals).

*Preparation.*—Hydrido-chloro-complexes of the type *trans*-[PtHCl(MR<sub>3</sub>)<sub>2</sub>] (M = P or As; R = alkyl or phenyl) are readily prepared by reducing the corresponding *cis*-dichloro-complexes *cis*-[PtCl<sub>2</sub>(MR<sub>3</sub>)<sub>2</sub>] with hydrazine hydrate. Other reducing agents were investigated only with reference to the preparation of *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] as listed below. The bromides may be prepared similarly but, in general, hydrides of the type [PtHX(MR<sub>3</sub>)<sub>2</sub>] (with X ≠ Cl) were prepared from the corresponding chlorides by metathetical replacements.

(1) Hydrazine hydrate is the most convenient reducing agent. When a suspension of *cis*-dichlorobis(triethylphosphine)platinum(II) with dilute aqueous hydrazine hydrate is heated at 90° the complex begins to dissolve, then almost immediately nitrogen is

<sup>2</sup> Chatt, Duncanson, and Shaw, *Chem. and Ind.*, 1958, 859.

<sup>3</sup> Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153; *J.*, 1961, 2605, 5507.

<sup>4</sup> Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, 14b, 738.

<sup>5</sup> Chatt and Shaw, *Chem. and Ind.*, 1960, 931.

<sup>6</sup> Lewis, Nyholm, and Reddy, *Chem. and Ind.*, 1960, 1386.

<sup>7</sup> Chatt, Hart, and Hayter, *Nature*, 1960, 187, 4731.

<sup>8</sup> Chatt and Shaw, *Chem. and Ind.*, 1961, 290.

<sup>9</sup> Vaska, *J. Amer. Chem. Soc.*, 1961, 83, 756.

<sup>10</sup> Malatesta, Angoletta, Araneo, and Canziani, *Angew. Chem.*, 1961, 73, 273.

<sup>11</sup> Malatesta, Freni, and Valenti, *Angew. Chem.*, 1961, 73, 273.

<sup>12</sup> Hayter, *J. Amer. Chem. Soc.*, 1961, 83, 1259.

<sup>13</sup> Vaska and DiLuzio, *J. Amer. Chem. Soc.*, 1961, 83, 1262.

<sup>14</sup> Vaska, *Chem. and Ind.*, 1961, 1402.

<sup>15</sup> Vaska and DiLuzio, *J. Amer. Chem. Soc.*, 1961, 83, 2784.

<sup>16</sup> Hieber and Linder, *Z. Naturforsch.*, 1961, 16b, 137.

<sup>17</sup> Chopoorian, Lewis, and Nyholm, *Nature*, 1961, 190, 528.

<sup>18</sup> Malatesta, in "Advances in the Chemistry of Co-ordination Compounds," ed. S. Kirschner, Macmillan, New York, 1961, p. 475.

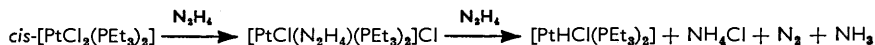
<sup>19</sup> Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.

<sup>20</sup> Chatt and Hayter, *J.*, 1961, 772.

<sup>21</sup> Owston, Partridge, and Rowe, *Acta Cryst.*, 1960, 13, 246.

<sup>22</sup> Chatt, *Proc. Chem. Soc.*, 1962, 318.

evolved. The chlorohydrido-complex, *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>], separates in *ca.* 90% yield as a colourless oil, which then solidifies. This reaction probably proceeds as follows:

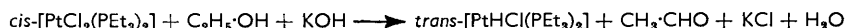


Similar reduction affords *trans*-[PtHBr(PEt<sub>3</sub>)<sub>2</sub>] and [PtHCl(PMe<sub>3</sub>)<sub>2</sub>], but the hydrido-complexes of the higher phosphines, PPr<sup>n</sup><sub>3</sub>, PEt<sub>2</sub>Ph, PEtPh<sub>2</sub>, and PPh<sub>3</sub> are better prepared in methyl or ethyl alcohol as solvent. The analogous arsine complex, *cis*-[PtCl<sub>2</sub>(AsEt<sub>3</sub>)<sub>2</sub>], in dilute aqueous hydrazine hydrate gives the hydridochloro-complex, *trans*-[PtHCl(AsEt<sub>3</sub>)<sub>2</sub>], in poor yield, much dark material being formed. However, a good yield results when reduction is carried out in dilute aqueous ammonia. This stabilises the product as the ammonia complex, [PtH(NH<sub>3</sub>)(AsEt<sub>3</sub>)<sub>2</sub>]Cl, which is converted into *trans*-[PtHCl(AsEt<sub>3</sub>)<sub>2</sub>] on cautious treatment with dilute hydrochloric acid at 0°.

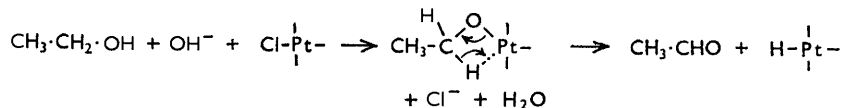
The dichloro-complex, *trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>], is not reduced, or only very slowly, by hydrazine hydrate under conditions used to reduce its *cis*-isomer. This is not surprising since the *cis*- is generally much more reactive than the *trans*-complex: thus in ethanolic solution it reacts *ca.* 10<sup>5</sup> times faster with pyridine than the *trans*-complex.<sup>19</sup>

(2) Lithium aluminium hydride in ether reduces both *cis*- and *trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] to the hydrido-material, *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>], but some metallic platinum is produced and this is not a convenient method. It has been extensively used in the preparation of similar hydrides of iron, ruthenium, and osmium.<sup>3,7</sup>

(3) When the complex *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] is heated in ethyl alcohol with potassium hydroxide (1 mol.) the hydrido-compound *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] is produced in *ca.* 90% yield, together with its equivalent of acetaldehyde:



Isopropyl alcohol reacts similarly, one mol. of acetone being formed in the process. We have proposed that these reductions proceed by hydride-ion transfer promoted by the base,<sup>8,23</sup> and this has been confirmed by tracer studies.<sup>24</sup>



This is a general reaction which has also been used to prepare hydrido-, carbonyl, and hydrido-carbonyl complexes of ruthenium, rhodium, osmium, and iridium.<sup>5,8,9,13-15</sup>

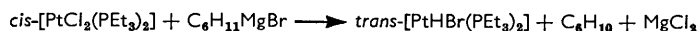
(4) Hot formic acid containing lithium chloride and a little water reduces *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] rapidly to the hydrido-material:



(5) Gaseous hydrogen reduces *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] in ethanol or in aqueous ammonia at 95°/50 atm., giving an excellent yield of the hydrido-complex, as does *cis*-[PtClPh(PEt<sub>3</sub>)<sub>2</sub>] with hydrogen at 20°/1 atm:



(6) Treatment of *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] with cyclohexylmagnesium bromide gives some of the hydridobromo-complex and presumably also cyclohexene:



Reaction between *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] and styrylmagnesium bromide also gives the hydridobromo-complex, as briefly reported previously.<sup>25</sup>

<sup>23</sup> Deno, Peterson, and Saines, *Chem. Rev.*, 1960, **60**, 7.

<sup>24</sup> Vaska and DiLuzio, verbally at 140th Meeting Amer. Chem. Soc., 1961 Abs. Papers, p. 49N.

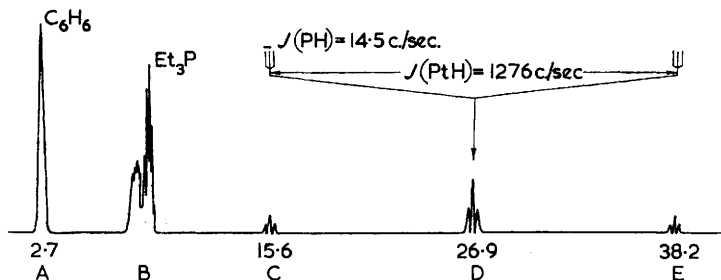
<sup>25</sup> Chatt and Shaw, *J.*, 1959, 4020.

(7) Pyrolysis of *trans*-[PtClEt(PEt<sub>3</sub>)<sub>2</sub>] at 180° gives the hydrido-complex (see "Alkylation," p. 5080).

(8) The chlorine atoms of these hydridochloro-complexes are very labile and readily replaced by other anionic ligands on treatment with the appropriate salt. Thus *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] is converted almost quantitatively into the corresponding bromide, iodide, cyanate, thiocyanate, nitro-, or cyanide complex by treatment with the corresponding alkali-metal salt in acetone or aqueous methanol, and into the nitrate by treatment with silver nitrate (1 mol.).

*Physical Properties of Platinum Hydrides.*—The hydrides are colourless and crystalline. The lower members are very soluble in organic solvents. The complex, *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>], is volatile, distilling at 130° (bath-temperature)/0.01 mm. and subliming slowly at 75°/0.01 mm., both with very little decomposition.

*Infrared Absorption Spectra.*—The infrared spectrum of each of the hydrido-complexes shows a band at just over 2000 cm.<sup>-1</sup> which is assigned to the Pt-H stretching mode,  $\nu(\text{Pt-H})$ . The values of  $\nu(\text{Pt-H})$  are given in the Experimental section. The assignment was confirmed by comparing the spectra of *trans*-[PtXCl(PEt<sub>3</sub>)<sub>2</sub>] (X = H and D) which have been reproduced in refs. 22 and 26. These two spectra also show bending modes [ $\delta(\text{Pt-H})$  and  $\delta(\text{Pt-D})$ ] at 821 and 588 cm.<sup>-1</sup>, respectively. The effects of different ligands in *trans*-position to the hydrogen atoms on  $\nu(\text{Pt-H})$  have been discussed before.<sup>2,27</sup>



Proton magnetic resonance spectrum of *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>]. (Units are  $\tau$ .)

The three complexes *trans*-[PtHX(PEt<sub>3</sub>)<sub>2</sub>] (where X = CN, OCN, or SCN) show strong absorptions at about 2000 cm.<sup>-1</sup> due to  $\nu(\text{C}\equiv\text{N})$ . To distinguish between bands due to  $\nu(\text{C}\equiv\text{N})$  and  $\nu(\text{Pt-H})$  the infrared absorption spectrum of the hydride has been compared with that of the corresponding deuteride, and the results are summarised in Table 1. The band at 813 cm.<sup>-1</sup> in the thiocyanate indicates that the nitrogen is attached to the platinum,<sup>28</sup> probably because the high *trans*-effect of the hydrogen favours the more ionic bonding, *i.e.*, Pt-N as opposed to Pt-S, in *trans*-position to itself.

TABLE 1.

Infrared spectra of *trans*-[PtHX(PEt<sub>3</sub>)<sub>2</sub>] in Nujol mull (X = -CN, -OCN, -NCS).

X	-CN	-OCN	-NCS	X	-CN	-OCN	-NCS
$\nu(\text{Pt-H})$ .....	2072m	2234s	2195m	$\nu(\text{C}\equiv\text{N})$ .....	2137vs	2192vs	2101vs
$\nu(\text{Pt-D})$ .....	1504m	1589m	1571s	$\nu(\text{S-C})$ .....	—	—	813m
$\rho^*$ .....	1.38	1.40	1.40	* $\rho$ = ratio of hydride to deuteride frequencies.			
$\delta(\text{Pt-H})$ .....	826m	840m	844ms				
$\delta(\text{Pt-D})$ .....	598m	—	604ms				
$\rho$ .....	1.38	—	1.40				

*Nuclear Magnetic Resonance.*—These spectra were kindly measured for us by Dr. N. Sheppard. The proton resonance of the hydridic hydrogen shows a large chemical shift

<sup>26</sup> Chatt and Shaw, XVIIIth Internat. Congress Pure Appl. Chem., Butterworths Scientific Publns., London, 1961, p. 147; "Chimica Inorganica," IV° Corso Estivo di Chimica, Varenna, 1959, Accad. naz. Lincei, Roma, 1961, p. 133.

<sup>27</sup> Chatt, Duncanson, Shaw, and Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

<sup>28</sup> Turco and Pecile, *Nature*, **191**, 66; Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

as listed in Table 2. The spectrum of *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] is shown diagrammatically in the Figure. There are five regions of absorption, A—E. The spectrum reproduced in ref. 26 was obtained from an older spectrometer too insensitive to detect the absorptions C and E. Band A is caused by the protons in the benzene solvent, B by those in the triethylphosphine ligands, and the triplets C, D, and E by the hydridic proton. The resonance of the hydridic proton is split to give the triplet structure D with peak intensities in the ratio 1 : 2 : 1 by the two equivalent <sup>31</sup>P nuclei of spin ½ (100% abundance), and this triplet is further split, giving two triplets, C and E by the <sup>195</sup>Pt nucleus of spin ½ (½ abundance). The absorption D comes from those molecules containing platinum isotopes of zero spin. The large coupling constant, *J*(Pt-H), of 1276 c./sec. is noteworthy.

TABLE 2.

Chemical shifts ( $\tau$ ) and phosphorus-hydrogen coupling constants [*J*(PH)] for compounds of the type *trans*-[PtHX(PEt<sub>3</sub>)<sub>2</sub>].

X	Solvent	$\tau$	<i>J</i> (PH) (c./sec.)	X	Solvent	$\tau$	<i>J</i> (PH) (c./sec.)
NO <sub>2</sub> .....	C <sub>6</sub> H <sub>6</sub>	33.8	15.5	I .....	C <sub>6</sub> H <sub>6</sub>	22.7	13
Cl .....	C <sub>6</sub> H <sub>6</sub>	26.9	14	NO <sub>2</sub> .....	"	29.7	16.5
	C <sub>2</sub> H <sub>5</sub> -OH	28.1	14	SCN .....	"	23.22	14
	CHCl <sub>3</sub>	29.0	14.5			27.9	14
Br .....	C <sub>6</sub> H <sub>6</sub>	25.6	15	CN .....	"	17.8	15.5

In Table 2 the ligands have been listed in order of increasing *trans*-effect. This is also approximately the order of decreasing  $\tau$  value, indicating some correlation between *trans*-effect and  $\tau$ ; the compounds having X = NO<sub>2</sub> or -SCN are anomalous. In the nitro-compound the value (29.7) is much higher than would be expected from the *trans*-effect series. This anomaly might be explained if the nitro-group were bonded through oxygen and not through nitrogen. This seems unlikely, however, since the infrared spectrum (Nujol mull) shows bands at 1339vs, 1316vs, 811m (sharp) cm.<sup>-1</sup> as would be expected for a nitro-complex, and no bands attributable to a nitrito-complex; in particular there was no band at about 1065 cm.<sup>-1</sup>.<sup>29</sup> The anomalies in the spectrum of the thiocyanate would be explained if the complex in the strong solution used for measuring the spectrum were a mixture of thiocyanate and isothiocyanate. The infrared spectrum indicates that the solid is an isothiocyanate but gives no evidence of isomerisation in solution.

*Reactions.*—A few simple reactions involving replacement of hydride and chloride ligands, alkylation, and addition of hydrogen chloride have been investigated.

(1) *Replacement of hydrogen by halogen.* The hydridic hydrogen is replaced with decreasing ease by reaction with (a) halogen, (b) hot aqueous halogen acid, and (c) aliphatic halogenohydrocarbons: *e.g.*,



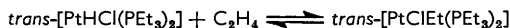
(2) *Deuteration.* Little exchange occurs when molten *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] is shaken with hot deuterium oxide. Exchange is faster in presence of hydrochloric acid (10<sup>-3</sup>M). Under the same conditions rapid exchange occurs with *trans*-[PtHX(PEt<sub>3</sub>)<sub>2</sub>] (X = -CN, -OCN, -SCN).

(3) *Replacement of chloride ion.* Chloride ion is replaced 10<sup>5</sup> times faster from *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>] than from *trans*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] by pyridine.<sup>19</sup> This is reflected in the ease of replacement by other anions (see the metathetical replacements mentioned above) and by ammonia. The latter gives a water-soluble salt, possibly [PtH(NH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>]Cl, which readily reverts to the hydridochloro-complex on acidification or evaporation on the solution. The evaporation may even be carried out on a steam-bath and open to the air without oxidation of the hydride.



<sup>29</sup> Penland, Lane, and Quagliano, *J. Amer. Chem. Soc.*, 1956, **78**, 887; Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

(4) *Alkylation.* The hydridochloro-complex reacts with ethylene in cyclohexane at 95°/40 atm., giving in 18 hours about 25% of the ethyl derivative.<sup>25</sup> This reaction is reversible [see preparation (7) p. 5078]:



This reaction is doubtless related to that described by Green and Nagy<sup>30</sup> who find that an alkyl group attached to the iron atom in, *e.g.*,  $[\text{FeEt}(\text{C}_5\text{H}_5)(\text{CO})_2]$  is converted into the olefin complex, *e.g.*,  $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{C}_2\text{H}_4)]^+$ , by hydride-ion abstraction with triphenylmethyl perchlorate. It seems probable that the  $\beta$ -hydrogen atom of the alkyl group migrates as a hydride ion, *via* the iron atom, to the reagent, while the olefin remains attached to the iron atom as an uncharged ligand. Our reaction above may similarly be explained by migration of the  $\beta$ -hydrogen atom to the metal, where it remains as an anionic ligand, and the olefin is eliminated.

(5) *Addition of hydrogen chloride.* Dry hydrogen chloride reacts with *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$  in ether, an unstable crystalline adduct,  $\text{PtHCl}(\text{PEt}_3)_2 \cdot \text{HCl}$ , being precipitated. This, on storage (except under hydrogen chloride), on being heated or on treatment with water, loses hydrogen chloride and reverts to the original hydridochloro-complex. Its solution in nitrobenzene is non-conducting. Its infrared spectrum in Nujol has a strong peak at 2254  $\text{cm}^{-1}$  and a shoulder at 2265  $\text{cm}^{-1}$ , both much higher than for the original hydridochloro-material. The adduct is probably a dihydridodichloro-platinum(IV) complex, formed as follows:



This is supported by the recent discovery of an analogous addition of hydrogen chloride to iridium(I) complexes of type  $[\text{IrCl}(\text{CO})(\text{PR}_2\text{Ph})]$  ( $\text{R} = \text{Et}^{\text{31}}$  or  $\text{Ph}^{\text{24}}$ ), to give stable and well-defined iridium(III) complexes of the type  $[\text{IrHCl}_2(\text{CO})(\text{PR}_2\text{Ph})_2]$ . The addition is also reminiscent of that<sup>32</sup> of methyl iodide to *trans*- $[\text{PtIme}(\text{PEt}_3)_2]$ , to form a platinumic complex  $[\text{PtI}_2\text{Me}_2(\text{PEt}_3)_2]$  sufficiently stable for isolation but nevertheless losing methyl iodide from its boiling benzene solution or from the solid at 80°/0.01 mm.

## EXPERIMENTAL

The complex platinumous halides were prepared by established methods. M. p.s were determined on a Kofler hot-stage and are corrected. Spence alumina (grade "H") was used for chromatography. The Pt-H stretching frequencies ( $\nu$ , in  $\text{cm}^{-1}$ ) are in hexane except when otherwise stated. A few stretching frequencies are given, *e.g.*,  $\nu(\text{C}\equiv\text{N})$  with the medium in parenthesis.

*Methods of Preparing trans-Hydridochlorobistriethylphosphineplatinum(II), trans-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>].—(1) Hydrazine hydrate.* A suspension of *cis*-dichlorobistriethylphosphineplatinum (1.005 g.) in water (10 c.c.) and hydrazine hydrate (0.5 c.c.) was heated on a steam-bath for 1 hr. The solid gradually dissolved, nitrogen was evolved, and a colourless oil formed. On cooling, the oil solidified to give almost pure *trans*-hydridochlorobistriethylphosphineplatinum(II) (0.82 g.), m. p. 80–81°. On cautious acidification of the mother-liquors with dilute hydrochloric acid a further quantity (0.05 g.) was obtained. Recrystallisation from aqueous methanol or light petroleum (b. p. 40–60°) gave the pure compound as prisms or needles m. p. 81–82°,  $\nu$  2183 (Found: C, 30.8; H, 6.65%; *M*, ebullioscopic in 0.43% benzene solution, 444; in 0.90% solution, 436.  $\text{C}_{12}\text{H}_{31}\text{ClP}_2\text{Pt}$  requires C, 30.8; H, 6.7%; *M*, 468).

(2) *Lithium aluminium hydride.* A solution of *trans*-dichlorobistriethylphosphineplatinum (0.75 g.) in ether (25 c.c.) was added dropwise at 0° to a suspension of lithium aluminium hydride (0.3 g.) in ether (25 c.c.). The suspension was stirred for 10 min. at 0°, then cooled to –20°, and dilute hydrochloric acid was added slowly. After removal of the precipitated platinum, *trans*-hydridochlorobistriethylphosphineplatinum was isolated from the ether layer

<sup>30</sup> Green and Nagy, *Proc. Chem. Soc.*, 1962, 74, and references therein.

<sup>31</sup> Chatt and Shaw, unpublished work.

<sup>32</sup> Chatt and Shaw, *J.*, 1959, 705.

and formed prisms (0.23 g.), m. p. 80—82°, from aqueous methanol. Similar results were obtained with *cis*-dichlorobistriethylphosphineplatinum.

(3) *Alcohol in presence of a base.* N-Aqueous potassium hydroxide solution (2.00 c.c.) was added to a solution of *cis*-dichlorobistriethylphosphineplatinum (1.00 g.) in boiling ethanol (25 c.c.), and the mixture was boiled. The distillate (ca. 10 c.c.) was collected during 35 min. in methanolic 2,4-dinitrophenylhydrazine sulphate (2,4-dinitrophenylhydrazine, 0.45 g.; sulphuric acid, ca. 0.4 g.; methyl alcohol, 30 c.c.; water, 3 c.c.). Acetaldehyde 2,4-dinitrophenylhydrazone (0.36 g.) was isolated and, recrystallised from ethanol, had m. p. and mixed m. p. 163—168°. The contents of the distillation flask were evaporated under reduced pressure and the residue was extracted with boiling light petroleum (b. p. 40—60°). Evaporation of this extract gave *trans*-hydrido-chlorobistriethylphosphineplatinum (0.84 g.), m. p. and mixed m. p. 79—81.5°.

(4) *Hot formic acid.* A mixture of *cis*-dichlorobistriethylphosphineplatinum(II) (0.5 g.), formic acid (10 c.c.), and water (10 c.c.) was heated at 90° for 15 min. during which an oil was deposited. Lithium chloride (0.5 g.) was added and heating continued for 2 min. Then the mixture was cooled and water added. The precipitated solid was collected and extracted with ether, leaving a residue of unchanged *cis*-dichlorobistriethylphosphineplatinum(II) (0.13 g.). The ethereal extract was evaporated and the residue recrystallised from light petroleum (b. p. 40—60°), to give *trans*-hydrido-chlorobistriethylphosphineplatinum (0.17 g.), m. p. 82—83°.

(5) *Gaseous hydrogen.* (a) From *cis*-dichlorobistriethylphosphineplatinum. (i) Into an autoclave (160 c.c.) containing *cis*-dichlorobistriethylphosphineplatinum (1.00 g.) and ethanol (25 c.c.), hydrogen was introduced to a pressure of 50 atm. at 20°. The mixture was then heated to 85° and agitated for 36 hr. Evaporation of the resultant solution and recrystallisation of the residue from light petroleum (b. p. 40—60°) (charcoal) afforded the hydrido-material (0.65 g.), m. p. 79—81°.

(ii) Treatment of *cis*-dichlorobistriethylphosphineplatinum (1.0 g.) in N-aqueous ammonia (40 c.c.) with hydrogen under the same conditions, followed by evaporation and recrystallisation, gave the hydrido-complex (0.35 g.).

(b) From *cis*-chloro(phenyl)bistriethylphosphineplatinum. A suspension of *cis*-chloro(phenyl)-bistriethylphosphineplatinum (0.5 g.) in ethanol (10 c.c.) was shaken in hydrogen (1 atom-equiv.) for 2 hr. Evaporation of the resultant solution and recrystallisation of the residue from light petroleum (b. p. 40—60°) gave *trans*-hydrido-chlorobistriethylphosphineplatinum (0.295 g.), shown to be identical with an authentic sample by means of its infrared spectrum.

(6) *Grignard reactions.* See ref. 25 for detail.

(7) *Pyrolysis of trans-chloro(ethyl)bistriethylphosphineplatinum.* *trans*-Chloro(ethyl)bistriethylphosphineplatinum (0.041 g.) was heated at 180° under nitrogen for 5 min. The residue was cooled and recrystallised from light petroleum (b. p. 40—60°), to give *trans*-hydrido-chlorobistriethylphosphineplatinum (0.020 g.), m. p. 82—83.5°.

*Hydrido-chlorobis(trimethylphosphine)platinum(II)*, [PtHCl(PMe<sub>3</sub>)<sub>2</sub>].—A suspension of *cis*-dichlorobis(trimethylphosphine)platinum (1.0 g.) in water (20 c.c.) containing hydrazine hydrate (1.0 c.c.) was heated under reflux for 1 hr. The mixture was acidified to pH 3 at 0° with dilute hydrochloric acid, and the product was extracted with benzene; this gave impure hydrido-chlorobis(trimethylphosphine)platinum(II), m. p. 132—137° (decomp.),  $\nu$  2182 (CCl<sub>4</sub>), which was too unstable for purification.

*trans-Hydrido-chlorobis(n-propylphosphine)platinum(II)*, *trans*-[PtHCl(PPr<sup>n</sup>)<sub>2</sub>].—A solution of *cis*-dichlorobis(n-propylphosphine)platinum(II) (0.98 g.) in methanol (8 c.c.) and hydrazine hydrate (0.5 c.c.) was heated under reflux for 1 hr., cooled, and just acidified with dilute hydrochloric acid. The resultant precipitate was collected and after recrystallisation from aqueous methanol and one from light petroleum (b. p. 60—80°) gave *trans*-hydrido-chlorobis(n-propylphosphine)platinum(II) as prisms (0.74 g.), m. p. 47—49°,  $\nu$  2183 (Found: C, 39.35; H, 7.8. C<sub>24</sub>H<sub>48</sub>ClP<sub>2</sub>Pt requires C, 39.15; H, 7.85%).

*trans-Hydrido-chlorobis(ethyldiphenylphosphine)platinum(II)*, *trans*-[PtHCl(PETPh<sub>2</sub>)<sub>2</sub>].—A suspension of *cis*-dichlorobis(ethyldiphenylphosphine)platinum (2.00 g.) in methanol (25 c.c.) and hydrazine hydrate (2 c.c.) was heated under reflux for 5 min., cooled, diluted with water, and acidified with dilute hydrochloric acid, and the product was taken up in benzene. The benzene extract on evaporation gave *trans*-hydrido-chlorobis(ethyldiphenylphosphine)platinum as needles (1.35 g.), m. p. 131—132.5° (from methanol),  $\nu$  2206 (Found: C, 50.95; H, 4.85. C<sub>28</sub>H<sub>31</sub>ClP<sub>2</sub>Pt requires C, 50.95; H, 4.75%).

*trans-Hydridochlorobistriphenylphosphineplatinum(II)*,  $\text{trans-[PtHCl(PPh}_3)_2]$ .—*cis*-Dichlorobistriphenylphosphineplatinum(II) (2.0 g.), ethanol (50 c.c.), and hydrazine hydrate (1.5 c.c.) were heated under reflux for 5 min., then cooled, and the white crystals were filtered off, washed with water, and recrystallised from benzene-methanol. Thus was obtained *trans-hydridochlorobistriphenylphosphineplatinum* as colourless prisms (1.08 g.), m. p. 215—220° (decomp.),  $\nu$  2220 (Found: C, 57.15; H, 4.2.  $\text{C}_{36}\text{H}_{31}\text{ClP}_2\text{Pt}$  requires C, 57.2; H, 4.15%).

*trans-Hydridobromobistriethylphosphineplatinum(II)*  $[\text{PtHBr(PEt}_3)_2]$ .—A suspension of *cis*-dibromobistriethylphosphineplatinum (0.50 g.) in water (5 c.c.) and hydrazine hydrate (0.2 c.c.) was boiled for 2 min., then cooled, and the resulting solid was collected and recrystallised from aqueous methanol, to give *trans-hydridobromobistriethylphosphineplatinum* (0.31 g.) as needles, m. p. 94—97°,  $\nu$  2178 (Found: C, 28.05; H, 6.05.  $\text{C}_{12}\text{H}_{31}\text{BrP}_2\text{Pt}$  requires C, 28.15; H, 6.1%),

*trans-Hydridochlorobistriethylarsineplatinum(II)*,  $\text{trans-[PtHCl(AsEt}_3)_2]$ .—A solution of *cis*-dichlorobistriethylarsineplatinum (3.6 g.) in water (80 c.c.) and aqueous ammonia (5 c.c.;  $d$  0.88) was treated with hydrazine hydrate (2.8 c.c.) and heated at 95° for 1 hr., then treated with charcoal and filtered. The filtrate was cooled to 0°, acidified with dilute hydrochloric acid, and extracted with light petroleum (b. p. 60—80°) containing a little ether. On evaporation this extract gave *trans-hydridochlorobistriethylarsineplatinum(II)* (1.9 g.), needles, m. p. 91—93° (from methanol),  $\nu$  2174 (Found: C, 25.8; H, 5.55.  $\text{C}_{12}\text{H}_{31}\text{ClP}_2\text{Pt}$  requires C, 25.95; H, 5.6%).

*Metathetical Replacements*.—*trans-Hydridonitratobistriethylphosphineplatinum*,  $[\text{PtH(NO}_3)(\text{PEt}_3)_2]$ . Silver nitrate (0.170 g.) in water (2 c.c.) and methanol (2 c.c.) was added to a solution of *trans-[PtHCl(PEt}\_3)\_2] (0.468 g.) in methanol. Silver chloride was filtered off and the filtrate evaporated. The residue was dissolved in ether, washed with water, dried ( $\text{MgSO}_4$ ), and evaporated to dryness, and the residue recrystallised from light petroleum (b. p. 60—80°), to give *trans-hydridonitratobistriethylphosphineplatinum* (0.26 g.) as prisms, m. p. 47—49°,  $\nu$  2242 (Found: C, 29.45; H, 6.4; N, 2.85.  $\text{C}_{12}\text{H}_{31}\text{NP}_2\text{PtO}_3$  requires C, 29.15; H, 6.3; N, 2.85%).*

*trans-Hydridobromobistriethylphosphineplatinum(II)*. A solution of the corresponding chloride (1.60 g.) and lithium bromide (6 g.) in acetone (45 c.c.) was boiled for 5 min. Evaporation of the acetone, addition of water, and recrystallisation of the residue from aqueous methanol gave the *trans*-hydridobromo-compound (1.75 g.) as needles, m. p. 94—98°.

*trans-Hydridobromobistriethylarsineplatinum(II)*,  $[\text{PtHBr(AsEt}_3)_2]$ . This complex was similarly prepared by heating the corresponding chloride (0.25 g.) with lithium bromide (1 g.) in acetone (15 c.c.) under reflux for 5 min. and formed needles (0.24 g.), m. p. 107—110° (from methanol),  $\nu$  2167 (Found: C, 24.15; H, 5.2.  $\text{C}_{12}\text{H}_{31}\text{As}_2\text{BrPt}$  requires C, 24.0; H, 5.2%).

*trans-Hydridoiodobistriethylphosphineplatinum(II)*,  $[\text{PtHI(PEt}_3)_2]$ . *trans*-Hydridochlorobistriethylphosphineplatinum (1.8 g.) in acetone (30 c.c.) was treated with sodium iodide (2.5 g.) and boiled for 5 min. The mixture was evaporated to dryness, water added to the residue, and the product isolated with ether. *trans-Hydridoiodobistriethylphosphineplatinum* was obtained as prisms (1.93 g.), m. p. 73—75° [from light petroleum (b. p. 60—80°)],  $\nu$  2156 (Found: C, 26.05; H, 5.65.  $\text{C}_{12}\text{H}_{31}\text{IP}_2\text{Pt}$  requires C, 25.75; H, 5.6%).

*trans-Hydridoiodobis(ethylidiphenylphosphine)platinum(II)*,  $[\text{PtHI(PeTPh}_2)_2]$ . A mixture of *trans-[PtHCl(PeTPh}\_2)\_2] (0.245 g.), acetone (5 c.c.), and sodium iodide (0.4 g.) was put aside at 20° for 5 min., then evaporated, and the residue was washed with water. Thus was obtained *trans-hydridoiodobis(ethylidiphenylphosphine)platinum*, needles (0.22 g.), m. p. 115—116° (from methanol),  $\nu$  2189 (Nujol mull) (Found: C, 44.85; H, 4.25.  $\text{C}_{24}\text{H}_{31}\text{IP}_2\text{Pt}$  requires C, 44.75; H, 4.15%).*

*trans-Hydridoiodobistriphenylphosphineplatinum(II)*,  $[\text{PtHI(PPh}_3)_2]$ . A mixture of *trans-[PtHCl(PPh}\_3)\_2] (0.11 g.), sodium iodide (0.25 g.), and acetone (6 c.c.) was heated under reflux for 10 min. and then evaporated. The residue was washed with water and recrystallised from benzene-methanol, to give *trans-hydridoiodobistriphenylphosphineplatinum* as prisms (0.10 g.), m. p. 195—212° (decomp.),  $\nu$  2186 (Found: C, 50.8; H, 3.6.  $\text{C}_{36}\text{H}_{31}\text{IP}_2\text{Pt}$  requires C, 51.0; H, 3.7%).*

*trans-Hydridoiodobistriethylarsineplatinum(II)*,  $[\text{PtHI(AsEt}_3)_2]$ . This product was prepared by heating under reflux the corresponding chloro-compound (0.50 g.) with sodium iodide in acetone for 5 min. and formed prisms (0.49 g.), m. p. 109—112° (decomp.) (from methanol),  $\nu$  2139 (Found: C, 22.4; H, 4.8.  $\text{C}_{12}\text{H}_{31}\text{As}_2\text{IPt}$  requires C, 22.25; H, 4.8%).

*trans-Hydridocyanatobistriethylphosphineplatinum(II)*,  $[\text{PtH(CNO)(PEt}_3)_2]$ . This was



prepared from the corresponding chloro-complex (0.41 g.) by heating under reflux with a solution of potassium cyanide (1.4 g.) in acetone (25 c.c.) for 40 min. After evaporation to dryness extraction of the residue with ether gave the required *cyanato-complex* (0.31 g.) as prisms, m. p. 65—66° [from light petroleum (b. p. 40—60°)],  $\nu$  2229s (benzene),  $\nu(\text{C}\equiv\text{N})$ , 2192vs (benzene) (Found: C, 33.15; H, 6.65; N, 3.4.  $\text{C}_{13}\text{H}_{31}\text{NOP}_2\text{Pt}$  requires C, 32.9; H, 6.6; N, 2.95%).

*trans-Hydridoisothiocyanatobistriethylphosphineplatinum(II)*,  $[\text{PtH}(\text{SCN})(\text{PEt}_3)_2]$ . The complex, *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$  (2.0 g.), was boiled with potassium thiocyanate (2.5 g.) in acetone (30 c.c.) for 10 min. The acetone was evaporated under reduced pressure, water added to the residue, and the product isolated with ether—light petroleum (b. p. 40—60°). *trans-Hydridoisothiocyanatobistriethylphosphineplatinum* was obtained as prisms (2.0 g.), m. p. 61—64° (from aqueous methanol),  $\nu$  2112,  $\nu(\text{C}\equiv\text{N})$  2078vs,  $\nu(\text{S}-\text{C})$  821m (benzene) (Found: C, 32.1; H, 6.2; N, 2.8.  $\text{C}_{13}\text{H}_{31}\text{NP}_2\text{PtS}$  requires C, 31.85; H, 6.35; N, 2.85%).

*trans-Hydridoisothiocyanatobistriethylarsineplatinum(II)*,  $[\text{PtH}(\text{SCN})(\text{AsEt}_3)_2]$ . This was prepared by heating the corresponding chloro-complex (0.5 g.) with a solution of potassium thiocyanate (1.5 g.) in acetone (5 c.c.) for 5 min. The acetone was removed, water added, and the precipitated solid recrystallised from methanol, to give the *thiocyanato-compound* as prisms, m. p. 56—57°,  $\nu$  2108 (Found: C, 27.2; H, 5.35; N, 2.95.  $\text{C}_{13}\text{H}_{31}\text{As}_2\text{NP}_2\text{S}$  requires C, 27.0; H, 5.4; N, 2.4%).

*trans-Hydridonitrobistriethylphosphineplatinum(II)*,  $[\text{PtH}(\text{NO}_2)(\text{PEt}_3)_2]$ . A mixture of the material *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$  (0.5 g.), sodium nitrite (1.5 g.), and acetone (20 c.c.) was heated under reflux for 1 hr., then evaporated, and the residue was washed with water. This gave *trans-hydridonitrobistriethylphosphineplatinum* as needles (0.46 g.), m. p. 95—97.5° [from light petroleum (b. p. 60—80°)],  $\nu$  2150 (Found: C, 30.0; H, 6.5; N, 3.15.  $\text{C}_{12}\text{H}_{31}\text{NP}_2\text{PtO}_2$  requires C, 30.1; H, 6.5; N, 2.95%).

*trans-Hydridocyanobistriethylphosphineplatinum(II)*,  $[\text{PtH}(\text{CN})(\text{PEt}_3)_2]$ . To a solution of the complex *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$  (0.467 g.) in methyl alcohol (15 c.c.) was added a solution of potassium cyanide (0.070 g.) in 4 : 1 v/v methyl alcohol—water (1.4 c.c.). After 10 min. at 20° the mixture was evaporated to dryness and the residue was taken up in ether and water. The ether layer was separated, dried ( $\text{MgSO}_4$ ), and evaporated. The residue recrystallised from light petroleum, to give *trans-hydridocyanobistriethylphosphineplatinum* (0.41 g.) as prisms, m. p. 106—107°,  $\nu$  2041,  $\nu(\text{C}\equiv\text{N})$  2135 (Found: C, 33.9; H, 6.8; N, 2.95.  $\text{C}_{13}\text{H}_{31}\text{NP}_2\text{Pt}$  requires C, 34.05; H, 6.8; N, 3.05%).

*Other Reactions.*—(1) *Deuteration.* *trans*-Hydridoisothiocyanatobistriethylphosphineplatinum(II) (0.10 g.) was heated with deuterium oxide (3 c.c.) containing concentrated hydrochloric acid (0.005 c.c.) at 90° for 1 min. After cooling, the solid was collected and recrystallised from light petroleum (b. p. 30—40°), giving prisms (0.25 g.), m. p. 63—65°. The infrared spectrum (in Nujol) of this product showed a strong band  $\nu(\text{Pt}-\text{D})$  at 1571  $\text{cm}^{-1}$  but a mere trace of a band due to Pt—H. The cyano- and the cyanato-complex were deuterated similarly.

(2) *Reaction with carbon tetrachloride.* A solution of *trans*-hydridochlorobistriethylphosphineplatinum(II) (0.05 g.) in carbon tetrachloride (1 c.c.) was left at room temperature for 6 weeks; it deposited *cis*-dichlorobistriethylphosphineplatinum(II) (0.04 g.), m. p. 191—193°.

(3) *Reaction with 1-bromobutane.* A solution of *trans*- $[\text{PtHBr}(\text{PEt}_3)_2]$  (0.237 g.) in 1-bromobutane (6 c.c.) was heated under reflux for 4 hr. After evaporation the residue recrystallised from methyl alcohol, giving *trans*-dibromobistriethylphosphineplatinum as yellow needles (0.225 g.), m. p. 136—136.5° (Found: C, 24.5; H, 5.1. Calc. for  $\text{C}_{12}\text{H}_{30}\text{Br}_2\text{P}_2\text{Pt}$ : C, 24.35; H, 5.3%).

(4) *Reaction with methyl iodide.* A solution of *trans*- $[\text{PtHI}(\text{PEt}_3)_2]$  (0.263 g.) in methyl iodide (5 c.c.) was heated under reflux for 30 min. and then put aside at 20° for 18 hr. Evaporation of the solution then gave *trans*-di-iodobistriethylphosphineplatinum as needles (0.25 g.), m. p. 135—135.5° (from methyl alcohol) (Found: C, 21.2; H, 4.4. Calc. for  $\text{C}_{12}\text{H}_{30}\text{I}_2\text{P}_2\text{Pt}$ : C, 21.0; H, 4.4%). Similar results were obtained with ethyl iodide.

(5) *Treatment with aqueous ammonia.* A suspension of *trans*-hydridochlorobistriethylphosphineplatinum(II) (0.10 g.) in aqueous ammonia (10 c.c.;  $d$  0.88) was heated on a steam-bath. The complex dissolved but was reprecipitated as an oil as the ammonia was driven off. The recovery was 90% and little or no decomposition of the chlorohydride could have taken place.

(6) *Reaction with ethylene.* Ethylene at 40 atm. was introduced into an autoclave containing *trans*-hydridochlorobis(triethylphosphine)platinum(II) (1.25 g.) in cyclohexane (75 c.c.).

The mixture was heated to 95° (the pressure rising to 80 atm.), agitated at this temperature for 18 hr., then cooled. The products were evaporated to dryness. The resultant solid was warmed with dilute aqueous ammonia, to remove unchanged starting material, and the residue recrystallised from methyl alcohol, to give *trans*-chloroethylbistriethylphosphineplatinum(II) (0.31 g.) as prisms, m. p. and mixed m. p. 54—56° (Found: C, 33.75; H, 7.15. Calc. for C<sub>14</sub>H<sub>35</sub>ClP<sub>2</sub>Pt: C, 33.9; H, 7.1%). The aqueous ammonia extract was acidified with hydrochloric acid, and the resultant precipitate isolated with light petroleum (b. p. 40—60°); it was the unchanged hydrido-complex (0.53 g.).

(7) *Reaction with bromine.* A 0.96N-solution (2.0 c.c.) of bromine in benzene was added to a solution of *trans*-hydrido-chlorobistriethylphosphineplatinum(II) (0.452 g.) in benzene. After 2 min. the solution was evaporated to dryness and the residue recrystallised from ethyl alcohol, to give *trans*-dibromobistriethylphosphineplatinum (0.45 g.), m. p. 137—138°.

(8) *Action of dry hydrogen chloride.* An excess of dry hydrogen chloride was passed into a solution of *trans*-hydrido-chlorobistriethylphosphineplatinum(II) (0.40 g.) in ether. White crystals were precipitated very rapidly. These were filtered off, washed with light petroleum (b. p. 30—40°), and dried. The product (0.42 g.) formed needles, decomposing at 82—100° (Found: C, 28.75; H, 6.45. C<sub>12</sub>H<sub>32</sub>Cl<sub>2</sub>P<sub>2</sub>Pt requires C, 28.6; H, 6.4%). On treatment with water or if heated at 120°, this complex lost hydrogen chloride to give *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>], quantitatively. The compound, C<sub>12</sub>H<sub>32</sub>Cl<sub>2</sub>P<sub>2</sub>Pt, was non-conducting in nitrobenzene solution.

*Determination of Dipole Moments.*—These were determined as described previously<sup>32</sup> and are listed in Table 3. The error is less than ±0.1 D. Atom polarisation was assumed to be 15% of the electron polarisation.

Infrared and nuclear magnetic resonance spectra were all determined as in ref. 3 (p. 2605) and that reproduced in the Figure at 56.45 Mc./sec., with benzene as internal standard ( $\tau = 2.7$ ).

TABLE 3.

Dipole moments of some hydridoplatinum(II) complexes in benzene at 25°.

	$10^8\omega$	$\Delta\epsilon/\omega$	$10^8\Delta n/\omega$	$-\Delta v/\omega$	$\tau^P$	$\epsilon^P$	$o^P$	$\mu(D)$
<i>trans</i> -[PtHCl(PEt <sub>3</sub> ) <sub>2</sub> ]	4.341	4.387						
	4.446	4.397						
	5.453	4.382						
	24.90		4.08					
	38.73		4.15					
	6.327			0.569				
	8.390			0.572	467.1	89.3	364.4	4.2
<i>trans</i> -[PtHCl(PPh <sub>3</sub> ) <sub>2</sub> ]	3.896	3.339						
	6.884	3.338						
	11.74		12.10					
	18.17		12.80					
	5.263			0.551				
	6.151			0.553	609.4	185.9	395.6	4.4
<i>trans</i> -[PtHBr(PEt <sub>3</sub> ) <sub>2</sub> ]	5.840	4.476						
	6.074	4.457						
	16.44		4.09					
	26.22		3.19					
	4.048			0.642				
7.410			0.601	511.2	88.7	409.2	4.45	
<i>trans</i> -[PtHI(PEt <sub>3</sub> ) <sub>2</sub> ]	3.591	4.212						
	4.453	4.243		(0.61)	535 *	(103)	417 *	4.5 *
<i>trans</i> -[PtH(SCN)(PEt <sub>3</sub> ) <sub>2</sub> ]	3.991	12.461		(0.58)	1232 *	(100)	1117 *	7.4 *
<i>trans</i> -[PtH(NO <sub>2</sub> )(PEt <sub>3</sub> ) <sub>2</sub> ]	5.801	7.904						
	7.114	7.905		(0.58)	793 *	(94)	685 *	5.8 *
<i>trans</i> -[PtH(CN)(PEt <sub>3</sub> ) <sub>2</sub> ]	5.401	7.189						
	6.146	7.184		(0.58)	698 *	(92)	592 *	5.4 *

\* Calc. by using estimated values of densities and refractivities, shown in parentheses.<sup>35</sup>

We thank Drs. N. Sheppard and L. H. Sutcliffe for the nuclear magnetic resonance data, and Dr. L. A. Duncanson and Dr. D. M. Adams for the infrared spectra.

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[Received, May 3rd, 1962.]