

1355. *Hydrido-complexes of Iridium(III) Stabilised by Tertiary Phosphines and Arsines*

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The preparation and properties of a series of iridium(III) hydrides of type $[\text{IrH}_x\text{Y}_{3-x}\text{L}_3]$ ($x = 1, 2, \text{ or } 3$; Y = halogen; L = tertiary phosphine or arsine) are described. The complexes were prepared by reacting trihalogeno-complexes $[\text{IrY}_3\text{L}_3]$ with alcohols with and without base and also by reduction of the trihalogeno-complexes with lithium aluminium hydride and lithium borohydride. Stereoisomers were obtained and the stereochemistry, based on dipole moments, infrared spectra, and nuclear magnetic resonance spectra, is discussed. Reactions of these hydrido-complexes with acids are described. Five-co-ordinate trihydrido-complexes $[\text{IrH}_3(\text{PR}_3)_2]$ were also prepared by lithium aluminium hydride or lithium borohydride reductions of trichlorotrisphosphine complexes. Dipole-moment data and infrared and nuclear magnetic resonance spectral data are given.

SINCE the discovery¹ of the volatile chlorohydride of platinum, *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$ a large number of transition-metal hydrides, stabilised by tertiary phosphines and tertiary arsines, has been reported.² We have also reported briefly a very convenient route to transition-metal hydrido-complexes by the action of an alcohol, usually in the presence of a

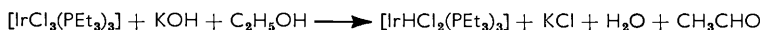
¹ J. Chatt, L. A. Duncanson, and B. L. Shaw, *Proc. Chem. Soc.*, 1957, 343.

² J. Chatt and B. L. Shaw, *J.*, 1962, 5075; see J. Chatt, *Proc. Chem. Soc.*, 1962, 318, and references therein.

base, on tertiary phosphine, or on tertiary arsine complexes of transition-metal halides.³⁻⁵ This route is particularly useful for the preparation of iridium hydrides of the type $[\text{IrH}_x\text{Y}_{3-x}(\text{MR}_3)_3]$ ($x = 1-3$; Y = halogen; M = P or As; R = alkyl or aryl group).

In this Paper we describe the preparation of six-co-ordinate hydrido-iridium(III) complexes by this and other reactions and also the preparation of a new class of five-co-ordinate trihydrido-iridium(III) complexes $[\text{IrH}_3(\text{PR}_3)_2]$ by lithium aluminium hydride or lithium borohydride reduction of trichlorotrisphosphine complexes $[\text{IrCl}_3(\text{PR}_3)_3]$. Whilst this work was progressing, others have also described some hydrido-iridium(III) complexes stabilised by tertiary phosphines, arsines, and stibines (particularly by triphenylphosphine), and we have repeated this work, where necessary, to show its relation to our work.⁶⁻¹⁴

Preparation of hydrido-iridium(III) complexes by reduction with alcohols. On treating the complexes $[\text{IrY}_3(\text{PR}_3)_3]$ ¹⁵ with boiling alcohols in the presence of a base, the halogen atoms are successively replaced by hydride ion according to the severity of the conditions, with the formation of the aldehyde or ketone corresponding to the alcohol. Thus, the yellow complex *trans*- $[\text{IrCl}_3(\text{PEt}_3)_3]$ with potassium hydroxide (1 mol.) in boiling ethanol for 1 hr. gave the yellow hydride $[\text{IrHCl}_2(\text{PEt}_3)_3]$ and acetaldehyde. The acetaldehyde



was distilled out of the reaction mixture and identified as its 2,4-dinitrophenylhydrazone; an 87% yield of the 2,4-dinitrophenylhydrazone being obtained. Similarly, a high yield of acetone 2,4-dinitrophenylhydrazone was obtained when propan-2-ol was used as reactant. The yellow complex *trans*- $[\text{IrCl}_3(\text{PEt}_2\text{Ph})_3]$ gave a 90% yield of the yellow monohydride $[\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3]$ [see configuration (I),] and a 90% yield of acetaldehyde 2,4-dinitrophenylhydrazone, when treated with potassium hydroxide (1 mol.) in boiling ethanol for 1 hr. On further treatment with alcoholic alkali, di- and tri-hydrido-complexes could be prepared. The various interconversion reactions and stereochemistry of these chlorohydrides stabilised by diethylphenylphosphine are summarised in the Figure. The configurations were assigned on the basis of dipole moment, nuclear magnetic resonance, and infrared data (see below).

Prolonged treatment (1½ days) of $[\text{IrCl}_3(\text{PEt}_2\text{Ph})_3]$ with potassium hydroxide (2 mol.) in ethanol gave a dihydrido-complex $[\text{IrH}_2\text{Cl}(\text{PEt}_2\text{Ph})_3]$ (III), which was also readily obtained (2-3 hr.) by reduction of $[\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3]$ (II) but with potassium hydroxide (1 mol.). It was most readily prepared (in 70% yield) by boiling a solution of the trichloro-complex in the high-boiling basic alcohol 2-diethylaminoethanol in the absence of an inorganic base. Replacement of all three chlorine atoms was obtained by refluxing a solution of the complex $[\text{IrCl}_3(\text{PEt}_2\text{Ph})_3]$ in the high-boiling 2-methoxyethanol (b. p. 124°) with potassium hydroxide (3 mol.). A mixture of the *trans*- and *cis*-trihydrido-complexes $[\text{IrH}_3(\text{PEt}_2\text{Ph})_3]$ [(IV) and (V), respectively] was formed, as shown by infrared spectroscopy, and the higher melting *cis*-isomer was isolated. The dihydrido-complex $[\text{IrH}_2\text{Cl}(\text{PEt}_2\text{Ph})_3]$ on treatment with potassium hydroxide (1 mol.) in hot ethanol readily gave the same mixture. In contrast, the analogous arsine complex $[\text{IrH}_2\text{Cl}(\text{AsEt}_2\text{Ph})_3]$

³ J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931.

⁴ J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1961, 290.

⁵ B. L. Shaw and J. Chatt, Proc. 7th Internat. Conf. Co-ordination Chem., Stockholm and Uppsala, 1962, p. 293.

⁶ L. Vaska, *J. Amer. Chem. Soc.*, 1961, **83**, 756.

⁷ L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1962, **84**, 4989.

⁸ L. Malatesta, M. Angoletta, A. Ananeo, and F. Canziani, *Angew. Chem.*, 1961, **73**, 273.

⁹ L. Malatesta, "Advances in the Chemistry of the Co-ordination Compounds," ed. Kirschner, Macmillan, New York, 1961, p. 475.

¹⁰ M. Angoletta, *Gazzetta*, 1962, **92**, 811.

¹¹ M. Angoletta and A. Araneo, *Gazzetta*, 1963, **93**, 1343.

¹² L. Malatesta, M. Angoletta, and G. Caglio, Proc. 8th Internat. Conf. Co-ordination Chem., Vienna, 1964, p. 210.

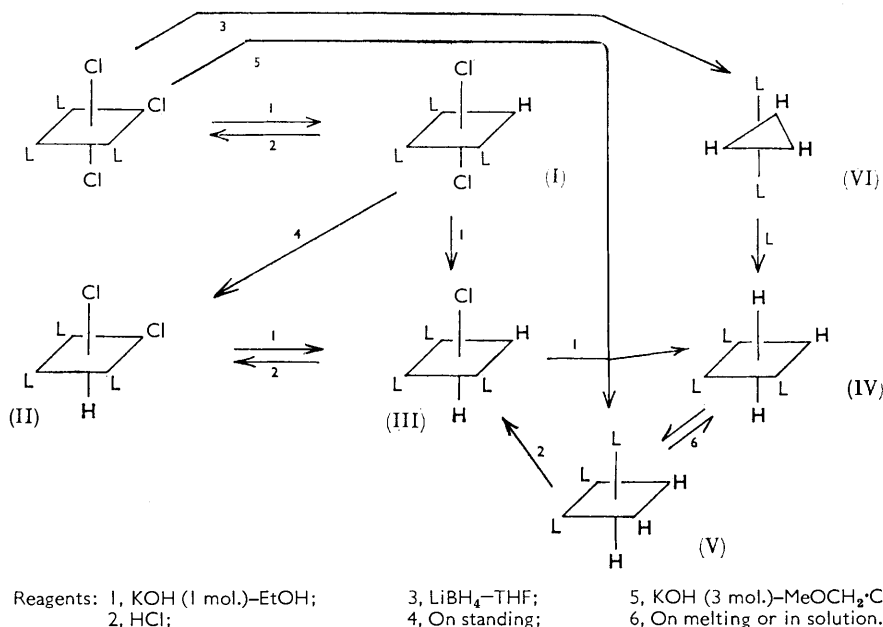
¹³ R. G. Hayter, *J. Amer. Chem. Soc.*, 1961, **83**, 1259.

¹⁴ J. Lewis, R. S. Nyholm, and G. K. N. Reddy, *Chem. and Ind.*, 1960, 1386.

¹⁵ J. Chatt, A. E. Field, and B. L. Shaw, *J.*, 1963, 3371.

was not obtained by treating the corresponding trichloro-complex with 2-diethylamino-ethanol nor by treating the monohydrido-complex $[\text{IrHCl}_2(\text{AsEt}_2\text{Ph})_3]$ with potassium hydroxide and ethanol; it was obtained only by treating the trihydride (see below) with hydrogen chloride (1 mol.). The trihydrides were generally more readily prepared by reductions with lithium aluminium hydride or lithium borohydride and are discussed below.

The hydrogen which is in *trans*-position to phosphorus of high *trans*-effect in the yellow monohydrido-complex $[\text{IrHCl}_2(\text{PET}_2\text{Ph})_3]$ of configuration (I) is very labile to dilute mineral acid. Thus, the addition of dilute hydrochloric acid to its ethanol solution gave a vigorous evolution of hydrogen and the yellow *trans*-trichloro-complex $[\text{IrCl}_3(\text{PET}_2\text{Ph})_3]$ in quantitative yield. On the other hand, hydrogen in *trans*-position to chlorine is stable to dilute hydrochloric acid. Thus, hydrochloric acid expelled only the hydrogen *trans* to phosphorus from the colourless dihydrido-complex $[\text{IrH}_2\text{Cl}(\text{PET}_2\text{Ph})_3]$ (III) and gave the colourless monohydrido-complex $[\text{IrHCl}_2(\text{PET}_2\text{Ph})_3]$ (II). Also on prolonged standing at room temperature crystals of the yellow isomer $[\text{IrHCl}_2(\text{PET}_2\text{Ph})_3]$ (I) partially isomerised into colourless isomer (II) but the arsenic analogue $[\text{IrHCl}_2(\text{AsEt}_2\text{Ph})_3]$ of configuration (I) is stable. The *cis*-trihydrido-complex $[\text{IrH}_3(\text{PET}_2\text{Ph})_3]$ (V) reacted with one mol. of hydro-



Preparation, stereochemistry and reactions of some iridium(III) hydrides stabilised by diethylphenylphosphine (L = PET_2Ph)

gen chloride in dry tetrahydrofuran to give the dihydrido-complex $[\text{IrH}_2\text{Cl}(\text{PET}_2\text{Ph})_3]$ (III) but with an excess of this reagent hydrogen (3 mol.) was evolved.

The hydrido-complexes containing diethylphenylphosphine have been the most extensively studied, but analogous hydrides stabilised by triethylphosphine, tri-*n*-propylphosphine, diethyl-*p*-methoxyphenylphosphine, triethylarsine, and diethylphenylarsine were also prepared and had similar properties. These compounds are listed in Table 1, which also contains several hydridobromides and hydrido-iodides. Monohydridodibromides $[\text{IrHBr}_2(\text{PET}_3)_3]$ and $[\text{IrHBr}_2(\text{PET}_2\text{Ph})_3]$ of configuration (I) were prepared by heating ethanolic solutions of the corresponding trichloro-complexes with potassium hydroxide (1 mol.) in the presence of an excess of lithium bromide. The isomers of configuration (II) were prepared from the trichloro-complexes by treatment with lithium bromide in boiling 2-methoxyethanol. Isomers of configuration (I) on storage at room

TABLE I
Hydrido-complexes of iridium(III)

Compound	Confign.	M. p.	Colour	$\nu(\text{Ir-H})$ (cm. ⁻¹)	(Nujol) *	(Benzene)
[IrHCl ₂ (PEt ₃) ₃]	(I)	83—84.5°	Yellow	2112s	2090	2090
[IrHCl ₂ (PEt ₃) ₃]	(II)	99.5—101	White	2213m	2194	2194
[IrHCl ₂ (PPr ⁿ) ₃]	(I)	70—71	Yellow	2167m	2092	2092
[IrHCl ₂ (PEt ₂ Ph) ₃]	(I)	118—120	Yellow	2045s	2069	2069
[IrHCl ₂ (PEt ₂ Ph) ₃]	(II)	170—178	White	2061m	2069	2069
[IrHCl ₂ (PEt ₂ Ph) ₃]	(II)	170—178	White	2031s	2069	2069
[IrHCl ₂ (PEt ₂ <i>p</i> -MeOC ₆ H ₄) ₃]...	(I)	140—143	Yellow	2232m	2186	2186
[IrHCl ₂ (AsEt ₃) ₃]	(I)	72.5—73.5	Yellow	2201m	2186	2186
[IrHCl ₂ (AsEt ₂ Ph) ₃]	(I)	110—113	Yellow	215s	2038	2038
[IrHCl ₂ (AsEt ₂ Ph) ₃]	(I)	99—100	Yellow	2110m	2100	2100
[IrHCl ₂ (AsEt ₂ Ph) ₃]	(I)	99—100	Yellow	2099s	2076	2076
[IrHCl ₂ (AsEt ₂ Ph) ₃]	(I)	99—100	Yellow	2055s	2076	2076
[IrHCl ₂ (AsEt ₂ Ph) ₃]	(II)	153—157	Yellow	2208	—	—
[IrHBr ₃ (PEt ₃) ₃]	(I)	93—95	Pale orange	2141m	2112	2112
[IrHBr ₃ (PEt ₃) ₃]	(II)	98—100.5	White	2213s	2198	2198
[IrHI ₃ (PEt ₃) ₃]	(II)	139.5—142	Cream	2222s	2188	2188
[IrHBr ₃ (PEt ₂ Ph) ₃]	(I)	121—123	Orange	2041s	2073	2073
[IrHBr ₃ (PEt ₂ Ph) ₃]	(I)	121—123	Orange	2042	2042	2042
[IrHBr ₂ (PEt ₂ Ph) ₃]	(II)	182—186	White	2227m	2225	2225
[IrHBr ₂ (PEt ₂ Ph) ₃]	(II)	182—186	White	2193m	2186	2186
[IrHI ₂ (PEt ₂ Ph) ₃]	(II)	185—195	Pale yellow	—	2220	2220
[IrH ₂ Cl(PEt ₂ Ph) ₃]	(III)	132.5—133.5	White	2178s	2171	2171
[IrH ₂ Cl(PEt ₂ Ph) ₃]	(III)	132.5—133.5	White	2018s	2020	2020
[IrH ₂ Br(PEt ₂ Ph) ₃]	(III)	132—133	White	2179s	2177	2177
[IrH ₂ Br(PEt ₂ Ph) ₃]	(III)	132—133	White	2020s	2030	2030
[IrH ₂ I(PEt ₂ Ph) ₃]	(III)	120.5—122	White	2162s	2167	2167
[IrH ₂ I(PEt ₂ Ph) ₃]	(III)	120.5—122	White	2023s	2036	2036
[IrH ₂ Cl(AsEt ₂ Ph) ₃]	(III)	105—107	Pale yellow	2159s	2168	2168
[IrH ₂ Cl(AsEt ₂ Ph) ₃]	(III)	105—107	Pale yellow	2061s	2058	2058
[IrH ₃ (PEt ₃) ₂]	(VI)	34	White	1931vs	1932	1932
[IrH ₃ (PEt ₂ Ph) ₂]	(VI)	78—80 (decomp.)	White	1950vs	1945	1945
[IrD ₃ (PEt ₂ Ph) ₂]	(VI)	78—80 (decomp.)	White	1404vs †	—	—
[IrH ₃ (PPh ₃) ₂]	(VI)	184—185 (decomp.) ‡	White	1948vs	Insol.	Insol.
<i>cis</i> -[IrH ₃ (PEt ₂ Ph) ₃]	(V)	105—107	White	2044vs	2025	2025
<i>cis</i> -[IrH ₃ (PEt ₂ Ph) ₃]	(V)	105—107	White	2026vs	2025	2025
<i>cis</i> -[IrH ₃ (PEt ₂ Ph) ₃]	(V)	105—107	White	2010vs	2025	2025
<i>trans</i> -[IrH ₃ (PEt ₂ Ph) ₃]	(IV)	62	White	2019m	2037	2037
<i>trans</i> -[IrH ₃ (PEt ₂ Ph) ₃]	(IV)	62	White	1725vs	1740	1740
<i>cis</i> -[IrH ₃ (PPh ₃) ₃]	(V)	233—235 (decomp.) ‡	White	2106vs	2090	2090
<i>cis</i> -[IrH ₃ (PPh ₃) ₃]	(V)	233—235 (decomp.) ‡	White	2094vs	2090	2090
<i>cis</i> -[IrH ₃ (PPh ₃) ₃]	(V)	233—235 (decomp.) ‡	White	2083vs	2090	2090
<i>trans</i> -[IrH ₃ (PPh ₃) ₃]	(IV)	225—227 (decomp.) ‡	White	2100m	2104	2104
<i>trans</i> -[IrH ₃ (PPh ₃) ₃]	(IV)	225—227 (decomp.) ‡	White	1771vs	1755	1755
<i>trans</i> -[IrH ₃ (PPh ₃) ₃]	(IV)	225—227 (decomp.) ‡	White	1750sh	1755	1755
<i>cis</i> -[IrH ₃ (AsEt ₂ Ph) ₃]	(V)	75	White	2072vs	2058	2058
<i>cis</i> -[IrH ₃ (AsEt ₂ Ph) ₃]	(V)	75	White	2057vs	2058	2058
<i>cis</i> -[IrH ₃ (AsEt ₂ Ph) ₃]	(V)	75	White	2022vs	2058	2058

* vs, very strong; s, strong; m, medium; sh, shoulder. † $\nu(\text{Ir-D})$. ‡ In vacuum.

temperature for a few days partly changed into isomers of configuration (II). Monohydridodi-iodo-complexes of configuration (II) were prepared like the bromo-complexes but attempts to make isomers of configuration (I) yielded only those of configuration (II). Generally the ease of isomerisation of configuration (I) into (II) increases in the order chloride < bromide < iodide, and triethylphosphine complexes isomerised more rapidly than diethylphenylphosphine complexes. The dihydridobromo- and dihydridoiodo-complexes [IrH₂X(PEt₂Ph)₃] were prepared by heating the corresponding trichloro-complexes with diethylaminoethanol solutions of lithium bromide and sodium iodide, respectively.

Preparations of trihydrido-complexes by lithium aluminium hydride or lithium borohydride reductions. Reduction of the *trans*-trichloro-complex [IrCl₃(PEt₂Ph)₃] with lithium aluminium hydride in ether gave a mixture from which only the yellow monohydride

$[\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3]$ (I) was isolated. When tetrahydrofuran was used as solvent, however, the major product was a five-co-ordinate monomeric trihydrido-complex $[\text{IrH}_3(\text{PEt}_2\text{Ph})_2]$ (ca. 50% yield); the *cis*-trihydrido-complex $[\text{IrH}_3(\text{PEt}_2\text{Ph})_3]$ (V) and occasionally the dihydridochloro-complex $[\text{IrH}_2\text{Cl}(\text{PEt}_2\text{Ph})_3]$ (III) were also obtained. Lithium borohydride reduction in tetrahydrofuran gave a similar yield of this five-co-ordinate trihydride. The triethylphosphine complex $[\text{IrH}_3(\text{PEt}_3)_2]$ was similarly prepared; this compound (m. p. 33—34°) was extremely soluble in organic solvents. Reduction of the pink diethylphenylphosphonium tetrachlorobis(diethylphenylphosphine)iridium(III) $(\text{PHEt}_2\text{Ph})[\text{IrCl}_4(\text{PEt}_2\text{Ph})_2]$ ¹⁵ with lithium aluminium hydride also gave a good yield of the five-co-ordinate trihydride $[\text{IrH}_3(\text{PEt}_2\text{Ph})_2]$. Lithium borohydride reduction of the triphenylphosphine complex $[\text{IrHCl}_2(\text{PPh}_3)_3]$ ⁶ in tetrahydrofuran gave the insoluble trihydridobis(triphenylphosphine)-iridium(III) complex $[\text{IrH}_3(\text{PPh}_3)_2]$ and triphenylphosphineborane, but apparently no other hydrido-complexes of iridium (evidence of infrared spectra). On the other hand, lithium aluminium hydride reduction gave mainly the *trans*-tristriphenylphosphine complex $[\text{IrH}_3(\text{PPh}_3)_3]$ and some of the bis-complex $[\text{IrH}_3(\text{PPh}_3)_2]$. From the lithium borohydride reductions of the triethylphosphine and triphenylphosphine complexes phosphineboranes were isolated, the phosphine ligand which is lost from the metal being taken up by borane; hydrido(tertiaryphosphine)aluminium complexes may be formed in the lithium aluminium hydride reductions. Similar reductions of the arsine complex $[\text{IrCl}_3(\text{AsEt}_2\text{Ph})_3]$ with either lithium borohydride or lithium aluminium hydride gave only the *cis*-trihydridotris(diethylphenylarsine) complex $[\text{IrH}_3(\text{AsEt}_2\text{Ph})_3]$, probably because diethylphenylarsine does not form such stable complexes with borane or aluminium hydride as diethylphenylphosphine. A trideuterido-complex $[\text{IrD}_3(\text{PEt}_2\text{Ph})_2]$ was also prepared by reduction with lithium aluminium deuteride. The trihydridobisphosphine complexes $[\text{IrH}_3(\text{PEt}_2\text{Ph})_2]$ and $[\text{IrH}_3(\text{PPh}_3)_2]$ quantitatively added another molecule of tertiary phosphine to give the *trans*-trihydridotrisphosphine complexes of configuration (IV). The trihydridobisphosphine complex $[\text{IrH}_3(\text{PEt}_2\text{Ph})_2]$ was shown to be a trihydride by treatment with hydrogen chloride in tetrahydrofuran; 2.80 mol. hydrogen chloride were consumed and 2.98 mol. hydrogen evolved (estimated by pumping into calibrated bulbs using a Toepler pump). The infrared spectrum of the metal complex product showed no iridium-hydrogen bonds to be left.

The pure *cis*- or pure *trans*-trihydrides $[\text{IrH}_3(\text{PEt}_2\text{Ph})_3]$ isomerised on melting and in benzene solutions at room temperature to give mixtures of both isomers and the *cis*-trihydridotris(triphenylphosphine) complex $[\text{IrH}_3(\text{PPh}_3)_3]$ on heating in tetrahydrofuran for several hours partly isomerised to the *trans*-isomer. However, the arsine complex *cis*- $[\text{IrH}_3(\text{AsEt}_2\text{Ph})_3]$ did not isomerise in solution or when heated above its melting point (75°) at 105°.

There have been several accounts of trihydrido-complexes of iridium(III) containing three triphenylphosphine ligands, *i.e.*, of formula $[\text{IrH}_3(\text{PPh}_3)_3]$, and some of this work requires clarification. Malatesta and co-workers,⁸⁻¹⁰ by heating iridium tribromide with triphenylphosphine and sodium borohydride in ethanol, obtained the two isomeric trihydrides $[\text{IrH}_3(\text{PPh}_3)_3]$ which they called α and β ; from the dipole-moment data and the presence of a very strong infrared absorption band at 1745 cm^{-1} the α - and β -isomers were identified as the *trans*- and *cis*-isomers, respectively (see Table 2). No nuclear magnetic resonance data were recorded for these two compounds but reactions with mineral and carboxylic acids were studied and in this way several complexes of type $[\text{IrH}_y\text{X}_{3-y}(\text{PPh}_3)_3]$ ($y = 1, 2$; X = halogen or carboxylate) were prepared.⁸⁻¹¹ By the reduction of the monohydrido-complex $[\text{IrHCl}_2(\text{PPh}_3)_3]$ with lithium aluminium hydride Hayter¹³ obtained a trihydride which from the reported infrared data appears to be the *trans*-isomer, but the dipole moment of 4.95D is far too high; he also made the corresponding deuteride and treated the trihydride with hydrochloric acid to give $[\text{IrH}_y\text{Cl}_{3-y}(\text{PPh}_3)_3]$ ($y = 1$ or 2). Recently Malatesta¹² described the preparation of the insoluble $[\text{IrH}_3(\text{Ph}_3\text{P})_2]$. The physical properties for the trihydrides $[\text{IrH}_3(\text{PPh}_3)_3]$ and $[\text{IrH}_3(\text{PPh}_3)_2]$ as reported in the literature are

TABLE 2

Some literature data on trihydrido-iridium complexes

Compound	M. p. (vac. decomp.)	$\nu(\text{Ir-H})$ (cm. ⁻¹)		Dipole moment (D)	Ref.
$[\text{IrH}_3(\text{PPh}_3)_3]$	227—229°	2100	1745 ^a	4.95	13
$[\text{IrD}_3(\text{PPh}_3)_3]$		1535	1255 ^a		13
α - $[\text{IrH}_3(\text{PPh}_3)_3]$	173 (decomp.)	2130	1750 ^b	2.73	8
	174 (decomp.)	2124	1745 ^b	2.70	9
	225				9
	220	2100	1730 ^b	2.3	10
β - $[\text{IrH}_3(\text{PPh}_3)_3]$		2075 ^b		4.30	8
	217	2083 ^b		4.30	9
	217	2080 ^b		3.5	10
$[\text{IrH}_3(\text{PPh}_3)_2]$	145 (decomp.)	1945 ^b		Insol.	12

^a In chloroform. ^b In Nujol.

given in Table 2. Comparison with the corresponding data relating to our preparations, listed in Tables 1 and 4, is not always good, but we have repeated our preparations and measurements and believe them to be correct.

Vaska^{6,7} has obtained a series of mono- and di-hydrido-complexes of iridium of general formulae $[\text{IrHX}_2\text{L}_3]$ and $[\text{IrH}_2\text{XL}_3]$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{or SbPh}_3$) by treating ammonium chloro- or bromo-iridate with an excess of the ligand L in various oxygenated solvents, particularly 2-methoxyethanol or ethylene glycol. These complexes were very insoluble; no nuclear magnetic resonance and very few dipole-moment measurements have been reported and generally the configurations of these complexes are not known. Lewis, Reddy, and Nyholm¹⁴ have also described the formation of a monohydridodibromo-complex $[\text{IrHBr}_2(\text{AsMe}_2\text{Ph}_3)]$ by heating iridium tribromide with an excess of ligand in alcohol in the presence of hypophosphorous acid.

Dipole moments. The dipole moments of the hydrido-complexes confirm their assigned configurations. They can be calculated, giving surprisingly good agreement with the measured values, if the moments of P-Ir-Cl , P-Ir-H , and H-Ir-Cl vectors are taken to be 6.9, 2.6, and 4.3D, respectively (negative end of dipole at R.H.S.). These three values were arrived at as follows: the moment of the trichloro-complex *trans*- $[\text{IrCl}_3(\text{PEt}_3)_3]$ is 6.9D and gives the first value; the moments of the yellow hydrides $[\text{IrHCl}_2(\text{PEt}_3)_3]$ and $[\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3]$ average at 2.6D, three configurations are possible for hydrides of this formula but only that of configuration (I) could possibly have such a low moment which therefore represents the moment of the vector P-Ir-H ; the value of 4.3D is the difference between the other two and is also very close to the dipole moment (4.1D) of the hydrido-platinum(II) complex *trans*- $[\text{PtHCl}(\text{PEt}_3)_2]$.²

Using these values one can easily calculate the expected moments for configuration (II), *i.e.*, $\sqrt{(6.9)^2 + (4.3)^2} = 8.1\text{D}$ and for configuration (III), *i.e.*, $\sqrt{(2.6)^2 + (4.3)^2} = 5.0\text{D}$; both very close to the observed values (see Table 4). The dipole moment (2.15D) of the trihydride *trans*- $[\text{IrH}_3(\text{PEt}_2\text{Ph})_3]$ points to the *trans*-structure, the rather low value probably being due to similar distortion to that found in *trans*- $[\text{PtHBr}(\text{PEt}_3)_2]$.¹⁶ One would therefore expect the *cis*-isomer to have a moment of $\sqrt{3} \times (2.15)^2 = 3.7\text{D}$, in good agreement with the observed value of 3.4D. In the triphenylphosphine complexes $[\text{IrH}_3(\text{PPh}_3)_3]$ agreement is less good but here the very bulky triphenylphosphine ligands would certainly cause distortions from octahedral symmetry. The almost zero dipole moments of the five-coordinate complexes $[\text{IrH}_3(\text{PR}_3)_2]$ agree with the trigonal-bipyramidal arrangement (VI).

We also find that the dipole moments of the complexes $[\text{IrHX}_2(\text{PEt}_2\text{Ph})_3]$ [configuration (II)] increase along the series $\text{Cl} < \text{Br} < \text{I}$, *i.e.*, 7.95, 8.3, and 8.65D, respectively; this may be caused by increasing back-donation of electrons from the metal to the halogen in the same order, or increasing distortion from a regular octahedral structure by the bulkier

¹⁶ P. G. Owston, J. Partridge, and J. M. Rowe, *Acta Cryst.*, 1960, **13**, 246.

halogens; a similar increase in dipole moments was found for the hydridoplatinum(II) complexes *trans*-[PtHX(PEt₃)₂] (X = Cl, Br, or I)² and is always found in platinum metal-halide complexes where the metal-halogen bond contributes directly to the molecular dipole moment. In contrast, the dipole moments of the isomers [IrHX₂(PR₃)₃] of configuration (I), where the two metal-halogen bond moments are in direct opposition, decrease in going from Cl to Br.

Infrared spectra. The iridium hydrido-complexes show strong or very strong infrared absorption bands at *ca.* 2000 cm.⁻¹ due to the iridium-hydrogen stretching mode. Generally monohydrides [IrHX₂L₃] of configuration (I) have much lower iridium-hydrogen stretching frequencies (2000—2100 cm.⁻¹) than the corresponding isomers of configuration (II) (2195—2220 cm.⁻¹). Evidently the hydrogen forms stronger bonds to iridium when it is in *trans*-position to halogen of low *trans*-effect than when it is in *trans*-position to the phosphine or arsine ligands of high *trans*-effect. This correlates with the reactivity of the hydrogen to acids; complexes containing hydrogen in *trans*-position to phosphine or arsine evolve hydrogen rapidly with acids, whereas hydrogen in *trans*-position to halogen is stable to dilute acids. The dihydrides of configuration (III) showed two bands, at *ca.* 2030 and 2170 cm.⁻¹, which we assign to the iridium-hydrogen bonds in *trans*-position to phosphine and to halogen, respectively. The trihydrido-complexes *cis*-[IrH₃L₃] (L = tertiary phosphine or arsine) in benzene solution showed a very strong band at 2020—2090 cm.⁻¹. The *trans*-isomers showed a medium intensity band at 2037—2104 cm.⁻¹, together with a very strong band at *ca.* 1750 cm.⁻¹, the second band is presumably associated with a vibration involving the two hydrogens in mutual *trans*-positions. The infrared spectra of these hydrido-complexes can therefore be used to determine their stereochemistry. A few monohydrido-complexes in benzene solution showed two iridium-hydrogen stretching modes, possibly due to the partial formation of a complex with the solvent but we have not investigated this further. As well as a strong band at 1950 cm.⁻¹ due to the stretching mode, the five-co-ordinated trihydride [IrH₃(PEt₂Ph)₂] showed a strong band at 877 cm.⁻¹ which shifted to 625 cm.⁻¹ on deuteration, and was therefore due to an iridium-hydrogen bending mode. The other hydrides showed a strong band (or bands) within the range 800—900 cm.⁻¹, presumably due to iridium-hydrogen bending modes. These assignments were not confirmed by deuteration studies but Vaska⁷ has confirmed this for the triphenylphosphine complex [IrHCl₂(PPh₃)₃].

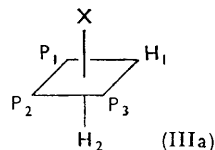
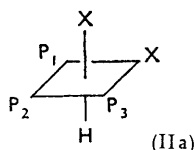
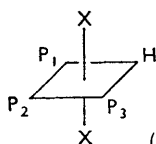
Nuclear magnetic resonance spectra. As in other transition-metal hydrido-complexes, the chemical shifts of the hydridic hydrogens are large (τ -values within the range 18—32). For the two monohydridodichloro-complexes of configuration (I) the τ -values are 22.55 but for the corresponding isomers of configuration (II) they are 31.6 and 31.2 (see Table 3). Also, the coupling constant for the interaction between a hydrogen nucleus and a phosphorus nucleus in mutual *cis*-positions is 11—21 c./sec. but for a phosphorus nucleus in *trans*-position it is 130—163 c./sec. Thus, the position and form of the resonance pattern of the hydrogen attached to the metal is very useful in determining the stereochemistry. In hydrides of configuration (I) the resonance pattern consists of two widely separated 1 : 2 : 1 triplets but in hydrides of configuration (II) these triplets are very close together, and for the complex [IrHCl₂(PEt₃)₃] configuration (II) they merge to give a quartet with intensity ratios of 1 : 3 : 3 : 1. The dihydride [IrH₂Cl(PEt₂Ph)₃] configuration (III) shows both types of resonance pattern and also some splitting due to coupling between the hydrogen nuclei. In the tertiary arsine monohydrido-complexes only single peaks were observed, and in the dihydrido-complex [IrH₂Cl(AsEt₂Ph)₃] the two resonance peaks for the two hydrogens were widely separated and split by mutual coupling as with the corresponding phosphine complex. The five-co-ordinate trihydrides gave simple spectra consisting of one triplet with intensity ratios 1 : 2 : 1 as one might expect for the trigonal bipyramidal structure (VI). The six-co-ordinate *cis*- and *trans*-trihydrides both gave one symmetrical resonance pattern but the peaks do not seem to have small integral ratios of intensities, have odd shapes, and have so far defied interpretation.

TABLE 3

Nuclear magnetic resonance data for hydrido-iridium(III) complexes in benzene solution, τ -values relative to SiMe_4 as internal standard, J -values in c./sec., measured at 60 Mc./sec.

Compound	Confign.*	τ	Coupling constants (J -values) * or multiplicity
$[\text{IrHCl}_2(\text{PET}_3)_3]$	(I)	22.55	$J_1 = J_3 = 19, J_2 = 163$
$[\text{IrHCl}_2(\text{PET}_3)_3]$	(II)	31.6	$J_1 = J_2 = J_3 = 15$
$[\text{IrHCl}_2(\text{PET}_2\text{Ph})_3]$	(I)	22.55	$J_1 = J_3 = 19, J_2 = 158$
$[\text{IrHCl}_2(\text{PET}_2\text{Ph})_3]$	(II)	31.2	$J_1 = J_3 = 12, J_2 = 18$
$[\text{IrHBr}_2(\text{PET}_3)_3]$	(I)	23.6	$J_1 = J_3 = 17, J_2 = 160$
$[\text{IrHBr}_2(\text{PET}_2\text{Ph})_3]$	(II)	30.4	$J_1 = J_3 = 11.6, J_2 = 18$
$[\text{IrHCl}_2(\text{AsEt}_2)_3]$	(I)	25.2	Singlet
$[\text{IrHCl}_2(\text{AsEt}_2\text{Ph})_3]$	(I)	25.55	Singlet
$[\text{IrH}_2\text{Cl}(\text{PET}_2\text{Ph})_3]$	(III)	H_1 18.6 H_2 31.5	$J_1 = J_3 = 19.9, J_2 = 125$ } Each peak was a doublet, $J_{\text{H}_1-\text{H}_2} = 8$
$[\text{IrH}_2\text{Cl}(\text{AsEt}_2\text{Ph})_3]$	(III)	H_1 24.3 H_2 35.0	Each peak was a doublet, $J_{\text{H}_1-\text{H}_2} = 8$
$[\text{IrH}_3(\text{PET}_3)_2]$	(VI)	20.7	1 : 2 : 1 triplet, $J = 13.5$
$[\text{IrH}_3(\text{PET}_2\text{Ph})_2]$	(VI)	19.9	1 : 2 : 1 triplet, $J = 13$
<i>cis</i> - $[\text{IrH}_3(\text{PET}_2\text{Ph})_3]$	(V)	23.0	Six peaks at τ 21.5, 21.9, 22.2, 23.5, 23.8, and 24.15, symmetrical about τ 23.0
<i>trans</i> - $[\text{IrH}_3(\text{PET}_2(\text{Ph}))_3]$	(IV)	21.73	Symmetrical quartet, central peaks stronger than outer ones. Peaks separated by 15 c./sec.
<i>cis</i> - $[\text{IrH}_3(\text{PPh}_3)_3]$	(V)	22.1	Six peaks, symmetrically arranged about τ 22.1
<i>cis</i> - $[\text{IrH}_3(\text{AsEt}_2\text{Ph})_3]$	(V)	24.9	Singlet

* Configurations with phosphorus and hydrogen atoms numbered as shown in formulæ (Ia)—(IIIa).



EXPERIMENTAL

Unless stated otherwise m. p.s were determined on a Kofler hot-stage apparatus and are corrected. All reactions involving complex hydrides were carried out under an atmosphere of nitrogen. Tetrahydrofuran was purified by distillation from sodium and benzophenone under nitrogen. Benzene, light petroleum, and diethyl ether were purified by distillation from phosphorus pentoxide under nitrogen.

Preparation of Monohydrido-complexes of Configuration (I) by Alcohol Reduction.—A general method for dichloro complexes. The corresponding tris(tertiary phosphine)- or tris(tertiary arsine)-iridium trichloride complex¹⁵ (*trans*-form) was dissolved in an alcohol (generally ethanol), the mixture heated to boiling and aqueous 1N-potassium hydroxide (1 ml.) added. The solution was heated under reflux for 1—2 hr., evaporated to dryness and the benzene-soluble portion of the residue recrystallised to give the required product. The following six compounds were prepared in this way.

Hyridodichlorotris(triethylphosphine)iridium(III), $[\text{IrHCl}_2(\text{PET}_3)_3]$. This was prepared from trichlorotris(triethylphosphine)iridium(III) (1.31 g.), potassium hydroxide (2.00 c.c.; 1N), and ethanol (25 c.c.). The mixture was refluxed for 70 min. and gave the required *product* as yellow plates (0.76 g.), m. p. 83—84.5° from aqueous methanol (Found: C, 35.2; H, 7.5. $\text{C}_{18}\text{H}_{46}\text{Cl}_2\text{IrP}_3$ requires C, 34.95; H, 7.5%).

Hyridodichlorotris(tri-n-propylphosphine)iridium(III), $[\text{IrHCl}_2(\text{PPr}_3)_3]$. This was prepared by boiling a mixture of trichlorotris(tri-n-propylphosphine)iridium(III) (0.778 g.), potassium hydroxide (1.05 c.c.; 1N), and ethanol (20 c.c.) for 2 hr. and formed yellow prisms (0.43 g.), m. p. 70—71°, from methanol (Found: C, 43.65; H, 8.65. $\text{C}_{27}\text{H}_{64}\text{Cl}_2\text{IrP}_3$ requires C, 44.1; H, 8.65%).

Hyridodichlorotris(diethylphenylphosphine)iridium(III), $[\text{IrHCl}_2(\text{PET}_2\text{Ph})_3]$. This was prepared from trichlorotris(diethylphenylphosphine)iridium(III) (1.59 g.), potassium hydroxide (2.1 c.c.; 1N), and ethanol (30 c.c.), the solution being refluxed for 1 hr. The required *compound* formed yellow plates (1.38 g.), m. p. 118—120° from ethanol (Found: C, 47.05; H, 6.1. $\text{C}_{30}\text{H}_{46}\text{Cl}_2\text{IrP}_3$ requires C, 47.25; H, 6.1%).

TABLE 4

Dipole moments of some hydrido-iridium(III) complexes in benzene at 25°

$10^3\omega$	$\Delta\epsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τP	ϵP	oP	$\mu(D)$
[IrHCl ₂ (PEt ₃) ₃] configuration (I)							
2.193	1.497	—	—	—	—	—	—
3.611	1.493	—	—	—	—	—	—
5.816	—	0.464	—	—	—	—	—
6.404	—	0.453	(0.46)	301.1	(149)	130 *	2.5 *
[IrHCl ₂ (PEt ₃) ₃] configuration (II)							
1.705	11.53	—	—	—	—	—	—
2.208	11.76	—	(0.46)	1484 *	(149)	1313 *	8.0 *
[IrHCl ₂ (PEt ₂ Ph) ₃] configuration (I)							
4.723	1.454	—	—	—	—	—	—
7.557	1.429	—	(0.46)	364 *	(193)	142 *	2.65 *
[IrHCl ₂ (PEt ₂ Ph) ₃] configuration (II)							
2.655	9.525	—	—	—	—	—	—
2.772	9.426	—	(0.46)	1511 *	(193)	1289 *	7.95 *
[IrHCl ₂ (AsEt ₃) ₃] configuration (I)							
5.724	1.073	—	—	—	—	—	—
6.687	1.079	—	(0.46)	306 *	(179)	100 *	2.2 *
[IrHCl ₂ (AsEt ₂ Ph) ₃] configuration (I)							
5.755	1.138	—	—	—	—	—	—
7.104	1.098	—	(0.46)	372 *	(223)	115 *	2.35 *
[IrHBr ₂ (PEt ₃) ₃] configuration (I)							
5.267	1.203	—	—	—	—	—	—
5.693	1.127	—	(0.55)	281 *	(154)	104 *	2.25 *
[IrHBr ₂ (PEt ₃) ₃] configuration (II)							
0.844	11.17	—	—	—	—	—	—
1.169	11.09	—	(0.55)	1610 *	(154)	1433 *	8.35 *
[IrHI ₂ (PEt ₃) ₃] configuration (II)							
3.951	10.61	—	—	—	—	—	—
4.239	10.56	—	—	—	—	—	—
11.01	—	—	0.599	—	—	—	—
17.06	—	—	0.621	1726	(165)	1536 *	8.65 *
[IrHBr ₂ (PEt ₂ Ph) ₃] configuration (I)							
2.369	1.000	—	—	—	—	—	—
3.782	1.023	—	(0.55)	314 *	(199)	86 *	2.05 *
[IrHBr ₂ (PEt ₂ Ph) ₃] configuration (II)							
4.791	9.211	—	—	—	—	—	—
8.738	9.246	—	—	—	—	—	—
18.53	—	10.22	—	—	—	—	—
25.13	—	10.01	—	—	—	—	—
8.839	—	—	0.543	—	—	—	—
9.592	—	—	0.553	1633	199	1405	8.3
[IrHI ₂ (PEt ₂ Ph) ₃] configuration (II)							
2.765	9.133	—	—	—	—	—	—
4.637	9.190	—	—	—	—	—	—
17.89	—	11.66	—	—	—	—	—
25.51	—	12.03	—	—	—	—	—
5.066	—	—	0.612	—	—	—	—
8.076	—	—	0.632	1780	209	1539	8.65

TABLE 4 (Continued)

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τ^P	ϵ^P	σ^P	$\mu(D)$
[IrH ₂ Cl(PEt ₂ Ph) ₃] configuration (III)							
5.648	4.228	—	—	—	—	—	—
5.698	4.254	—	—	—	—	—	—
20.28	—	9.25	—	—	—	—	—
20.46	—	9.57	(0.45)	733 *	188 *	517 *	5.05 *
[IrH ₂ Br(PEt ₂ Ph) ₃] configuration (III)							
5.045	4.497	—	—	—	—	—	—
7.771	4.510	—	(0.55)	739 *	(191)	574 *	5.3 *
[IrH ₂ I(PEt ₂ Ph) ₃] configuration (III)							
4.903	4.968	—	—	—	—	—	—
5.729	4.988	—	(0.62)	897 *	(196)	672 *	5.75 *
[IrH ₂ Cl(AsEt ₂ Ph) ₃] configuration (III)							
2.660	3.352	—	—	—	—	—	—
3.795	3.335	—	—	—	—	—	—
42.43	—	8.59	—	—	—	—	—
24.49	—	9.01	—	—	—	—	—
5.708	—	—	0.508	—	—	—	—
8.190	—	—	0.501	679	179	474	4.8
<i>cis</i> -[IrH ₃ (PEt ₂ Ph) ₃] configuration (V)							
3.234	2.271	—	—	—	—	—	—
2.617	2.211	—	—	—	—	—	—
16.03	—	7.88	—	—	—	—	—
24.77	—	8.34	—	—	—	—	—
3.484	—	—	0.431	—	—	—	—
3.550	—	—	0.451	439	176	236	3.4
<i>trans</i> -[IrH ₃ (PEt ₂ Ph) ₃] configuration (IV)							
2.303	1.172	—	—	—	—	—	—
3.207	1.158	(8.11)	(0.441)	298 *	176 *	96 *	2.2 *
<i>cis</i> -[IrH ₃ (Ph ₃ P) ₃] configuration (V)							
2.060	1.951	—	—	—	—	—	—
1.687	1.936	—	(0.420)	566 *	(280)	244 *	3.5 *
<i>trans</i> -[IrH ₃ (Ph ₃ P) ₃] configuration (IV)							
2.290	1.334	—	—	—	—	—	—
6.447	1.363	—	—	—	—	—	—
13.93	—	12.02	—	—	—	—	—
14.93	—	11.06	—	—	—	—	—
5.515	—	—	0.417	—	—	—	—
2.601	—	—	0.423	462	280	140	2.6
<i>cis</i> -[IrH ₃ (AsEt ₂ Ph) ₃] configuration (V)							
2.57	2.44	—	—	—	—	—	—
4.21	2.48	—	—	—	—	—	—
11.97	—	6.05	—	—	—	—	—
6.60	—	6.07	—	—	—	—	—
6.225	—	—	0.530	—	—	—	—
6.450	—	—	0.527	535	179	329	4.0
[IrH ₃ (PET ₂ Ph) ₂] configuration (VI)							
3.028	0.561	—	—	—	—	—	—
5.163	0.552	—	—	—	—	—	—
19.145	—	7.36	—	—	—	—	—
20.57	—	7.66	—	—	—	—	—
5.37	—	—	0.447	—	—	—	—
5.777	—	—	0.460	163	129	15	0.85
[IrH ₃ (PET ₃) ₂] configuration (VI)							
3.234	0.427	—	—	—	—	—	—
4.056	0.483	—	(0.500)	118 *	(92)	12 *	0.8 *

* Calc. by using estimated values of densities and refractivities, shown in parentheses.

Hydridodichlorotris(diethyl-p-methoxyphenylphosphine)iridium(III), $[\text{IrHCl}_2(\text{PEt}_2\text{MeOC}_6\text{H}_4)_3]$. This was prepared by boiling for 70 min. a mixture of trichlorotris(diethyl-*p*-methoxyphenylphosphine)iridium(III) (0.50 g.), potassium hydroxide (0.59 c.c.; 1N), and methanol (12 c.c.) for 70 min. and formed yellow plates (0.25 g.), m. p. 140—143° from ethanol (Found: C, 46.6; H, 6.25. $\text{C}_{33}\text{H}_{52}\text{Cl}_2\text{IrO}_3\text{P}_3$ requires C, 46.5; H, 6.15%).

Hydridodichlorotris(triethylarsine)iridium(III), $[\text{IrHCl}_2(\text{AsEt}_3)_3]$. Prepared by boiling for 1 hr. a mixture of trichlorotris(triethylarsine)iridium(III) (0.79 g.), potassium hydroxide (1.0 c.c.; 1N), and ethanol (25 c.c.), the complex formed yellow prisms (0.71 g.), m. p. 72.5—73.5° from aqueous methanol (Found: C, 28.8; H, 6.2. $\text{C}_{18}\text{H}_{46}\text{As}_3\text{Cl}_2\text{Ir}$ requires C, 28.9; H, 6.1%).

Hydridodichlorotris(diethylphenylarsine)iridium(III), $[\text{IrHCl}_2(\text{AsEt}_2\text{Ph})_3]$. Prepared by boiling for 2 hr. a mixture of trichlorotris(diethylphenylarsine)iridium(III) (0.98 g.), potassium hydroxide (1.05 c.c.; 1N), and ethanol (25 c.c.), this complex formed yellow plates (0.56 g.), m. p. 110—112° from methanol (Found: C, 40.25; H, 5.25. $\text{C}_{30}\text{H}_{46}\text{As}_3\text{Cl}_2\text{Ir}$ requires C, 40.3; H, 5.2%). This compound exhibited polymorphism and was also obtained as yellow needles, m. p. 99—100° from methanol.

Hydridodibromotris(triethylphosphine)iridium(III), $[\text{IrHBr}_2(\text{PEt}_3)_3]$. A mixture of *trans*-trichlorotris(triethylphosphine)iridium(III) (0.653 g.) and lithium bromide in boiling ethanol (25 c.c.) was treated with aqueous potassium hydroxide (1.05 c.c.; 1N) and the boiling continued for 3 hr. The solvent was removed *in vacuo* and the ether-soluble portion of the residue recrystallised from methanol to give *hydridodibromotris(triethylphosphine)iridium(III)*, configuration (I), as orange needles (0.34 g.), m. p. 93—95° (Found: C, 30.7; H, 6.6. $\text{C}_{18}\text{H}_{46}\text{Br}_2\text{IrP}_3$ requires C, 30.55; H, 6.55%).

Hydridodibromotris(diethylphenylphosphine)iridium(III), $[\text{IrHBr}_2(\text{PEt}_2\text{Ph})_3]$ was similarly prepared from *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (0.797 g.), lithium bromide (2.5 g.), aqueous potassium hydroxide solution (1.05 c.c.; 1N), and ethanol (20 c.c.), and formed orange prisms (0.47 g.), m. p. 121—123° from light petroleum (b. p. 40—60°) (Found: C, 42.55; H, 5.45. $\text{C}_{30}\text{H}_{46}\text{Br}_2\text{IrP}_3$ requires C, 42.3; H, 5.45%).

Hydridodichlorotris(triethylphosphine)iridium(III) by lithium aluminium hydride reduction. A mixture of *trans*-trichlorotris(triethylphosphine)iridium(III) (1.0 g.), lithium aluminium hydride (0.4 g.), and ether (30 c.c.) was heated under reflux for 1 hr. and then hydrolysed with ethanol. The solvent was removed under reduced pressure and the required product isolated with ether. It formed yellow plates (0.55 g.), m. p. 83—84.5° from methanol, identical with the sample prepared as above.

Preparation of Monohydrido-complexes of Configuration (II) by Alcohol Reduction.—*Hydridodichlorotris(triethylphosphine)iridium(III)*, $[\text{IrHCl}_2(\text{PEt}_3)_3]$. A mixture of trichlorotris(triethylphosphine)iridium(III) (1.306 g.), aqueous potassium hydroxide solution (6 c.c.; 1N), and ethanol (40 c.c.) was heated under reflux for 24 hr. and then acidified with dilute hydrochloric acid. The mixture was evaporated to dryness and the benzene-soluble residue recrystallised from light petroleum (b. p. 60—80°) to give white prisms (0.36 g.), m. p. 99.5—101° of the complex (Found: C, 34.9; H, 7.4%).

Hydridodichlorotris(diethylphenylphosphine)iridium(III), $[\text{IrHCl}_2(\text{PEt}_2\text{Ph})_3]$. This was similarly prepared from trichlorotris(diethylphenylphosphine)iridium(III) (0.796 g.), aqueous potassium hydroxide (3 c.c.; 1N), and ethanol (25 c.c.). The solution was boiled for 18 hr. and the product isolated as above, colourless needles (0.34 g.), m. p. 168—178° (decomp.) from light petroleum (b. p. 80—100°) (Found: C, 47.6; H, 6.2%).

Hydridodibromotris(diethylphenylphosphine)iridium(III), $[\text{IrHBr}_2(\text{PEt}_2\text{Ph})_3]$. *trans*-Trichlorotris(diethylphenylphosphine)iridium(III) (1.0 g.) and lithium bromide (2.0 g.) were dissolved in 2-methoxyethanol and the solution was heated under reflux for 3½ hr. The mixture was cooled, water added, and the resultant white precipitate recrystallised from methanol to give the complex as white prisms (0.81 g.), m. p. 182—187° (Found: C, 42.5; H, 5.45%). This compound was also prepared in *n*-propanol as solvent in 50% yield by an analogous method.

Hydridodi-iodotris(triethylphosphine)iridium(III), $[\text{IrHI}_2(\text{PEt}_3)_3]$. Similarly, a 2-methoxyethanol solution (25 c.c.) of *trans*-trichlorotris(triethylphosphine)iridium(III) (0.50 g.) and sodium iodide (2 g.) was boiled for 2½ hr. to give the required product as pale yellow prisms (0.37 g.), m. p. 129.5—142° from methanol (Found: C, 27.15; H, 5.8. $\text{C}_{18}\text{H}_{46}\text{I}_2\text{IrP}_3$ requires C, 27.0; H, 5.8%).

Hydridodi-iodotris(diethylphenylphosphine)iridium(III), $[\text{IrHI}_2(\text{PEt}_2\text{Ph})_3]$. This was similarly

prepared by boiling a 2-methoxyethanol solution (45 c.c.) of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (1.0 g.) and sodium iodide (2 g.) and formed yellow prisms (0.49 g.), m. p. 185—195° (decomp.) from light petroleum (b. p. 80—100°) (Found: C, 38.25; H, 4.9. $C_{30}H_{46}I_2IrP_3$ requires C, 38.1; H, 4.9%).

Preparation of Dihydrido-complexes of Configuration (III) by Alcohol Reduction.—*Dihydrido-chlorotris(diethylphenylphosphine)iridium(III)*, $[IrH_2Cl(PEt_2Ph)_3]$. *Method 1.* A mixture of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (0.796 g.), ethanol (50 c.c.), and aqueous potassium hydroxide solution (2 c.c.; IN), was heated under reflux for 1½ days. The solvent was then removed under reduced pressure and the water-insoluble portion of the residue was recrystallised from methanol to give *dihydrido-chlorotris(diethylphenylphosphine)iridium(III)* as white prisms (0.37 g.), m. p. 132.5—133.5° (Found: C, 49.45; H, 6.45. $C_{30}H_{47}ClIrP_3$ requires C, 49.45; H, 6.5%).

Method 2. A 2-diethylaminoethanol (25 c.c.) solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (1.0 g.) was heated under reflux for 2½ hr., cooled, water added, and the product isolated with benzene. It formed white prisms (0.65 g.) from methanol, identical with those prepared by Method 1.

Dihydridobromotris(diethylphenylphosphine)iridium(III), $[IrH_2Br(PEt_2Ph)_3]$. A 2-diethylaminoethanol (25 c.c.) solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (0.5 g.) and lithium bromide (2 g.) was boiled for 2½ hr. and the required *product* isolated as in Method 2 above. It formed white prisms (0.27 g.), m. p. 132—133° from methanol (Found: C, 46.7; H, 6.05. $C_{30}H_{47}BrIrP_3$ requires C, 46.65; H, 6.15%).

Dihydridoiodotris(diethylphenylphosphine)iridium(III), $[IrH_2I(PEt_2Ph)_3]$. This was prepared by boiling a 2-diethylaminoethanol (25 c.c.) solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (0.5 g.) and sodium iodide (1 g.) for 2 hr. and isolating as above. It formed white prisms (0.31 g.), m. p. 120.5—122° from ethanol (Found: C, 43.9; H, 5.85. $C_{30}H_{47}IIrP_3$ requires C, 43.95; H, 5.8%).

Preparation of Trihydrido-complexes.—*Trihydridobis(diethylphenylphosphine)iridium(III) and cis-trihydridotris(diethylphenylphosphine)iridium(III)*. Lithium aluminium hydride (0.35 g.) was added portionwise over 10 min. to a stirred solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (1.0 g.) in tetrahydrofuran (15 c.c.). The mixture was heated under reflux for 1 hr., cooled, and hydrolysed with wet tetrahydrofuran. Ether was added, the solvents removed under reduced pressure and the product isolated with light petroleum (b. p. 40—60°). The crude product, on digesting with methanol, yielded crystals which on recrystallisation from methanol or light petroleum (b. p. 40—60°) gave *trihydridobis(diethylphenylphosphine)iridium(III)* (0.33 g.) as white prisms, m. p. 78—80° (decomp.) (Found: C, 45.55; H, 6.65; Cl, 0.0%; *M*, cryoscopically in benzene, 536. $C_{20}H_{33}IrP_2$ requires C, 45.55; H, 6.35; Cl, 0.0%; *M*, 528). On concentrating the methanol washings *cis-trihydridotris(diethylphenylphosphine)iridium(III)* (0.05 g.) was obtained as colourless needles (m. p. 107—109°) from methanol or light petroleum (b. p. 40—60°) (Found: C, 52.15; H, 7.1%; *M* (ebullioscopically in 0.43% benzene solution, 698. $C_{30}H_{48}IrP_3$ requires C, 51.95; H, 6.95%; *M*, 694). Although the infrared absorption spectrum of the crude reaction product indicated the presence of *trans*-trihydridotris(diethylphenylphosphine)iridium(III) (see below) it was not isolated, but occasionally a little dihydrido-chlorotris(diethylphenylphosphine)iridium(III) was obtained from this reaction and shown to be identical with a sample prepared as above.

Alternative preparations of trihydridobis(diethylphenylphosphine)iridium(III). (i) Lithium borohydride (0.4 g.) was added portionwise over 3 hr. to a stirred boiling solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (1.0 g.) in tetrahydrofuran (15 c.c.). After 4 hr. the mixture was cooled and hydrolysed with a mixture of methanol (5 c.c.) and tetrahydrofuran (5 c.c.). Evaporation of the solvent and extraction with light petroleum (b. p. 60—80°) gave the required product (0.33 g.) as prisms from methanol. The infrared spectrum of the crude petroleum extract indicated that no other hydrides were present.

(ii) A slurry of diethylphenylphosphonium tetrachlorobis(diethylphenylphosphine)iridium(III) (0.5 g.) in tetrahydrofuran (20 c.c.) was heated with lithium aluminium hydride (0.3 g.) for 2½ hr. Hydrolysis and isolation as in (i) gave the required product (0.28 g.). The infrared spectrum of the crude petroleum extract indicated that small amounts of *cis*- and *trans*-trihydridotris(diethylphenylphosphine)iridium(III) were present.

Trideuteridobis(diethylphenylphosphine)iridium(III), $[IrD_2(PEt_2Ph)_2]$. A solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (0.4 g.) and lithium aluminium deuteride

(0.1 g.) in tetrahydrofuran (8 c.c.) was heated under reflux for 20 min. After cooling, the mixture was hydrolysed by deuterium oxide (0.5 c.c.). Anhydrous sodium sulphate was added and after 1 hr. the mixture was filtered, the solvent removed under reduced pressure, and the residue recrystallised from light petroleum (b. p. 40—60°) to give trideuteridobis(diethylphenylphosphine)iridium(III) as colourless prisms (0.06 g.), m. p. 76—78° (decomp.). The infrared spectrum contained no bands due to iridium hydrides.

Trihydridobis(triethylphosphine)iridium(III), $[\text{IrH}_3(\text{PEt}_3)_2]$.—(i) By lithium aluminium hydride reduction. Similarly, *trans*-trichlorotris(triethylphosphine)iridium(III) (1.0 g.) was reduced by lithium aluminium hydride (0.35 g.) in tetrahydrofuran and the product isolated with light petroleum (b. p. 40—60°) to give *trihydridobis(triethylphosphine)iridium(III)* (0.12 g.) as white prisms, m. p. 33—34° from methanol (Found: C, 33.3; H, 8.1. $\text{C}_{12}\text{H}_{33}\text{IrP}_2$ requires C, 33.4; H, 7.7%). The infrared spectrum of the crude product indicated that both *cis*- and *trans*-isomers were present, but these were not isolated.

(ii) By lithium borohydride reduction. A mixture of *trans*-trichlorotris(triethylphosphine)iridium(III) (1.0 g.) in tetrahydrofuran (15 c.c.) was reduced with lithium borohydride (0.4 g.) as for the diethylphenylphosphine complex. The light petroleum (b. p. 60—80°) extract of the crude reaction product deposited triethylphosphineborane (0.05 g.) as colourless needles, m. p. 45—48° (lit., 46°) (Found: C, 53.55; H, 13.5. Calc. for $\text{C}_6\text{H}_{18}\text{BP}$: C, 54.6; H, 13.75%). The petroleum mother liquors were evaporated to dryness and the residue was recrystallised from methanol to give the required trihydride (0.12 g.), m. p. 33—34°.

Trihydridobis(triphenylphosphine)iridium(III), $[\text{IrH}_3(\text{PPh}_3)_2]$. A suspension of hydridodichlorotris(triphenylphosphine)iridium(III) (1.0 g.) (prepared according to Vaska⁹) in boiling tetrahydrofuran (20 c.c.) was treated portionwise with lithium borohydride (0.4 g.) over 3 hr. The mixture was then evaporated to dryness and the residue extracted with methanol (3 × 15 c.c.), benzene (3 × 15 c.c.), and then continuously with tetrahydrofuran in a Soxhlet apparatus to give *trihydridobis(triphenylphosphine)iridium(III)* as a white powder (0.35 g.), m. p. 184—185° (vac. decomp.) (Found: C, 59.9; H, 4.9; Cl, 0.0; P, 8.0. $\text{C}_{36}\text{H}_{33}\text{IrP}_2$ requires C, 60.05; H, 4.6; Cl, 0.0; P, 8.6%). The combined methanol, benzene, and tetrahydrofuran extracts were evaporated to dryness and the residue was recrystallised from methanol to give triphenylphosphineborane as colourless needles, m. p. 185° (Found: C, 79.1; H, 6.9; B, 3.6. Calc. for $\text{C}_{18}\text{H}_{18}\text{BP}$: C, 78.35; H, 6.55; B, 3.9%).

Alternative preparations of cis-trihydridotris(diethylphenylphosphine)iridium(III).—(i) A mixture of dihydridochlorotris(diethylphenylphosphine)iridium(III) (0.31 g.), ethanol (15 c.c.), and aqueous potassium hydroxide (0.5 c.c.; 0.85N) was boiled for 20 min. During this time a 94% yield of acetaldehyde was collected as its 2,4-dinitrophenylhydrazone. The reaction mixture was evaporated to give an oil whose infrared spectrum showed both *cis*- and *trans*-trihydridotris(diethylphenylphosphine)iridium(III) to be present. Recrystallisation gave a low yield of the *cis*-isomer identical with an authentic sample.

(ii) A mixture of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (1.21 g.), 2-methoxyethanol (20 c.c.), and aqueous potassium hydroxide (1 c.c.; 5N) was heated under reflux for 4 hr. The mixture was then cooled and the product isolated by adding water and benzene. It formed white plates (0.36 g.), from light petroleum (b. p. 30—40°), identical with an authentic sample.

trans-Trihydridotris(diethylphenylphosphine)iridium(III). A solution of diethylphenylphosphine (0.09 g.) and trihydridobis(diethylphenylphosphine)iridium(III) (0.24 g.) in tetrahydrofuran (2 c.c.) was heated under reflux for 1 hr. The solvent was evaporated under reduced pressure and the residue recrystallised from methanol to give *trans-trihydridotris(diethylphenylphosphine)iridium(III)* as colourless needles (0.08 g.), m. p. 58—62° (Found: C, 51.7; H, 7.0%).

cis-Trihydridotris(diethylphenylarsine)iridium(III), $[\text{IrH}_3(\text{AsEt}_2\text{Ph})_3]$. A mixture of *trans*-trichlorotris(diethylphenylarsine)iridium(III) (1.0 g.), lithium aluminium hydride (0.4 g.), and tetrahydrofuran (10 c.c.) was heated under reflux for 1.75 hr. After hydrolysis with wet tetrahydrofuran the mixture was evaporated to dryness and the light petroleum (b. p. 40—60°)-soluble fraction recrystallised from methanol to give *cis-trihydridotris(diethylphenylarsine)iridium(III)* (0.21 g.) as white needles, m. p. 75° (Found: C, 43.95; H, 5.95. $\text{C}_{30}\text{H}_{48}\text{As}_3\text{Ir}$ requires C, 43.65; H, 5.85). The infrared spectrum of the crude petroleum extract showed that no other hydrides were present. When lithium borohydride was used as reducing agent a similar yield was obtained.

trans-Trihydridotris(triphenylphosphine)iridium(III). *Method 1*. A mixture of hydridodichlorotris(triphenylphosphine)iridium(III)⁶ (1.0 g.), lithium aluminium hydride (0.4 g.), and

tetrahydrofuran (15 c.c.) was heated under reflux for 1 hr. Wet tetrahydrofuran was then added and the tetrahydrofuran-soluble portion recrystallised from tetrahydrofuran to give *trans*-trihydrido-tris(triphenylphosphine)iridium(III) as white needles, m. p. 225—227° (vac. decomp.) [Found: C, 65.45; H, 5.45%; *M* (ebullioscopically in 0.62% benzene solution), 993. Calc. for $C_{54}H_{48}IrP_3$: C, 66.04; H, 4.98%; *M*, 982].

Method 2. A mixture of triphenylphosphine (0.27 g.), trihydrido-bis(triphenylphosphine)-iridium(III) (0.75 g.), and tetrahydrofuran (15 c.c.) was heated under reflux until most of the solid material had dissolved (40 min.). The hot mixture was filtered and the filtrate concentrated under reduced pressure and cooled to give the required product (1.0 g.), m. p. 225—227° (vac. decomp.).

cis- and trans-Trihydrido-tris(triphenylphosphine)iridium(III). A mixture of iridium trichloride (1.5 g.), triphenylphosphine (5.2 g.), and ethanol (30 c.c.) was stirred and heated under reflux for 20 min. Sodium borohydride (0.6 g.) was then added and the mixture heated under reflux for a further 3 hr. and then cooled. The solid product was washed with hot light petroleum (b. p. 60—80°) and extracted with benzene to give a soluble fraction rich in the *trans*-isomer. The two fractions were recrystallised from tetrahydrofuran to give, respectively, *cis*-trihydrido-tris(triphenylphosphine)iridium(III) as colourless cubes, m. p. 233—235° (vac. decomp.) [Found: C, 66.4; H, 5.65; Cl, 0.0%; *M* (ebullioscopically in 0.744% benzene solution), 977] and the *trans*-isomer as needles, m. p. 225—227° (vac. decomp.).

Isomerisation of Hydrido-dichloro-tris(triethylphosphine)iridium(III), Configuration (I) to Configuration (II).—The yellow isomer, configuration (I), was sealed under nitrogen and stored in the dark for 6 months at room temperature, during which time it became completely white. The infrared spectrum showed the solid to be identical with hydrido-dichloro-tris(triethylphosphine)iridium(III), configuration (II).

Isomerisation of Hydrido-dibromo-tris(triethylphosphine)iridium(III), Configuration (I) to Configuration (II).—A sample of the yellow isomer of configuration (I) was put aside for 6 weeks during which time it became almost completely white. On recrystallisation from methanol, *hydrido-dibromo-tris(triethylphosphine)iridium(III)* configuration (II) (82%) was obtained as white prisms, m. p. 98—100.5° (Found: C, 30.8; H, 6.6%).

Isomerisation of Trihydrido-tris(diethylphenylphosphine)iridium(III).—(i) A benzene solution of the pure *cis*-isomer or the pure *trans*-isomer slowly deposited crystals whose m. p. (ca. 60—80°) and infrared spectra indicated that they were a mixture of *cis*- and *trans*-isomers.

(ii) Pure *cis*-isomer was heated in an infrared hot cell at 110° for 5 min. The infrared spectrum indicated that a mixture of *cis*- and *trans*-isomers was present.

Attempted Isomerisation of cis-Trihydrido-tris(diethylphenylarsine)iridium(III).—After being heated in an infrared hot-cell at 110° for 15 min. the infrared spectrum of the complex was unchanged.

Isomerisation of cis-Trihydrido-tris(triphenylphosphine)iridium(III).—A solution of the hydride (0.1 g.) in tetrahydrofuran (10 c.c.) was refluxed overnight. The solvent was evaporated off and the infrared spectrum of the residue indicated that a mixture of *cis*- and *trans*-isomers were present. Extraction with benzene left a solid, m. p. 225—227° (vac. decomp.) and infrared spectrum identical with the *trans*-isomers. On concentrating the benzene solution the *cis*-isomer was obtained as colourless cubes, m. p. 232—234° (vac. decomp.) infrared spectrum identical with authentic *cis*-isomer.

Reaction between Hydrido-dichloro-tris(triethylphosphine)iridium(III), Configuration (I), and Hydrochloric Acid.—A solution of the hydrido-complex (0.10 g.) in methanol (4 c.c.) was treated with concentrated hydrochloric acid (0.05 g.). There was a vigorous evolution of hydrogen and, on adding a few drops of water, *trans*-trichloro-tris(triethylphosphine)iridium(III) (0.084 g.) separated, identical with an authentic sample.

Reaction between cis-Trihydrido-tris(diethylphenylphosphine)iridium(III) and Hydrogen Chloride. A solution of *cis*-trihydrido-tris(diethylphenylphosphine)iridium(III) (0.184 g.) in tetrahydrofuran (5.5 c.c.) containing hydrogen chloride (1 mol.) was put aside for 18 hr. Evaporation of the solvent and recrystallisation of the residue from light petroleum (b. p. 60—80°) gave dihydrido-dichloro-tris(diethylphenylphosphine)iridium(III) (0.153 g.) identical with an authentic sample.

Reaction between cis-Trihydrido-tris(diethylphenylarsine)iridium(III) and Hydrogen Chloride. A solution of the trihydride (0.32 g.) in tetrahydrofuran (5 c.c.) containing dry hydrogen chloride (1 mol.) was set aside overnight. The solvent was evaporated and the residue recrystallised

from light petroleum (b. p. 60—80°) to give *dihydrido*chloro*tris*(diethylphenylarsine)iridium(III) as pale yellow needles (0.23 g.), m. p. 105—107° (Found: C, 41.95; H, 5.55; Cl, 4.25. $C_{30}H_{47}As_3ClIr$ requires C, 41.9; H, 5.5; Cl, 4.25%).

*Reaction between cis-Trihydrido*tris(diethylphenylarsine)iridium(III) and Hydrogen Chloride. A solution of *cis*-trihydrido*tris*(diethylphenylarsine)iridium(III) (0.09 g.) in tetrahydrofuran (5 c.c.) containing hydrogen chloride (2 mol.) was set aside overnight. The solvent was evaporated and the residue recrystallised from methanol to give *hydrido*dichloro*tris*(diethylphenylarsine)iridium(III) as pale yellow needles (0.033 g.) m. p. 153—157° (Found: C, 40.6; H, 5.25; Cl, 7.35. $C_{30}H_{46}As_3Cl_2Ir$ requires C, 40.3; H, 5.3; Cl, 7.9%).

Determination of Dipole Moments.—These were determined as described previously¹⁷ and are listed in Table 4. The error is less than $\pm 0.1D$ for moments $> 2.5D$ but may be greater for moments $< 2.5D$. Atom polarisation was assumed to be 15% of electron polarisation.

We thank Drs. N. Sheppard and D. T. Thompson for the nuclear magnetic resonance data, Dr. D. M. Adams for the infrared spectra, and Dr. J. M. Davidson for quantitative determination of the volume of hydrogen evolved by acids.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, HEAVY ORGANIC CHEMICALS DIVISION,
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[Received, June 29th, 1965.]

¹⁷ J. Chatt and B. L. Shaw, *J.*, 1959, 705.
