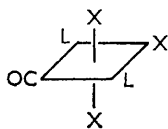


320. Carbonyl and Hydridocarbonyl Complexes of Iridium(III) Halides Stabilised by Tertiary Phosphines, Arsines, and Stibines.

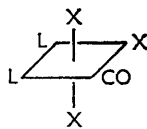
By J. CHATT, N. P. JOHNSON, and B. L. SHAW.

The preparation and properties of new iridium(III) complexes of the type $[\text{IrX}_3(\text{CO})\text{L}_2]$ ($\text{X} = \text{halogen}$; $\text{L} = \text{tertiary phosphine, arsine, or stibine}$) are described. In two cases all three possible isomers have been prepared. Two isomeric hydridocarbonyl complexes; $[\text{IrHCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_2]$ and a binuclear complex $[\text{Ir}_2\text{H}_2\text{Cl}_4(\text{CO})_2(\text{PEt}_3)_2]$ are also described. Infrared, nuclear magnetic resonance, and dipole-moment data are given.

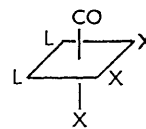
In this Paper we describe the preparation and properties of a new series of iridium(III) carbonyl complexes of the type $[\text{IrX}_3(\text{CO})(\text{MR}_3)_2]$ ($\text{X} = \text{Cl or Br}$; $\text{M} = \text{P, As, or Sb}$; $\text{R} = \text{alkyl or aryl}$) and some derived hydridocarbonyl complexes. For the new octahedral complexes of IrX_3 the three configurations shown below are possible ($\text{L} = \text{MR}_3$).



Configuration (I)



Configuration (II)



Configuration (III)

We have devised general routes to complexes of both configurations (I) and (II) and have prepared several examples of each type; in two cases (with $\text{R} = \text{Et}$ and Bu^n) we have prepared all three isomers.

Complexes of Configuration (I).—The most convenient route to chloro-complexes of configuration (I) was to add the tertiary phosphine, arsine, or stibine (2 mol.) to a 2-methoxyethanol solution of chloroiridous acid, prepared *in situ* from chloroiridic acid by reduction with warm 2-methoxyethanol, and then to pass carbon monoxide through the boiling mixture for several hours (usually *ca.* 6). The isomer of configuration (II) was formed as an intermediate (see below) but under the high temperature conditions used slowly isomerised to the more stable isomer of configuration (I), which crystallised on cooling or on addition of water. The complexes prepared in this way are shown in Table 1, their low dipole moments of 2.35—3.3D (see Table 3) confirmed their configuration.

Two complexes $[\text{IrCl}_3(\text{CO})(\text{PEt}_3)_2]$ and $[\text{IrCl}_3(\text{CO})(\text{AsEt}_2\text{Ph})_2]$ of configuration (I) were also prepared by treating the complexes $[\text{IrCl}_3(\text{PEt}_3)_3]$ and $[\text{IrCl}_3(\text{AsEt}_2\text{Ph})_3]$, respectively, with carbon monoxide under pressure (55—65 atm.) at 55—75°. Also a bromo-complex $[\text{IrBr}_3(\text{CO})(\text{PEt}_2\text{Ph})_2]$ of configuration (I) was prepared by treating the corresponding chloro-complex with an excess of lithium bromide in boiling 2-methoxyethanol, and the

TABLE I.

Some iridium(III) carbonyl complexes.

Complex	Confign.	Colour	M. p.	$\nu(\text{CO})$ (cm. ⁻¹)		
				Nujol	C ₆ H ₆	CHCl ₃
[IrCl ₃ (CO)(PEt ₃) ₂]	I	Pale yellow	159—161°	2031	2041	2050
"	II	Yellow	114—116	2073	2088	2095
"	III	Colourless	189—192	2050	insol.	2062
[IrCl ₃ (CO)(PBu ⁿ) ₂]	I	Pale yellow	93—96	2034	2037	2047
"	II	Yellow	87—89	2028	2090	2094
"	III	Colourless	140—144	2047	2050	2060
[IrCl ₃ (CO)(PEt ₂ Ph) ₂] ...	I	Pale yellow	182—183	2070	2069	2063
"	II	Yellow	175—182	2081	2105	2109
[IrBr ₃ (CO)(PEt ₂ Ph) ₂] ...	I	Yellow	176—178	2056	2064	
[IrCl ₃ (CO)(AsEt ₃) ₂]	II	Yellow	95—101	2060	2077	2081
[IrCl ₃ (CO)(AsEt ₂ Ph) ₂] ...	I	Pale yellow	140—143	2057	2057	2062
"	II	Yellow	149—153	2065	2080	2085
[IrCl ₃ (CO)(SbPr ⁿ) ₂]	I	Yellow	102—105	2020	2029	2038

complex [IrCl₃(CO)(AsEt₂Ph)₂] of configuration (I) by isomerisation of its isomer of configuration II in boiling 2-methoxyethanol under carbon monoxide for 8 hours.

Complexes of Configuration (II).—These were obtained by using similar reaction mixtures but with reaction times of only 15—20 minutes. The products crystallised on cooling or on addition of water, and their high dipole moments (*ca.* 9.5D) were in agreement with configuration (II).

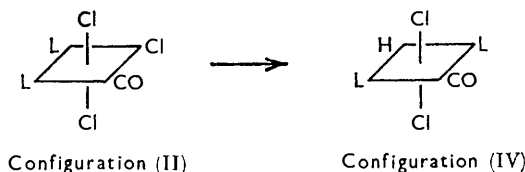
Complexes of Configuration (III).—The yellow tri-*n*-butylphosphine complex [IrCl₃(CO)(PBuⁿ)₂] of configuration (II) on storage at room temperature for 4 months was almost completely converted into a colourless isomer which must have the remaining configuration (III). The very high dipole moment of 12.35D is in agreement with this assignment. An ethanol solution of the triethylphosphine complex [IrCl₃(CO)(PEt₃)₂] of configuration (I) after being boiled for 3 hours and then kept for three months at room temperature deposited a colourless isomer which was unfortunately too insoluble in benzene for dipole-moment determination but must have been the remaining isomer, of configuration (III). The colour, high melting point, and low solubility in non-polar solvents are in agreement with this configuration. Also its carbonyl stretching frequency is almost identical with that for the complex [IrCl₃(CO)(PBuⁿ)₂] of configuration (III) (see Table I). Attempts to prepare other complexes of configuration (III) by heating solutions of the corresponding isomers of configurations (I) or (II) gave mixtures which could not be separated.

Physical Properties.—These iridium(III) carbonyl complexes showed a very intense absorption band at *ca.* 2000—2100 cm.⁻¹ due to a carbonyl stretching mode of vibration. The values of these stretching frequencies together with the configurations, colours, and melting points of the various iridium(III) carbonyl complexes are given in Table I.

Conversion to Hydridocarbonyl Complexes.—We have also investigated the action of alkali and ethanol on the diethylphenylphosphine complexes [IrCl₃(CO)(PEt₂Ph)₂] of both configurations (I) and (II) in an attempt to make hydridocarbonyl complexes. Many tertiary phosphine complexes of Group-VIII metal halides on treatment with alcohols in the presence of a base are smoothly converted into metal hydride complexes.¹ Treatment of the complex [IrCl₃(CO)(PEt₂Ph)₂] of configuration (II) with potassium hydroxide in boiling ethanol gave an excellent yield of a yellow monohydrido-carbonyl [IrHCl₂(CO)(PEt₂Ph)₂] shown by its low dipole moment and n.m.r. spectrum to have configuration (IV). Migration of the phosphine ligand from mutual *cis*- to mutual *trans*-positions had occurred during the reduction.

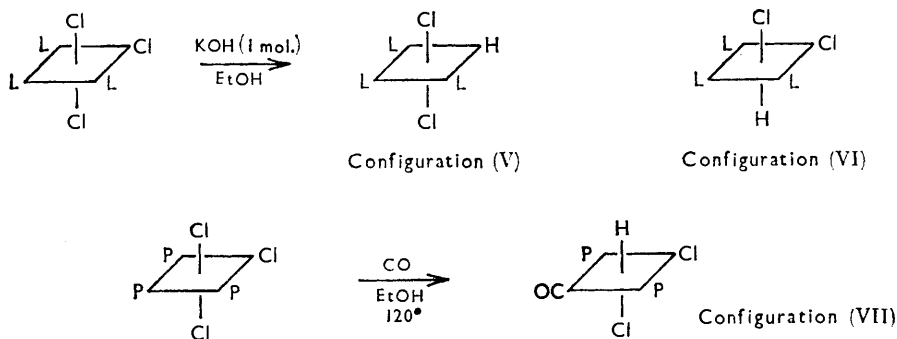
In contrast, the complex [IrCl₃(CO)(PEt₂Ph)₂] of configuration (I) was recovered

¹ Chatt and Shaw, *J.*, 1962, 5075, and references therein.



unchanged after treatment with potassium hydroxide in boiling ethanol. This is surprising since this trichloro-complex and the hydridochloro-complex of configuration (IV) have the same arrangement of phosphine and carbon monoxide ligands. It appears that, in these octahedral complexes, chlorine in a *trans*-position to either another chlorine or to carbon monoxide as ligands is inert to substitution by hydrogen, with alcoholic potash as reagent. On the other hand, chlorine in a *trans*-position to phosphine is readily substituted. This has been found in other iridium(III) complexes. Thus, *trans*-[IrCl₃(PEt₂Ph)₃] reacts readily with ethanol and potassium hydroxide (1 mol.) to give the monohydrido-complex [IrHCl₂(PEt₂Ph)₃] of configuration (V) in which only the chlorine in a *trans*-position to phosphine has been replaced, although the complex of configuration (VI) is the more stable and indeed the solid of configuration (V) changes to (VI) on storage.^{2,3}

The monohydride [IrHCl₂(CO)(PEt₂Ph)₂] of configuration (IV) was also formed by treating the trichloro-complex *trans*-[IrCl₃(PEt₂Ph)₃] in ethanol with carbon monoxide at 77°/70 atm. for 16 hours but under more drastic conditions (120°/78 atm. for 18 hours) it gave a white isomeric hydridocarbonyl complex [IrHCl₂(CO)(PEt₂Ph)₂] of configuration (VII). This isomer was also obtained by treatment of chloroiridic acid in boiling ethanol with carbon monoxide followed by addition of diethylphenylphosphine. Possibly a planar chlorocarbonyl complex of iridium(I) *trans*-[IrCl(CO)(PEt₂Ph)₂] was formed as intermediate and added hydrogen chloride to its octahedral positions to give the hydridocarbonyl complex [IrHCl₂(CO)(PEt₂Ph)₂] of configuration (VII). Complexes of type *trans*-[IrCl(CO)(PR₃)₂] are known to add hydrogen chloride rapidly to give hydridocarbonyl complexes [IrHCl₂(CO)(PR₃)₂]^{4,5} and are formed by the addition of tertiary phosphines to solutions obtained by treatment of sodium chloroiridite in ethanol with carbon monoxide in the absence of mineral acid. A bromo-hydridocarbonyl complex [IrHBr₂(CO)(PEt₂Ph)₂] of configuration (VII) was similarly prepared by treating sodium bromoiridate with carbon monoxide in ethanol followed by the addition of diethylphenylphosphine.



The configurations (IV) and (VII) of the two isomeric hydridocarbonyl complexes [IrHCl₂(CO)(PEt₂Ph)₂] follow from their dipole moments of 1.2 and 5.1D, respectively, and from their n.m.r. spectra. Nuclei of hydrogen atoms directly attached to transition

² Chatt and Shaw, *Chem. and Ind.*, 1960, 931.

³ Shaw and Chatt, Proceedings of the 7th Internat. Conf. on Co-ord. Chem., Stockholm, 1962.

⁴ Vaska and DiLuzio, verbally at 140th Meeting, Amer. Chem. Soc., 1961, Abs. Papers, p. 49N.

⁵ Chatt, Johnson, and Shaw, unpublished work.

metals have large chemical shifts, the two isomers had chemical shifts of τ 19.0 and 26.0, respectively. The resonances were split by interaction with two equivalent phosphorus nuclei into symmetrical 1:2:1 triplets with coupling constants J 16 and 12 c./sec., respectively, confirming the *cis*-arrangement of the phosphine ligands relative to the hydride ligand in both isomers. In transition-metal hydrides containing phosphine

TABLE 2.
Some iridium(III) hydridocarbonyl complexes.

Complex	Confign.	Colour	M. p.	$\nu(\text{CO})$ † (cm^{-1})	$\nu(\text{Ir-H})$ (cm^{-1})	n.m.r. (C_6H_6)
$[\text{IrHCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_2]$	(IV)	Yellow	110—112°	2101(N) 2109(N)	2008(N)	$\tau_{\text{H}} = 19.0$
$[\text{IrHCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_2]$	(VII)	Colourless	123—136 *	2105(B) 1987(sh) 2032(N)	2008(B) 2237(N)	$J = 16$ c./sec. $\tau_{\text{H}} = 26.05$
$[\text{IrHBr}_2(\text{CO})(\text{PEt}_2\text{Ph})_2]$	(VII)	Colourless	140—144 *	2033(B) 2039(Ch)	2194(B) 2205(Ch)	$J = 12$ c./sec.
$[\text{Ir}_2\text{H}_2\text{Cl}_4(\text{CO})_2(\text{PEt}_3)_2]$	—	Colourless	170—190 *	2035(N) 2038(B) 2058(N)	2232(N) 2193(B) 2242(N)	

* With decomp. † (N) Nujol mull; (B) benzene solution; (Ch) = chloroform solution.

ligands the hydrogen and phosphorus nuclei always couple, but the coupling is much larger when they are in mutually *trans*-positions; J is then of the order of 80—150 c./sec., but in a *cis*-position J is only 12—24 c./sec. Also a hydride ligand *trans* to a phosphine invariably has a much smaller chemical shift than one *trans* to a chloride ligand.⁶ The assigned configurations fit these observations. The bromo-complex $[\text{IrHBr}_2(\text{CO})(\text{PEt}_2\text{Ph})_2]$ has configuration (VII), as shown by its moment of 5.35D.

These hydride complexes showed a very strong band at 2030—2100 cm^{-1} ($\text{C}\equiv\text{O}$ stretch) and also a strong band at *ca.* 2200 cm^{-1} [configuration (VII)] or *ca.* 2000 cm^{-1} [configuration (IV)] due to the iridium-hydrogen stretching vibration (see Table 2).

A colourless dinuclear dihydrogen complex $[\text{Ir}_2\text{H}_2\text{Cl}_4(\text{CO})_2(\text{PEt}_3)_2]$ was obtained by treatment of a boiling 2-methoxyethanol solution containing chloroiridous acid, hydrochloric acid, and triethylphosphine with carbon monoxide. This must be bridged through two chlorine atoms because both $\nu(\text{Ir-H})$ and $\nu(\text{C}\equiv\text{O})$ (Table 2) are too high to allow for these being bridging groups. Indeed, $\nu(\text{Ir-H})$ is so high that the hydrogen is very probably *trans* to chlorine.

EXPERIMENTAL

Melting points (Table 1) were determined on a Kofler hot-stage apparatus and are corrected. Operations involving free tertiary phosphines or arsines were carried out in an atmosphere of nitrogen.

Trichloro(carbonyl)bis(triethylphosphine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{PEt}_3)_2]$ Configuration (I).—A solution of *trans*-trichlorotris(triethylphosphine)iridium(III) (1.0 g.) in acetone (15 c.c.) was heated with carbon monoxide (65 atm.) at 55° for 20 hr. in a rocking autoclave. The mixture was evaporated to dryness and recrystallised from methanol to give *trichlorocarbonyl*bis(*triethylphosphine*)iridium(III) configuration (I) as prisms (0.57 g.) (Found: C, 27.95; H, 5.45. $\text{C}_{13}\text{H}_{30}\text{Cl}_3\text{IrOP}_2$ requires C, 27.75; H, 5.35%).

Trichloro(carbonyl)bis(diethylphenylarsine)iridium(III) $[\text{IrCl}_3\text{CO}(\text{AsEt}_2\text{Ph})_2]$ Configuration (I).—A solution of *trans*-trichlorotris(diethylphenylarsine)iridium(III) (1.5 g.) in ethanol (25 c.c.) was heated under carbon monoxide (55 atm.) at 73° for 16 hr. in a rocking autoclave. The mixture was evaporated to dryness and the residue recrystallised from methanol to give *trichloro(carbonyl)bis(diethylphenylarsine)iridium(III)* configuration (I) as needles (0.07 g.) (Found: C, 34.05; H, 4.1. $\text{C}_{21}\text{H}_{30}\text{As}_2\text{Cl}_3\text{IrO}$ requires C, 33.75; H, 4.05%).

General Preparation of Trichloro(carbonyl)iridium(III) Complexes of Type $[\text{IrCl}_3(\text{CO})(\text{MR}_2)_2]$

⁶ Shaw and Sheppard, unpublished work.

Configurations (I) and (II).—The tertiary phosphine, arsine, or stibine (*ca.* 2 mol.) was added to a solution of chloroiridic acid, prepared from chloroiridic acid, 2-methoxyethanol, and hydrochloric acid. Carbon monoxide was then passed through the boiling solution, for 1—6 hr. to give isomers of configuration (I) or *ca.* 15—20 min. for isomers of configuration (II). The preparation described immediately below has been given in slightly more detail than the others, as a typical example.

Trichloro(carbonyl)bis(triethylphosphine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{PEt}_3)_2]$ *Configuration (I).*—A solution of chloroiridic acid (5.00 g.) in 2-methoxyethanol (50 c.c.) containing hydrochloric acid (1 c.c.) was heated on a steam-bath until it became brownish yellow. Triethylphosphine (3.1 g.) was added, and the mixture heated under reflux for 6 hr. and cooled; the product then separated as yellow prisms (3.65 g.; m. p. 159—161°) from methanol. Its identity was proved by its infrared spectrum.

Trichloro(carbonyl)bis(triethylphosphine)iridium(III) *Configuration (II).*—This was prepared in 62% yield after boiling for 15 min. and formed needles from methanol (Found: C, 27.95; H, 5.45%).

Trichloro(carbonyl)bis(tri-n-butylphosphine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{PBu}_3)_2]$ *Configuration (I).*—This was obtained in 34% yield after boiling for 3 hr. and formed *prisms* from methanol (Found: C, 41.15; H, 7.25. $\text{C}_{25}\text{H}_{54}\text{Cl}_3\text{IrOP}_2$ requires C, 41.05; H, 7.45%).

Trichloro(carbonyl)bis(tri-n-butylphosphine)iridium(III) *Configuration (II).*—This was obtained in 51% yield after boiling for 15 min. and formed *prisms* from light petroleum (b. p. 40—60°) (Found: C, 41.35; H, 7.55%).

Trichloro(carbonyl)bis(diethylphenylphosphine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{PEt}_2\text{Ph})_2]$ *Configuration (I).*—This was prepared in 70% yield after boiling for 6½ hr. and formed *needles* from ethanol (Found: C, 38.55; H, 4.65. $\text{C}_{21}\text{H}_{30}\text{Cl}_3\text{IrOP}_2$ requires C, 38.3; H, 4.6%).

Trichloro(carbonyl)bis(diethylphenylphosphine)iridium(III) *Configuration (II).*—This was obtained in 64% yield after boiling for 20 min. and formed *prisms* from ethanol (Found: C, 37.9; H, 4.85%).

Trichloro(carbonyl)bis(triethylarsine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{AsEt}_3)_2]$ *Configuration (II).*—This was obtained in 59% yield after boiling for 1¾ hr. and formed *needles* from methanol (Found: C, 24.1; H, 4.8. $\text{C}_{13}\text{H}_{30}\text{As}_2\text{Cl}_3\text{IrO}$ requires C, 24.0; H, 4.65%).

Trichloro(carbonyl)bis(diethylphenylarsine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{AsEt}_2\text{Ph})_2]$ *Configuration (II).*—This was obtained in 51% yield after boiling for 1½ hr. and formed *needles* from ethanol (Found: C, 33.8; H, 4.15; Cl, 14.3. $\text{C}_{21}\text{H}_{30}\text{As}_2\text{Cl}_3\text{IrO}$ requires Cl, 14.25%).

Trichloro(carbonyl)bis(tri-n-propylstibine)iridium(III) $[\text{IrCl}_3(\text{CO})(\text{SbPr}_3)_2]$ *Configuration (I).* This was obtained in 40% yield after boiling for 1 hr. and formed *prisms* from light petroleum (b. p. 30—40°) (Found: C, 27.85; H, 5.25. $\text{C}_{19}\text{H}_{42}\text{Cl}_3\text{IrOSb}_2$ requires C, 27.55; H, 5.1%).

Tribromo(carbonyl)bis(diethylphenylphosphine)iridium(III) $[\text{IrBr}_3(\text{CO})(\text{PEt}_2\text{Ph})_2]$ *Configuration (I).*—A solution of trichloro(carbonyl)bis(diethylphenylphosphine)iridium(III) configuration (I) (1.0 g.) and lithium bromide (2 g.) in 2-methoxyethanol (25 c.c.) was heated under reflux for 22 hr., cooled, and diluted with water, and the precipitate recrystallised from ethanol to give the tribromo-complex as *needles* (0.63 g.) (Found: C, 32.5; H, 3.95. $\text{C}_{21}\text{H}_{30}\text{Br}_3\text{IrP}_2\text{O}$ requires C, 31.85; H, 3.8%).

Isomerisation of Trichloro(carbonyl)bis(diethylphenylarsine)iridium(III) of Configuration (II) to Configuration (I).—A solution of the isomer of configuration (II) (2.0 g.) in 2-methoxyethanol (35 c.c.) was heated under reflux for 8 hr. with a stream of carbon monoxide passing through the solution. The solution was then cooled, water added, and the precipitate crystallised from light petroleum (b. p. 80—100°) to give trichloro(carbonyl)bis(diethylphenylarsine)iridium(III) configuration (I) as *needles* (1.39 g.) (Found: C, 34.1; H, 4.25%). The mixed melting point with the starting material (m. p. 147—152°) was 122—140°. The configuration of this product was confirmed by its dipole moment, which was virtually identical with that of an authentic specimen.

Trichloro(carbonyl)bis(triethylphosphine)iridium(III) *Configuration (III).*—A solution of trichloro(carbonyl)bis(triethylphosphine)iridium(III) configuration (I) (0.50 g.) in ethanol (25 c.c.) was heated under reflux for 3 hr. and put aside for 3 months at 20°; *trichloro(carbonyl)bis(triethylphosphine)iridium(III) configuration (III)* separated and was crystallised, forming *prisms* (0.27 g.) from methylene chloride-methanol (Found: C, 27.75; H, 5.5%).

Trichloro(carbonyl)bis(tri-n-butylphosphine)iridium(III) *Configuration (III).*—Trichloro(carbonyl)bis(tri-n-butylphosphine)iridium(III) configuration (II) (0.67 g.) was put aside at

TABLE 3
The dipole moments of some carbonyl and hydridocarbonyl complexes of iridium(III).

$10^3\omega$	$\Delta\epsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τ^P	ϵ^P	o^P	μ (D)
6.204	1.806						
7.338	1.806		(0.52)	297 *	(118)	161 *	2.8 *
4.802	17.74						
7.263	17.79		(0.52)	1989 *	(118)	1853 *	9.5 *
3.976	1.296						
6.628	1.294		(0.52)	315 *	(174)	115 *	2.35 *
4.884	13.95						
7.189	14.02		(0.52)	2062 *	(173)	1863 *	9.55 *
1.964	24.38						
3.488	25.35						
4.550	26.04		(0.52)	3323 *	(173)	3124 *	12.35 *
9.003	2.183						
18.72	2.142		(0.52)	392 *	(148)	222 *	3.3 *
4.661	15.697						
6.953	15.686		(0.52)	2071 *	(148)	1901 *	9.65 *
5.512	15.73						
9.478	15.83						
38.20		6.26					
40.85		6.41					
7.913			0.657				
8.591			0.652	2031	118	1896	9.65
2.649	1.660						
3.104	1.664						
4.855	1.625						
17.10		8.77					
19.60		8.66					
3.68			0.543				
5.36			0.560	363	160	179	2.95
6.198	14.37						
8.293	14.36		(0.55)	2132 *	(148)	1962 *	9.8 *
2.490	1.119						
5.376	1.048						
32.09		6.14					
39.81		6.30					
7.532			0.584				
7.727			0.582	308	166	117	2.4
3.210	1.875						
5.294	1.832		(0.55)	417 *	(156)	238 *	3.4 *
4.932	0.567						
5.477	0.578		(0.46)	195 *	(143)	31 *	1.2 *
3.819	4.833						
6.150	4.807		(0.46)	695 *	(143)	531 *	5.1 *
3.819	4.833						
6.150	4.807		(0.55)	751 *	(149)	580 *	5.35 *

* Calculated by using estimated values of densities and refractivities, shown in parentheses.⁷ Chatt and Shaw, *J.*, 1959, 705, 4020; 1960, 1718.

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room temperature (20°) for 4 months. Recrystallisation from methanol then gave the isomer of configuration (III) as *needles* (0.25 g.) (Found: C, 41.2; H, 7.45%).

Hydridodichloro(carbonyl)bis(diethylphenylphosphine)iridium(III) Configuration (IV).—Method 1. A mixture of trichloro(carbonyl)bis(diethylphenylphosphine)iridium(III) configuration (II) (1.98 g.), aqueous potassium hydroxide (1.0N; 3.15 c.c.), and ethanol (50 c.c.) was heated under reflux for 15 min. The solution was evaporated to dryness and the residue twice recrystallised from methanol in an atmosphere of carbon dioxide to give the product as *needles* (0.92 g.) (Found: C, 40.4; H, 5.0. $C_{21}H_{31}Cl_2IrOP_2$ requires C, 40.4; H, 5.0%).

Method 2. A solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (1.5 g.) in ethanol (25 c.c.) was heated under carbon monoxide at 77°/73 atm. for 16 hr. On cooling a yellow precipitate formed, which when crystallised from methanol in an atmosphere of carbon dioxide gave the product as *needles* (0.52 g.) (Found: C, 40.1; H, 5.0%).

Hydridodichloro(carbonyl)bis(diethylphenylphosphine)iridium(III) [IrHCl₂(CO)(PEt₂Ph)₂] Configuration (VII).—Method 1. A solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (2.0 g.) in ethanol (25 c.c.) was heated under carbon monoxide for 18 hr. at 120°/78 atm. The product separated on cooling and on recrystallisation from methanol formed *prisms* (0.61 g.) (Found: C, 40.45; H, 5.15; Cl, 11.8%; *M*, ebullioscopically in 1.490% solution in benzene, 645. $C_{21}H_{31}Cl_2IrOP_2$ requires Cl, 11.35%; *M*, 625). The compound was non-conducting in nitrobenzene.

Method 2. A solution of chloroiridic acid (3.36 g.) in ethanol (50 c.c.) was heated under reflux for 2 hr. with carbon monoxide bubbling through the solution. Diethylphenylphosphine (3.04 g.) was then added after cooling; the solution was reheated to boiling under nitrogen and cooled, the required product separated as *white prisms* (3.52 g.), m. p. 123—136° (decomp.). The infrared spectrum of this compound was identical with that prepared by method 1.

Hydridodibromo(carbonyl)bis(diethylphenylphosphine)iridium(III) [IrHBr₂(CO)(PEt₂Ph)₂] Configuration (VII).—Carbon monoxide was bubbled through a boiling solution of sodium bromoiridate (3.9 g.) in ethanol (70 c.c.) for 18 hr. The solution was cooled, diethylphenylphosphine (1.33 g.) added, and the mixture heated to boiling, filtered, and allowed to cool. The product formed *prisms* (1.55 g.) from ethanol (Found: C, 35.6; H, 4.5. $C_{21}H_{31}Br_2IrOP_2$ requires C, 35.35; H, 4.4%).

Dihydridodi-μ-chloro-dichloro(dicarbonyl)bis(triethylphosphine)di-iridium(III) [IrHCl₂(CO)PEt₃]₂.—A mixture of chloroiridic acid (7.45 g.) and concentrated hydrochloric acid (1.5 c.c.) in 2-methoxyethanol (50 c.c.) was heated on a water-bath. Triethylphosphine (2.30 g.) was then added and the solution heated under reflux for 2 hr. with carbon monoxide bubbling through it. On cooling, the product separated and when recrystallised from 2-methoxyethanol formed *prisms* (2.54 g.) (Found: C, 20.8; H, 4.0%; *M*, ebullioscopically in 1.97% chloroform solution, 841. $C_{14}H_{32}Cl_4Ir_2O_2P_4$ requires C, 20.5; H, 3.95%; *M*, 821). Triethylphosphine (2.26 g.) was added to the mother-liquors from the above, and the solution was heated under reflux under nitrogen for 3 hr. On cooling, trichloro(carbonyl)bis(triethylphosphine)iridium(III) configuration (I) separated as pale yellow prisms (3.46 g.), m. p. 156—158°. The infrared spectrum of this product was identical with the spectrum of the authentic material.

Determination of Dipole Moments.—The method of determination and meaning of the symbols are as described previously.⁷

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