# 1257. *Far-infrared Spectra of Some Halogeno–Iridium*(III) *Complexes;* trans-*Effects in Iridium*(III) *Complexes*

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Far-infrared absorption spectra of a series of halogeno–iridium(III) complexes containing tertiary arsines or phosphines as ligands have been recorded from 450—220 cm.$^{-1}$. Bands due to iridium–chlorine stretching modes are very strong, and readily identified by replacing chloride with other ligands, *e.g.*, hydride, bromide, or iodide. The iridium–chlorine stretching frequencies depend mainly on the ligand in *trans*-position, and occur within the ranges 320—303 cm.$^{-1}$ (*trans*-chlorine), 278—262 cm.$^{-1}$ (*trans*-tertiary phosphine or tertiary arsine), and 249—246 cm.$^{-1}$ (*trans*-hydrogen), but depend very little on ligands in *cis*-positions. Some iridium–bromine stretching frequencies have also been recorded. The spectra are a very useful aid in assigning stereochemistry. There is also good correlation between decreasing iridium–chlorine stretching frequency (bond strength) and lability of the chlorine towards nucleophilic substitution.

IT is well known that the lability of a given ligand and also the strength of a bond it forms with a metal atom can be markedly affected by other ligands. The effects have been demonstrated best in square planar complexes of platinum(II), where the lability of a ligand depends mainly on the "*trans*-effect" of the ligand in *trans*-position.[1] Unfortunately, very little is known about bond energies in such complexes, but the metal–ligand atom stretching frequency probably gives a good indication of the relative values of metal–ligand bond strengths for a given series of closely related compounds. For platinum(II) the platinum–hydrogen,[2] platinum–carbon,[3] and platinum–chlorine [4] stretching frequencies are all sensitive to the nature of the other ligands, particularly the ligand in *trans*-position. With a few exceptions, good correlation is obtained between these stretching frequencies and the *trans*-effects of the ligand in *trans*-position, *i.e.*, increasing *trans*-effect causes a decreasing frequency (bond strength).

We have now recorded the far-infrared spectra of some chloroiridium(III) complexes, and find that iridium–chlorine stretching frequencies depend markedly on the ligands in *trans*-position. The Table lists the frequencies of the infrared absorption bands for these complexes within the range 450—220 cm.$^{-1}$. The bands due to iridium–chlorine stretching are very strong or strong, and easily identified.

An iridium–chlorine stretching frequency occurs at 296 cm.$^{-1}$ in $K_3IrCl_6$,[3a] and other transition metal–chlorine stretching frequencies occur within this range and are usually strong or very strong, *e.g.*, platinum–chlorine,[4] gold–chlorine,[5] iridium–chlorine,[6,7] and many others.[5-7]

In practically all the cases we have studied, the assignments of iridium–chlorine stretching bands have been confirmed by substitution of the chlorine by another ligand, as described below. Values of iridium–chlorine stretching frequencies fall naturally into three groups depending on the *trans*-ligands, *viz.*, 320—303 cm.$^{-1}$ (*trans*-chlorine), 278—262 cm.$^{-1}$ (*trans*-tertiary phosphine or -tertiary arsine) and 249—246 cm.$^{-1}$ (*trans*-hydrogen). Frequencies due to other vibrations are recorded in the Table; they were generally not assigned,

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[1] See F. Basolo and R. G. Pearson, " Mechanism of Inorganic Reactions," Wiley, New York, 1958, pp. 172—192 for a review.

[2] J. Chatt, L. A. Duncanson, B. L. Shaw, and L. M. Venanzi, *Discuss. Faraday Soc.*, 1958, **26**, 131.

[3] D. M. Adams, J. Chatt, and B. L. Shaw, *J.*, 1960, 2047.

[3a] D. M. Adams and H. A. Gebbie, *Spectrochim. Acta*, 1963, **19**, 925.

[4] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J.*, 1964, 734.

[5] G. E. Coates and C. Parkin, *J.*, 1963, 421.

[6] J. Lewis, R. S. Nyholm, and G. A. Rodley, *J.*, 1965, 1483.

[7] D. M. Adams, *Proc. Chem. Soc.*, 1961, 335.

but a few iridium–bromine stretching frequencies came within the range of our instrument, and are shown in italics.

*Assignment of the Metal–Chlorine Stretching Frequencies.*—These assignments were based on changes in the spectrum when chlorine was substituted by another ligand. For example, yellow trichloroiridium(III) complexes of type $[IrCl_3L_3]$ (L = tertiary phosphine or tertiary arsine) are known to have the *trans*-structure (I).[8] One would expect three infrared active iridium–chlorine stretching vibrations for complexes of this type, but in fact we find that all show only two very strong absorptions (within the ranges 320—303 and 278—262 cm.$^{-1}$). Presumably one iridium–chlorine absorption is so weak as to be undetectable. This could be due to the two bonds to *trans*-chlorines being so nearly collinear that the symmetric stretching vibration causes hardly any dipole moment change and hardly any absorption.† These two bands disappear when the chlorine atoms are replaced by bromine, iodine or hydrogen, *e.g.*, the compound *trans*-$[IrCl_3(PEt_2Ph)_3]$ shows

Far infrared absorptions for some halogeno–iridium(III) complexes; iridium–bromine stretching frequencies are in italics. Error $< \pm 2$ cm.$^{-1}$

| Compound | Configuration | Frequency of other bands in cm.$^{-1}$ | $\nu$(Ir–Cl) cm.$^{-1}$ | | |
|---|---|---|---|---|---|
| | | | Trans Cl | Ligand P or As | Atom H |
| *trans*-$[IrCl_3(PEt_3)_3]$ | I | 440w, 389w, 303w * | 313vs | 262vs | |
| *trans*-$[IrI_3(PEt_3)_3]$ | I | 426m, 383w, 328w | | | |
| $[IrHCl_2(PEt_3)_3]$ | II | 431m, 384w | 314vs | | |
| $[IrICl_2(PEt_3)_3]$ | II | 444w, 434w, 391w,* 380w | 312vs | | |
| *trans*-$[IrCl_3(P^nPr_3)_3]$ | I | 419m, 381m | 313vs | 268vs | |
| $[IrHCl_2(P^nPr_3)_3]$ | II | 417m, 373w | 308vs | | |
| *trans*-$[IrCl_3(PMe_2Ph)_3]$ | I | 437m, 426m, 414m, 359s, 324s,* 303s * | 315vs | 276vs | |
| *trans*-$[IrBr_3(PMe_2Ph)_3]$ | I | 437m, 427m, 413m, 356m, 340m, 320w, 308w, *ca.* 220m | | | |
| *trans*-$[IrI_3(PMe_2Ph)_3]$ | I | 427w, 410w | | | |
| $[IrHCl_2(PMe_2Ph)_3]$ | II | 437w, 415m, 357m, 325m,* 301m * | 313vs | | |
| $[IrHCl_2(PMe_2Ph)_3]$ | IV | 446m, 433w, 417m, 358s, 348w, 316w | | 273vs | 246vs |
| $[IrHI_2(PMe_2Ph)_3]$ | IV | 448w, 433m,* 418m, 386w,* 375w,* 361m, 316w, 288w | | | |
| $[IrH_2Cl(PMe_2Ph)_3]$ | III | 444w, 420m, 364m, 346m, 322m, 281w | | | 249vs |
| $[IrBrCl_2(PMe_2Ph)_3]$ | II | 437s, 426m, 413m, 360m, 323s,* 303s * | 314vs | | |
| $[IrICl_2(PMe_2Ph)_3]$ | II | 435s, 426m, 413s, 356m, 306s | 317vs | | |
| $[IrCl_2(CN)(PMe_2Ph)_3]$ | II | 439m, 425m,* 417m, 347m, 328s, 301s | 315s | | |
| $[IrCl_2(SCN)(PMe_2Ph)_3]$ | II | 441m, 418m, 356w, 328s | 315s | | |
| $[HPMe_2Ph][IrCl_4(PMe_2Ph)_2]$ | | 419m, 400m | 303vs | | |
| $[Me_4N][IrCl_4(PMe_2Ph)_2]$ | | 418m | 305vs | | |
| *trans*-$[IrCl_3(PEt_2Ph)_3]$ | I | 444m, 403m,* 392m | 314vs | 266vs | |
| *trans*-$[IrBr_3(PEt_2Ph)_3]$ | I | 441m, 405m, 391m, 326w, 267w, *222*s | | | |
| *trans*-$[IrI_3(PEt_2Ph)_3]$ | I | 439m, 402m,* 389m, 323w | | | |
| $[IrHCl_2(PEt_2Ph)_3]$ | II | 459m, 444m, 407w, 262w | 307vs | | |
| $[IrHBr_2(PEt_2Ph)_3]$ | II | 441m, 412m, 403m,* 328m, 301w, 253w, *225*s | | | |
| $[IrHCl_2(PEt_2Ph)_3]$ | IV | 398w, 328w | | 262vs | 248s |
| $[IrHBr_2(PEt_2Ph)_3]$ | IV | 451m, 402m,* 389m, 357w, 325w, 258w | | | |
| $[IrHI_2(PEt_2Ph)_3]$ | IV | 444w, 408w, 395w, 355w, 324w | | | |
| $[IrH_2Cl(PEt_2Ph)_3]$ | III | 448m, 407w, 327w, 323w * | | | 247vs |
| $[IrH_2Br(PEt_2Ph)_3]$ | III | 448m, 412w,* 402m, 326m, 263w | | | |
| $[IrH_2I(PEt_2Ph)_3]$ | III | 448m, 415w,* 405m, 326m, 315w,* 271w | | | |
| $[IrICl_2(PEt_2Ph)_3]$ | II | 443m, 389m | 318vs | | |
| $[IrBr_2Cl(PEt_2Ph)_3]$ | II | 443m, 403m,* 389m, 326m, 304w, *230*s | | 270vs | |
| *trans*-$[IrCl_3(P^nPr_2Ph)_3]$ | I | 465m, 446m, 412m, 390m, 242m | 318vs | 268vs | |
| $[IrHCl_2(P^nPr_2Ph)_3]$ | II | 448m, 408m, 392m, 299w | 315s | | |
| *trans*-$[IrCl_3(P^nBu_2Ph)_3]$ | I | 418m, 394m | 312vs | 269vs | |
| *trans*-$[IrCl_3(PMePh_2)_3]$ | I | 446m, 415m | 320vs | 277vs | |
| *trans*-$[IrCl_3(AsEt_3)_3]$ | I | 343m | 311vs | 275vs | |
| $[IrHCl_2(AsEt_3)_3]$ | II | 345m | 312vs | | |
| *trans*-$[IrCl_3(AsMe_2Ph)_3]$ | I | 316s,* 253m | 308vs | 278vs | |
| *trans*-$[IrBr_3(AsMe_2Ph)_3]$ | I | 314s, 306s, 283m, 297m, 242m | | | |

* Shoulder.

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† We are grateful to a referee for pointing this out.

[8] J. Chatt, A. E. Field, and B. L. Shaw, *J.*, 1963, 3371.

two very strong bands at 314 and 266 cm.$^{-1}$, as well as other weaker bands within the range 450—220 cm.$^{-1}$. In the infrared (i.r.) spectrum of the corresponding bromide, *trans*-$[IrBr_3(PEt_2Ph)_3]$, the two very strong bands have disappeared, but the rest of the spectrum is very similar except for an extra band at 222 cm.$^{-1}$, assigned to an iridium–bromine stretching mode of vibration. Similarly for the iodo-complex *trans*-$[IrI_3(PEt_2Ph)_3]$, except that bands due to iridium–iodine stretch are below 220 cm.$^{-1}$. Of the two i.r. absorption bands at 314 and 266 cm.$^{-1}$, due to iridium–chlorine stretching modes of vibration, the one at lower frequency is assigned to the chlorine in *trans*-position to phosphorus on the following evidence. When *trans*-$[IrCl_3(PEt_2Ph)_3]$ is treated with a hot ethanolic solution of potassium hydroxide (1 mol.) the chlorine atom *trans* to phosphorus is replaced by hydrogen to give the yellow hydro-complex $[IrHCl_2(PEt_2Ph)_3]$, configuration (II) ($Y = H$, $L = PEt_2Ph$); the configuration of this compound is based on its low dipole moment (2·55 *D*) [9] and also in the nuclear magnetic resonance (n.m.r.) pattern of the hydride ligand.[10] This yellow monohydro-complex showed only one band due to an iridium–chlorine stretching vibration; this was at 307 cm.$^{-1}$, the low frequency band having disappeared. Moreover, when this yellow hydride *trans*-$[IrHCl_2(PEt_2Ph)_3]$ of configuration (II) was treated with nitric acid in the presence of sodium iodide, hydrogen was evolved and the monoiodo-complex $[IrICl_2(PEt_2Ph)_3]$, of configuration (II) ($Y = I$, $L = PEt_2Ph$), was formed. As expected, this compound showed only one band due to iridium–chlorine stretch (antisymmetric), and this was at 318 cm.$^{-1}$. Moreover, the dibromohydro-complex $[IrHBr_2(PEt_2Ph)_3]$, configuration (II) ($Y = H$), when treated with hydrochloric acid gave the corresponding dibromo-chloro-complex $[IrClBr_2(PEt_2Ph)_3]$, configuration (II) ($Y = Cl$, $L = PEt_2Ph$ or Br replacing the other two Cl). This compound had an iridium–chlorine stretching frequency at 270 cm.$^{-1}$ and a band at 230 cm.$^{-1}$ assigned to an iridium–bromine stretching frequency.

A similar but more extensive study of dimethylphenylphosphine complexes was made. These compounds had the advantage that the $^1H$ n.m.r. spectrum of the phosphine ligands were used to confirm the stereochemistry. We have shown [11] that when two dimethylphenylphosphine ligands are in mutual *trans*-positions the methyl protons couple equally with both phosphorus nuclei (virtual coupling) and give a narrow triplet, intensity ratios 1 : 2 : 1. In contrast, a dimethylphenylphosphine ligand without another phosphine in *trans*-position gives a 1 : 1 doublet. The n.m.r. spectra of all the dimethylphenylphosphine complexes shown in Table 1 were in agreement with their assigned stereochemistries (the data will be published later). The trichloro-complex *trans*-$[IrCl_3(PMe_2Ph)_3]$, configuration (I), showed two very strong bands at 313 and 268 cm.$^{-1}$, due to iridium–chlorine stretching frequencies. These were absent in the corresponding tribromo- and tri-iodo-complexes. The yellow hydro-complex $[IrHCl_2(PMe_2Ph)_3]$, configuration (II) ($Y = H$, $L = PMe_2Ph$), showed only one iridium–chlorine stretching frequency, at 313 cm.$^{-1}$, and when treated with sodium iodide and nitric acid it gave the dichloroiodo-complex $[IrICl_2(PMe_2Ph)_3]$, configuration (II) ($Y = I$), or with hydrobromic acid the corresponding bromodichloro-complex. A thiocyanato-complex $[IrCl_2(SCN)(PMe_2Ph)_3]$, configuration (II) ($Y = SCN$), was similarly prepared from the hydride, nitric acid, and potassium thiocyanate. All these dichloro-complexes showed only one iridium–chlorine stretching band, and this at a frequency $>300$ cm.$^{-1}$. Complexes of type $[IrYCl_2(PMe_2Ph)_3]$, configuration (II) with $Y = I$ or CN, were also prepared by treating the corresponding trichloro-complex with sodium iodide (excess) or sodium cyanide (1 mol.), showing that chlorine in *trans*-position to phosphine is more labile than chlorine in *trans*-position to chlorine (which required treatment with an excess of sodium iodide in boiling methyl isopropyl ketone for two days to effect complete replacement.) When treated with boiling 2-diethylaminoethanol the trichloro-complex *trans*-$[IrCl_3(PMe_2Ph)_3]$ gave the dihydro-complex

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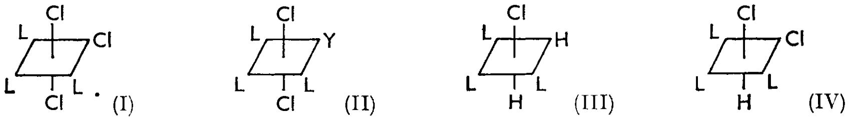
[9] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931.

[10] B. L. Shaw and J. Chatt, Proceedings of the 7th I.C.C.C., Stockholm and Uppsala, June 1962, p. 293.

[11] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279.

$[IrH_2Cl(PMe_2Ph)_3]$, which by analogy with the corresponding diethylphenylphosphine complex $[IrH_2Cl(PEt_2Ph)_3]$ [10] has the configuration (III) (L = $PMe_2Ph$). The proton magnetic resonance spectrum of the methyl groups and also of the hydride ligands confirm this stereochemistry, and will be discussed in a future Paper. The compounds $[IrH_2Cl(PMe_2Ph)_3]$ and $[IrH_2Cl(PEt_2Ph)_3]$ had iridium–chlorine stretching frequencies at 249 and 247 cm.$^{-1}$ respectively; the assignment was confirmed for the compound $[IrH_2Cl(PEt_2Ph)_3]$ by making the corresponding bromide and iodide.



Configurations of irridium(III) complexes L = Neutral ligand Sometimes Br or I replace Cl.

On treatment with dilute hydrochloric acid the hydrogen in *trans*-position to phosphorus was replaced by chlorine, giving white monohydro-complexes of configuration (IV) [10] (L = $PMe_2Ph$ and $PEt_2Ph$, respectively). These compounds each had two iridium–chlorine stretching frequencies, $[IrHCl_2(PMe_2Ph)_3]$ at 273 and 246 cm.$^{-1}$ and $[IrHCl_2(PEt_2Ph)_3]$ at 262 and 248 cm.$^{-1}$. Clearly the two higher frequencies correspond to chlorines in *trans*-position to phosphorus and the two lower ones to the chlorines in *trans*-position to hydrogen. Corresponding bromohydro- and hydroiodo-complexes were also made, and their i.r. spectra helped to confirm the assignment. As will be seen from the Table, various other chloro-, bromo-, iodo- and hydro-complexes were prepared and their far infrared spectra recorded; these were wih the phosphines $PEt_3$, $PPr_3{}^n$, $PPr_2{}^nPh$, $PBu_2{}^nPh$, $PMePh_2$ and also with the arsines $AsEt_3$ and $AsMe_2Ph$. In all cases the numbers of and frequencies of the bands due to iridium–chlorine stretching modes were in excellent agreement with those of the corresponding complexes containing dimethylphenylphosphine or diethylphenylphosphine as ligands. In addition, i.r. spectra of salts of the ion $[IrCl_4(PMe_2Ph)_2]^-$ were recorded. This ion has previously been shown to have *trans*-configuration,[11] and only one iridium–chlorine stretching frequency was therefore observed (at 305 and 303 cm.$^{-1}$ for the two salts).

*Discussion of the Iridium–Chlorine Stretching Frequencies.*—Our results show that the i.r. spectra of chloro-iridium(III) complexes in the region of metal–chlorine stretching frequencies are a valuable aid in assigning stereochemistry. They are also very useful for comparing iridium–chlorine bond strengths. We assume that a decreasing iridium–chlorine stretching frequency corresponds to a decreasing force constant, *i.e.*, bond strength. This is probably true, since the complexes being compared are of similar type. Our results indicate that hydride as *trans*-ligand causes the greatest weakening of the iridium–chlorine bond. A *trans*-hydride ligand gave the lowest platinum–chlorine stretching frequency observed in the extensive series of chloro-platinum(II) complexes studied by Adams, Chatt, Gerratt, and Westland.[4] This was attributed to an inductive electron release mechanism by the weakly electronegative hydride ligand, *i.e.*, chlorine in *trans*-position to hydride carries more negative charge than chlorine in *trans*-position to chlorine, and the bond it forms to the platinum will be weaker and probably longer (the Pt–Br distance in trans-$[PtHBr(PEt_3)_2]$ is 2·56 Å whilst the radius sum is only 2·42 Å).[12]

We suggest that a similar inductive mechanism operates in our iridium(III) complexes. An alternative description is that a chlorine atom with hydrogen or phosphorus in *trans*-position contributes more of its character to the bonding molecular orbitals than does a chlorine atom with another chlorine atom in *trans*-position.

Decreasing iridium–chlorine stretching frequency in these hydro-complexes is paralleled by an increasing lability towards chemical attack, *e.g.*, when the complex $[IrH_2Cl(PEt_2Ph)_3]$ is treated with sodium iodide, the chlorine is readily replaced by iodine, but we find that

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

with chlorine in *trans*-position to chlorine metathetical replacement by iodine requires high temperatures and very long reaction times (see the Experimental section for examples). Decreasing platinum–chlorine stretching frequency in platinum(II) complexes is usually paralleled by increased lability, *e.g.*, the chlorine of the hydro-complex trans-$[PtHCl(PEt_3)_2]$ is very labile to nucleophilic substitution.[4,13]

Similarly, tertiary phosphines and tertiary arsines in *trans*-position to chlorine cause low iridium–chlorine stretching frequencies and high lability of the chlorine, *e.g.*, the trichloro-complex *trans*-$[IrCl_3(PEt_3)_3]$ when treated with sodium iodide in hot acetone for 3 min. gives the monoiodo-complex $[IrICl_2(PEt_3)_3]$, configuration (II) ($Y = I, L = PEt_3$), but to replace the other two chlorines a $3\frac{1}{2}$ hr. treatment in boiling methyl ethyl ketone is necessary. $d_\pi$–$d_\pi$-Bonding between phosphine and iridium could either strengthen or weaken an iridium–chlorine bond in *trans*-position, depending on the direction of the electron donation in the $d_\pi$–$d_\pi$- or $d_\pi$–$p_\pi$-bonding between iridium and chlorine. However, we think the major factor weakening the iridium–chlorine bond in the *trans*-position is inductive electron release by the phosphine [phosphorus has a similar electronegativity to hydrogen (2·1)]. Dipole moment measurements show that there is a large electron drift from phosphorus to *trans*-chlorine in the trichloro-complexes of type *trans*-$[IrCl_3(PR_3)_3]$, configuration (I); these have moments of *ca.* 7·0 *D*.[8]

The effects of *cis*-ligands on iridium–chlorine stretching frequencies were small, *e.g.*, in the series of complexes of type $[IrYCl_2(PMe_2Ph)_3]$, configuration (II) with Y = Cl, H, Br, I, SCN or CN, values for ν (Ir–Cl) were 315, 313, 314, 317, 315 and 315 cm.$^{-1}$ respectively. Similarly, changes in the phosphine or arsine ligands in *cis*-positions had little effect on the iridium–chlorine stretching frequencies.

Environmental effects in the solid state often do change absorption frequencies and cause bands to split. However, for the compounds described in this Paper the correlation of iridium–stretching frequencies with stereochemistry is so good that solid state interactions must affect these frequencies approximately equally, or must be small. In no case did we find an iridium–chlorine frequency band to be split.

*Preparation of the Complexes.*—The trichloro- and various hydro-complexes were prepared by known methods and several of them have been described previously.[8–10,14] The tri-iodo-complexes $[IrI_3(PR_3)_3]$ were prepared from the trichloro-complexes by prolonged treatment with sodium iodide in a ketonic solvent; an alcoholic solvent must not be used since the alcohol would react to give iridium hydride complexes.[9,14–16] The tribromo-complexes $[IrBr_3L_3]$ (L = tertiary phosphine or tertiary arsine) were prepared from sodium bromoiridate and the neutral ligand reacting in aqueous methyl ethyl ketone (again an alcoholic solvent must be avoided). The complexes containing mixed halides and also the thiocyanato- and cyano-complexes are of a new type: they were prepared either (1), by treating a hydride with mineral acid in the presence of the required anion, or (2), by making use of the different reactivities of the iridium–chlorine bonds, and replacing reactive chlorine with other anions by metathesis.

## EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. All reactions involving free tertiary phosphines or arsines or hydro-complexes were carried out under nitrogen.

*Spectra.*—The infrared spectra (450—220 cm.$^{-1}$) of the complexes as Nujol mulls supported on polyethylene plates were recorded on a Grubb–Parsons D.B.3/D.N.2 spectrometer calibrated with water vapour. The errors are $< \pm 2$ cm.$^{-1}$.

*Preparation of Trihalide Complexes.*—trans-*Trichlorotris*(*dimethylphenylphosphine*)*iridium*(III); $[IrCl_3(PMe_2Ph)_3]$. Concentrated hydrochloric acid (0·5 ml.) was added to a solution

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[13] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J.*, 1961, 2207.

[14] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1961, 290.

[15] J. Chatt, R. S. Coffey, and B. L. Shaw, unpublished work.

[16] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 2784.

of chloroiridic acid (2·30 g.) in 2-methoxyethanol (25 ml.), and the solution warmed until it became greenish-brown. Dimethylphenylphosphine (3·18 g.) was added to the cold solution, which was then heated under reflux for 1½ hr. and cooled, when a mixture of pink and yellow crystals separated. The mixture was extracted with benzene, which dissolved the yellow crystals. Evaporation of the benzene solution under reduced pressure gave a yellow solid, which when recrystallised from benzene–methanol gave trans-*trichlorotris(dimethylphenylphosphine)iridium*(III) as yellow prisms (2·41 g.), m. p. 238—241° (Found: C, 40·3; H, 4·65. $C_{24}H_{33}IrP_3$ requires C, 40·4; H, 4·65%). The pink residue when recrystallised from methanol gave *dimethylphenylphosphonium tetrachlorobis(dimethylphenylphosphine)iridate*(III) as pink prisms (1·07 g.), m. p. 165—168° (decomp.) (Found: C, 38·3; H, 4·55. $C_{24}H_{34}Cl_4IrP_2$ requires C, 38·5; H, 4·57%). Molar conductivity in nitrobenzene at 20°, 16·1 mho ($10^{-3}$M solution.)

*Tetramethylammonium tetrachlorobis(dimethylphenylphosphine)iridate*(III); $[Me_4N][IrCl_4(PMe_2Ph)_2]$. A solution of dimethylphenylphosphonium tetrachlorobis(dimethylphenylphosphine)iridate(III) (0·1 g.) in boiling methanol (5·0 ml.) was added to a solution of tetramethylammonium chloride (0·4 g.) in boiling methanol (1·0 ml.). The hot filtered solution gave on cooling the *tetramethylammonium iridate* as pink prisms (0·046 g.), m. p. 265—267° (decomp.) (Found: C, 35·1; H, 4·9; N, 2·4. $C_{20}H_{34}Cl_2IrNP_2$ requires C, 35·1; H, 5·0; N, 2·0%). Molar conductivity in nitrobenzene at 20°, 21·4 mho ($10^{-3}$M solution).

trans-*Tribromotris(dimethylphenylphosphine)iridium*(III); $[IrBr_3(PMe_2Ph)_3]$. Dimethylphenylphosphine (1·10 g.) was added to a solution of sodium bromoiridate (2·45 g.) in water (2·0 ml.) and methyl ethyl ketone (10 ml.). After heating the mixture under reflux for 3 hr. it was cooled, and the product filtered off. Recrystallisation from methyl ethyl ketone gave the *complex* as orange prisms (1·09 g.), m. p. 216—220° (decomp.) (Found: C, 34·1; H, 3·9; Br, 27·8. $C_{24}H_{33}Br_3IrP_3$ requires C, 34·1; H, 3·9; Br, 28·3%).

trans-*Trichlorotris(methyldiphenylphosphine)iridium*(III); $[IrCl_3(PMePh_2)_3]$. Concentrated hydrochloric acid (0·25 ml.) was added to a solution of chloroiridic acid (0·697 g.) in 2-methoxyethanol (25 ml.) and the solution warmed until it became greenish-brown. Methyldiphenylphosphine (1·16 g.) was added to the cold solution, which was then heated under reflux for 40 min. and cooled. The yellow crystals which separated were recrystallised from methyl ethyl ketone to give the *complex* as yellow prisms (1·19 g.), m. p. 240—246° (Found: C, 52·5; H, 4·5. $C_{24}H_{39}Cl_3IrP_3$ requires C, 52·2; H, 4·4%).

trans-*Tribromotris(dimethylphenylarsine)iridium*(III); $[IrBr_3(AsMe_2Ph)_3]$. Dimethylphenylarsine (2·45 g.) was added to a solution of sodium bromoiridate (3·36 g.) in water (10 ml.) and methyl ethyl ketone (20 ml.). After heating the solution under reflux for 1½ hr., partial evaporation of the solvent under reduced pressure gave a brown solid, which when recrystallised from methyl ethyl ketone yielded the *complex* as orange prisms (1·42 g.), m. p. 206—208° (Found: C, 29·5; H, 3·4. $C_{24}H_{33}As_3Br_3Ir$ requires C, 29·6; H, 3·4%).

*Preparation of Hydrides.—Dichlorohydrotris(dimethylphenylphosphine)iridium*(III), configuration (II); $[IrHCl_2(PMe_2Ph)_3]$. Aqueous N-potassium hydroxide (1·05 ml.) was added to a suspension of *trans*-trichlorotris(dimethylphenylphosphine)iridium(III) (0·712 g.) in boiling methanol (25 ml.). The solution was heated under reflux for 50 min., cooled, and the solvent removed under reduced pressure. A benzene extract of the residue was evaporated to dryness under reduced pressure to give a yellow solid which when recrystallised from methanol gave the *dichlorohydro-complex*, as yellow needles (0·475 g.), m. p. 163—165° (decomp.) (Found: C, 42·7; H, 5·1. $C_{24}H_{34}Cl_2IrP_3$ requires C, 42·5; H, 5·1%). ν(Ir–H) 2070 cm.$^{-1}$ (Nujol), 2042 cm.$^{-1}$ (benzene solution).

*Dichlorohydrotris(di-n-propylphenylphosphine)iridium*(III), configuration (II); $[IrHCl_2(PPr_2^nPh)_3]$. Aqueous N-potassium hydroxide (1·05 ml.) was added to a solution of *trans*-trichlorotris(di-n-propylphenylphosphine)iridium(III) (0·846 g.) in a mixture of boiling ethanol (15 ml.) and benzene (5 ml.). The solution was heated under reflux for 1 hr., cooled, and the solvent removed under reduced pressure. A benzene extract of the residue was evaporated to dryness under reduced pressure to give a yellow solid which, when recrystallised from ethanol, gave the *dichlorohydro-complex*, as yellow prisms (0·59 g.), m. p. 147—149° (Found: C, 51·5; H, 7·0; Cl, 8·6. $C_{36}H_{58}Cl_2IrP_3$ requires C, 51·5; H, 6·9; Cl, 8·4%). ν(Ir–H), 2035 cm.$^{-1}$ (Nujol), 2040 cm.$^{-1}$ (benzene solution).

*Hydrodi-iodotris(dimethylphenylphosphine)iridium*(III), configuration (IV); $[IrHI_2(PMe_2Ph)_3]$. *trans*-Trichlorotris(dimethylphenylphosphine)iridium(III) (1·5 g.) and sodium iodide (3·0 g.) were dissolved in 2-methoxyethanol (25 ml.) and the solution heated under reflux for 30 hr.

After cooling, water was added, and the solution extracted with dichloromethane. Evaporation of the extract under reduced pressure gave a pale yellow solid, which when recrystallised from light petroleum (b. p. 80—100°) gave the *hydrodi-iodo-complex* as pale yellow prisms (1·01 g.), m. p. 151—170° (decomp.) (Found: C, 34·0; H, 4·3. $C_{24}H_{34}I_2IrP_3$ requires C, 33·5; H, 4·0%. ν(Ir–H) 2204m, 2168s cm.$^{-1}$ (Nujol), 2171 cm.$^{-1}$ (benzene solution).

*Chlorodihydrotris(dimethylphenylphosphine)iridium*(III), configuration (III); [$IrH_2Cl(PMe_2Ph)_3$]. A solution of *trans*-trichlorotris(dimethylphenylphosphine)iridium(III) (1·0 g.) and lithium chloride (2 g.) in 2-diethylaminoethanol (25 ml.) was heated under reflux for 2½ hr. and cooled; water was added, and the product isolated in benzene. Evaporation of the solvent under reduced pressure gave a dark oil, from which a colourless solid deposited. Recrystallisation from light petroleum (b. p. 60—80°) gave the *chlorodihydro-complex*, as colourless prisms (0·57 g.), m. p. 122—124° (Found: C, 45·1; H, 5·5. $C_{24}H_{35}ClIrP_3$ requires C, 44·8; H, 5·5%). ν(Ir–H) 2204, 2010 cm.$^{-1}$ (Nujol), 2174, 2010 cm.$^{-1}$ (benzene solution).

*Dichlorohydrotris(dimethylphenylphosphine)iridium*(III), configuration (IV); [$IrHCl_2(PMe_2Ph)_3$]. A solution of chlorodihydrotris(dimethylphenylphosphine)iridium(III) (0·15 g.) in ethanol (4 ml.) was treated with N-hydrochloric acid (2·24 ml.) in ethanol (4 ml.). The solution was put aside for 4 days at room temperature, when a colourless deposit formed. Recrystallisation from ethanol gave the *dichlorohydro-complex*, as colourless prisms (0·114 g.), m. p. 178—182° (Found: C, 42·6; H, 4·9. $C_{24}H_{34}Cl_2IrP_3$ requires C, 42·5; H, 5·1%). ν(Ir–H) 2212, 2183, 2167 cm.$^{-1}$ (Nujol), 2182 cm.$^{-1}$ (benzene solution).

*Hydride Substitution Reactions.—Bromodichlorotris(dimethylphenylphosphine)iridium*(III), configuration (II); [$IrBrCl_2(PMe_2Ph)_3$]. 1·15N-Hydrobromic acid (0·26 ml. was added to a solution of dichlorohydrotris(dimethylphenylphosphine)iridium, configuration(II), (0·20 g.) in hot ethanol (15 ml.). On cooling, the *bromodichloro-complex* was deposited as pale yellow needles (0·198 g.), m. p. 216—225° (Found: C, 38·1; H, 4·5. $C_{24}H_{33}BrCl_2IrP_3$ requires C, 38·1; H, 4·4%).

*Dibromochlorotris(diethylphenylphosphine)iridium*(III), configuration (II); [$IrBr_2Cl(PEt_2Ph)_3$] N-Hydrochloric acid (0·5 ml.) was added to a solution of dibromohydrotris(diethylphenylphosphine)iridium(III), configuration (II), (0·425 g.) in methanol (25 ml.). A yellow solid eparated, which when recrystallised from ethanol gave the *dibromochloro-complex*, as pale yellow needles (0·15 g.), m. p. 230—245° (decomp.) (Found: C, 40·7; H, 5·05. $C_{30}H_{45}Br_2ClIrP_3$ requires C, 40·7; H, 5·1%).

*Dichloroiodotris(dimethylphenylphosphine)iridium*(III), configuration (II); [$IrICl_2(PMe_2Ph)_3$]. N-Nitric acid (0·25 ml.) was added to a solution of dichlorohydrotris(dimethylphenylphosphine)-iridium(III), configuration (II), (0·17 g.) and sodium iodide (0·2 g.) in acetone (10 ml.). The solution was put aside at 20° for 30 min., and then evaporated to dryness under reduced pressure. A dichloromethane extract of the residue was evaporated to dryness under reduced pressure to give a yellow solid, which on recrystallisation from dichloromethane–methanol gave the *dichloro-complex* as orange micro-prisms (0·135 g.), m. p. 215—225° (Found: C, 35·7; H, 4·0. $C_{24}H_{33}Cl_2IIrP_3$ requires C, 35·9; H, 4·1%).

*Dichloroiodotris(diethylphenylphosphine)iridium*(III), configuration (II); [$IrICl_2(PEt_2Ph)_3$]. N-Nitric acid (0·25 ml.) was added to a solution of dichlorohydrotris(diethylphenylphosphine)-iridium(III), configuration (II) (0·19 g.) and sodium iodide (0·4 g.) in acetone (10 ml.). The solution was stood at 20° for 30 min. and then evaporated to dryness under reduced pressure. A dichloromethane extract of the residue, evaporated to dryness under reduced pressure gave a yellow solid, which on recrystallisation from dichloromethane–methanol gave the *dichloroiodo-complex*, as orange yellow prisms (0·123 g.), m. p. 224—237° (Found: C, 40·4; H, 5·1. $C_{30}H_{45}Cl_2IIrP_3$ requires C, 40·6; H, 5·1%. 0·009523 g. compound gave 0·00549 g. silver halides, calc. 0·00559 g.).

*Dichlorothiocyanototris(dimethylphenylphosphine)iridium*(III), configuration (II); [$IrCl_2(SCN)(PMe_2Ph)_3$]. 2N-Nitric acid (0·6 ml.) was added to a solution of dichlorohydrotris-(dimethylphenylphosphine)iridium(III), configuration (II), (0·34 g.) and potassium thiocyanate (1·0 g.) in acetone (10 ml.). The solution was heated to boiling, and after a further 20 min. at room temperature the solvent was removed under reduced pressure to give a yellow solid. This, on recrystallisation from methanol, gave the *dichlorothiocyanato-complex*, as yellow prisms (0·268 g.), m. p. 91—104° (decomp.) (Found: C, 40·6; H, 4·7; Cl, 9·5; N, 1·9. $C_{25}H_{33}Cl_2IrNP_3S$ requires C, 40·8; H, 4·5; Cl, 9·6; N, 1·9%).

*Metathetical Replacement Reactions.—Dichloroiodotris(dimethylphenylphosphine)iridium*(III), configuration (II); $[IrICl_2(PMe_2Ph)_3]$. Sodium iodide (1·0 g.) was added to a solution of *trans*-trichlorotris(dimethylphenylphosphine)iridium(III) (0·5 g.) in methyl ethyl ketone (10 ml.) and the solution boiled under reflux for 3½ hr. The solvent was removed under reduced pressure. A benzene extract of the residue, on evaporation to dryness under reduced pressure, gave the dichloroiodocomplex, as orange-yellow prisms (0·249 g.), m. p. 215—225°, shown to be identical with an authentic sample by its i.r. spectrum.

*Dichlorocyanotris(dimethylphenylphosphine)iridium*(III), configuration (II); $[IrCl_2(CN)(PMe_2Ph_3]$. Sodium cyanide (0·106 g.) was added to a solution of *trans*-trichlorotris-(dimethylphenylphosphine)iridium(III) (0·712 g.) in ethanol (25 ml.), and the solution boiled under reflux for 3 hr. Addition of water to the old solution afforded a yellow solid which, when recrystallised from ethanol, gave the *dichlorocyano-complex*, as pale yellow needles (0·622 g.), m. p. 204—207° (decomp.) (Found: C, 42·7; H, 4·5; Cl, 10·2; N, 2·1. $C_{25}H_{33}Cl_2IrNP_3$ requires C, 42·7; H, 4·7; Cl, 10·1; N, 2·0%).

*Dichloroiodotris(triethylphosphine)iridium*(III), configuration (II); $[IrICl_2(PEt_3)_3]$. Sodium iodide (0·30 g.) was added to a solution of *trans*-trichlorotris(triethylphosphine)iridium(III) (0·33 g.) in acetone (10 ml.). The solution was boiled for 3 min. and then evaporated to dryness under reduced pressure. The residue was washed with water to give a yellow solid, which when recrystallised from acetone gave the *dichloroiodo-complex*, as yellow prisms (0·34 g.), m. p. 123—132° (decomp.) (Found: C, 28·9; H, 5·9. $C_{18}H_{45}Cl_2IIrP_3$ requires C, 29·0; H, 6·1%). 0·009088 g. compound gave 0·00643 g. silver halides, calc. 0·00634 g.).

trans-*Tri-iodotris(triethylphosphine)iridium*(III); $[IrI_3(PEt_3)_3]$. A solution of *trans*-trichlorotris(triethylphosphine)iridium(III) (1·0 g.) and sodium iodide (2·0 g.) in methyl ethyl ketone (25 ml.) was heated under reflux for 3½ hr. After cooling, the solvent was removed under reduced pressure. A chloroform extract of the residue, on evaporation to dryness, gave a red solid, which when recrystallised from light petroleum (b. p. 80—100°) gave the *tri-iodo-complex* as red prisms (0·46 g.), m. p. 158—163° (Found: C, 23·35; H, 4·8. $C_{18}H_{45}I_3IrP_3$ requires C, 23·3; H, 4·9%).

trans-*Tri-iodotris(dimethylphenylphosphine)iridium*(III); $[IrI_3(PMe_2Ph)_3]$. A solution of *trans*-trichlorotris(dimethylphenylphosphine)iridium(III) (0·6 g.) and sodium iodide (1·2 g.) in methyl isopropyl ketone (25 ml.) was heated under reflux for 48 hr. After cooling, the solvent was removed under reduced pressure. A dichloromethane extract of the residue, on evaporation to dryness under reduced pressure, gave a dark red solid, which after several recrystallisations from methyl ethyl ketone gave the *tri-iodo-complex* as red prisms (0·12 g.), m. p. 230—238° (Found: C, 29·7; H, 3·6. $C_{24}H_{33}I_3IrP_3$ requires C, 29·3; H, 3·4%).

trans-*Tri-iodotris(diethylphenylphosphine)iridium*(III); $[IrI_3(PEt_2Ph)_3]$. A solution of *trans*-trichlorotris(diethylphenylphosphine)iridium(III) (0·5 g.) and sodium iodide (1·0 g.) in methyl ethyl ketone (25 ml.) was heated under reflux for 3 hr. After cooling, the solvent was removed under reduced pressure. A dichloromethane extract of the residue, on evaporation to dryness under reduced pressure, gave a dark red solid which, when recrystallised from methyl ethyl ketone, gave the *tri-iodo-complex* as red prisms (0·25 g.), m. p. 213—223° (Found: C, 33·6; H, 4·1; I, 35·5. $C_{30}H_{45}I_3IrP_3$ requires C, 33·6; H, 4·2; I, 35·5%).

*Dihydroiodotris(diethylphenylphosphine)iridium*(III), configuration (IV); $[IrH_2I(PEt_2Ph)_3]$. A solution of chlorodihydrotris(diethylphenylphosphine)iridium(III) (0·5 g.) and sodium iodide (2·0 g.) in acetone (25 ml.) gave an immediate precipitate of sodium chloride when boiled. The cold solution was put aside at room temperature for 20 hr., when the solvent was removed under reduced pressure. The benzene extract of the residue was evaporated under reduced pressure to give a white solid, which when recrystallised from ethanol gave the *dihydroiodo-complex* as colourless prisms (0·25 g.), m. p. 118—120°, shown to be identical with an authentic sample by its i.r. spectrum, $\nu$(Ir–H) 2162, 2023 cm.$^{-1}$ (Nujol), 2167, 2036 cm.$^{-1}$ (benzene solution).

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