are: F_2SNCFO, −39.7;[2] SF_5NSF_2, −54.8;[14] C_2F_5-$NSFCF(CF_3)_2$, 26.2.[10] The spectra were found to show temperature dependence (see Figure 1). A neat sample yielded sharp doublet structure (J = 19 cps) at −60° for both the CFO and SF fluorine signals. This fine structure disappeared, the peaks broadened, and the chemical shift between the CFO and SF signals decreased as the sample temperature was raised (δ 58 ppm at −60° and δ 55 ppm at + 70°). The temperature dependence is believed to be the result of an exchange process with a rate at room temperature of the same order of magnitude as the spin coupling.[15] The exchange rate was lowered when the sample was diluted with 1,1,2-trichloro-1,2,2-trifluoromethane; hence the process may be intermolecular. The high Trouton constant (26.7) also suggests association.

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Stereochemical Course of Addition of Hydrogen Halides to Iridium(I) Complexes. The Effect of Solvents

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Convincing evidence for kinetically controlled *trans* addition of halogens, alkyl halides, acetyl halides, and hydrogen halides to *trans*-$[(C_6H_5)_2CH_3P]_2Ir(CO)Cl$[1] has been augmented by recent studies[2] which indicate that the addition of methyl bromide or methyl iodide to *trans*-$[(C_6H_5)(CH_3)_2P]_2IrCOCl$ is stereospecifically *trans*. In contrast to these reports is the generalized *cis* addition of diatomic molecules (X–Y) to planar *trans*-$[(C_6H_5)_3P]_2Ir(CO)Cl$ discussed by Vaska.[3] *cis*-Addition products were also reported by others.[4]

Gaseous hydrogen halides (HX) and crystalline *trans*-$[(C_6H_5)_3P]_2Ir(CO)Y$ (Y is a halogen) react to give octahedral *cis*-addition products (*i.e.*, H and X *cis*).[5] The addition of a diethyl ether solution of HBr to a benzene solution of *trans*-$[(C_6H_5)_2CH_3P]_2Ir(CO)Cl$ was reported to give a mixture of products with H and Br in *trans* as well as *cis* positions.[1] This same mixture was obtained in a similar reaction between HCl and *trans*-$[(C_6H_5)_2CH_3P]_2Ir(CO)Br$. Similar results, that is the formation of a single product (mixture), have been reported for the reaction of HCl and *trans*-$[(C_6H_5)_3P]_2Ir(CO)Br$ and the reaction of *trans*-$[(C_6H_5)_3P]_2Ir(CO)Cl$ and HBr.[6] Although it would seem from these results that the hydrogen halide addition reaction may not be stereospecific, it has been suggested that the observed mixtures of *cis* and *trans* products may result from stereoselectivity in the original oxidative-addition reaction, followed by subsequent isomerization reactions.[1] This proposal remains to be investigated. The effect of solvents on the stereochemical course of oxidative-addition reactions has not been carefully examined as yet. That the solvent can play a significant role in determining the stereochemistry of certain oxidative-addition reactions has been recently reported.[7] Herein we report experiments which indicate that the addition of hydrogen halide (HX) to square-planar iridium(I) complexes is stereospecifically *cis* in benzene solution. Mixtures of *cis* and *trans* products are obtained in benzene–methanol solution. The stereochemical course of HX addition in other solvents has also been investigated. Experiments designed to determine the origin of the mixtures of *cis*–*trans* products are described.

Experimental Section

Reagents.—Reagent grade benzene was distilled and stored over molecular sieve. Reagent grade chloroform was passed through an alumina column just prior to use. All other solvents which were of reagent grade quality were stored over molecular sieve and used without any further treatment. Matheson anhydrous halogen halides were used without further treatment. Anhydrous hydrogen chloride which was passed through concentrated sulfuric acid gave the same results as the untreated anhydrous hydrogen chloride. The iridium complexes were prepared as previously described.[1,8]

General Method.—Approximately 100 mg of iridium complex was placed in a flask which was purged with nitrogen or argon. Sufficient solvent (*e.g.*, 15 ml of dry benzene, 15 ml of benzene–5 ml methanol, 15 ml of benzene–5 ml of acetonitrile, 60 ml of dichloromethane, 15 ml of dimethylformamide, or 30 ml of chloroform) was added to dissolve the iridium complex completely. Special precautions were taken to avoid exposure of these solutions to atmospheric oxygen. Solutions of the anhydrous hydrogen halide in the respective solvents were added dropwise to the yellow solution of the iridium(I) complex, with efficient stirring, until the solution became colorless or until no further color change was observed. At this point argon or nitrogen was immediately bubbled into the solution and the solvent was then stripped on a rotary evaporator. The solid was washed with ether and dried. Similar products were obtained when the volume of solvent was reduced, and diethyl ether, hexane, or methanol was added to precipitate the white solids. Recrystallization of the white solids from benzene–methanol, benzene–hexane, or dichloromethane–ethanol gave decomposition products which were generally yellow. Attempted recrystallization of $[(CH_3C_6H_4)_3P]_2ClIrCO\cdot HBr$ from benzene–methanol, for example, gave a product with no detectable ν_{Ir-Cl}. Thin layer chromatography was conducted on precoated silica gel plates (Brinkmann Instruments,

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TABLE I

SELECTED INFRARED FREQUENCIES (cm^{-1}) OF PRODUCTS FROM REACTIONS OF HYDROGEN HALIDES (HX) AND *trans*-$L_2Ir(CO)Y$ IN BENZENE (Y IS HALOGEN OR PSEUDOHALOGEN; L IS PHOSPHINE OR ARSINE)

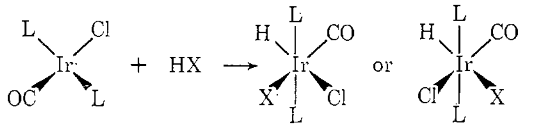
L	Y	HX	Ir–H[b]	IrC–O[a]	Ir–Cl[b]
$(C_6H_5)_3P$	Cl	HBr	2239 (2226)[a]	2044	263
$(C_6H_5)_3P$	Cl	HI	2240 (2228)[a]	2044	262
$(C_6H_5)_2CH_3P$	Cl	HBr	2218 (2208)[a]	2043	266
$(p\text{-}CH_3C_6H_4)_3P$	Cl	HBr	2220 (2227)[a]	2042	267
$(C_6H_5)_3As$	Cl	HBr	2200	2043	269
$(C_6H_5)_3P$	Br	HCl	2226 (2218)[a]	2045	307
$(C_6H_5)_2CH_3P$	Br	HCl	2208 (2208)[a]	2043	303
$(C_6H_5)_3P$	I	HCl	2190 (2200)[a]	2046	305
$(C_6H_5)_3P$	NCS	HCl	2237 (2220)[a]	2047	309, 260
$(C_6H_5)_3P$	NCO	HCl	2236	2045	308, 259[c]
$(C_6H_5)_3P$	N_3	HCl	2238	2044	309, 260[c]

[a] In CH_2Cl_2 solution. [b] In Nujol mulls. [c] No evidence for anion Y in product.

Inc.) with benzene–chloroform (9:1) as eluent. Spots were developed with iodine vapor and identified by comparison of R_f values of authentic samples. Infrared spectra were obtained in Nujol mulls between cesium iodide or polyethylene plates. Solution spectra were obtained in 1-mm CaF_2 cells or 1-mm polyethylene cells. Most of the $L_2YIr(CO)\cdot HX$ adducts have CO stretching bands which are split in the solid state with bands of varying intensities at approximately 2050 and 2020 cm^{-1}. All the compounds have a single CO stretching frequency at 2045 ± 2 cm^{-1} in dichloromethane solution.

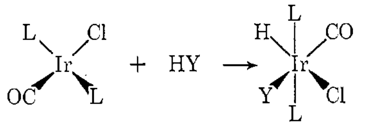
Results and Discussion

The products formed by the addition of hydrogen halides to *trans*-halobis(arylphosphine)carbonyliridium(I) have been previously well characterized.[1,5] Among the eight geometrical isomers possible for products of each of the reactions shown in Tables I and II, the five isomers with *cis*-phosphine ligands can be excluded on the basis of nmr studies with methylated phosphines. A triplet due to virtual coupling of the PCH_3 group with a *trans*-phosphorus atom is observed in hydrogen halide adducts of *trans*-chlorobis(methyldiphenylphosphine)carbonyliridium(I).[1] If the phosphines are *cis*, the PCH_3 group gives rise to a doublet. *trans* H–P or *trans* H–CO isomers are also not in accord with the high ν_{Ir-H} values observed for the HX adducts.[9] The isomer with *trans* H–CO is also excluded because of the absence of *trans* H–CO vibrational interaction.[10] Thus the remaining isomers are the *cis* (1) or *trans* (2) HX addition products shown in eq 1. (L is phosphine.)



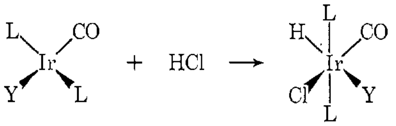
1 2 (1)

The infrared Ir–Cl stretching frequency is highly dependent on the ligand *trans* to the Cl atom; thus Cl *trans* to CO has absorption frequencies in the 305–310-cm^{-1} region and the Cl *trans* to H has absorption frequencies in the 255–269-cm^{-1} region.[1,2,9] As shown in Table I, the addition of hydrogen halides (HY) to chloroiridium(I) complexes in benzene solutions gives only products with Ir–Cl frequencies in the 262–269-cm^{-1} region. This indicates that the Cl atom is *trans* to the hydride ligand in each of the products and is in accord with *cis* addition of HY (eq 2). The formation of a single isomer in these reactions was also demonstrated by thin layer chromatography. Addition of



(2)

HCl to *trans*-$L_2Ir(CO)Y$ in benzene solution (eq 3) gives products with ν_{Ir-Cl} frequencies in the 303–305-cm^{-1} region, indicative of products with Cl *trans* to CO.



(3)

The addition of HCl in benzene solution is thus *cis*. The addition of HCl to the complexes where Y is NCO or N_3 leads to products in which Y is rapidly displaced by a second Cl atom. This rapid substitution of NCO and N_3 contrasts to the relatively slower substitution of the other halogens in benzene solution. The addition of HCl to *trans*-$[(C_6H_5)_3P]_2Ir(CO)NCS$ in benzene solution gives an addition product in which the Ir–NCS bond is retained, but the 309- and 260-cm^{-1} frequencies indicate the existence of *cis* and *trans* isomers.

As indicated by data in Table II, and using arguments detailed above, it is apparent that the addition of hydrogen halide to halocarbonyliridium(I) complexes is also *cis* in chloroform solution. Contrary to the earlier report,[1] we found that under strictly anhydrous conditions the addition of an ethereal solution of HCl to a solution of *trans*-$[CH_3(C_6H_5)_2P]Ir(CO)Br$ in benzene gives only the *cis*-addition product (ν_{Ir-Cl} 303 cm^{-1}) and that similar addition of HBr to *trans*-$[CH_3(C_6H_5)_2P]_2Ir(CO)Cl$ gives only the *cis*-addition product (ν_{Ir-Cl} 266 cm^{-1}). As indicated in Table II the same mixture of *cis* and *trans* isomers with ν_{Ir-Cl} at 308 and 262 cm^{-1} is obtained when these two reactions are conducted in wet benzene–ether. The data in Table II further reflect the formation of mixtures of *cis* and *trans* isomers upon the addition of hydrogen halides to iridium(I) complexes in solvents such as dichloromethane, dimethylformamide, benzene–acetonitrile, and benzene–methanol. The presence of *cis* and *trans* isomers was also demonstrated by thin layer chromatography.

Preliminary investigation was focused on the origin of

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(9) See ref 5 and references therein.

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TABLE II

SELECTED INFRARED FREQUENCIES (CM^{-1}) OF PRODUCTS FROM REACTIONS OF HYDROGEN HALIDES (HX) AND *trans*-$L_2Ir(CO)Y$ IN VARIOUS SOLVENTS (Y IS HALOGEN OR PSEUDOHALOGEN; L IS PHOSPHINE OR ARSINE)

L	Y	HX	Solvent	Ir–H	IrC–O	Ir–Cl
$(C_6H_5)_3P$	Cl	HBr	C_6H_6–CH_3OH	2235	2074 w, 2020 vs.	307, 264
$(C_6H_5)_3P$	Cl	HBr	C_6H_6–CH_3CN	2239	2021	305, 264
$(C_6H_5)_3P$	Cl	HBr	$HC(O)N(CH_3)_2$	2227, 2235 sh	2021	306, 258
$(C_6H_5)_3P$	Cl	HBr	$CHCl_3$	2238	2019	264
$(C_6H_5)_2CH_3P$	Cl	HBr	C_6H_6–CH_3OH	2216, 2204	2044	304, 265
$(C_6H_5)_3As$	Cl	HBr	C_6H_6–CH_3OH	2200	2020	306 vw, 263 vw
$(C_6H_5)_3P$	Br	HCl	C_6H_6–CH_3OH	2236	2021	308, 260
$(C_6H_5)_3P$	Br	HCl	C_6H_6–CH_3CN	2235	2020	306, 259
$(C_6H_5)_3P$	Br	HCl	$HC(O)N(CH_3)_2$	2236, 2225	2020	308, 259
$(C_6H_5)_3P$	Br	HCl	$CHCl_3$	2226	2022	306
$(C_6H_5)_2CH_3P$	Br	HCl	C_6H_6–CH_3OH	2216, 2204	2044	310, 264
$(C_6H_5)_3P$	I	HCl	C_6H_6–CH_3OH	2235, 2203	2018	300, 256
$(C_6H_5)_3P$	Cl	HI	C_6H_6–CH_3OH	2210[a]	2047[a]	306, 260
$(C_6H_5)_3P$	Cl	HI	C_6H_6–CH_3CN	2218[a]	2045[a]	306, 258
$(C_6H_5)_3P$	Cl	HI	$HC(O)N(CH_3)_2$	2208[a]	2047[a]	305
$(C_6H_5)_3P$	Cl	HBr	CH_2Cl_2	2228	2021	305, 256
$(C_6H_5)_3P$	Br	HCl	CH_2Cl_2	2228	2050, 2020	306, 260 vvw
$(C_6H_5)_2CH_3P$	Cl	HBr	C_6H_6–$(C_2H_5)_2O$ (wet)	2214, 2205	2044	308, 262
$(C_6H_5)_2CH_3P$	Br	HCl	C_6H_6–$(C_2H_5)_2O$ (wet)	2245, 2220	2030, 2020	308, 261

[a] In CH_2Cl_2 solution; all other frequencies in Nujol.

mixtures of *cis* and *trans* isomers in ionizing solvents, contrasted to the stereospecifically *cis* products obtained in benzene. Among the numerous routes by which mixtures of isomers can originate, the following most obvious pathways were briefly considered.

(1) **Isomerization during Work-up.**—Far-infrared spectra (ν_{Ir-Cl} frequencies) of products in the benzene reaction solution were virtually identical with the solid-state spectra of products obtained by either stripping the solvent or precipitation with methanol, hexane, or diethyl ether. This indicates that isomerization during work-up is not significant under mild conditions. An nmr spectrum of the solution of reactants HBr and *trans*-$[P(CH_3)(C_6H_5)_2]_2IrCOCl$ in benzene showed a triplet at τ 8.05 denoting the *trans* orientation of phosphine ligands. This spectrum is identical with that of the products obtained after precipitation with methanol. Rearrangements of phosphine ligands with variation of solvent such as was observed in the addition of allylic halides to iridium(I) complexes can thus be excluded.[7]

(2) **Substitution of Halogen in a Six-Coordinate Product.**—Treatment of a solution of 50 mg of $[CH_3(C_6H_5)_2P]_2Ir(CO)Br \cdot HBr$ with 100 mg of tetramethylammonium chloride in 5 ml of methanol gave a product which had an infrared spectrum indicating Cl incorporation in both *cis* and *trans* positions relative to the hydride. Similar treatment of $[CH_3(C_6H_5)_2P]_2Ir(CO)Br \cdot HBr$ with anhydrous hydrogen chloride in dry benzene solution resulted in no detectable substitution of Br by Cl atoms. Treatment of *trans*-$[(C_6H_5)_3P]_2Ir(CO)Cl$ with excess HBr in benzene–methanol results in a product with no ν_{Ir-Cl}.

(3) **Substitution of Halogen before Addition.**—Exchange reactions of square-planar d^8 rhodium complexes are extremely rapid.[11] When a solution of 100 mg of *trans*-bromobis(triphenylphosphine)carbonyliridium(I) in 10 ml of benzene was treated with a solution of 100 mg of tetramethylammonium chloride in 5 ml of methanol, a yellow product with ν_{Ir-Cl} at 314 cm^{-1} was obtained within 2 min.

These results indicate that the addition of anhydrous hydrogen halide (HX) to *trans*-halobis(arylphosphine)-carbonyliridium(I) complexes gives *cis* HX adducts in benzene or chloroform. In the presence of solvents such as methanol, acetonitrile, water, or dimethylformamide, which have the capacity of solvating ions, mixtures of *cis* and *trans* isomers are formed. Whether these isomers result from rapid exchange of halide ions before the addition reaction or exchange of halide ions in the products remains to be explored.

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Reactions of Eight-Coordinate Metal Cyanide Complexes. II.[1] Interaction of Octacyanomolybdate(IV) with Uranyl Salts

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The addition of amine molecules to octacyanomolybdate(IV) results in the formation of red compounds for

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