anthroline is effectively removing some of the catalyst from the reaction chain. Pyridine competes with *o*-phenanthroline for the rhodium(I), and to whatever extent it forms complexes with the labile metal, the catalyzed pyridination is carried on. The slower rate is the result of the decreased effective catalyst concentration. The smaller inhibition of the alcohol catalyst compared with [Rh(CO)$_2$Cl]$_2$ can also be accounted for. As *o*-phenanthroline removed rhodium(I), the excess alcohol was able to produce more while, with the [Rh(CO)$_2$Cl]$_2$ catalyst, only a fixed amount of rhodium(I) was available.

The question still remained about the synthesis of [Rh(phen)$_2$Cl$_2$]Cl. Closer scrutiny of the procedure indicated that the catalyst, hydrazinium chloride, was added in sufficient quantity to reduce more than half of the rhodium present. Furthermore, the reaction was carried out in boiling 50% ethanol. It may have been that the chain mechanism, with rhodiums exchanging oxidation states, did not occur. Instead, all of the rhodium was reduced, underwent ligand exchange, and was reoxidized by the reducing and oxidizing agents present in the reaction mixture.

Conclusion

The author feels that many of the data presented in this paper are inconsistent with the catalytic species in the pyridination of hexachlororhodate ion being a hydride. On the other hand, nothing presented here or elsewhere is inconsistent with the catalyst being a rhodium(I) complex. The reagents which have been shown to produce hydrido complexes have previously been used in such large quantities that the small amounts of reduced rhodium needed to bring about catalysis could easily have been formed. When the amounts of the promoters are reduced to a minimum, it is found that rhodium(I) compounds are more active than hydride ion. Since rhodium(I) does not form hydrido complexes under the reaction conditions, it seems necessary to conclude that it is the primary catalytic agent.

CONTRIBUTION FROM THE VENABLE LABORATORIES, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA   27514

Stereochemistry of Oxidative Addition Reactions of Iridium(I) Complexes[1,2]

BY JAMES P. COLLMAN[3] AND CURTIS T. SEARS, JR.

A study has been made of the stereochemistry of the oxidative addition reactions of halogens, hydrogen halides, alkyl halides, and acetyl halides with *trans*-[IrCl(CO)((C$_6$H$_5$)$_2$PCH$_3$)$_2$]. The stereochemistry of the resulting octahedral complexes has been assigned by a combination of nmr and far-infrared spectroscopy. Evidence supporting a kinetically controlled *trans* addition is reported. Reactions with mercuric chloride and perfluoroalkyl iodides are also described.

Oxidative addition reactions involving four- and five-coordinate d^8 complexes is a subject of considerable current interest.[4-6] Impetus is given to this research by the number of homogeneous catalysts which are d^8 complexes and whose mode of action involves oxidative addition and its reverse, reductive elimination.[4] To understand the detailed mechanisms by which such homogeneous catalysts act requires a knowledge of the stereochemical course of these reactions. The two-stage oxidative addition of five-coordinate d^8 complexes has been shown to be *cis*.[4] Herein is described

our investigation of the stereochemistry of oxidative additions involving planar four-coordinate complexes.

When this project was begun, the only definitive stereochemical information concerning oxidative additions with four-coordinate complexes were the results of Basolo[7] on platinum(II) amine complexes and Vaska's[8] addition of oxygen to *trans*-halogenocarbonyl-bis(triphenylphosphine)iridium(I) (1, X = Cl). Reaction of chlorine with the platinum(II) complexes afforded octahedral products in which the chlorine atoms were *trans*;[7] however, it is not clear that this configuration results from kinetic or thermodynamic control. *cis* addition is clearly indicated in the formation of [IrX(CO)((C$_6$H$_5$)$_3$P)$_2$O$_2$]. The apparent *cis* elimination of chlorine from tetrachlorobis(tri-*n*-

(1) This work was supported by the National Science Foundation, The Advanced Research Projects Agency (Contract SD-100), and the Alfred P. Sloan Foundation.

(2) Abstracted from the Ph.D. dissertation of C. T. Sears, University of North Carolina, 1966.

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(4) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966), and references therein.

(5) J. Chatt and S. A. Butler, *Chem. Commun.*, 501 (1967).

(6) M. A. Bennett and D. L. Milner, *ibid.*, 581 (1967).

(7) F. Basolo, J. C. Bailar, and B. R. Tarr, *J. Am. Chem. Soc.*, **72**, 2433 (1950).

(8) L. Vaska, *Science*, **140**, 809 (1963); J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *ibid.*, **155**, 709 (1967).

propylphosphine)platinum(IV) reported by Chatt[9] might be used to advocate the *cis* mode of addition by applying the principle of microscopic reversibility.
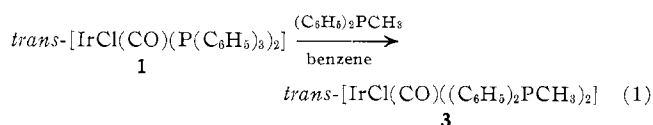
During the course of the present investigation it was established that the addition of hydrogen to 1[10] and related planar iridium(I)[11] and rhodium(I)[5] complexes is *cis*.[12] Recently a preliminary report[13a] described *cis* addition of *gaseous* hydrogen halides to solid [IrCl(CO)(P(C₆H₅)₃)₂]. The results presented herein, however, show that *in solution* preferential *trans* addition takes place.[13b]

Reaction of a molecule X₂ (X ≠ Cl) with *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) (1) could give rise to six isomers. If, as might be expected, the phosphine liquids remain *trans*, then only two isomers (2a and 2b) are possible as a result of *cis* and *trans* addition, respectively

1, L = P(C₆H₅)₃   2a   2b
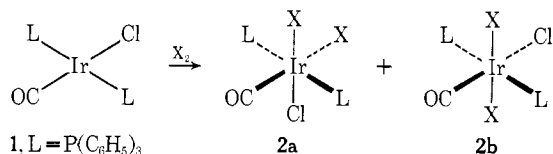
Jenkins and Shaw[14] have demonstrated that it is possible to determine the relative positions of methyl-substituted phosphine ligands by nmr spectroscopy. In complexes having mutually *trans* phosphines the proton nmr spectrum of the PCH₃ groups exhibits a triplet because of strong coupling between the *trans* phosphorus atoms. However, if the phosphines are *cis*, they behave as isolated units, and the PCH₃ group gives rise to a doublet. In order to apply this technique to the present problem, it was necessary to prepare methylated phosphine complexes analogous to 1. This now famous iridium(I) carbonyl complex (1) was first prepared in 1959 by Angoletta[15] from Ir(CO)₃Cl but this method has been little used, probably because of the toil required to prepare substantial quantities of Ir(CO)₃Cl. The usual method for preparing 1 involves heating triphenylphosphine with an iridium(III) or -(IV) salt in the presence of an oxygenated solvent such as ethylene glycol[10] or preferably dimethylformamide.[16] When alkyl-substituted phosphines are employed, this method fails to produce carbonyl complexes analogous to 1. *trans*-Chlorocarbonylbis(diphenylmethylphosphine)iridium(I) (3) was prepared from 1 by phosphine exchange (eq 1).[16a,17] It should be noted this type

of thermodynamically controlled exchange cannot be used to form the analogous triphenylarsine complex inasmuch as triphenylphosphine is more strongly bound to iridium. More recently, complexes such as 3 have been prepared by reducing iridium salts in a stream of carbon monoxide in hot β-methoxyethanol and then adding the desired phosphine or arsine.[18]

$$trans\text{-}[IrCl(CO)(P(C_6H_5)_3)_2] \xrightarrow[benzene]{(C_6H_5)_2PCH_3}$$
$$\mathbf{1}$$
$$trans\text{-}[IrCl(CO)((C_6H_5)_2PCH_3)_2] \quad (1)$$
$$\mathbf{3}$$

The nmr spectrum of 3 revealed the expected methyl triplet verifying the *trans* disposition of the two phosphine ligands. Using this test, *trans* arrangement of the phosphine ligands was verified for all of the octahedral iridium(III) complexes prepared from 3 (see Table I).

Once the phosphines in the octahedral adducts were shown to be *trans*, it became possible to elucidate the remaining stereochemistry by use of infrared spectroscopy. Jenkins and Shaw[19] measured the far-infrared spectra of a series of octahedral iridium(III) halide complexes and demonstrated that the iridium-chlorine stretching frequency depends primarily on the nature of the ligand *trans* to the chlorine and is insensitive to the *cis* ligands.

To determine the stretching frequency of iridium-chlorine bonds *trans* to a carbonyl, trichlorocarbonylbis(diphenylmethylphosphine)iridium(III) (4) was prepared by treating 3 with chlorine.

4, X = Cl
5, X = Br
6, X = I
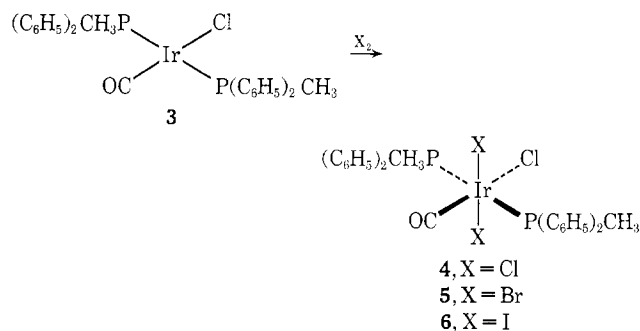
The proton nmr of 4 exhibits a PCH₃ triplet at τ 7.60 establishing the stereochemistry as shown. Two iridium–chlorine absorptions were observed at 330 and 310 cm⁻¹, in the far-infrared spectrum of 4. On the basis of Shaw's studies[19] the absorption at 330 cm⁻¹ is assigned to the two mutually *trans* chlorines and the one at 310 cm⁻¹ to the chlorine *trans* to the carbonyl. The absence of an additional iridium–chlorine stretching mode can be explained by the failure of a symmetrical stretching motion of the collinear chlorine atoms to produce a dipole change. A similar effect was noted by Shaw.[19]

Treatment of the chloro complex 3 with bromine and iodine afforded [IrClBr₂(CO)((C₆H₅)₂PCH₃)₂] (5) and [IrCl₂(CO)((C₆H₅)₂PCH₃)₂] (6), respectively. Thin layer chromatography indicated the formation of single

(9) J. Chatt, *J. Chem. Soc.*, 3201 (1950).

(10) L. Vaska and J. W. Diluzio, *J. Am. Chem. Soc.*, **84**, 679 (1962).

(11) L. Vaska and D. L. Catone, *ibid.*, **88**, 5324 (1966).

(12) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

(13) (a) L. Vaska, *J. Am. Chem. Soc.*, **88**, 5325 (1966). (b) After submission of this paper a report appeared describing the far-infrared spectra of related adducts. It was concluded that the configurations of these adducts were the result of *cis* addition: M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

(14) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(15) M. Angoletta, *Gazz. Chim. Ital.*, **89**, 2359 (1959).

(16) (a) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89**, 844 (1967); (b) K. Vrieze, J. P. Collman, C. T. Sears, and M. Kubota, *Inorg. Syn.*, **10**, in press.

(17) Exchange reactions of this type have been reported in the case of the rhodium complex isostructural with 1: H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.*, 358 (1960).

(18) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 604 (1967).

(19) J. M. Jenkins and B. L. Shaw, *ibid.*, 6789 (1965).

TABLE I

PROTON NMR SPECTRA

Compound	Chemical shift[a]		
	P–CH₃		Other signals
[IrCl(CO)((C₆H₅)₂PCH₃)₂] (**3**)	7.75 (T)[b]		
[IrBr(CO)((C₆H₅)₂PCH₃)₂] (**9**)	7.65 (T)		
[IrCl₃(CO)((C₆H₅)₂PCH₃)₂] (**4**)	7.60 (T)		
[IrClBr₂(CO)((C₆H₅)₂PCH₃)₂] (**5**)	7.60 (T)		
[IrClI₂(CO)((C₆H₅)₂PCH₃)₂] (**6**)	7.62 (T)		
[IrCl₂CH₃(CO)((C₆H₅)₂PCH₃)₂] (**7**)	7.51 (T)		9.64 (T)[b] Ir–CH₃
[IrClBrCH₃(CO)((C₆H₅)₂PCH₃)₂] (**8A**)	7.49 (T)		9.48 (T) Ir–CH₃
[IrClBrCH₃(CO)((C₆H₅)₂PCH₃)₂] (**8B**)	7.49 (T)		9.65 (T) Ir–CH₃
[IrCl₂H(CO)((C₆H₅)₂PCH₃)₂] (**11**)	7.52 (T)		. . .
[IrCl₂(CH₃CO)(CO)((C₆H₅)₂PCH₃)₂] (**12**)	7.42 (T)		9.30 (S) COCH₃
[IrClBrH(CO)((C₆H₅)₂PCH₃)₂][c] (**14**)	7.40 (T), 7.43 (T)		. . . . . .
[IrClBr(CH₃CO)(CO)((C₆H₅)₂PCH₃)₂][c] (**15**)	7.42 (T)		9.20 (S), 9.30 (S) COCH₃

[a] Chemical shifts reported in τ values relative to tetramethylsilane (τ 10) in CDCl₃ using a Varian Associates A-60 spectrometer. Coupling patterns are indicated by (T) triplet and (S) singlet. [b] All apparent coupling constants for triplets (separation between central and outer peak) were found to be 10 cps. [c] A mixture of isomers is present.

isomers of **5** and **6**, and their nmr spectra demonstrated that the phosphines remained *trans* (Table I). The frequency of the iridium–chlorine stretching absorption, in both cases, corresponds to that of a chlorine *trans* to the carbonyl (Table II) and suggests *trans* addition as illustrated. The stereochemistry of the addition is apparently unaffected by the nature of the solvent, since the results are identical when the reaction is carried out in benzene or glacial acetic acid. Because we had previously found methanol to affect halogen exchange in analogous rhodium(III) complexes,[2] it was necessary to show that methanol employed in the purification step had not caused isomerization. In the case of iodine addition, a modified work-up using nonpolar solvents gave the same results. Additional support for the improbability of isomerization during purification was obtained by heating a mixture of [IrCl₃(CO)((C₆H₅)₂PCH₃)₂] and [IrBr₃(CO)((C₆H₅)₂PCH₃)₂] in a benzene–methanol solution under reflux. Thin layer chromatography established that halogen exchange had not taken place.

The alternative reaction, addition of chlorine to bromocarbonylbis(diphenylmethylphosphine)iridium(I), could not be used for this stereochemical study because chlorine was found to cleave iridium–bromine bonds.

These methods were then applied to the addition of methyl halides to the iridium(I) complexes. The triphenylphosphine complex **1** adds methyl iodide[20,21] but not methyl chloride. However, methyl chloride readily combines with the diphenylmethylphosphine complex **3**. It is generally found that increasing σ-donor characteristics of the ligands attached to four-coordinate d⁸ compounds enhances their reactivity toward alkyl halides, hydrogen halides, and oxygen.[22] The methyl chloride adduct **7** exhibited iridium–chlorine stretching absorption at 305 and 257 cm⁻¹ corresponding to chlorine *trans* to carbon monoxide and methyl, respectively. No absorption was found for mutually *trans* chlorines. Thus the configuration of

(20) R. F. Heck, *J. Am. Chem. Soc.*, **86**, 2796 (1964).
(21) P. B. Chock and J. Halpern, *ibid.*, **88**, 3511 (1966).
(22) See, for example, ref 5.

TABLE II

INFRARED DATA

Compound	$\nu(CO)$,[a] cm⁻¹	$\nu(Ir-Cl)$,[b] cm⁻¹
[IrCl(CO)((C₆H₅)₂PCH₃)₂] (**3**)	1960	312
[IrBr(CO)((C₆H₅)₂PCH₃)₂] (**9**)	1960	. . .
[IrCl₃(CO)((C₆H₅)₂PCH₃)₂] (**4**)	2060	330, 310
[IrClBr₂(CO)((C₆H₅)₂PCH₃)₂] (**5**)	2060	310
[IrClI₂(CO)((C₆H₅)₂PCH₃)₂] (**6**)	2060	308
[IrCl₂CH₃(CO)((C₆H₅)₂PCH₃)₂] (**7**)	2025	305, 257
[IrClBrCH₃(CO)((C₆H₅)₂PCH₃)₂] (**8A**)	2025	302
[IrClBrCH₃(CO)((C₆H₅)₂PCH₃)₂] (**8B**)	2025	255
[IrCl₂H(CO)((C₆H₅)₂PCH₃)₂] (**11**)	2050	310, 260
[IrCl₂(CH₃CO)(CO)((C₆H₅)₂PCH₃)₂] (**12**)	2050	310, 296
[IrClBrH(CO)((C₆H₅)₂PCH₃)₂] (**14**)	2045	311, 263
[IrClBr(CH₃CO)(CO)((C₆H₅)₂PCH₃)₂] (**15**)	2050	309, 297
[IrClIR_F(CO)((C₆H₅)₂PCH₃)₂] (**16, 17, 18**)	2060	315

[a] KBr pellets recorded on a Perkin-Elmer Model 237 grating spectrophotometer. [b] Benzene solution in 1.0-mm polyethylene cells recorded on a Perkin-Elmer Model 521 spectrophotometer.

the adduct is established as depicted for **7**, but the stereochemical course of the addition is not revealed.
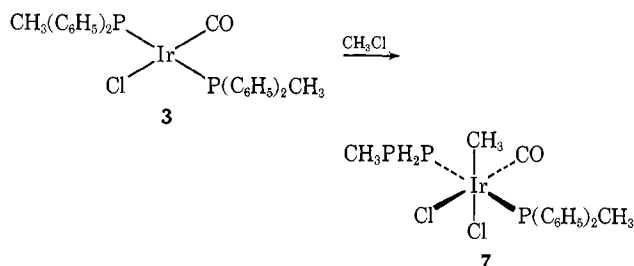
Treatment of **3** with methyl bromide afforded bromochloromethylcarbonylbis(diphenylmethylphosphine)-iridium(III) (**8**) in 54% yield. Both the crude product precipitated from the reaction mixture by the addition of *n*-hexane and the analytical sample resulting from recrystallization from benzene–methanol have a single iridium–chlorine stretching frequency at 302 cm⁻¹. Thus the adduct **8** has configuration **A** with methyl and bromine *trans*—apparently the result of *trans* addition. An alternative structure involving methyl *trans* to CO can be disregarded in view of structure **7** and the constant CO frequencies exhibited by methyl halide adducts.

The alternative isomer was obtained from the addition of methyl chloride to *trans*-bromocarbonylbis(diphenylmethylphosphine)iridium(I) (9) and precipitation with *n*-hexane. The crude white powder exhibited little absorption in the region 300–310 cm^{-1} but an iridium–chlorine band was found at 255 cm^{-1}. This indicates that the adduct 8 has configuration **B**—the result of *trans* addition. After recrystallization from benzene–methanol, the infrared spectrum of this adduct showed a peak of diminished intensity at 255 cm^{-1} and a new absorption band at 302 cm^{-1}. Heating a solution of 8, configuration **B**, in benzene–methanol at the reflux temperature for 3 hr resulted in complete isomerism to 8, configuration **A**. Thus the addition of methyl chloride to 9 is stereospecific, *trans*, and the result of *kinetic control*. Addition of methyl iodide to 3 gives a similar product 10 whose configuration is **A**. The ease with which configuration **B** isomerizes to **A** illustrates the danger in concluding that the configurations of the products observed from oxidative addition reactions are kinetically determined. This is particularly evident in the case of the analogous rhodium complexes which are much more labile than the iridium compounds.


configuration **A**
8, X = Br
10, X = I
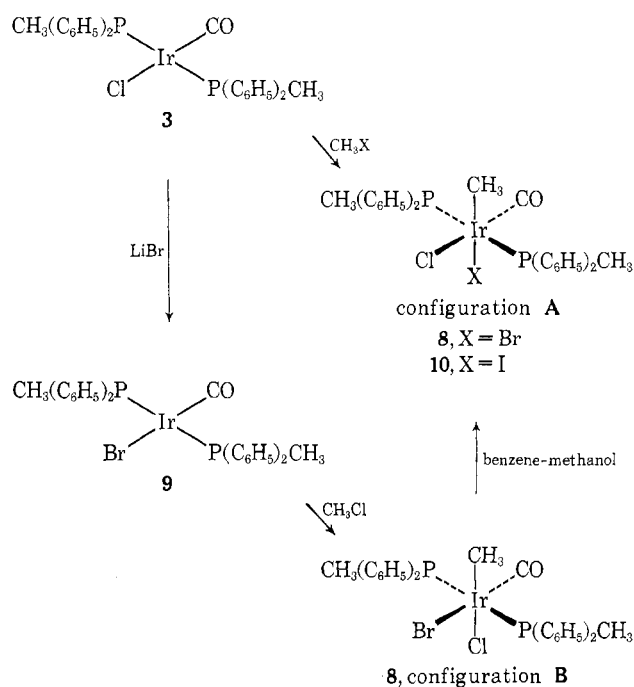
8, configuration **B**

The lability of a halogen *trans* to a methyl group is suggested by reaction of 8 (configuration **A**) with lithium chloride in tetrahydrofuran to form the dichloride complex 7 in excellent yield.[23]

Chock and Halpern[21] studied the kinetics of the addition of methyl iodide to the planar iridium(I) complex 1. They point out the similarity with respect to activation parameters and solvent dependence between this oxidative addition reaction and the alkylation of tertiary amines. A highly polar transition state

was suggested for the oxidative addition reaction. It seems likely that the isomerization from configuration **B** to **A** involves a similar intermediate—probably a five-coordinate complex cation.

Hydrogen chloride, acetyl chloride, and mercuric chloride[24] react with 3 to form octahedral adducts having the stereochemistry shown, 11–13. The stereochemical course of these reactions is uncertain, and attempts to clarify this problem by using mercuric bromide were frustrated by intermolecular halogen interchange. This facile halogen exchange may have taken place prior to oxidative addition. Four-coordinate complexes such as 3 are known to be exceptionally reactive toward nucleophilic substitution.[17]

11. Z = H
12. Z = CH$_3$CO
13. Z = HgCl
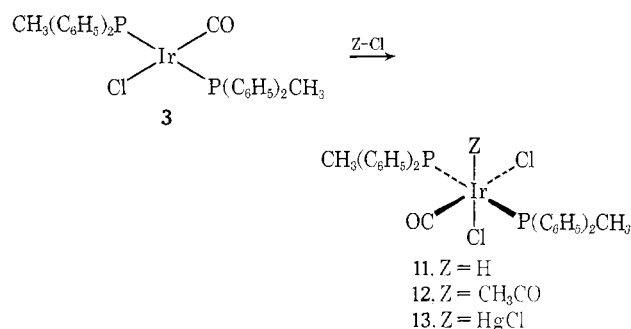
Treatment of 3 with either dry hydrogen bromide or acetyl bromide afforded a mixture of two stereoisomers. The absence of any other products such as those arising from halogen exchange was shown by thin layer chromatography and elemental analyses. The same mixtures were obtained from treatment of the bromo complex 9 with hydrogen chloride or acetyl chloride. Prolonged heating of the mixture of isomers (14A and 14B) in benzene–methanol did not produce a significant change in the isomer ratio suggesting that the system is at equilibrium. It is possible that isomerism occurs in the work-up of 14 and 15 rather than during the addition reactions.

A   B
14. Z = H
15. Z = CH$_3$CO
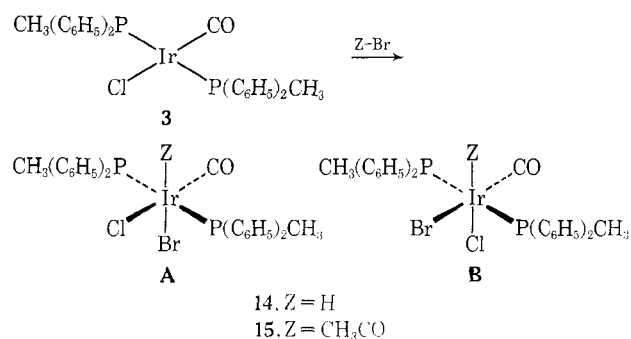
Another attempt to form a single stereoisomer of 15 was made by treating the methyl bromide adduct 8A with carbon monoxide. No reaction was observed, although carbonylation has been reported in the closely related complex, [RhClICH$_3$(CO)((n-C$_4$H$_9$)$_3$P)$_2$].[20]

In the course of this work, addition of perfluoroalkyl iodides to the iridium(I) complex (3) has been studied. The adducts 16, 17, and 18 seem to be single stereo-

(23) It would be satisfying to *prove* that the halogen *trans* to the methyl is more labile than one *trans* to the carbonyl; however, it is not possible to do so because the conditions necessary for halogen exchange will lead to isomerization.

(24) Previous examples of such mercuric halide additions have been described: R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5336 (1965).

isomers as indicated by their homogeneity on thin layer chromatograms and the presence of a single iridium-chlorine stretching frequency. Lacking a model for the frequency of an iridium–chlorine stretching mode for a chlorine *trans* to a perfluoroalkyl group, we are unable to assign a configuration to these adducts.

$$[IrCl(CO)(P(C_6H_5)_2CH_3)_2] + R_FI \longrightarrow$$
$$\mathbf{3}$$
$$[IrClIR_F(CO)(P(C_6H_5)_2CH_3)_2]$$
$$\mathbf{16}, R_F = CF_3$$
$$\mathbf{17}, R_F = C_2F_5$$
$$\mathbf{18}, R_F = n\text{-}C_3F_7$$
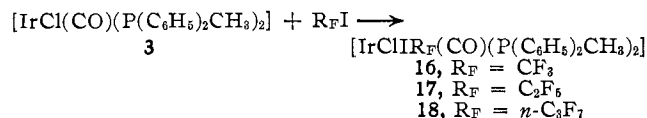
Experimental Section

General Material.—Refluxing and stirring of solutions of iridium carbonyl complexes were performed under nitrogen. Stripping of solvents was performed at reduced pressure with a rotatory evaporator.

Chlorocarbonylbis(diphenylmethylphosphine)iridium(I) (3).—This compound was prepared as previously described.[16a] *Anal.* Calcd for $C_{27}H_{26}ClOP_2Ir$: C, 49.35; H, 3.99; Cl, 5.40; P, 9.44. Found: C, 49.67; H, 4.02; Cl, 5.05; P, 9.18.

Bromocarbonylbis(diphenylmethylphosphine)iridium(I) (9).—A procedure analogous to that used for preparation of chlorocarbonyl **3** gave a 62% yield of **9**. *Anal.* Calcd for $C_{27}H_{26}$-$BrOP_2Ir$: C, 46.23; H, 3.73; P, 8.38; Br, 11.39. Found: C, 46.42; H, 3.99; P, 8.78; Br, 11.00.

Trichlorocarbonylbis(diphenylmethylphosphine)iridium(III) (4).—To a solution of 0.20 g (0.30 mmole) of chlorocarbonyl **3** in 30 ml of methylene chloride was added an excess of a solution of chlorine in methylene chloride. After stirring for 30 min, the solution was evaporated to dryness under reduced pressure. Recrystallization of the residue from methylene chloride–methanol afforded 0.16 g (73%) of yellow crystals. *Anal.* Calcd for $C_{27}H_{26}Cl_3OP_2Ir$: C, 44.55; H, 3.60; Cl, 14.61; P, 8.51. Found: C, 44.76; H, 3.72; Cl, 14.19; P, 8.38.

Chlorodibromocarbonylbis(diphenylmethylphosphine)iridium(III) (5). Procedure A.—To 0.33 g (0.5 mmole) of chlorocarbonyl **3** dissolved in 30 ml of benzene was added 1 equiv of bromine in benzene and the mixture was stirred for 1 hr. Upon addition of hexane, the small amount of white precipitate which formed was discarded. The volume of the yellow solution was reduced on a rotatory evaporator until the product separated as a yellow powder, which was washed with *n*-hexane and air-dried. The product recrystallized from benzene–methanol or methylene chloride–methanol had far-infrared spectra identical with that of the unrecrystallized powder.

Procedure B.—To 0.20 g (0.3 mmole) of chlorocarbonyl **3** in 50 ml of glacial acetic acid was added an excess of bromine in acetic acid. The mixture was stirred for 1 hr. The solution was poured into a benzene–water mixture and the benzene layer separated and evaporated to dryness under reduced pressure. Recrystallization of the residue from benzene–methanol afforded 0.060 g (25%) of yellow crystals. *Anal.* Calcd for $C_{27}H_{26}$-Br_2ClOP_2Ir: C, 39.76; H, 3.17; Br, 17.63; Cl, 4.35; P, 7.61. Found: C, 39.91; H, 3.34; Br, 17.76; Cl, 4.20; P, 7.57.

Chlorodiiodocarbonylbis(diphenylmethylphosphine)iridium(III) (6). Procedure A.—To a solution of 0.40 g (0.6 mmole) of chlorocarbonyl **3** in 20 ml of benzene was added 0.16 g of iodine in 20 ml of benzene. The mixture was stirred for 1 hr. Upon the addition of hexane and reduction of the volume of solution, the orange product precipitated. Recrystallization from benzene–cyclohexane afforded 0.19 g (35%) of **6**.

Procedure B.—To 0.40 g (0.6 mmole) of chlorocarbonyl **3** in 20 ml of glacial acetic acid was added 0.16 g of iodine and the mixture stirred for 1 hr. The solution was poured into a benzene–water mixture, and the benzene layer was separated and evaporated to dryness under reduced pressure. Recrystallization of the residue from benzene–methanol afforded 0.465 g (85%) of orange crystals. *Anal.* Calcd for $C_{27}H_{26}ClI_2OP_2Ir$: C, 35.60; H, 2.87; P, 6.79; I, 27.86. Found: C, 35.96; H, 3.06; P, 6.99; I, 27.76.

Tribromocarbonylbis(diphenylmethylphosphine)iridium(III).—To 0.20 g (0.28 mmole) of bromocarbonyl **9** in 20 ml of benzene was added an excess of bromine in benzene and the mixture was stirred for 15 min. Upon the addition of methanol, the product separated and was collected by filtration. Recrystallization from benzene–methanol afforded 0.16 g (67%) of the yellow crystals. Infrared absorption (KBr) occurred at 2060 cm^{-1} (CO). *Anal.* Calcd for $C_{27}H_{26}Br_3OP_2Ir$: C, 37.65; H, 3.04; P, 7.19; Br, 27.93. Found: C, 38.77; H, 3.23; P, 7.57; Br, 27.93.

Attempted Halogen Exchange between Trichlorocarbonylbis-(diphenylmethylphosphine)iridium(III) and Tribromocarbonylbis(diphenylmethylphosphine)iridium(III).—Ten milligrams of both trichloro- and tribromocarbonylbis(diphenylmethylphosphine)iridium(III) were dissolved in 5 ml of a benzene–hexane mixture (50:50 v/v). A thin layer chromatogram on silica gel showed two spots. A similar mixture was prepared in a benzene–methanol (50:50 v/v) mixture and heated at the reflux temperature for 15 min. Thin layer chromatography showed only two spots, indicating that halogen exchange had not occurred; neither did the addition of chlorocarbonyl **3** to the solution cause exchange.

Dichloromethylcarbonylbis(diphenylmethylphosphine)iridium-(III) (7). Procedure A.—Methyl chloride (5 ml) was condensed in a glass tube of approximately 30-ml volume, which contained 0.40 g (0.6 mmole) of chlorocarbonyl **3**. The tube was sealed and allowed to stand at room temperature for 3 days. Excess methyl chloride and solvent were allowed to evaporate. Repeated recrystallization from benzene–methanol afforded 0.10 g (24%) of the snow white crystals. *Anal.* Calcd for $C_{28}H_{29}Cl_2OP_2Ir$: C, 47.54; H, 4.13; Cl, 10.02; P, 8.76. Found: C, 47.17; H, 4.36; Cl, 9.52; P, 8.51.

Procedure B.—A mixture of 0.10 g (0.13 mmole) of bromochloromethylcarbonyl **8A** and 2.0 g of lithium chloride in 50 ml of tetrahydrofuran was heated at reflux for 6 hr. The mixture was allowed to cool to room temperature and poured into a benzene–water mixture. The benzene layer was separated and evaporated to dryness under reduced pressure. Recrystallization from benzene–methanol afforded 0.065 g (71%) of **7**, identified by comparative thin layer chromatography on silica gel with an authentic sample prepared by procedure A and by its far-infrared spectrum.

Bromochloromethylcarbonylbis(diphenylmethylphosphine)-iridium(III) (8). Configuration A.—A solution of 0.5 g (0.76 mmole) of chlorocarbonyl **3** in 20 ml of toluene was treated with 5 ml of methyl bromide at room temperature for 1 hr. A Dry Ice condenser was used to return methyl bromide to the reaction vessel. At the end of this period, the condenser was removed and the excess methyl bromide was allowed to evaporate.

A large volume of hexane was added to precipitate the product, which was washed with hexane. The far-infrared spectrum of the crude product exhibits only one iridium–chlorine absorption at 302 cm^{-1}. Recrystallization afforded 0.33 g (54%) of the white product. Infrared absorption (KBr) occurred at 2025 cm^{-1} (CO) and (C_6H_6) at 302 cm^{-1} (Ir–Cl). *Anal.* Calcd for $C_{28}H_{29}BrClOP_2Ir$: C, 44.72; H, 3.75; Br, 10.63; Cl, 4.72; P, 8.24. Found: C, 44.41; H, 4.23; Br, 10.00; Cl, 4.62; P, 8.10.

Configuration B.—Methyl chloride (10 ml) was condensed in a medium-walled glass tube of approximately 30-ml capacity, which contained a solution of 0.5 g (0.7 mmole) of bromocarbonyl **9** in 10 ml of benzene. The tube was sealed and allowed to stand at room temperature for 5 days. Excess methyl chloride was then allowed to evaporate and the remaining solution was taken to dryness under reduced pressure. The far-infrared spectrum of the crude product shows a predominance of **8B** (infrared absorption at 255 cm^{-1} (Ir–Cl)), although a trace of configuration **A** was observed. The nmr spectrum exhibits only one signal attributable to a methyl group directly bonded to iridium: a triplet at τ 9.65, which corresponds to a methyl group *trans* to Cl. This indicates that configuration **B** accounts for greater

than 90% of the sample. Attempted purifications from non-polar solvents failed. Recrystallization from benzene–methanol decreased the ratio of **8B** to **8A**.

Isomerization of Configuration B of Bromochloromethylcarbonylbis(diphenylmethylphosphine)iridium(III) (8) to Configuration A.—A solution of 0.10 g of **8B** in 50 ml of a benzene–methanol (90:10 v/v) mixture was refluxed for 3 hr. The solution was evaporated to dryness under reduced pressure. The residue recrystallized from benzene–methanol had an iridium–chlorine absorption band at 302 cm^{-1}; no absorption was observed at 255 cm^{-1}.

Chloroiodomethylcarbonylbis(diphenylmethylphosphine)iridium(I) (10).—A solution of 0.30 g (0.45 mmole) of chlorocarbonyl **3** in 15 ml of methyl iodide was stirred at room temperature for 15 min. The solution was evaporated to dryness under reduced pressure. Recrystallization from benzene–methanol afforded 0.29 g (81%) of white crystals. Infrared absorption (KBr) occurred at 2030 cm^{-1} (CO) and (C$_6$H$_6$) at 300 cm^{-1} (Ir–Cl); nmr (CDCl$_3$) occurred at (P–CH$_3$) τ 7.40 triplet ($J = 10$ cps) and (Ir–CH$_3$) τ 9.25 triplet ($J = 10$ cps). *Anal.* Calcd for C$_{28}$H$_{29}$ClIOP$_2$Ir: C, 42.09; H, 3.65; Cl, 4.44; I, 15.88; P, 7.76. Found: C, 42.35; H, 3.80; Cl, 4.91; I, 16.00; P, 7.85.

Dichlorohydridocarbonylbis(diphenylmethylphosphine)iridium(III) (11).—To a solution of 0.15 g (0.23 mmole) of chlorocarbonyl **3** in 20 ml of benzene was added an excess of dry hydrogen chloride in diethyl ether. The yellow solution instantly turned colorless. The volume of solution was reduced under vacuum. Upon the addition of methanol, the product precipitated and was collected by filtration, washed with methanol, and air dried; yield, 0.090 g (56%). Infrared absorption (KBr) occurred at 2225 cm^{-1} (Ir–H). *Anal.* Calcd for C$_{27}$H$_{27}$Cl$_2$OP$_2$Ir: C, 46.76; H, 3.92; Cl, 10.24; P, 8.94. Found: C, 47.09; H, 3.90; Cl, 10.56; P, 8.85.

Acetyldichlorocarbonylbis(diphenylmethylphosphine)iridium(III) (12).—To a solution of 0.40 g (0.6 mmole) of chlorocarbonyl **3** in 30 ml of benzene was added an excess of acetyl chloride, and the mixture was stirred for 15 min. The mixture was evaporated to dryness under reduced pressure. Recrystallization of the residue from methylene chloride–methanol afforded 0.26 g (59%) of the white product. Infrared absorption (KBr) occurred at 2050 cm^{-1} (CO) and 1630 cm^{-1} (acetyl CO). *Anal.* Calcd for C$_{29}$H$_{29}$OCl$_2$P$_2$Ir: C, 47.35; H, 3.97; P, 8.43. Found: C, 47.61; H, 4.15; P, 8.67.

Dichlorocarbonylbis(diphenylmethylphosphine)monochloromercuryiridium(III) (13).—To 0.33 g (0.5 mmole) of chlorocarbonyl **3** in 30 ml of benzene was added an excess of a solution of mercuric chloride in methanol. The solution turned colorless immediately. The volume of solution was reduced until the product precipitated. The precipitate was washed with methanol. Recrystallization from methylene chloride–methanol afforded 0.37 g (80%) of long white needles. Infrared absorption (KBr) occurred at 2045 cm^{-1} (CO) and (C$_6$H$_6$) at 320, 305, and 270 cm^{-1} (Ir–Cl). *Anal.* Calcd for C$_{27}$H$_{26}$Cl$_3$HgOP$_2$Ir: C, 34.92; H, 2.82; Cl, 11.45; P, 6.67; Hg, 21.61. Found: C, 34.92; H, 3.34; Cl, 11.66; P, 6.71; Hg, 21.19.

Bromochlorohydridocarbonylbis(diphenylmethylphosphine)iridium(III) (14). Procedure A.—To 0.15 g (0.23 mmole) of chlorocarbonyl **3** dissolved in 30 ml of benzene was added an excess of a solution of dry hydrogen bromide in diethyl ether. The solution instantly became colorless. The volume of solution was reduced. Addition of methanol gave white crystals which were collected by filtration, washed with methanol, and air dried; yield, 0.119 g (65%). Infrared absorption (KBr)

occurred at 2210 cm^{-1} (Ir–H) and 2045 cm^{-1} (CO) and (C$_6$H$_6$) at 311 and 268 cm^{-1} (Ir–Cl). *Anal.* Calcd for C$_{27}$H$_{27}$BrClOP$_2$Ir: C, 43.94; H, 3.69; Br, 10.82; Cl, 4.81; P, 8.40. Found: C, 43.95; H, 3.79; Cl, 4.52; Br, 10.94; P, 8.28.

Procedure B.—To 0.20 g (0.29 mmole) of bromocarbonyl **9** dissolved in 10 ml of benzene was added an excess of dry hydrogen chloride in diethyl ether and the solution was stirred for 10 min. The volume of solution was reduced, and upon the addition of methanol the product precipitated. The product was washed with methanol and air dried; yield, 0.075 g (37%). Infrared absorption (KBr) occurred at 2210 cm^{-1} (Ir–H) and 2045 cm^{-1} (CO) and (C$_6$H$_6$) at 310 and 265 cm^{-1} (Ir–Cl). *Anal.* Calcd for C$_{27}$H$_{27}$BrClOP$_2$Ir: C, 43.94; H, 3.69; P, 8.28; total halogen as AgX, 2.400 mg for 5.095-mg sample. Found: C, 44.34; H, 3.76; P, 8.19; AgX, 2.288 mg.

Acetylbromochlorocarbonylbis(diphenylmethylphosphine)iridium(III) (15). Procedure A.—To 0.40 g (0.56 mmole) of bromocarbonyl **9** in 30 ml of benzene was added an excess of acetyl chloride and the mixture was stirred for 10 min. The solution was evaporated to dryness and the residue was reg crystallized from methylene chloride–methanol affording 0.195 - (44%) of the pale yellow crystals. Infrared absorption (KBr) occurred at 2050 cm^{-1} (CO) and 1630 cm^{-1} (acetyl CO). *Anal.* Calcd for C$_{29}$H$_{29}$BrClO$_2$P$_2$Ir: C, 44.66; H, 3.74; Cl, 4.55; Br, 10.25; P, 7.94. Found: C, 44.83; H, 3.93; Cl, 4.25; Br, 10.34; P, 7.91.

Procedure B.—To a benzene solution of chlorocarbonyl **3** was added an excess of acetyl bromide under the same conditions used in procedure A. Thin layer chromatography and infrared and nmr spectra show the same mixture of isomers was formed as in procedure A.

Procedure C.—A solution of 0.65 g of bromochloromethylcarbonyl **8A** in 20 ml of methylene chloride was treated with 50 psi of carbon monoxide at 80° for 24 hr. An infrared spectrum of the reaction mixture indicated that no reaction occurred.

Chloroiodo(trifluoromethyl)carbonylbis(diphenylmethylphosphine)iridium(III) (16).—Into a solution of 0.33 g (0.5 mmole) of chlorocarbonyl **3** in 20 ml of benzene was bubbled trifluoromethyl iodide for 3 min. The solvent was removed and recrystallization of the residue from benzene–methanol afforded 0.21 g (49%) of orange plates. *Anal.* Calcd for C$_{28}$H$_{26}$ClF$_3$IOP$_2$Ir: C, 39.43; H, 3.04; Cl, 4.04; F, 6.68; I, 14.88; P, 7.27; mol wt, 853. Found: C, 39.72; H, 3.57; Cl, 3.94; F, 6.36; I, 15.30; P, 7.13; mol wt, 788.

Chloroiodo(pentafluoroethyl)carbonylbis(diphenylmethylphosphine)iridium(III) (17).—Pentafluoroethyl iodide was bubbled into a solution of 0.33 g (0.5 mmole) of chlorocarbonyl **3** for 3 min. The reaction mixture was worked up in the same manner as in the preparation of **16**. *Anal.* Calcd for C$_{29}$H$_{26}$ClF$_5$IOP$_2$Ir: C, 38.62; H, 2.88; Cl, 3.93; F, 10.53; I, 14.07; P, 6.86; mol wt, 903. Found: C, 37.96; H, 3.17; Cl, 3.91; F, 10.22; I, 14.60; P, 6.58; mol wt, 812.

Chloroiodo(heptafluoro-n-propyl)carbonylbis(diphenylmethylphosphine)iridium(III) (18).—Upon dropwise addition of heptafluoro-n-propyl iodide to 0.40 g (0.6 mmole) of chlorocarbonyl **3** dissolved in 20 ml of benzene, an immediate color change from yellow to orange was observed. The solvent was removed under reduced pressure and recrystallization of the residue from methylene chloride–methanol afforded 0.39 g (68%) of orange prisms. *Anal.* Calcd for C$_{30}$H$_{26}$ClF$_7$IOP$_2$Ir: C, 37.81; H, 2.75; Cl, 3.72; F, 13.96; I, 13.32; P, 6.50; mol wt, 953. Found: C, 37.61; H, 2.83; Cl, 4.95; F, 12.34; I, 14.13; P, 6.65; mol wt, 864.