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Preparation and Interconversion of Two Isomeric Iridium Trihydrides

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The preparation, separation, and structural characterization of *a,b,c*-trihydrido-*f*-carbonylbis(triphenylphosphine)iridium(III) and *a,b,f*,-trihydrido-*d*-carbonylbis(triphenylphosphine)iridium(III) are described. The kinetics of interconversion of the two isomers and of the displacement of H_2 from both isomers by triphenylphosphine have been measured and indicate that interconversion occurs via reversible reductive elimination/oxidation sequence. Both the isomerization and substitution reactions are postulated to involve the intermediate $IrH(CO)P_2$. The relationship of the present results to other studies of the stereochemistry of oxidative additions to square-planar iridium(I) complexes is discussed.

Introduction

The reactions corresponding to eq 1, where P = Ph_3P and

$$\mathrm{IrCl(CO)P_2 + L \xrightarrow{NaBH_4} IrH(CO)LP_2} \qquad (1)$$

L = phosphine,[1,2] olefin,[2,3] CO,[1] H_2,[4] or R_3MH[2] (M = Si, Ge, Sn), provide a useful general synthesis for a family of analogous iridium(I) and iridium(III) hydride complexes.

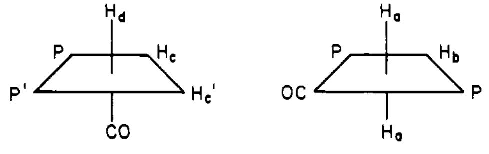
In the course of studying the synthetic scope of this reaction, a species was frequently obtained, either as the major, or a minor, product which seemed to be the trihydride, $P_2(CO)H_3Ir$, previously reported by Malatesta.[4] In accord with this earlier work, the complexity of the IR spectrum of the trihydride suggested the presence of at least two isomers. However, in our preparations, the relative intensities of the carbonyl and hydride bands were quite variable from one preparation to another and, more importantly, were often found to vary with time. An investigation was therefore undertaken with the objective of isolating and fully characterizing these hydrides and determining the reason for the variability in their relative amounts in the reaction product.

A second important reason for our interest in these trihydrides was their relationship to the group 4 hydride complexes $IrH_2(CO)(MR_3)P_2$, which are notable for their unusual stereochemistry[5] (M = Si, Ge, Sn).

Results and Discussion

Preparation and Characterization of *fac*- and *mer*-$IrH_3(CO)P_2$. A slight modification of the reported synthesis[4] permitted the mixed isomers to be prepared in good yield. Fractional crystallization yielded samples of each isomer of such a purity that neither could be detected in the other by IR spectroscopy (>95% purity). The IR spectra of the two pure isomers in the carbonyl/hydride region are shown in Figure 1. The strong band at 1780 cm^{-1} in one of the isomers is indicative of trans hydrides and fixes the hydride positions as facial and meridional in the two isomers, as originally suggested by Malatesta.[4] The complete structures of the *mer* and *fac* isomers were derived from ^1H and ^{31}P NMR studies. Because of long measurement times, the NMR spectra were usually those of the starting isomer contaminated by small amounts of the other isomer produced by spontaneous isomerization. By remeasurement of spectra at intervals, it was shown that, under a hydrogen atmosphere, both isomers undergo spontaneous interconversion to equilibrium in a few hours at room temperature and that the two isomers coexist with a slight excess of the *fac* isomer. A number of earlier reports of these trihydrides failed to observe the existence of a dynamic equilibrium between the two isomers.[1,4,6,7] That the isomers are in equilibrium was, however, concluded by Burnett et al. on the basis of indirect evidence.[8] Similarly, there have been a number of reports of the ^1H NMR spectra of the two trihydride isomers, but no complete assignment for the *fac* isomer has been reported.[9] The complete assignments for the ^1H and ^{31}P NMR spectra are therefore presented in Table I.

Table I. ^1H and ^{31}P NMR Parameters of *mer* and *fac* Isomers[a]



Chemical Shifts,[b] δ

H_d	−10.20	H_a	−10.06
H_c	−11.42	H_b	−10.54
P	6.55	P	15.48

Coupling Constants (^1H Spectra),[c] Hz

H_d-H_c	2.4	H_a-P	16.6
H_d-P	18.1	H_b-P	19.5
H_c-P'	123.1	H_a-H_b	4.6
H_c-P	−18.1		
H_c-H_c'	~5		
P-P'	~8		

Coupling Constants (^{31}P Spectra),[c] Hz

H_d-P	18.0	H_a-P	17.0
H_c-P'	123.0	H_b-P	20.0
H_c-P	18.0		

[a] All spectra recorded in CH_2Cl_2 at 25 °C. [b] Proton values relative to Me_4Si; phosphorus relative to 85% H_3PO_4. [c] Coupling constants for *fac* isomer obtained by spectral simulation.

Kinetics of Interconversion of the Two Isomers. The rates of isomerization of each of the two isomers were studied under a range of experimental conditions. Some values for the rate and equilibrium constants for reaction 2 are listed in Table

$$mer \underset{k_R}{\overset{k_F}{\rightleftharpoons}} fac \qquad (2)$$

II. Values for the rate constants k_F and k_R were estimated by two independent methods: first, from the initial rates of reaction, determined by computer extrapolation of experi-

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Table II. Rate and Equilibrium Constants for the Isomerization Reactions[a]

$[H_2]$[b]	$k_F \times 10^2$,[c] min^{-1}	$k_R \times 10^2$,[c] min^{-1}	$k_F \times 10^2$,[d,e] min^{-1}	$(k_F + k_R) \times 10^2$,[d,e] min^{-1}	$k_R \times 10^2$,[d,e] min^{-1}	$(k_F + k_R) \times 10^2$,[d,f] min^{-1}	K_{eq}
100	0.83	0.91	1.27	2.11	0.84	2.16	1.5
75	1.20	1.50	1.04	1.80	0.76	1.67	1.3
50	1.70	2.41	1.07	1.73	0.66	2.17	1.6
25	1.40	1.41	1.15	1.93	0.78	1.96	1.5
0	1.40	1.26					

[a] All rates measured in methylene chloride at 25 °C. [b] The percentage of H_2 in a H_2/N_2 mixture above the solution. [c] Estimated from initial rates. [d] Derived from slopes of plots of linearized rate law. This treatment could not be applied when no H_2 was present since the trihydrides decomposed without achieving equilibrium. [e] Starting from pure *mer* isomer. [f] Starting from pure *fac* isomer.

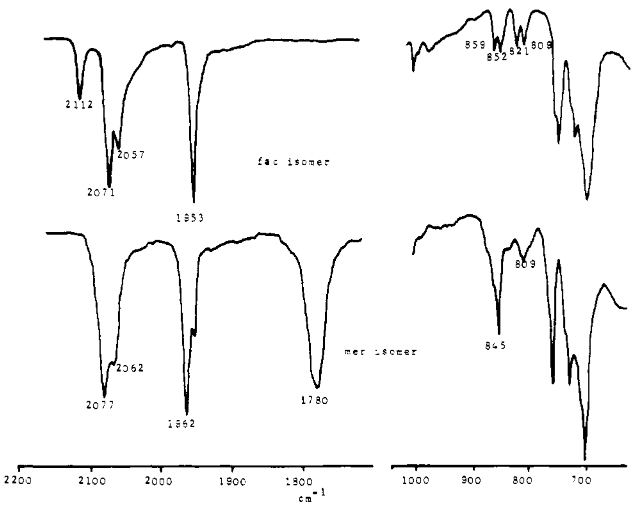
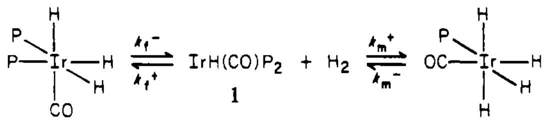


Figure 1. Infrared spectra of pure *fac* and *mer* isomers in the Ir–H and CO regions (measured as Nujol mulls).

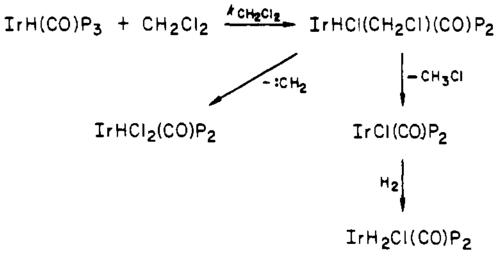
mental data to zero time, and second, by fitting the data to a model rate law which assumed the achievement of equilibrium from either reactant by a first-order process. The first method gave k_F and k_R directly and independently. The second method gave k_F and $(k_F + k_R)$ when starting from pure *mer* isomer and $(k_F + k_R)$ when starting from pure *fac* isomer. Although the scatter of the results derived from initial rate measurements is rather large due to experimental error in the initial conditions, the overall agreement between the values of k_F and k_R from the two methods is quite good. Further, the results support a model by which both isomers interconvert by a unimolecular rate controlling process.

The two most plausible mechanisms which fit the requirements of first order in iridium complex and lack of dependence $[H_2]$ are (i) a unimolecular, intramolecular isomerization which is completely represented by reaction 2 and (ii) a slow unimolecular loss of H_2 by the reductive elimination followed by a rapid readdition of H_2 to the coordinatively unsaturated intermediate, as shown in eq 3. Provided the rates of hydrogen loss are very slow compared to hydrogen addition to **1**, mechanism 3 is indistinguishable from (2) on the basis of the evidence presented so far.



(3)

The fact that equilibrium is not achieved, due to a side reaction with methylene chloride solvent, in the absence of externally supplied hydrogen, suggests the possibility that (3) occurs. This is even more strongly supported by the observation that a nitrogen purge of either, or both, isomers in methylene chloride leads to the slow, but eventually complete, disappearance of the trihydrides and the appearance of $IrCl(CO)P_2$, $IrCl_2H(CO)P_2$, and $IrClH_2(CO)P_2$. These are the products expected from the oxidative addition of CH_2Cl_2 to **1** by eq 4.



(4)

In the presence of even low concentrations of externally supplied hydrogen, the reaction of methylene chloride is too slow to compete effectively with H_2 for **1** (vide infra).

Kinetics of Triphenylphosphine Substitution into the *mer* and *fac* isomers. It has been known for some time that the trihydrides are a useful source of the transient **1** and that a variety of new complexes can be prepared by trapping **1** with various ligands or oxidative addends. For example, equilibrium 5 is known to be established, presumably via the intermediacy of **1**.[1,8]

$$IrH_3(CO)P_2 + P \overset{k_D}{\rightleftharpoons} IrH(CO)P_3 + H_2 \qquad (5)$$

Since triphenylphosphine evidently competes effectively with H_2 for **1**, a study of the kinetics of the forward reaction (5) was carried out. With use of relatively high phosphine concentrations, the back-reaction was suppressed and the overall reaction obeyed a pseudo-first-order rate law.

The rates of the reactions of both the *mer* and the *fac* isomers were determined and the results are summarized in Table III. The rate law was again determined both by initial rate measurements and by fitting the data to a model rate law based on the assumption that the rate-controlling step is a unimolecular loss of dihydrogen from the trihydride complexes. As in the case of the isomerization reaction the scatter of the initial rate data is large. Nevertheless, the conclusion that the reactions of both *mer* and *fac* trihydrides are independent of phosphine concentration and first order in iridium complex is reasonably established.

The most significant feature of the data listed in Table III is the close similarity of the rate constants for dihydrogen dissociation, k_D, to those for the rates of isomerization, k_F and k_R. If the rates of isomerization and phosphine substitution of the trihydrides are both controlled by the rate of hydrogen dissociation, then the rate of isomerization can be equal to or less than that of phosphine substitution. The fact that observed rates of isomerization are slightly higher than those of phosphine substitution is expected since addition of H_2 to the square-planar intermediate, **1**, can lead to both reactant and product, while addition of phosphine can only lead to product. The near equality of the rates of hydrogen loss from the *mer* and *fac* trihydrides in CH_2Cl_2, coupled with the slight preponderance of *fac* isomer at equilibrium, indicates that the rate of hydrogen addition to **1** to form *fac* isomer is slightly faster than the formation of *mer* isomer.

Table III. Rate Constants for Phosphine Substitution Reactions at 25 °C

[P], mM	10^{-2}[Ir],[a] mM	solvent	reactant	initial rate,[b] min^{-1}	final abs	$k_D \times 10^2$,[c] min^{-1}	$k_D \times 10^2$,[d] min^{-1}
10	5	CH_2Cl_2	*fac*				1.21
5	5	CH_2Cl_2	*fac*				1.40
2.5	5	CH_2Cl_2	*fac*				1.60
10	5	CH_2Cl_2	*mer*				1.17
5	5	CH_2Cl_2	*mer*				1.30
2.5	5	CH_2Cl_2	*mer*				1.50
5	7.5	CH_2Cl_2	*fac*				1.00
5	2.5	CH_2Cl_2	*fac*				1.20
5	7.5	CH_2Cl_2	*mer*				1.29
5	2.5	CH_2Cl_2	*mer*				1.20
10	5	toluene	*fac*	0.0113	0.613	1.84	1.85
5	5	toluene	*fac*	0.0107	0.591	1.81	1.80
2.5	5	toluene	*fac*	0.0102	0.629	1.62	1.76
10	5	toluene	*mer*	0.0146	1.084	1.35	1.61
5	5	toluene	*mer*	0.0117	1.112	1.05	1.46
2.5	5	toluene	*mer*	0.0130	1.063	1.22	1.41
5.0	7.5	toluene	*fac*	0.0163	0.830	1.96	2.09
5	5	toluene	*fac*	0.0103	0.550	1.87	2.06
5	2.5	toluene	*fac*	0.0057	0.276	2.06	
5	7.5	toluene	*mer*	0.0127	1.000	1.27	
5	5	toluene	*mer*	0.0089	0.682	1.30	
5	2.5	toluene	*mer*	0.0042	0.313	1.34	

[a] Nominal gravimetric concentrations. Subject to relatively large error due to small amounts of material used. [b] Initial slope of absorbance vs. time plot obtained by curve fitting. [c] Obtained by division of initial slope by final absorbance. Values for CH_2Cl_2 solutions not included due to lack of final absorbance data. [d] Derived from slopes of plots of linearized rate law.

Reaction of $IrH(CO)P_3$ with CH_2Cl_2. The reaction of $IrH(CO)P_3$ with CH_2Cl_2 was found to occur in the reactions of the trihydrides with triphenylphosphine when CH_2Cl_2 was used as solvent. Although the reaction rate for phosphine substitution was fast compared to the methylene chloride reaction, the side reaction had a serious effect on the kinetic analysis at longer reaction times and the phosphine substitution data required correction. The kinetics of the methylene chloride reaction were briefly studied. In the presence of excess phosphine, the iridium complex reacted according to a pseudo-first-order rate law with a rate constant inversely proportional to the phosphine concentration.

If it is assumed that the reactant is in equilibrium with **1** and that **1** reacts irreversibly with CH_2Cl_2 to give chlorinated products such as shown in eq 4, the rate law will be of the form

$$\frac{-d[Ir]}{dt} = k_a[Ir] = \frac{k_{CH_2Cl_2}K_P[CH_2Cl_2][Ir]}{[P]} \qquad (6)$$

where K_P is the equilibrium constant for the equilibrium

$$IrH(CO)P_3 \underset{k_{+p}}{\overset{k_{-p}}{\rightleftharpoons}} IrH(CO)P_2 + P \qquad (7)$$

k_a is the observed apparent first-order rate constant, [Ir] = [$IrH(CO)P_3$], and $k_{CH_2Cl_2}$ is the bimolecular rate constant for reaction of **1** with CH_2Cl_2. The integrated form of this rate law corresponds to the experimental observation and predicts that the slope of a plot of k_a vs. 1/[P] will equal $k_{CH_2Cl_2}K_P[CH_2Cl_2]$. The relevant data are shown in Table IV. Since the value of k_{-p} is known from previous work,[10] the value for the competition parameter $k_{CH_2Cl_2}/k_{+p}$ can be evaluated. The very small value of ca. 5×10^{-6} accounts for the facts that reaction of **1** with solvent was not found to be a problem in earlier studies of its reaction with group 4 hydrides[10,11] and that H_2 readily suppresses the decomposition of the trihydrides in CH_2Cl_2. The fact that **1** reacts with methylene chloride at all is indicative of its relatively great reactivity in comparison to other square-planar rhodium(I) and iridium(I) complexes.

Stereochemical Aspects of Oxidative Addition to Square-Planar Iridium(I) Complexes. Of the dozens of examples of oxidative addition to complexes of the general formula $IrX(CO)P_2$, the overwhelming majority give products in which the two phosphine ligands are trans to each other.[12-14] In cases where the reaction is concerted, this stereospecificity is explained by a movement of the X and CO ligands from a collinear relationship to the metal, to an angular relationship where they occupy a common edge on the opposite side of the product polyhedron to the incoming addend.[11,12] In the few exceptional cases of oxidative addition to $IrX(CO)P_2$ where products have cis phosphines, the stereospecificity is ascribed to an analogous ligand motion, but in this case, it is the phosphines rather than X and CO ligands which migrate.[11]

Table IV. Rate Constants for Reaction of $IrH(CO)P_3$ with CH_2Cl_2 at 25 °C

[P], mM	[P]/[Ir]	$k_a \times 10^3$, min^{-1}	$k_{CH_2Cl_2}K_P \times [CH_2Cl_2] \times 10^5$, min^{-1}
10	200	1.4	1.4
5	100	3.5	1.7
2.5	50	6.4	1.6

One of the interesting aspects of the oxidative additions which produce the *mer* and *fac* isomers of $IrH_3(CO)P_2$ is that both types of reactant deformation appear to occur with the common addend H_2. This contrasts with the behavior of group 4 hydrides, which induce stereospecific migration of phosphines to give products with the same stereochemistry as the *fac* trihydride. While it is reasonable that the stereochemistry of **2** should be more favorable than **3** since it is easier for the phosphines and silicon to be coplanar with H than with CO, there is clearly not much steric bias favoring **2** over **4**. There is, however, a statistical bias favoring **2** over **4** by a factor of 2, and this combined with relatively minor solvation and electronic effects could be sufficient to diminish the equilibrium concentration of isomer **4** below the easily detectable limit. The possible existence of subdetectable amounts of **3** has previously been postulated to explain the H/D exchange of **2** with excess silane.[5]

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(10) J. P. Fawcett and J. F. Harrod, *Can. J. Chem.*, **54**, 3106 (1976).

(11) J. F. Harrod, C. A. Smith, and K. A. Than, *J. Am. Chem. Soc.*, **94**, 8321 (1972).

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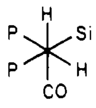

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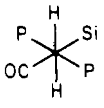

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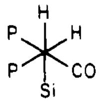

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The observations of Longato et al. on the stereochemistry of H_2 adducts of $IrX(CO)P_2$, where X is a σ-bonded carborane,[15] also provide evidence for the relatively delicate balance of kinetic, steric, and solvation effects which govern the stereochemistry of adducts such as those described above. In the case of the carborane complexes, reaction with H_2 in solvents of low polarity gives primary products with stereochemistries analogous to **2** and **3** in a ratio of ca. 6:4, much the same as observed with the trihydrides.[17] In addition, traces of the isomer with stereochemistry **4** were also detected. Unlike the trihydrides, the above isomer ratio does not correspond to equilibrium and the isomer of stereochemistry **2** converts entirely to **3** stereochemistry in solvents of moderate polarity. Furthermore, ligating solvents of high polarity such as acetonitrile induce the complete conversion of **2** stereochemistry to **4** while not affecting the isomer with stereochemistry **3**. It appears, therefore, that the addition of group 4 hydrides to **1** and the addition of H_2 to the carborane complex, or the square-planar complex, **1**, kinetically favor the isomer in which the phosphine ligands have migrated to positions trans to the incoming addend and cis to each other. In both the silyl and carborane products, the thermodynamically favored isomers appear to be those in which the three bulky ligands are coplanar with a hydride and can presumably adopt bond angles relative to each other considerably greater than 90°.[18] The absence of severe steric constraints in the trihydrides accounts for the presence of roughly equal amounts of two isomers at equilibrium.

Other effects such as trans effects and molecular polarity are no doubt important in determining the prevalence of the various possible isomers, but their quantitative significance is difficult to assess. The large trans effects of group 4 ligands may disfavor isomers such as **4** by greatly weakening the hydride bond and accelerating reductive elimination of H_2.

Experimental Section

All solvents were dried, distilled, and degassed before use.

Preparation and Purification of *fac*- and *mer*-$IrH_3(CO)P_2$. The procedure used was a modification of that previously described.[4] A suspension of *trans*-$IrCl(CO)P_2$ (0.5 g) and sodium borohydride (0.15 g) was stirred in freshly distilled acetonitrile (5 mL) for 24 h under a hydrogen atmosphere. After evaporation of solvent in a stream of hydrogen, the product was extracted into toluene (6 mL) under hydrogen and filtered. Careful addition of hexane (6 mL) to the filtrate induced crystallization of the *mer* isomer. Leaving the latter mixture for 24 h under hydrogen eventually gave the *mer* isomer in ca. 55% yield, on the basis of $IrCl(CO)P_2$. If the *mer* isomer was filtered off shortly after addition of the first 6 mL aliquot of hexane and the filtrate was treated with more hexane (10 mL) and cooled to −20 °C, the *fac* isomer crystallized and was recovered in ca. 30% yield.

Kinetic Measurements. The rates of isomerization of the *fac* and *mer* isomers were followed by monitoring the appearance or disappearance of the infrared band at 1780 cm^{-1} due to the *mer* isomer. Reactions were in solution under appropriate mixtures of H_2 and N_2, and the progress of reaction was monitored by periodic transfer of samples to gas-tight 1 mm path length sodium chloride cells for IR measurement. The fact that the 1780-cm^{-1} band obeyed Beer's law was established by independent dilution experiments on the pure *mer* isomer.

The substitution of triphenylphosphine into the *mer* and *fac* trihydrides was followed by continuously monitoring the appearance of the 330-nm absorption band of $IrH(CO)P_3$. Reactions were carried out under nitrogen in airtight quartz cuvettes. Several test experiments were carried out in the dark, with only periodic exposure to the spectrometer source. No measurable contribution of photochemical decomposition of either of the trihydrides was detected.

The reaction of $IrH(CO)P_3$ with CH_2Cl_2 was followed by continuously monitoring the disappearance of the 330-nm band of the reactant. None of the products had significant absorbance at that wavelength.

Treatment of Data. Rate constants for the equilibration reactions were obtained from slopes of plots of the lhs of eq 8 and 9 for the *mer* isomer and eq 10 for the *fac* isomer.[16]

$$\ln\left(\frac{A_0 - A_{eq}}{A - A_{eq}}\right) = (k_F + k_R)t \tag{8}$$

$$\frac{A_0 - A_{eq}}{A_0}\ln\left(\frac{A_0 - A_{eq}}{A_t - A_{eq}}\right) = k_F t \tag{9}$$

$$\ln\left(\frac{A_{eq}}{A_{eq} - A_t}\right) = (k_F + k_R)t \tag{10}$$

A is the absorbance at 1780 cm^{-1}, and the subscripts zero, eq, and t refer to initial and final absorbances and absorbance at time t.

The reaction of $IrH(CO)P_3$ with CH_2Cl_2 follows the same rate law as the group 4 hydride reaction.[10] The simplifying assumption that $k_{-p} \gg k_{CH_2Cl_2}$ yields eq 6.

Values of k_D for the reactions of the trihydrides with triphenylphosphine in CH_2Cl_2 were determined by an arithmetic iteration procedure as follows. (i) An approximate value of k_D was determined from the standard first-order equation (11) with use of the maximum

$$\ln\left(\frac{[Ir]_{eq}}{[Ir]_{eq} - [Ir]_t}\right) = k_D t \tag{11}$$

concentration achieved by $IrH(CO)P_3$ as the value for $[Ir]_{eq}$. (ii) From the approximate value of k_D, an approximate value of t for 99% reaction of the trihydride was calculated. (iii) The data for [Ir] beyond the 99% reaction time was used to calculate k_a. (iv) This value of k_a was used in the standard consecutive first-order reaction rate law, eq 12 to compute an improved value of k_D. (v) The improved value

$$\ln\left(e^{-k_a t} - \frac{[Ir]_t}{[Ir]_{eq}}\right) = k_D t \tag{12}$$

of k_D was used to calculate better values of $[Ir]_{eq}$ and the 99% reaction time with (11), and the whole process was reiterated. Usually, four reiterations gave excellent straight-line plots of the lhs of (12) vs. t and values of k_a that agreed well with values determined independently from studies of the reaction of $IrH(CO)P_3$ with CH_2Cl_2.

Acknowledgment. The financial support of this work by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. *fac*-$IrH_3(CO)P_2$, 16971-55-4; *mer*-$IrH_3(CO)P_2$, 36606-40-3; *trans*-$IrCl(CO)P_2$, 59246-46-7; $IrH(CO)P_3$, 17250-25-8; CH_2Cl_2, 75-09-2.

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(15) B. Longato, F. Moradini, and S. Bresadola, *Inorg. Chem.*, **15**, 650 (1976); B. Longato and S. Bresadola, *Inorg. Chim. Acta*, **33**, 189 (1979).

(16) These are standard equations for unimolecular approach to equilibrium.

(17) The analogy is with the relative positions of the reactant and addend ligands, not the absolute positions of the product ligands.

(18) In the structurally analogous $[IrH_2(CO)P_3]^+$ species the angles between mutually cis phosphines are 101°.[19]

(19) P. Bird, J. F. Harrod, and K. A. Than, *J. Am. Chem. Soc.*, **96**, 1222 (1974).