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Mechanism of Oxidative Addition of Allylic Halides to Iridium(I) Complexes

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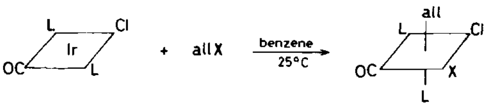
A detailed study has been made of the oxidative addition reaction of allylic halides to IrCl(CO)(P-(CH$_3$)$_2$C$_6$H$_5$)$_2$ in benzene and in methanol. In benzene the reaction probably occurs by way of a π-allyl intermediate. This reacts with anion to give a product with a σ-allyl group bonded to the metal cis *to the added anion. Both crotyl and α-methylallyl chlorides give the same products since they form the same π-allyl. In methanol the π-allyl is not an intermediate since crotyl chloride and α-methylallyl chloride give different σ-allyl products with the metal atom bonding predominantly to the carbon atom bearing the chloride. The anion which add in methanol can be one added to the solution and it bonds* trans *to the σ-allyl group. A modified S$_N$2 mechanism with double-bond participation is proposed for both solvents.*

Introduction

The *cis* addition of allylic halides to IrCl(CO)-(PMe$_2$Ph)$_2$ to give isomer I, reported by Deeming and Shaw [2], is unique for oxidative addition of alkyl halides to planar four-coordinated metal complexes.

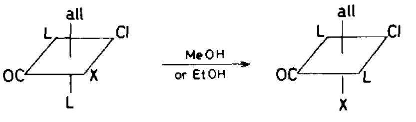


(1)

all = CH$_2$=CR–CH$_2$
R = H, Cl, CH$_3$
X = Cl, Br
L = P(CH$_3$)$_2$C$_6$H$_5$

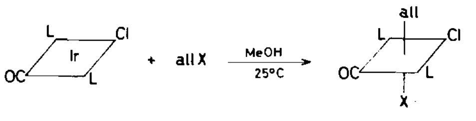
While H$_2$ and sometimes HX add to complexes of the type *trans*-IrX(CO)L$_2$ to give *cis* adducts, alkyl halides generally form products with the alkyl and added halogen groups *trans* to each other [3]. Reaction (1) is also unusual because the phosphine ligands are *cis* to each other in the product [4].

Deeming and Shaw also observed that recrystallization of isomer I from methanol or ethanol resulted in complete isomerization to the *trans* isomer II.



I II (2)

Furthermore when the oxidative addition reaction is carried out in methanol, the *trans* isomer is formed directly.



II (3)

These results raise several interesting possibilities. The *cis* addition in benzene may be an example of concerted oxidative addition, since orbital symmetry arguments show that *cis* adducts should form in concerted addition [5]. There could be solvent control over the mechanism with concerted addition favored in a nonpolar solvent such as benzene. In a polar solvent such as methanol, a two-step mechanism with ionic intermediates might be favored (S$_N$2 mechanism).

$$\mathrm{IrCl(CO)L_2 + all\,X \rightarrow IrCl(CO)L_2(all)^+ + X^-} \quad (4)$$

$$\mathrm{IrCl(CO)L_2all^+ + X^- \rightarrow IrCl(CO)L_2(all)X} \quad (5)$$

Such a two-step mechanism would lead directly to the favored *trans* products, II.

It is also possible that *cis* addition is common in oxidative addition but that rapid isomerization to the *trans* isomer immediately follows. Product work-up would show only the more stable *trans* isomer. Alternatively, it may be that the allyl group is special either because of its double bond, or because it can form π-allyl complexes. In fact Shaw and Deeming isolated the π-allyl complex, III, in several cases and showed that it reacted with halide ions to form *trans*-isomers of the σ-allyl complexes [2].

The structure of III has been determined by X-ray diffraction in the case of Ir(C$_3$H$_5$)Cl(CO)(PMe$_2$Ph)$_2$-PF$_6$ [6]. The structure is shown in Figure 1.

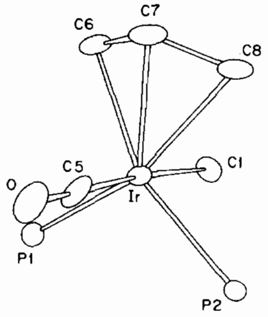
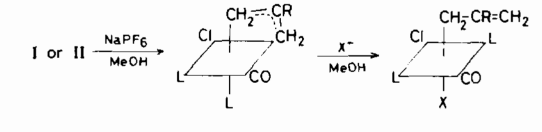


Fig. 1. A perspective view of the coordination geometry about the iridium atom in $Ir(\eta^3\text{-}C_3H_5)Cl(CO)P(CH_3)_2C_6H_5^+$.



III

II

(6)

Because of these interesting questions, it was decided to investigate the mechanism of oxidative addition of allyl halides to $IrCl(CO)(PMe_2Ph)_2$ in methanol and in benzene in some detail. We report product and rate studies using substituted allyl halides, external anion trapping experiments and the reaction with optically active (+)-$CH_2{=}CHCHClCH_3$.

Finally, some observations on reactions of alkyl and allyl sulfonates with iridium(I) complexes were also made. The third general mechanism for oxidative addition reactions of alkyl halides involves free radical formation [5]. It is generally considered that alkyl sulfonates are not susceptible to this free radical path [7, 8]. They are instead very prone to react by the two step, or S_N2 mechanism.

Experimental

$IrCl(CO)(PMe_2Ph)_2$ was prepared by a modification of the procedure by Deeming and Shaw [9]. 1.2 g hydrated $IrCl_3$ (Matthey-Bishop, Inc.) and 0.6 g LiCl were added to 16 ml 95% ethanol. The solution was bubbled with carbon monoxide and heated at reflux for 16–20 hours, until it turned from dark brown to straw yellow. The solution was then cooled slowly to room temperature, carbon monoxide bubbling was discontinued, and 1.1 ml dimethylphenylphosphine was added immediately. Upon stirring, there was a vigorous release of carbon monoxide and a white precipitate formed. Cooling to −10 °C caused further precipitation of the white $IrHCl_2(CO)(PMe_2Ph)_2$. The product was filtered in the air, washed with a small amount of cold acetone, and dried. A good yield for the reaction was 1.31 g (70%). An equivalent of 1 *M* sodium methoxide in methanol was added to a suspension of 1 g of the iridium hydrochloride in 5 ml of nitrogen-saturated methanol; a yellow precipitate formed immediately. The mixture was refluxed under nitrogen until the yellow precipitate completely dissolved. Cooling to −10 °C gave the yellow crystalline $IrCl(CO)(PMe_2Ph)_2$ which was then filtered and dried. The iridium(I) complex reacts completely with oxygen on exposure to air over several days, and was therefore stored under nitrogen.

$IrBr(CO)(PMe_2Ph)_2$ was prepared from $IrCl(CO)(PMe_2Ph)_2$ by halogen exchange. 0.9 g LiBr was dissolved in 5 ml nitrogen-saturated methanol, 0.2 g $IrCl(CO)(PMe_2Ph)_2$ was added, and the mixture was refluxed until all of the iridium complex dissolved. The solution was cooled, filtered, and washed with a small amount of cold methanol. The infrared spectrum of the yellow product was identical to that of $IrCl(CO)(PMe_2Ph)_2$ except for the complete absence of an Ir-Cl stretching frequency. The uv–vis spectrum of $IrBr(CO)(PMe_2Ph)_2$ in methanol exhibited absorption maxima at 433, 375, and 338 nm whereas $IrCl(CO)(PMe_2Ph)_2$ has absorption maxima at 428, 373, and 337 nm.

$IrCl(CO)(PPh_3)_2$ was prepared by a literature method [10]. $IrBr(CO)(PPh_3)_2$ was prepared by the reaction of $IrCl(CO)(PPh_3)_2$ with a 50-fold molar excess of LiBr in tetrahydrofuran at room temperature for one hour. The solvent was evaporated, the lithium salts were extracted with water, and the water-insoluble product was recrystallized from nitrogen-saturated benzene. Infrared spectroscopy was used to confirm that the product was not contaminated with $IrCl(CO)(PPh_3)_2$.

Reagent grade benzene was heated to reflux over sodium wire and distilled in an atmosphere of nitrogen. Other solvents were purchased reagent grade and used without further purification. Allylic halides were obtained commercially (usually from Aldrich Chemical Company) and were purified by simple distillation, except for 3-chloro-1-butene and 1-chloro-2-butene, which were fractionally distilled at reduced pressure to separate the desired compound from small amounts of the allylically-related isomer. The two isomers were stored in the dark in refrigeration at −30 °C to prevent isomerization to an equilibrium mixture of isomers. Nmr spectroscopy was used to show that isomeric purity was greater than 95% in both cases. Also, it was shown that neither halide isomerised in methanol, chloroform, or benzene at room temperature over six hours.

Optically active 3-chloro-1-butene was prepared by a modification of the method of Young and Caserio [11]. A mixture of 34.8 g of 3-butene-2-ol and 59.2 g of phthalic anhydride in 35 ml dry pyridine was heated on the steam bath for one hour, during which time the phthalic anhydride completely dissolved. The solution was cooled, ice and chloroform were added, and then 80 ml concentrated (12 *M*) HCl was slowly added. The product, 3-butene-2-ol monophthalate, was extracted into chloroform, the solution was washed with water and dried over Na_2SO_4 and the chloroform was removed by vacuum distillation. To a solution of 78 g of the product oil in 400 ml acetone was added 138 g of brucine. This mixture was heated on the steam bath and sufficient acetone was added so that all solids dissolved. The solution was cooled; the resulting white crystalline precipitate was predominantly the least soluble diastereomer of the phthalate ester-brucine salt. Multiple recrystallizations in acetone of this solid increased diastereomeric purity. The soluble diastereomer was purified by multiple solvent evaporations followed by filtration. Addition of 4 *M* HCl to the brucine salts and extraction with diethyl ether produced (+)-3-butene-2-ol monophthalate from the least acetone-soluble salt and the (–) enantiomer from the acetone-soluble salt. Addition of the ester oils to aqueous NaOH, steam distillation, ane extraction of the distillate with diethyl ether produced the enantiomeric allylic alcohols. To 4 ml of dry allylic alcohol was added 11.2 ml tributylamine and 51 ml dry butyl ether in a flask topped with a $CaCl_2$ drying tube. The solution was colled to –10 °C, and 2.4 ml $SOCl_2$ was added dropwise over one-half hour with rapid stirring of the solution. When the reaction was complete, the butyl ether layer was quickly separated from the oily layer of $(n\text{-}C_4H_9)_3N$ HCl and washed with aqueous $NaHCO_3$. The ether solution was distilled at atmospheric pressure and the distillate collected from 40 °C to 80 °C. The product was a solution in butyl ether of partially resolved $CH_2{=}CHCHClCH_3$ and $CH_3CH{=}CHCH_2Cl$, with the secondary halide typically present in two-fold molar excess over the primary halide. (–)-1-butene-3-ol, derived from the (–)-phthalate ester, reacts with thionyl chloride to give (+)-3-chloro-1-butene. Based upon an estimate for the optical rotation of enantiomerically pure (+)-$CH_2{=}CHCHClCH_3$, $[\alpha]_D^{20} = +61°$, the optical purity of the (+)-enantiomer used in this study was 42% and the optical purity of the (–)-enantiomer was 25%. The butyl ether solution of a mixture of primary and secondary halides was used in reactions with $IrCl(CO)(PMe_2Ph)_2$. Over a period of several hours at room temperature, methanol or benzene solutions of the alkyl halide mixture do not lose optical activity.

Allyl methanesulfonate, $CH_2{=}CHCH_2OSO_2CH_3$, and homoallyl methanesulfonate, $CH_2{=}CHCH_2CH_2OSO_2CH_3$, were prepared by the addition of methylsulfonyl chloride to the alcohols in dry pyridine at –10 °C. The reaction mixtures were stored at –10 °C for one hour, then the products were extracted with cold ether, pyridine was removed by precipitation as pyridinium ion with conc. H_2SO_4, and the ether filtrate was washed with aq. $NaHCO_3$ and dried with $CaCl_2$. Removal of the ether gave colorless or slightly yellow oils. The products were stored at –30 °C.

The rates of oxidative addition of allylic halides to $IrCl(CO)(PMe_2Ph)_2$ in benzene were followed on a Cary 14 UV–Vis Spectrophotometer, thermostated to 25.0 ± 0.2 °C. In a typical kinetic run, 3 ml of a 5×10^{-5}–3×10^{-4} *M* nitrogen-saturated solution of $IrCl(CO)(PMe_2Ph)_2$ was syringed under nitrogen into a uv–vis cuvette which had a teflon needle-valve top. A microliter quantity of a dilute solution of the halide in benzene was then added, the cell was closed and shaken, and the decrease in intensity of the 378 nm absorption peak ($\epsilon = 4.4\ (\pm 0.1) \times 10^3 M^{-1}\ cm^{-1}$) of the iridium(I) complex as a function of time was followed on the spectrophotometer. Equal concentrations of halide and iridium(I) were used when allyl chloride and allyl bromide were the reactants; plots of $\log(t_{1/2})$ *vs.* log(initial iridium concentration) were linear with slope = –0.90 for allyl bromide and slope = –1.00 for allyl chloride, indicating that the reactions are first order in iridium(I) concentration. The initial iridium(I) concentration varied from 3.2×10^{-5} to 3.8×10^{-4} *M*. The allyl chlorides, 3-chloro-2-methyl-1-propene, 1-chloro-2-butene, and 3-chloro-1-butene, were allowed to react in greater than 10-fold molar excess with $IrCl(CO)(PMe_2Ph)_2$. Plots of log $A_{378\,nm}$ against time were generally linear over greater than four half-lives. The halide concentrations were usually varied over the range 1×10^{-3}–1×10^{-2} *M* and graphs of first order rate constants *versus* halide concentration were linear and had zero intercept. Thus, these reactions follow a second order rate law (first order in iridium and first order in halide), and no competing reactions are kinetically evident.

The rates of oxidative addition of allylic halides to $IrCl(CO)(PMe_2Ph)_2$ in methanol, chloroform, and acetonitrile were studied on a stopped-flow apparatus previously described [12]. For all kinetic runs, reactant solutions were nitrogen-saturated, the halide concentrations were kept in greater than 10-fold molar excess over the iridium(I) concentrations, and the reactants and mixing chamber of the stopped-flow apparatus were maintained at 25.0 ± 0.5 °C. The loss of intensity of an iridium(I) absorption peak (373 nm in methanol and 377 nm in acetonitrile and chloroform) was monitored as a function of time. The iridium(I) complex was quite stable in methanol and acetonitrile, but decomposed completely over several hours in nitrogen-saturated chloroform. However, this decomposition was much slower than the oxidative addition, and the product of the decomposition had no effect upon the rate of oxidative addition with the allylic halides. Under conditions of excess halide (3×10^{-3}–5×10^{-2} *M* halide, 2×10^{-4} *M* iridium(I)) the reactions were all first order in iridium over at least three half-lives; plots of first-order rate constants *versus* halide concentrations were linear with zero intercept.

The rates of isomerization of allyliridium(III) complexes of configuration I (*cis* isomers) in

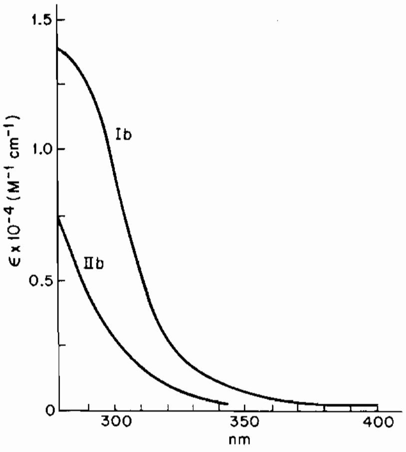


Fig. 2. Visible–uv spectral changes in isomerization of Ib to IIb in methanol.

methanol were determined by rapidly dissolving the solids in methanol in a capped uv–vis spectrophotometer cuvette and recording the decrease in absorbance at 285 nm as a function of time at 25.0 ± 0.2 °C. A Cary 14 UV–Vis Spectrophotometer was used. Complexes of configuration I always had larger extinction coefficients at 285 nm than the configuration II (*trans*) complexes to which they isomerize.

The external ion-incorporation experiment was performed in the following manner:

To a solution of 0.030 g $IrBr(CO)(PMe_2Ph)_2$ and 0.15 g LiBr in 3.0 ml nitrogen-saturated methanol was added dropwise with stirring a stoichiometric amount of 10% allyl chloride in methanol. Methanol was pumped off from the colorless solution on the vacuum line until most of the white crystalline product came out of solution. The product was filtered, washed twice with cold methanol to remove any residual LiBr, and dried. The infrared spectrum (nujol mull) showed a complete absence of an absorption peak at 310 cm^{-1}. When the same procedure was followed, but only 0.06 g of LiBr used, a very weak absorption peak at 310 cm^{-1} was observed. When allyl chloride was added to $IrBr(CO)(PMe_2Ph)_2$ in the absence of LiBr, a strong 310 cm^{-1} infrared peak was observed in the product. When 0.15 g LiBr was mixed with a methanolic solution of 0.030 g of this product and allowed to stand at room temperature for 20 minutes, the isolated compound showed the same high intensity for the 310 cm^{-1} absorption peak as the original.

Optical rotations were measured on a Cary 60 Optical Rotary Dispersion–Circular Dichroism Spectrophotometer. All measurements were made at 20 °C, with cell path length = 1 cm. The optical rotation of reactants and oxidative addition products were recorded for the wavelength region 600–350 nm.

All reactions with iridium(I) complexes were performed under a nitrogen atmosphere. Nmr spectra were taken on a Perkin Elmer-Hitachi R20-B Spectrophotometer. Infrared spectra were taken on a Beckman IR 12 Spectrometer.

Most of the allylic halide adducts of $IrCl(CO)(PMe_2Ph)_2$ used in this study had been prepared by Deeming and Shaw [2], and product purity was confirmed by comparison with their spectral and m.p. data. The previously unreported oxidative additions of 3-chloro-1-butene and 1-chloro-2-butene to $IrCl(CO)(PMe_2Ph)_2$ gave white crystalline solids in methanol. The molecular structures were assigned by nmr spectroscopy and by comparison of the infrared spectra to those of similar compounds prepared by Deeming and Shaw (see Results).

Results

Isomerization Studies

Benzene as solvent

Two compounds of configuration II, (all = C_3H_5 and X = Br and Cl) were dissolved in benzene and heated to 60 °C for one hour. No isomerization to configuration I was observed in either case. However, the configuration I isomers (*cis*) slowly isomerize to II (*trans*) after one day at room temperature. Nmr spectroscopy was used to monitor this reaction since I and II have completely different coupling patterns for the methyl groups on the phosphine ligands (II exhibits two overlapping triplets and I shows a second-order pattern of overlapping doublets).

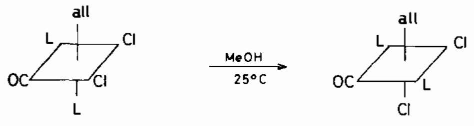
Thus in benzene isomers II are thermodynamically stable and isomers I are the kinetically-controlled oxidative addition products of reaction. This excludes an oxidative addition pathway involving initial formation of II followed by isomerization to I, the observed product.

Methanol and chloroform as solvents

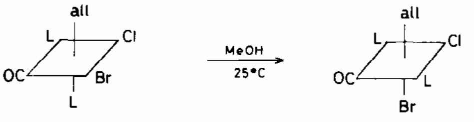
Since compounds of configuration I are thermodynamically unstable in methanol, reaction (2), it is possible that in methanol isomers I are initially formed by oxidative addition, followed by isomerization to II.

This possibility, however, can be excluded by comparison of the oxidative addition rate with the rate of isomerization of I under suitable conditions. The reactions of allyl chloride and allyl bromide with $IrCl(CO)(PMe_2Ph)_2$ obey a rate law which is first order in each reactant. When allyl halide concentrations are made sufficiently high so that all of the iridium(I) is consumed in less than 1 second, a scan of the 285–350 nm spectral region 20 seconds after mixing the reactants showed no evidence of intermediates of configuration I. If isomers I were intermediates, they should have been observed spectrally since they differ markedly in extinction coefficient from isomers II in the region 285–330 nm and since the isomerization I → II in methanol requires much longer than 20 seconds for completion.

The isomerizations were studied by adding Ia and Ib as solids to methanol and observing the change in absorbance at 285 nm at 25 °C.



Ia IIa



Ib IIb

all = C_3H_5
L = PMe_2Ph

Both compounds isomerize according to a first order rate law, with half-lives of 38 seconds for Ia and 52 seconds for Ib. The reactant and product spectra for the isomerization of Ib to IIb are given in Fig. 2.

In addition, the oxidative addition of allyl bromide to $IrCl(CO)(PMe_2Ph)_2$ in methanol was monitored as a function of time at both 373 and 280 nm, using stopped-flow spectrophotometry. This reaction gives a mixture of isomers of $IrClBr(CO)L_2$-(all) in which the phosphines are always *trans* to each other, but either Cl or Br can be *trans* to CO (*vide infra*).

$$IrCl(CO)(PMe_2Ph)_2 + CH_2{=}CHCH_2Br \rightarrow IrClBr(CO)(PMe_2Ph)_2(C_3H_5) \qquad (7)$$

$IrBr_2(CO)(PMe_2Ph)_2$ may also have formed.

At 373 nm, only the reactant $IrCl(CO)(PMe_2Ph)_2$ absorbs significantly. At 280 nm, the reactant has an extinction coefficient, ϵ, equal to $1.04(\pm 0.05) \times 10^4$ M^{-1} cm^{-1}, and the mixture of *trans* products has $\epsilon = 5.6(\pm 0.01) \times 10^3$ M^{-1} cm^{-1}. Spectral monitoring of reaction (7) shows a decrease in absorbance as a function of time at the same rate at both 280 nm and 373 nm. This demonstrates that compounds Ia and Ib are not present in significant quantity during the reaction course and that the observed mixture of products having *trans* phosphine ligands is kinetically-controlled.

These experiments rule out reaction (1) followed by (2) as the pathway for oxidative addition in methanol. Further support for this conclusion is the fact that reaction (7) gives a mixture of products whereas isomerization of Ib in methanol produces only a single isomer, IIb [2].

The reaction of allyl bromide with $IrCl(CO)(PMe_2Ph)_2$ in chloroform occurs upon mixing; an nmr spectrum of the reaction solution taken 10 minutes later shows a product with *trans*-phosphine ligands, IIb. This reaction does not proceed through formation of Ib as an intermediate since Ib isomerizes to IIb with a half-life of about 50 minutes in chloroform at 25 °C.

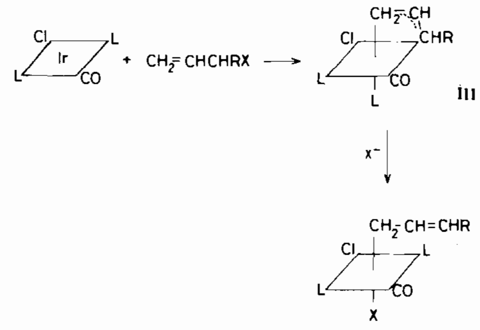
Position of Substitution of Allylic Group

There are a number of mechanisms by which an allylic halide can react with a nucleophile to give 1,3 rearranged products.

$$CH_2{=}CH{-}CHRX + N \rightarrow {}^{+}NCH_2{-}CH{=}CHR + X^{-} \qquad (8)$$

The classical S_N2' mechamism, in which the nucleophile reacts directly with the γ-carbon atom, has fallen into disrepute [13]. Other mechanisms are a direct (1,3) sigmatropic shift (allowed for certain nucleophiles) and reactions in which carbonium ions or ion-pairs are formed.

An additional mechanism exists for transition metal nucleophiles such as $IrCl(CO)L_2$. Formation of the π-allyl complex, III, could be followed by conversion to the σ-allyl species with rearrangement. In this case it is expected that the primary σ-allyl isomer will form in preference to the secondary σ-allyl because of the greater thermodynamic stability of the former.



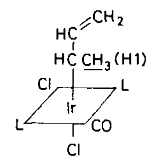
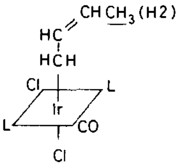
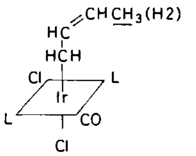
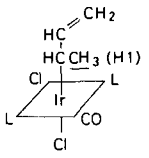
(9)

To determine whether allylic rearrangement occurs in the reaction of allylic halides with $IrCl(CO)(PMe_2Ph)_2$, 3-chloro-1-butene (α-methylallyl chloride) and 1-chloro-2-butene (crotyl chloride) were used as reactants in both methanol and benzene. In methanol α-methylallyl chloride and the iridium (I) complex react to give a mixture containing 75 ± 5% of IIc and 25 ± 5% of IId.

Crotyl chloride reacted to give a different mixture containing 71 ± 5% of IId and 29 ± 5% of IIc. The products were identified by nmr and infrared spectroscopy (see Table I).

This observation of different product ratios for the two isomeric halides rules out a common inter-

TABLE I. NMR and Infrared Spectral Data for the Reaction of $IrCl(CO)(PMe_2Ph)_2$ with 3-Chloro-1-butene or 1-Chloro-2-butene.

Reactant	Product IR Absorption[a]		Product NMR Absorption[b]	
	Maxima (cm^{-1})	Assignment	Maxima (δ, ppm)	Assignment[c]
$CH_2{=}CHCHClCH_3$	2037, 2032	ν(CO)	1.14d 3:1 intensity ratio	H1
	1635	ν(C=C)	1.40d	H2
	306	ν(Ir–Cl)	2.00–2.25dt	PMe_2Ph
	248	ν(Ir–Cl)	4.46–5.46	vinyl protons
			7.3–7.9	PMe_2Ph
	 75%	 25%		
$CH_3CH{=}CHCH_2Cl$	2038, 2027	ν(CO)	1.40d 2.4:1 intensity ratio	H2
	1653, 1635	ν(C=C)	1.14d	H1
	305	ν(Ir–Cl)	2.00–2.25dt	PMe_2Ph
	248	ν(Ir–Cl)	4.46–5.46	vinyl protons
			7.3–7.9	PMe_2Ph
	 71 %	 29 %		

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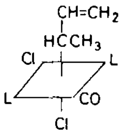
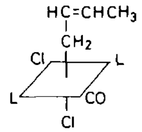
[a] Spectra measured in $CDCl_3$ solution. [b] Spectra measured in nujol. [c] d = doublet, dt = two overlapping triplets, H1, H2 = methyl protons shown in Structures.



IIc
75 ± 5%



IId
25 ± 5%

mediate, such as a free carbonium ion or a π-allyl species. Furthermore the products are the result of kinetic control, for α-methylallyl chloride at least, since heating the 75/25 mixture of IIc and IId for one hour at 60 °C in methanol causes isomerization to a 24/76 mixture, similar to that found for crotyl chloride.

One possible origin of the product mixtures is rapid isomerization of the halide by the iridium (I) complex prior to product formation. However, reaction of a four-fold molar excess of α-methylallyl chloride with the iridium(I) complex in methanol, monitored by nmr spectroscopy, resulted in unreacted starting material of 95% purity.

When a solution of crotyl chloride in benzene was added to a benzene solution of $IrCl(CO)(PMe_2Ph)_2$, a product of configuration I was obtained; α-methylallyl chloride, however, gives a mixture of isomers of configuration I and II. Isomer II results in part from isomerization of I in the presence of local high concentrations of the allyl halide since the percentage of isomer II can be minimized by using dilute solutions of the halide to prepare the adduct. It was not possible to determine by nmr spectroscopy at which allyl carbon the iridium is bonded since the methyl resonance on the allyl ligand for the adducts of configuration I is located beneath the phosphine methyl resonances. Assignment by the vinyl resonance pattern was also not possible because of the low solubility of the product in benzene. Attempts were made to isolate the *cis* products by precipitation with hexane and by evaporation of solvent; this produced oils which could be crystallized by pumping on the vacuum line. Nmr and infrared spectra showed that the same product, an 80% IId/20% IIc mixture (±5%), is obtained starting from either 3-chloro-1-butene or 1-chloro-2-butene. The same mixture is obtained from the reaction of either halide with the iridium(I) complex in benzene followed by *cis* → *trans* isomerization by methanol addition.

External-Ion Incorporation Experiments

The reaction of a methanolic solution of $IrBr(CO)(PMe_2Ph)_2$ with allyl chloride results in a mixture of isomers [20]. The nmr spectrum of the product mixture is consistent with the presence of only complexes with the phosphine ligands *trans* to each other. The solid state product infrared spectrum shows the presence of chlorine *trans* to carbonyl.

The reaction of a methanolic solution of $IrBr(CO)(PMe_2Ph)_2$ with allyl chloride in the presence of a 35-fold molar excess of LiBr gives a product whose solid state infrared spectrum shows the complete absence of bands assignable to chloride *trans* to carbonyl. Control experiments (see Experimental) showed that the bromide incorporation occurred during, and not subsequent to, the oxidative addition reaction (chloride *trans* to carbonyl in this iridium(III) complex is substitution inert). These results are consistent with the reaction scheme:

$$IrBr(CO)L_2 + C_3H_5Cl \rightarrow IrBr(CO)L_2(C_3H_5)^+ + Cl^- \qquad (10)$$

$$IrBr(CO)L_2(C_3H_5)^+ + Br^- \rightarrow IrBr(CO)L_2(C_3H_5)Br \qquad (11)$$

The mixture of products obtained when excess bromide ion is not present is attributed to the very rapid reaction

$$IrBr(CO)L_2 + Cl^- \rightarrow IrCl(CO)L_2 + Br^- \qquad (12)$$

These iridium(I) complexes are substitution labile. The same explanation was given by Deeming and Shaw [2].

A similar experiment could not be performed for the oxidative addition reaction in benzene because of the lability of halides *trans* to phosphine ligands in complexes of configuration I; as a result, it is impossible to distinguish interception of an ionic intermediate from ligand substitution on the six-coordinate products by external ions.

As already mentioned, the π-allyl ion, III, as its PF_6^- salt reacts with halide ion in methanol to give the *trans* adduct of structure II [2]. When 0.07 mmol of $IrCl(\pi\text{-allyl})(CO)(PMe_2Ph)_2^+\ PF_6^-$ was treated with 0.5 ml of a benzene solution of 0.06 mmol of $(n\text{-}C_4H_9)_4NBr$, the complex dissolved to give a yellow oil layer and a colorless solution layer. The yellow oil was identified as $(n\text{-}C_4H_9)_4NPF_6$. The benzene solution contained compound Ib, the *cis* isomer. This was identified by its nmr spectrum, its visible–uv spectrum, and by comparing its rate of isomerization to configuration II in a 28 volume percent methanol–benzene mixture with that of authentic Ib.

Due to the low solubility of the π-allyl salt in benzene, it was not possible to measure its rate of reaction with Br^-. This rate would have to exceed the rate of oxidative addition of allyl bromide with $IrCl(CO)(PMe_2Ph)_2$ for the π-allyl ion to be an intermediate in the overall reaction.

Of interest is the fact that reaction of the π-allyl complex with halide in methanol results in formation of the σ-allyl complex with *trans* phosphines (equation 6) while in benzene the *cis* isomer is obtained. One explanation is that the reaction in methanol proceeds through formation of the σ-allyl *cis*-phosphine isomer as the intermediate, which then isomerizes to the *trans*-phosphine isomer. This is possible because the rate of reaction of the π-allyl complex with chloride ion (half-life 280 seconds) is slower than the *cis–trans* isomerization rate (half-live 38 seconds).

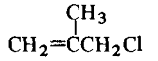
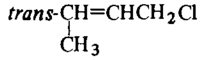
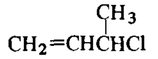
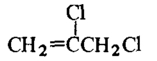
Optical Activity Experiments

A solution consisting of 50% butyl ether, 17% $CH_3{=}CHCH_2Cl$, and 33% $CH_2{=}CHCHClCH_3$ ($[\alpha]_D^{20} = +25^\circ$) was mixed with a 10% molar excess of $IrCl(CO)(PMe_2Ph)_2$ (0.21 mmol) in 3.3 ml of methanol. Complete formation of the iridium(III) product occurred within time of mixing. An optical rotary dispersion (ORD) spectrum taken of the product solution within eight minutes after addition of the halide showed no optical rotation in the region 600–380 nm. The oxidative addition product was isolated as a crystalline solid. An nmr spectrum in $CDCl_3$ taken of the product showed the presence of a mixture of secondary and primary allyliridium adducts. The crystalline product was redissolved in methanol and an ORD spectrum taken, which also exhibited no rotation. The experiment was repeated on a large scale and 0.17 g of the oxidative addition product was dissolved in 3.0 ml methanol. This solution exhibited no optical rotation under extreme scale expansion; from this experiment it was concluded that if the product possesses any optical rotation, its upper limit is $[\alpha]_D^{20} = 0.45^\circ$.

Reaction of the iridium(I) complex with a molar excess of the halide solution did not produce loss of optical activity in the unreacted halide. This experiment indicates that racemization of all optically active halide molecules in solution prior to oxidative addition does not occur. However, racemization within the reaction encounter complex prior to the oxidative addition step is not ruled out by this experiment (see Discussion).

A similar set of experiments were performed with benzene as the solvent, but an nmr spectrum of the product solution showed it to contain 90% of the primary allyliridium complex of configuration II, rather than the expected mixture of isomers of configuration I and II. Therefore, no conclusion could be made about the stereochemistry of formation of

TABLE II. Second Order Rate Constants for Oxidative Addition Reactions at 25 °C.[a]

Allylic Halide	$k(M^{-1}\ s^{-1})$, benzene	$k(M^{-1}\ s^{-1})$, methanol	$k(M^{-1}\ s^{-1})$, chloroform	$k(M^{-1}\ s^{-1})$, acetonitrile
1. $CH_2{=}CHCH_2Cl$	22 (±1)	980 (±40)	231 (±16)	410 (±30)
2.  $CH_2{=}\overset{CH_3}{C}CH_2Cl$	2.4 (±.3)	59 (±10)	–	–
3.  *trans*-$\underset{CH_3}{CH}{=}CHCH_2Cl$	2.8 (±.1)	34 (±4)	–	–
4.  $CH_2{=}CH\overset{CH_3}{C}HCl$	9.9 (±.4)	230 (±3)	–	–
5.  $CH_2{=}\overset{Cl}{C}CH_2Cl$	–	67 (±3)	–	–
6. $CH_2{=}CHCH_2Br$	421 (±25)	1450 (±200)	–	–

[a]Products of configuration I are formed in benzene, and of configuration II in methanol, chloroform and acetonitrile.

the α-methylallyl chloride adduct of $IrCl(CO)(PMe_2Ph)_2$ which has configuration I. Presumably the relatively high concentration of halide present caused the formation of isomer II to predominate. The high halide concentration was necessary in order to detect the optical rotation.

Substituent and Solvent Effects upon Rates of Oxidative Addtion

The rates of addition of the halides $CH_2{=}CHCH_2Br$, $CH_2{=}CClCH_2Cl$, *trans*-$CH_3CH{=}CHCH_2Cl$ and $CH_2{=}CHCHClCH_3$ in all solvents could be obtained by monitoring the decrease in absorbance of the 373 nm absorption maximum of the iridium(I) complex on a stopped-flow apparatus at 25 ± 0.5 °C. The halides were present in sufficient excess so that pseudo-first order conditions held. In each case, the reactions were first order in iridium concentration and plots of the pseudo-first order rate constants against halide concentration were linear with zero intercept, indicating the rate law (13).

$$\text{rate} = k[IrCl(CO)L_2]\,[allX] \qquad (13)$$

Reaction of the same halides with the iridium(I) complex in benzene were considerably slower and could be followed on a conventional spectrophotometer either under pseudo-first order conditions or using equal concentrations of the iridium complex and halide. In both cases, the rate law (13) was followed.

Second-order rate constants are given in Table II along with solvent and product identity. One striking trend is the approximately equal decrease in rate upon methyl substitution at the β- and γ-carbons of allyl chloride. Also, the rate decreases are less for methyl substitution at the α-carbon; the trend occurs in both solvents. This suggests some interaction of the double bond with the iridium in the activation step. If simple S_N2-type attack of the iridium nucleophile on the carbon bearing the halogen were the mechanism, the greatest rate reduction should have occurred for methyl substitution at the α-carbon [15].

That allyl bromide reacts only 1.5 times more rapidly than allyl chloride in methanol is surprising since alkyl bromides usually react 50–100 times faster than alkyl chlorides [16]. The latter is more typical of the relative carbon–halogen bond strengths. The anomalous result of the allyl halide reaction again suggests some interaction with the double bond. The more electronegative chlorine would favor π-complex formation compared to bromine. The rate retardation found for the β-chloro substituent is not inconsistent. Electronegative groups on the β-carbon have a large deactivating effect in S_N2 reactions [17].

Osborn found no spectroscopic evidence for a π-bonded allyl halide–platinum(0) complex prior to oxidative addition [18]. We could find no spectral evidence for formation of such an intermediate in the iridium(I)–allyl halide case.

The reactions of all the allyl halides in Table II are 11.5–44 times faster in methanol than in benzene. This behavior is often observed when there is increased charge separation in the transition state for a reaction. However, the rate increases for oxidative addition are less than for reactions where there is a full development of charge, as in reactions of amines with alkyl halides [19].

The absolute rates of reaction of the allyl halides are unusually large as shown in Table II. The rate constant for allyl bromide in benzene of 421 M^{-1} sec^{-1} may be compared with the rate constant for the reaction of methyl iodide with $IrCl(CO)(PMe_2Ph)_2$ in benzene, 4.7×10^{-2} M^{-1} sec^{-1} [20]. Usually methyl iodide and allyl bromide react at similar rates with common nucleophiles [21]. The high rate ratio of 10^4 is again suggestive of an interaction between the metal atom and the double bond which stabilizes the transition state.

Reaction of Alkyl Sulfonates with $IrCl(CO)(PPh_3)_2$ and $IrCl(CO)(PMe_2Ph)_2$

Strope and Shriver have shown that millimolar concentrations of $CH_3OSO_2CF_3$ and $IrCl(CO)(PPh_3)_2$ react in benzene over a period of hours at room temperature to produce $Ir(CH_3)(OSO_2CF_3)Cl(CO)(PPh_3)_2$ [22]. We have used $CH_3OSO_2CH_3$, $CH_2{=}CHCH_2OSO_2CH_3$, and$CH_2{=}CHCH_2CH_2OSO_2CH_3$ as substrates for reaction with $IrCl(CO)(PPh_3)_2$ in order to compare relative reactivities. Methyl methanesulfonate was found not to react with the iridium complex after several days in benzene or chloroform at 25 °C, and homoallyl methanesulfonate is unreactive in chloroform at 25 °C over 24 hours.

Allyl methanesulfonate, however, reacts with $IrCl(CO)(PPh_3)_2$ in seconds in either chloroform or benzene when both reactants are used in tenth molar concentrations. Monitoring of this reaction by nmr spectroscopy showed incremental decreases in the allyl substrate resonances upon addition of $IrCl(CO)(PPh_3)_2$ simultaneously with appearance of a new singlet at 2.78, which was 16 Hz upfield from the methyl singlet of the unreacted methanesulfonate group; this new resonance may be due to $CH_3SO_2O^-$ coordinated to the metal. Addition of hexane to a benzene solution of the product produced a pale yellow oil. Infrared bands of the oil and tentative assignments are given in Table III. The absence of a band in the 245–315 cm^{-1} region attributable to Ir–Cl is puzzling, but the other bands are consistent with formation of an iridium(III) oxidative addition product. No attempt was made to obtain an elemental analysis of the product because of the facile reversibility of the reaction.

The reaction of allyl methanesulfonate with $IrCl(CO)(PMe_2Ph)_2$ in benzene yields a product having *trans* phosphine ligands. Failure to form isomers having *cis* phosphines, as were obtained in reactions of allylic halides, may be rationalized by the poor coordinating ability of the methanesulfonate group. Dissociation of this ligand could result in rapid isomerization of an initially formed *cis* phosphine isomer to the *trans* phosphine geometry.

The reaction of $IrCl(CO)(PPh_3)_2$ with allyl chloride in either benzene or chloroform also results in formation of a product with configuration II. This is not unexpected since steric repulsion of the bulky phosphine ligands would be severe in the *cis* isomer of configuration I. Thus formation of *cis* isomers in benzene is not a universal property of oxidative addition reaction of $IrCl(CO)L_2$ complexes.

TABLE III. Infrared Spectral Data, $IrCl(CO)(PPh_3)_2$ + $CH_2{=}CHCH_2OSO_2CH_3$ Reacted in Chloroform.

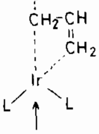
Absorption Maximum (cm^{-1})	Intensity	Assignment
2050	v. strong	ν(CO)
1618	v. weak	ν(C=C)
~1200	v. strong	ν(SO)
1335	medium	ν(SO)

Discussion

A free radical chain mechanism can be ruled out as a common mechanism by the regiospecific results found in methanol for $CH_3CH{=}CHCH_2Cl$ and $CH_2{=}CHCHClCH_3$. It is also improbable in the case of benzene because of the constant ratio of rates in the two solvents for different allyl halides (Table II) and because of the rapid reaction of allyl methanesulfonate in benzene. Also Osborn was unable to inhibit the reaction of allylic halides with $IrCl(CO)(PMe_3)_2$ in benzene by free radical scavengers [18].

A mechanism of concerted addition in methanol is ruled out by the experiments in which external ions were incorporated in the product, and also by the *trans* structure of the product (external-ion incorporation is also evidence against a radical cage mechanism as the predominant pathway). In benzene the best evidence against a concerted mechanism is the similar rate behavior for different halides in both methanol and benzene. In particular, it is unlikely that $CH_2{=}CHCHCH_3Cl$ would react faster than $CH_3CH{=}CHCH_2Cl$ in a concerted process.

The simplest mechanism that can accommodate all the experimental results but one, is the two-step S_N2 mechanism in both solvents, but with some modification due to the allylic double bond. The nucleophilic iridium atom attacks the carbon atom bearing the leaving halide in the usual way. However, some assistance is gained by the double bond also coordinating to the iridium atom. The phosphine ligands must move slightly to allow this to occur. The transition state in both solvents would resemble an unsymmetric π-allyl complex, as in IV.



IV

In methanol, and other coordinating solvents, a solvent molecule would attack at the position marked by the arrow. This would lead to the formation of the *trans* solvato complex, which would readily undergo solvent replacement by any anion in solution. In benzene, for steric reasons probably, such solvation cannot easily occur. The phosphine groups would move down further and the symmetric π-allyl complex, III, would form. This would eventually react with halide ion to form the *cis*-isomer, as demonstrated in the Results section. Both crotyl chloride and α-methylallyl chloride would give predominantly the same σ-allyl product in which the primary carbon is bonded to iridium [24]. In methanol some formation of a π-allyl complex might happen, to account for the 20% isomerization which is observed.

The modified S_N2 mechanism is also consistent with the rapid reaction of allyl methanesulfonate with both $IrCl(CO)(PPh_3)_2$ and $IrCl(CO)(PMe_2Ph)_2$. The failure of methyl methanesulfonate to react is attributed to a very slow rate of reaction, since the product appears to be stable [23]. A remote double bond, as in homoallyl methanesulfonate, is not very activating.

The one experimental observation which does not fit the above mechanism is the complete racemization found with optically active $CH_2{=}CH{-}CHCH_3Cl$. One explanation is that racemization of the organic halide is induced by the iridium(I) complex *before* oxidative addition occurs. The observation that $IrCl(CO)(PMe_2Ph)_2$ does not cause complete racemization when mixed with a molar excess of optically active allyl halide could mean that racemized allyl halide does not substantially escape the solvent cage prior to oxidative addition.

A closely related study is that of Otsuka and Ataka [25] on the reaction of α-bromopropionic esters with $Rh(CNR)_4^+$. When an optically active halide was used, racemization before oxidative addition was shown to take place. The $O{=}C(OR)CHCH_3Br$ structure is quite similar to $CH_2{=}CHCHCH_3Br$ and Rh(I) and Ir(I) are isoelectronic.

Stille and Becker [26] observed only partial inversion of configuration at carbon in the oxidative addition of benzyl halides to tris(triethylphosphine)palladium(0). Partial loss of stereochemistry was explained as due to a competitive one electron-transfer process occurring in the solvent cage or due to scrambling in a trigonal bipyramidal transition state. Benzyl halides are similar to allyl halides in their ability to form both σ- and π-complexes.

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