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Mechanistic Studies of Oxidative Addition to Low-Valent Metal Complexes. 6.[1,2] Stereochemistry at Carbon in Addition of Alkyl Halides to Iridium(I)

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The stereochemical changes at carbon during oxidative addition of an alkyl halide to carbonylchlorobis(tertiary phosphine)iridium(I) have been investigated by NMR methods, using diastereomeric β-fluoroalkyl bromides. Also, the addition of optically active ethyl α-bromopropionate has been reexamined. In all cases studied complete loss of stereospecificity at carbon was observed.

Introduction

The term "oxidative addition" has been proposed to describe a large class of reactions in which coordinatively unsaturated, low-valent metal complexes are converted to complexes of higher coordination number and oxidation state.[4,5] While a great number of reactions which fall into this class have been reported,[6] at the outset of this work relatively little mechanistic information was known about these reactions. One important question is whether the similarities between reactions of this type reflect *mechanistic* similarities or whether, instead, these reactions comprise a variety of different mechanistic processes which lead to the same net *stoichiometric* changes.

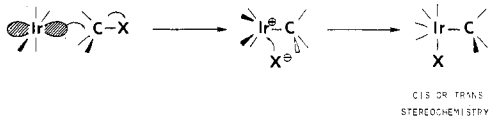
Oxidative addition of alkyl halides is of particular interest for several reasons. First, such reactions are important in many aspects of organo–transition metal chemistry such as the synthesis of transition-metal alkyls,[7] coupling reactions involving transition-metal reagents,[8] and catalytic processes such as the Monsanto acetic acid synthesis.[9] Second, a variety of experimental techniques are well established for mechanistic study of organic reactions of alkyl halides; many of these should be applicable here as well. Finally, organic reactions of alkyl halides exhibit considerable mechanistic variety, so this should be a favorable case for determining whether more than one mechanism might be operative for oxidative addition. A brief review of this topic, which emphasizes systems involving palladium complexes, has recently appeared.[10]

Much of the previous work on oxidative addition has employed the coordinatively unsaturated d^8 complexes of the type *trans*-$IrCl(CO)(PR_3)_2$ (**1**), which are easy to handle and versatile in reactivity, and their reactions can be conveniently followed by changes in IR and NMR spectra. The well-known PPh_3 complex **1d**, however, only reacts readily with the most active alkyl halides such as methyl, benzyl, and allyl halides. Complexes containing more electron-releasing alkylphosphines are considerably more reactive; many of the studies here employ *trans*-$IrCl(CO)(PMe_3)_2$ (**1a**), thus permitting study on a wider variety of alkyl halides, including those which permit stereochemical studies.

$$\underset{\mathbf{1}}{\textit{trans}\text{-}Ir(PR_3)_2COCl} + RX \rightarrow Ir(PR_3)_2(CO)(R)ClX$$

$PR_3 = PMe_3$ (**1a**), PMe_2Ph (**1b**), $PMePh_2$ (**1c**), PPh_3 (**1d**), $AsMe_2Ph$ (**1e**)

Two basic mechanisms had previously been proposed for oxidative addition of alkyl halides. Kinetic studies of the addition of methyl iodide[11] and benzylic halides[12] to **1d** were consistent with an S_N2-type mechanism, with the metal center acting as nucleophile using the nonbonding electrons in the d_{z^2} orbital. An alternative proposal was for a concerted reaction wherein the metal inserts into the C–X bond.[13] Here



(1)

the σ-bonding electrons in the C–X bond can donate to a vacant orbital on Ir; retrodonation (from a filled d_{xz} or d_{yz}) into the σ* orbital on the alkyl halide would cause bond making and breaking (see eq 2). These two pathways should

(2)

cis addition

be readily distinguishable on the grounds of stereochemistry at carbon: the first requires inversion at the reacting carbon atom; the second requires retention. In this paper we report several such studies, which show for certain types of alkyl halides that *loss* of stereochemistry occurs, indicating that a third mechanism is followed in these cases. In the following paper[14] the nature of this mechanism and its scope will be discussed. Further papers will concern the mechanism of oxidative addition on complexes of Pt(0) and Pd(0). Preliminary accounts of parts of this work have appeared previously.[15,16] Very recently, a detailed account of the mechanism of reaction of Ni(0) complexes with aryl halides has appeared.[48]

Results and Discussion

Prior to our work, it had been reported that the addition of optically active ethyl α-bromopropionate to *trans*-$IrCl(CO)(PMePh_2)_2$ (**1c**), followed by cleavage with Br_2 to regenerate the alkyl bromide, gave 67% net overall retention; this was interpreted as predominant retention in *both* steps—oxidative addition and reductive cleavage.[13] This

(1) Part 4: A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7832–7833 (1974).
(2) Part 5: J. A. Osborn in "Organotransition Metal Chemistry", Y. Ishii and M. Tsutsui, Eds., Plenum Press, New York, 1975, pp 65–80.
(3) (a) Department of Chemistry, University of Notre Dame, Notre Dame, Ind. 46556. (b) Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France.
(4) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 54 (1968).
(5) J. Halpern, *Acc. Chem. Res.*, **3**, 386–392 (1970).
(6) A. J. Deeming, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **9**, 118 (1972).
(7) G. W. Parshall and J. J. Mrowca, *Adv. Organomet. Chem.*, **7**, 157 (1968).
(8) See, for example: M. F. Semmelhack, *Org. React. (N.Y.)*, **19**, 115–198 (1972); J. Schwartz, D. W. Hart, and J. L. Holden, *J. Am. Chem. Soc.*, **94**, 9269–9271 (1972); L. S. Hegedus, S. M. Lo, and D. E. Bloss, *ibid.*, **95**, 3040–3042 (1973).
(9) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974, p 209.
(10) J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, **10**, 434–442 (1977).
(11) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511–3514 (1966).
(12) J. Halpern and P. B. Chock, *Proc. Int. Conf. Coord. Chem., 10th*, 135 (1967).
(13) R. G. Pearson and W. R. Muir, *J. Am. Chem. Soc.*, **92**, 5519–5520 (1970).
(14) J. A. Labinger, J. A. Osborn, and N. J. Coville, *Inorg. Chem.*, following paper in this issue.
(15) J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Am. Chem. Soc.*, **94**, 4043–4044 (1972).
(16) J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Am. Chem. Soc.*, **95**, 7908–7909 (1973).

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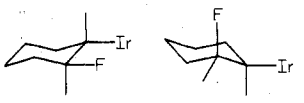
conclusion was clearly not on firm ground, since brominative cleavage of coordinatively saturated transition-metal alkyls often results in inversion.[17] Since such ambiguity is inherent in the use of measurements involving optical rotations (barring a crystallographic determination of absolute configuration), we chose to design alkyl halides for which NMR studies would provide the desired stereochemical information. The use of 2-fluoroalkyl halides appeared particularly attractive since the presence of the 2-F substituent not only provides an additional NMR probe but also shifts the resonances for protons attached to the same carbon strongly downfield, avoiding their being obscured by the PMe_3 resonances. We thus discuss in turn the reactions of a secondary and primary unactivated 2-fluoroalkyl bromide, respectively, with Ir(I). Subsequently, with consideration of Pearson's results using optically active $CH_3CHBrCOOEt$, the reaction of a suitably fluorine-labeled α-bromo ester was investigated. Finally since these latter studies were not compatible with Pearson's work, we decided to reinvestigate his experiments.

cis- **and** *trans*-**2-Bromofluorocyclohexane (2a, 2b).** Both substrates were prepared by literature methods and then ^1H and ^{19}F NMR spectra measured at variable temperature (see the Experimental Section). Both substrates reacted with **1a** although the rate of reaction was highly variable. In our initial studies, **2b** in CH_2Cl_2, the ^{19}F resonance at 88.3 ppm decreased while a new signal appeared to 64.2 ppm. Simultaneous monitoring by IR showed these changes to be associated with the formation of the oxidative addition adduct. The signal at 64.2 ppm seemed to be a rather poorly resolved quartet (separation ca. 50 Hz), apparently indicating that the product consisted of a single isomer with fluorine axial. We were thus initially led to the erroneous conclusion that the reaction was stereospecific and occurred with inversion.[18] However, with careful isolation and purification of the product, a ^{19}F spectrum (at 94.1 MHz) of higher quality could be obtained, which showed clearly to consist of a strong doublet (J_{F-H} = 48 ± 2 Hz) centered at 64.1 ppm, with an additional resonance separated by ca. 60 Hz from the downfield arm of the doublet (intensity ca. 10% of total). The spectrum at 56.4 MHz shows essentially the same pattern except the separation of the outer peak decreases to ca. 37 Hz. Thus the spectrum results from the presence of two species. This was later confirmed by the presence of two resonances in the heteronuclear proton-decoupled ^{19}F spectrum in which, incidently, also ^{11}F–^{31}P coupling was evident.

The reaction of **1a** with **2a** was found to give a spectrum *identical* with the above, showing the two products must result in *loss of stereochemistry* at carbon. The two most likely isomers would seem to be



a b

The ^{19}F of structure a would thus give rise to the strong doublet, and structure b would give rise to a quartet; presumably the outer peaks would be too weak to observe. However, chemical shift differences between axial and equatorial fluorines are usually much greater than 0.7 ppm (e.g., 4 ppm in *trans*-$C_6H_{10}FBr$ and 20.5 ppm in fluorocyclohexane), and it seems unreasonable that the resonances would be so close. Another possibility is that the large steric bulk of the Ir group forces the ring out of the chair conformation (e.g., twist boat) where conceivably the two isomers might have the fluorine atom in more closely similar environments. A third possibility is the two signals result from two different stereochemistries at the Ir center, but this appears unlikely since only a single Ir–Cl stretching bond is observed in the infrared. The ^1H spectrum was not informative (see the Experimental Section).

Table I. NMR Parameters for PhCHFCH(H,D)Br

parameter	3a	3b	3c
$\delta(H_1)$	5.54	5.57	5.60
$\delta(H_2)$	*b*	*c*	3.47
$\delta(H_3)$	*b*	3.60	*d*
F shift,[a] ppm	99.7	100.2	100.1
$^2J_{H_1F}$, Hz	47.1	47.2	47.2
$^3J_{H_2F}$, Hz	26.1	4.0[c]	26.0
$^3J_{H_3F}$, Hz	14.8	14.8	2.0[d]
$^3J_{H_1H_2}$, Hz	3.9	<1[c]	3.9
$^3J_{H_1H_3}$, Hz	7.6	7.8	<2[d]
$^3J_{H_2H_3}$, Hz	11.3	1.6	1.5–2

[a] Relative to external CF_3COOH. [b] AB pattern in the region δ 3.3–3.7; shift difference between H_2 and H_3 0.071 ppm. [c] D substituted for H_2 in this isomer. [d] D substituted for H_3 in this isomer.

It was claimed that this addition does not occur.[19,20] However, the adduct has been conclusively identified by elemental analysis and by its mass spectrum where a group of peaks in the parent-ion region show the expected relative intensities for a complex containing one Ir, one Cl, one Br, and thirteen C atoms. The addition of **1a** with *trans*-2-bromomethoxycyclohexane was also studied. However the ^1H resonance for the proton *gem* to the MeO group was masked by the strong singlet due to that group, and no stereochemical information was obtained.

1-Bromo-2-fluoro-2-phenylethane-*1***-***d*$_1$. Our experience with **2** led us to examine a primary alkyl halide, both to simplify NMR spectra and to see whether a different mechanism was operative. The preparation of the substrate deserves comment. Undeuterated $PhCHFCH_2Br$ (**3a**) has been prepared from the reaction of styrene with *N*-bromoacetamide in anhydrous HF;[21] (*RR*,*SS*)- and (*RS*,*SR*)-PhCHFCHDBr (**3b**, **3c**) should be similarly accessible from *cis*- and *trans*-PhCH=CHD, respectively. Previous preparations of these deuterated styrenes have given relatively poor yields and isotopic purity.[22] We obtained an improved preparation: hydroboration of phenylacetylene-*d* with disiamylborane, followed by protonolysis with acetic acid, gave a good yield (observed by NMR on the reaction mixture) of *cis*-PhCH=CHD; however, extensive polymerization occurred on attempted isolation, probably initiated by radicals generated from boron-containing byproducts. This was avoided by using 8-hydroxyquinoline for protonolysis, leading to a stable dialkylborinic ester of the latter,[23] from which the labeled styrene could be separated by distillation. The trans isomer was analogously obtained from phenylacetylene, with use of DOAc followed by sodium 8-quinolinolate. Both products were obtained in ca. 40% yield and >95% isotopic and isomeric purity.

The reactions with *N*-bromoacetamide/HF proceed normally but not perfectly stereospecifically: each isomer was contaminated with about 15–20% of the other epimer (see ^{19}F spectra). The ^1H and ^{19}F NMR parameters are listed in Table

(17) M. D. Johnson, *Acc. Chem. Res.*, **11**, 57–65 (1978), and references therein.
(18) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 612–613 (1970).
(19) F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.*, **93**, 6339–6340 (1971).
(20) It is clear that this claim is not correct. However, many of these reactions are highly sensitive to conditions, including purity of reagents and solvents as well as presence of oxygen,[14] which may explain the failure to observe any reaction in some cases.
(21) F. L. M. Pattison, D. A. V. Peters, and F. H. Dean, *Can. J. Chem.*, **43**, 1689–1699 (1965).
(22) (a) M. Buza and E. I. Snyder, *J. Am. Chem. Soc.*, **88**, 1161–1165 (1966); (b) J. W. Cornforth, J. W. Redmond, H. Eggerer, W. Buckel, and C. Gutschow, *Eur. J. Biochem.*, **14**, 1–13 (1970).
(23) K. Torssell, *Prog. Boron Chem.*, **1**, 369 (1964), and references therein.

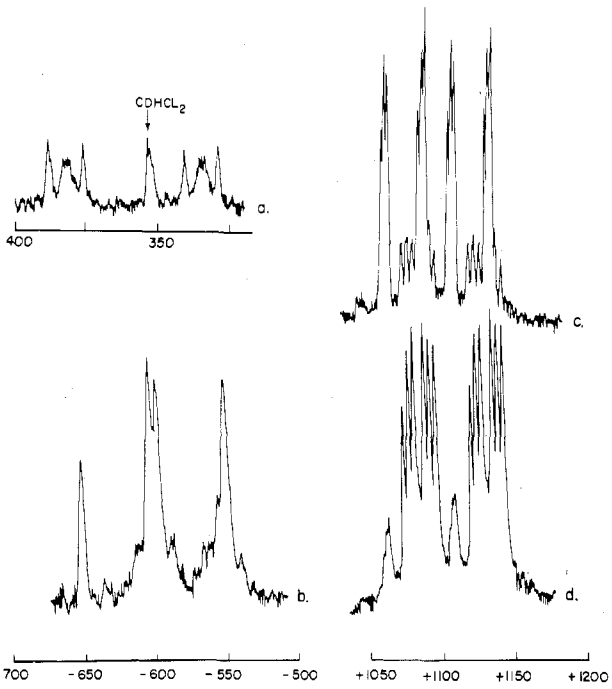
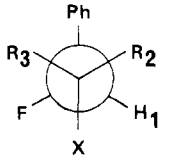


Figure 1. Spectra of products from either **3b** or **3c** to give **4a** + **4b**: (a) ^1H, 60 MHz, CD_2Cl_2 (Hz from Me_4Si); H_1 region only; (b) ^{19}F, 94.1 MHz, CH_2Cl_2 (Hz from internal C_6F_6). Spectra of starting materials: (c) ^{19}F of **3b** ($CDCl_3$, Hz from C_6F_6); (d) ^{19}F of **3c** ($CDCl_3$, Hz from C_6F_6). Note that each contains ca. 15–20% of each other.

I. The calculated coupling constants indicate that the predominant conformer is



3, X = Br
4, X = IrClBr(CO)$(PMe_3)_2$

a, $R_2 = R_3 = H$
b, $R_2 = D$, $R_3 = H$
c, $R_2 = H$, $R_3 = D$

The ^{19}F spectra of **3b** and **3c** are shown in Figure 1. A notable feature is the isotope shift for the ^{19}F signals in **3b** and **3c**—about 10.5 Hz or 0.11 ppm. This results from the differing relative orientations of F with respect to H and D in the two isomers; similar shifts have been observed, e.g., in $CF_2{=}CHD$, where the isotope shift is 0.05 ppm.[24]

Reactions of **3** with **1a** give the oxidative adducts **4**, which were fully characterized (see the Experimental Section); again, *the key result is that the products formed from either* **3b** *or* **3c** *have identical* ^1H *and* ^{19}F *spectra* (Figure 1). Thus complete racemization, leading to an equal mixture of **4b** and **4c**, accompanies this oxidative addition reaction. NMR parameters and assignments are given in Table II. (Assignments of geometry from coupling constants are based upon the assumption that the Karplus relationship for vicinal coupling constants remains valid;[25] although $^3J_{HF}$ is sensitive to other structural factors as well, it generally follows this relationship.[26]) The ^{19}F spectrum consists of a sharp double doublet (**4c**) overlapping a broad doublet (**4b**) which differ in chemical shift by 0.28 ppm; this was confirmed both by measuring the spectrum at a different frequency (54.1 vs. 94.1 MHz) and by the ^1H-decoupled spectrum, which shows two triplets ($^4J_{PF}$ = 1.0 Hz) of equal intensity. The larger isotope shift in **4** compared to that in **3** presumably results from the greater conformational preference due to the greater steric bulk of Ir and its associated ligands: this is also manifested in the relative magnitudes of the vicinal coupling constants.

Table II. NMR Parameters for IrClBr(CH(H,D)CHFPh)(CO)$(PMe_3)_2$

parameter	4a	4b	4c
$\delta(H_1)$	5.40	5.36	5.36
F shift,[a] ppm	85.9	86.2	86.0
$^2J_{H_1F}$, Hz	47.1	47.5 ± 1	47.5 ± 1
$^3J_{H_2F}$, Hz	52.3	*c, d*	52.2 ± 1
$^3J_{H_3F}$, Hz	11.5	*d*	<2[c]
$^3J_{H_1H_2}$, Hz	2.0	<1[c]	<3
$^3J_{H_1H_3}$, Hz	12.2	12.2	<3[c]
$^2J_{H_2H_3}$, Hz	*b*	*b*	*b*

[a] Relative to external CF_3COOH. [b] Resonances for H_2 and H_3 were not observed, but by fitting calculated spectra of H_1 and F resonances for undeuterated **4a**, it was calculated that $^2J_{H_2H_3}$ = −14 Hz, and the chemical shift difference between them is 12 Hz. [c] D substituted for H. [d] The fine structure of F resonance was not resolved; the total width of each half of doublet is ca. 30 Hz.

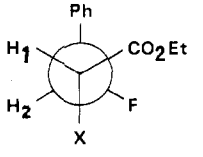
Table III. NMR Parameters for Isomers of $PhCHFCHBrCO_2Et$

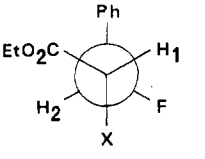
parameter[a]	(*RS,SR*)-5a	(*RR,SS*)-5b
$\delta(H_1)$	4.45	4.56
$\delta(H_2)$	5.77	5.72
$\delta(CH_3)$	1.28	1.06
$\delta(CH_2)$	4.25	4.02
δ(Ph)	7.34	7.31
F shift,[b] ppm	85.2	100.6
$^2J_{H_2F}$, Hz	45.3	46.0
$^3J_{H_1F}$, Hz	6.9	12.6
$^3J_{H_1H_2}$, Hz	9.5	8.5

[a] ^1H spectrum measured at 100 MHz in $CDCl_3$. [b] ^{19}F at 94.15 MHz in acetone-d_6; shift relative to external CF_3COOH.

Ethyl 2-Bromo-3-fluoro-3-phenylpropionate. The results cited earlier for ethyl α-bromopropionate apparently indicated that it undergoes oxidative addition with some stereospecificity,[13] although whether inversion or retention takes place is not clear. Since this contrasts with the results found here for simple primary and secondary alkyl bromides, it appeared desirable to prepare an α-halo ester suitable for NMR study. (*RS,SR*)-$PhCHFCHBrCO_2Et$ (**5a**) has been prepared from ethyl *trans*-cinnamate with *N*-bromoacetamide/HF,[27] while the RR,SS isomer (**5b**) can be similarly obtained from ethyl *cis*-cinnamate although not stereospecifically: some epimerization occurs during reaction, and careful distillation gave at best a 60:40 mixture of **5b**:**5a**. NMR parameters are given in Table III; coupling constants suggest less predominance of a single conformer than in **3**, as might be expected since both Br and CO_2Et are sterically large.

Both **5a** and the isomeric mixture (henceforth called simply





5a, X = Br
6a, X = IrClBr(CO)$(PMe_3)_2$

5b
6b

5b) react rapidly with **1a**. Again the ^1H and ^{19}F NMR spectra (Figure 2a,b) of the products are identical for the two isomers

(24) H. Batiz-Hernandez and R. A. Bernheim, *Prog. Nucl. Magn. Reson. Spectrosc.*, **3**, 63 (1967).
(25) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870–2871 (1963).
(26) (a) K. L. Williamson, Y. F. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Am. Chem. Soc.*, **90**, 6717–6722 (1968); (b) A. M. Ihrig and S. L. Smith, *ibid.*, **92**, 759–763 (1970).
(27) A. K. Bose, K. D. Das, and P. T. Funke, *J. Org. Chem.*, **29**, 1202–1206 (1964).

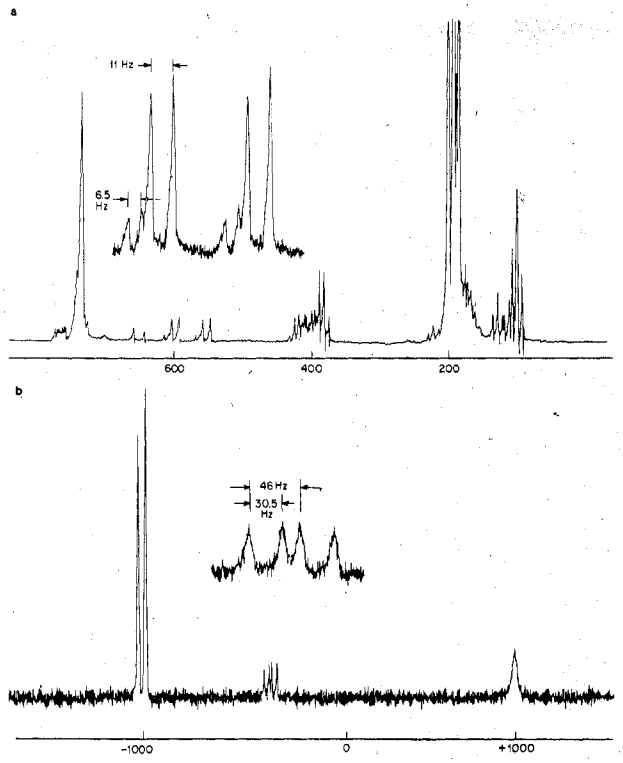


Figure 2. (a) ^1H NMR spectrum of the reaction mixture $Ir(PMe_3)_2COCl + PhCHFBrCO_2Et$ in acetone-d_6 recorded at 100 MHz. (b) Fourier transform ^{19}F NMR spectrum of the reaction mixture $Ir(PMe_3)_2COCl + PhCHFCHBrCO_2Et$ recorded in acetone at 94.1 MHz (shift (Hz) relative to internal C_6F_6).

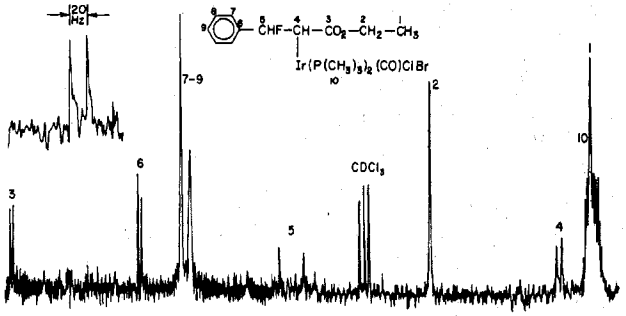


Figure 3. ^{13}C NMR spectrum of **6b** recorded at 25.2 MHz in $CDCl_3$.

of starting alkyl halide, showing that a nonspecific process is operative here as well. In this case an unequal mixture of the two diastereomeric adducts **6a** and **6b** is obtained. Parameters and assignments are given in Table IV: the ratio **6a**:**6b** is about 1:4.5. In addition, both ^1H and ^{19}F spectra show a third component. The extra peaks in the ^1H spectrum are readily assigned to ethyl *trans*-cinnamate; the nature of the species giving rise to the broad ^{19}F signal (at 1000 Hz below C_6F_6) has not been ascertained (vide infra).

Recrystallization led to substantial enrichment in **6b**, which could be obtained in >95% isomeric purity. The ^{13}C spectrum was recorded to confirm the geometric assignments, since they depend upon assumption of the conformation shown for **6**, which is not as confidently made as in **4** because of the bulky CO_2Et group. However, as the ^{13}C spectrum shows (Figure 3), the large value of $^3J_{CF}$ (20.0 ± 1.0 Hz) indicates that CO_2Et and F are trans in the major conformer.[28] The H-decoupled ^{19}F spectrum of **6b** shows a double doublet, indicating the two phosphorus nuclei are nonequivalent ($^4J_{PF}$ = 2.0, 3.8 Hz); since the ^1H spectrum indicates this adduct (and all others studied) has trans phosphine ligands, this nonequivalence must result from the presence of chiral centers on the alkyl group. (See the following section.)

The ability to isolate one diastereomer in pure form makes it possible *to exclude the possibility that epimerization occurs subsequent to stereospecific formation of* **6**: solutions of **6b** show no NMR changes over long periods of time. Also, no changes are observed when more **1a** is added to a solution of **6b**. This rules out the possibility that the alkyl group is transferred from product to unreacted starting Ir(I) complex with inversion (such transfers have been observed in some systems[30]), which could have led to overall nonstereospecificity.

Reactions of these alkyl halides were also examined with *trans*-$IrCl(CO)L_2$, where L = PMe_2Ph (**1b**), $PMePh_2$ (**1c**), and $AsMe_2Ph$ (**1e**). In all cases, NMR spectra of the adducts formed (Table V) indicate a single isomer is the sole product, with structure analogous to **6b**. However, here, as well, both **5a** and **5b** give this same product, so loss of stereospecificity

Table IV. NMR Parameters for $IrClBr(CH(CO_2Et)CHFPh)(CO)(PMe_3)_2$

parameter[a]	6a	6b
$\delta(H_1)$	*b*	*b*
$\delta(H_2)$	5.85	5.72
$\delta(CH_3)$	1.13	1.01
$\delta(CH_2)$	*c*	3.93
F shift,[d] ppm	83.5	75.5
$^2J_{H_2F}$, Hz	46.6	46.2
$^3J_{H_1F}$, Hz	30.5	ca. 5
$^3J_{H_1H_2}$, Hz	6.5	10.5

[a] In acetone-d_6. [b] Not observed, masked by other peaks. [c] Region too complex to assign (mixture of isomers). [d] Shifts relative to external CF_3COOH.

Table V. NMR Parameters for $IrClBr(CH(CO_2Et)CHFPh)(CO)L_2$

	L		
parameter[a]	PMe_2Ph	$AsMe_2Ph$	$PMePh_2$
$\delta(H_2)$	4.78	4.88	4.69
F shift,[b] ppm	76.0	76.0	74.7
$^2J_{H_2F}$, Hz	45.6	45.7	45.3
$^3J_{H_1F}$, Hz	*c*	6.1	*c*
$^3J_{H_1H_2}$, Hz	11.0	10.7	10.7

[a] See structure **6** for definitions. [b] Relative to external CF_3CO_2H. [c] Not resolvable because of P–F coupling.

Table VI. Parent-Ion Region of Mass Spectrum of $IrClBr(2\text{-}FC_6H_{10})(CO)(PMe_3)_2$

	intensity[a] for $IrC_{13}H_{28}OFClBrP_2$	
m/e	obsd	calcd
586	0.334	0.373
587	0.057	0.081
588	1.0	1.0
589	0.169	0.169
590	0.843	0.848
591	0.143	0.130
592	0.179	0.195
593	0.030	0.034

[a] Relative to intensity of *m/e* 588 peak defined as 1.0.

(28) While the applicability of the Karplus relationship to $^3J_{CF}$ is not as well documented as for other nuclei, there are several supporting examples known.[29] For comparison, the corresponding $^3J_{CF}$ in **5a** and **5b** are 1.1 and 9.9 Hz, respectively, in accord with the relative predominance of the conformer with F and CO_2Et trans.

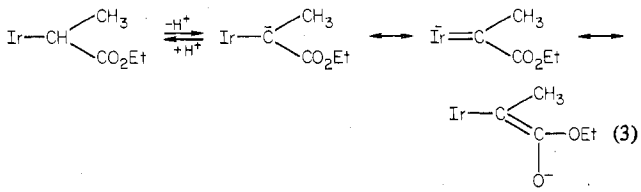
(29) (a) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 7107–7120 (1970); (b) D. A. Doddrell, C. Charrier, and J. D. Roberts, *Proc. Natl. Acad. Sci. U.S.A.*, **67**, 1649 (1970); (c) F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2361–2369 (1971).

(30) (a) D. Dodd and M. D. Johnson, *Chem. Commun.*, 1371–1372 (1971); (b) J. H. Espenson and J. S. Shveima, *J. Am. Chem. Soc.*, **95**, 4468–4469 (1973).

is still occurring; changing L here apparently does not bring about a change in mechanism. Probably the greater steric bulk of these ligands results in a greater difference in the transition states leading to the two diastereomeric products, leading to a much stronger preference for one product over the other.

Ethyl (*R*)-(+)-α-Bromopropionate. While it is not inconceivable that $CH_3CHBrCO_2Et$ and $PhCHFCHBrCO_2Et$ might react with **1** by completely different mechanisms, the striking contrast between our results just cited and those reported earlier[13] appeared to warrant a reinvestigation of the earlier work. Ethyl (*R*)-(+)-α-bromopropionate (**7**) was prepared in essentially 100% optical purity by esterification of commercially available (*S*)-(+)-lactic acid, followed by reaction with PBr_3. This procedure is a substantial improvement over the resolution method used previously, which gave only 18–20% optical purity.[13] Reactions with Ir(I) complexes **1a–c** gave the adducts $IrClBr(CH(CO_2Et)CH_3)(CO)L_2$ (**8a–c**), which were isolated and fully characterized. Specific rotations for each adduct were determined on two to five independent samples; all fell in the range 0 ± 0.5°, showing that essentially complete racemization occurs in these reactions.[31]

Again, there are possible mechanisms by which racemization might occur subsequent to or during a stereospecific oxidative addition process. (Note however no prior racemization occurs since unreacted alkyl halide remains optically active.) One such involves deprotonation of the chiral carbon to form a stabilized carbanion (eq 3). Indeed, the reaction of **7** with



(3)

$PMePh_2$, which presumably goes by a normal S_N2 process, gives the racemic phosphonium salt. When this reaction was run in CH_3OD, the product is entirely $CH_3CD(CO_2Et)PMePh_2^+Br^-$, indicating that exchange of this α proton is responsible for the racemization. However, when the reaction of **7** with **1a** was carried out in the presence of CH_3OD, no deuterium incorporation was found in the racemic product, excluding this pathway. Still another possibility would be interconversion with isomeric $IrClBr(CH_2CH_2CO_2Et)(CO)L_2$ via β-hydride elimination and readdition.[32] However, the latter isomer can be prepared independently[14] and shows no sign of any such interconversion even at much higher temperatures than those employed in these reactions. Further it should be noted that β-hydride elimination to the olefin complex and readdition will not in itself effect racemization unless the olefin can dissociate from the metal and coordinate on the opposite face; no trace of free olefin was ever detected in any reactions of **7**.

The ^1H NMR spectra of the adducts **8** demonstrate the effect of the chiral center, which again renders the phosphorus nuclei nonequivalent; the signals for the ligand methyl protons do not fit patterns expected for an $X_nAA'X'_n$ system in which the two A nuclei are chemically (but not magnetically) equivalent.[33] The diastereotopic protons of the methylene carbon in the CO_2Et moiety also show nonequivalence, with the chemical shift difference (determined by analyzing the pattern as an ABX_3 system[34]) increasing with steric bulk (0 Hz for **7**, 12.5 Hz for **8a**, 43.4 Hz for **5b**, and 52.9 Hz for **8c** (at 100 MHz)). Furthermore, the ^{31}P spectrum of **8a** shows an AB quartet rather than a singlet (which is observed for $IrClIMe(CO)(PMe_3)_2$, which has no chiral ligand). The chemical shift difference between the two nuclei is 4.0 ppm, and $^2J_{PP}$ = 408.2 Hz, in good agreement with values typical of related complexes with trans phosphine ligands.[35]

Possibility of a Competing Mechanism. All of the results reported here are consistent with a mechanism (or mechanisms, perhaps) which results in complete loss of stereospecificity at carbon during oxidative addition. In the following paper[14] we shall present evidence in favor of a radical chain process to account for this, but that mechanism is not operative for all types of alkyl halides. We have therefore examined the possibility that an alternate mechanism, with different stereochemical results, might become competitive under certain reaction conditions. In particular, a nucleophilic pathway might be thought to be viable, especially for the α-halo esters. Reactions of **5** and **7** were carried out in higher polar solvents, *N*-methylpyrrolidone and *N*,*N*-dimethylformamide. For **7**, no difference was observed: although oxidative addition is faster than in nonpolar solvents such as benzene, the products **8** are still totally racemic. (No deuterium incorporation from CH_3OD was observed here either, excluding the possibility that proton exchange facilitated by polar conditions is responsible for racemization.) Radical inhibitors such as galvinoxyl still slow reaction,[14] without changing the stereochemical result. Hence there is no evidence for any competition by a stereospecific, nucleophilic pathway for reactions for **7**, even under conditions which should most strongly favor such competition.

With **5** the results are more complex: polar solvents strongly enhance formation of side products (see above), ethyl *trans*-cinnamate, and the species responsible for the broad, high-field ^{19}F signal. However, the ratio of isomers **6a** and **6b** remains unchanged, even if galvinoxyl is added. Thus, while there may be an alternate mechanism operating, it cannot lead to the normal product. One reasonable possibility is that an S_N2 process occurs to give an unstable intermediate (eq 4). Indeed,

$$\mathbf{1} + \mathbf{5} \rightarrow \underset{\mathbf{9}}{PhCHFCH(CO_2Et)IrCl(CO)L_2^+Br^-} \xrightarrow{\text{fast}} FIrCl(CO)L_2^+Br^- + PhCH{=}CHCO_2Et \quad (4)$$

on treatment of adduct **6** with $AgPF_6$, which precipitates AgBr and hence should lead to the hypothesized intermediate **9**, ethyl *trans*-cinnamate is indeed formed. The Ir-containing product exhibits a ^{19}F signal of similar appearance to, but different chemical shift from, that of the side product of the oxidative addition reaction. This suggests tentative identification of the latter as $IrClBrF(CO)(PMe_3)_2$, while the product of the Ag^+ reaction would be $IrClF(CO)(PMe_3)_2(solvent)^+PF_6^-$.

While the experiment appears consistent with a competing S_N2-type process, it appears most surprising that **5** should undergo nucleophilic reaction more readily than **7**; both the increased steric bulk and the β-fluoride[36] would be expected to disfavor such a process for **5**. A nonstereospecific competing mechanism remains a possibility for both **5** and **7**; a reasonable possibility might be a metal-assisted S_N1-like reaction, resembling reactions of alkyl halides with Ag^+. Clearly, however,

(31) For comparison, the sample of **7** used in the prior study[13] had a specific rotation of −6°; the adduct **8c** was claimed to have $[\alpha]_D$ = −20°. A correspondingly stereospecific reaction with our sample of **7** would have given a specific rotation of +96° for **8c**.

(32) For an example of such an isomerization (not reversible, however), see M. A. Bennett, R. Charles, and T. R. B. Mitchell, *J. Am. Chem. Soc.*, **100**, 2737–2743 (1978).

(33) R. K. Harris, *Can. J. Chem.*, **42**, 2275–2281 (1964).

(34) P. L. Corio, "Structure of High-resolution NMR Spectra", Academic Press, New York, 1966, pp 298–299.

(35) (a) J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, **2**, 346 (1969); (b) E. G. Finer and R. K. Harris, *Prog. NMR Spectrosc.*, **6**, 61 (1970); (c) J. G. Verkade, *Coord. Chem. Rev.*, **9**, 1–106 (1972–1973); (d) S. O. Grim and R. A. Ference, *Inorg. Nucl. Chem. Lett.*, **2**, 205 (1966); (e) A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc. A*, 1826–1831 (1971).

(36) For example, the relative reactivities of CH_3CH_2Br and FCH_2CH_2Br toward PhS^- are 8:1: A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, pp 2–34.

for both primary and secondary simple alkyl bromides and for α-bromo esters, the primary mechanism for oxidative addition is one which is totally nonstereospecific.

Experimental Section

Materials and Apparatus. Iridium trichloride hydrate was obtained from Engelhard Industries and from Matthey-Bishop. Phosphine ligands, solvents, and organic halides were commercial samples used as received except when indicated otherwise. All reactions involving iridium(I) complexes were carried out under inert atmosphere. Instrumentation used includes: IR, Perkin-Elmer Models 337 and 457; NMR, Varian Models HA-100 and XL-100; mass spectra, AEI MS-9; optical rotation, Perkin-Elmer Model 141 scanning polarimeter. Melting points were determined on samples in open capillary tubes and are uncorrected. Elemental analyses were performed by Bernhardt, Dornis and Kolbe, Galbraith, and Chemalytics Laboratories.

Preparation of Iridium(I) Complexes. The general route to *trans*-$IrCl(CO)L_2$ complexes[37] proved highly erratic and unreliable in our hands; alternate methods were employed. **1c** (L = $PMePh_2$) was prepared from **1d** (L = PPh_3) by metathetical exchange.[38] An attempt to use the same method with PMe_3 led instead to $Ir(CO)(PMe_3)_4^+Cl^-$, which was converted to **1a** by heating in vacuo.[39] **1b** could not be prepared by exchange, probably because of formation of $IrCl(CO)(PMe_2Ph)_3$;[40] instead, treatment of an ethanol suspension of $[Ir(1,5\text{-cyclooctadiene})L]_2$[41] with 4 equiv of PMe_2Ph, followed by bubbling CO through the resulting red solution until it became pale yellow and concentrating with a stream of N_2, gave yellow crystals of **1b** in 65% yield. The $AsMe_2Ph$ analogue **1e** was prepared similarly. For all complexes, spectral properties agreed with those previously reported.[37]

1-Bromo-2-fluoro-2-phenylethane and Deuterated Derivatives. The undeuterated compound **3a** was made by the literature procedure.[21] *cis*-Styrene-*d* was prepared as follows: phenylacetylene-d[22b] (14.3 g, 0.14 mol) was added at 0 °C to a solution of disiamylborane, prepared from 23.1 g (0.32 mol) of 2-methyl-2-butene and 150 mL of BH_3·THF (1 M). After 1 h at 0 °C, 8-hydroxyquinoline (46 g, 0.32 mol) was added, and the mixture was stirred overnight at room temperature and then poured into water and extracted with pentane. The organic layer was thoroughly washed to remove all THF, dried, and concentrated and then either distilled (room temperature (2×10^{-5} torr)) or chromatographed on neutral alumina until all traces of the green fluorescence due to the quinolinolate–boron complex were gone. *trans*-Styrene-*d* was prepared similarly by using ordinary phenylacetylene and deuterolyzing with acetic-*d* acid followed by excess sodium 8-quinolinolate. Yields of purified product range from 20–40%; ^1H NMR shows each product is >95% isotopically and isomerically pure. Conversion to **3b** and **3c** proceeded as with the undeuterated analogue; each was obtained in 80–85% isomeric purity. NMR parameters are given in Table I.

Ethyl 2-Bromo-3-fluoro-3-phenylpropionate. The *RS,SR* isomer (**5a**) was obtained from ethyl *trans*-cinnamate as described in the literature.[27] Ethyl *cis*-cinnamate was prepared by hydrogenating ethyl phenylpropiolate over $Rh(norbornadiene)(PMe_2Ph)_3^+PF_6^- \text{–} HClO_4$ in acetone;[42] use of this catalyst gives the product in 95% yield and >95% purity, far superior to results reported with Pd–$BaSO_4$.[43] Addition of *N*-bromoacetamide–HF as before gave a 60:40 mixture of **5a** and the *RR,SS* isomer **5b**; slow distillation at 0.35 torr on a Nester-Faust adiabatic Teflon-coated spinning-band column gave an initial fraction containing **5a** and **5b** in 40:60 ratio; no higher enrichment of **5b** could be obtained.

Ethyl (*R*)-(+)-α-Bromopropionate. (*S*)-(+)-Lactic acid (Sigma Chemicals) was esterified[44] and brominated with PBr_3[45] by literature methods. The specific rotation for the product (neat) was +31.9°, corresponding to an optical purity of 97–100%, depending upon which literature value is used.[45,46]

Formation of Oxidative Adducts. General Comments. Reactions of Ir(I) complexes with alkyl halides are frequently dependent upon conditions, as will be discussed in the following paper.[14] In general the simple alkyl bromides such as **3** react only very slowly with **1a** at room temperature and much faster at elevated temperatures, especially with added radical initiator; however, no difference in stereochemical results was ever observed in comparing products made under differing conditions. Reactions can be easily monitored by the disappearance of yellow color and/or the IR peak at 1945–1955 cm^{-1}.

Bromocarbonylchloro(2-fluorocyclohexyl)bis(trimethylphosphine)iridium(III). *trans*- and *cis*-2-Bromofluorocyclohexane (**2**) were prepared by literature methods.[47] A solution of 0.4 g of **1a** and 1.8 g of *trans*-**2** in 5 mL of benzene was heated under argon at 55 °C for 40 h. Removal of volatiles and trituration with ether gave the product as a white powder (0.17 g, 30%): IR (Nujol) 2020 (C=O), 306 cm^{-1} (Ir–Cl); ^1H NMR ($CDCl_3$) δ 1.7 (PCH_3 + cyclohexyl protons), 4.76 (br, J_{HF} = 48 Hz, CHF); ^{19}F NMR (CH_2Cl_2) 64.2 (b d, J_{HF} = 48 Hz), 63.5 ppm (b d or possible q), in ratio 9:1 (shifts relative to external trifluoroacetic acid). The mass spectrum cuts off at *m/e* 593; the relative intensities of the peaks in the parent region (*m/e* 586–593) agree closely with predicted values for a molecule with one Ir, one Cl, one Br, and thirteen C atoms (Table VI). Anal. Calcd for $C_{13}H_{28}BrClFIrOP_2$: C, 26.51; H, 4.79; Br, 13.57; Cl, 6.02; F, 3.23; P, 10.52. Found: C, 26.71; H, 4.88; Br, 13.76; Cl, 5.82; F, 3.07; P, 10.66.

Bromocarbonylchloro(2-fluoro-2-phenylethyl)bis(trimethylphosphine)iridium(III) (4a). A solution of 0.2 g of **1a** and 0.3 g of **3a** in 1 mL of benzene was allowed to stand for 1 week at room temperature. Removal of volatiles and trituration with hexane gave the product **4a** as an off-white powder (0.14 g, 45%): IR (Nujol) 2037 (C=O), 311 cm^{-1} (Ir–Cl). NMR parameters for this compound as well as the deuterated analogue (prepared similarly from **3b** or **3c**) are listed in Table II. The mass spectrum contains the expected envelope in the parent-ion region (*m/e* 608–615), shifted to 1 higher *m/e* unit in the deuterated compound. Anal. Calcd for $C_{15}H_{26}BrClFIrOP_2$: C, 29.50; H, 4.31; Br, 13.10; Cl, 5.82; F, 3.11. Found: C, 29.17; H, 4.19; Br, 13.13; Cl, 5.74; F, 3.00.

Bromo(1-(carboethoxy)-2-fluoro-2-phenylethyl)carbonylchlorobis(trimethylphosphine)iridium(III) (6). A solution of 130 mg of **5a** in 1 mL of CH_2Cl_2 was added to 125 mg of **1a**; after the yellow color faded (several minutes), evaporation of volatiles and trituration with hexane gave **6** as a white powder (130 mg, 60%) which was recrystallized from CH_2Cl_2–ligroin: mp 136–138 °C; IR (Nujol) 2041 (C=O), 1705 (ester C=O), 310 cm^{-1} (Ir–Cl). NMR parameters are listed in Table IV. Anal. Calcd for $C_{18}H_{30}BrClFIrO_2P_2$: C, 31.70; H, 4.43; F, 2.78. Found: C, 31.60; H, 4.25; F, 2.52.

The analogous complex with dimethylphenylphosphine ligands was prepared similarly (reaction time 18 h) in 65% yield and recrystallized as above: mp 150–154 °C; IR 2026 (C=O), 1705 (ester C=O), 312 cm^{-1} (Ir–Cl). Anal. Calcd for $C_{28}H_{34}BrClFIrO_3P_2$: C, 41.70; H, 4.25; F, 2.25. Found: C, 42.03; H, 4.39; F, 2.25. Compounds with dimethylphenylarsine and methyldiphenylphosphine were generated under similar conditions and examined by NMR without isolation. NMR parameters for all three are given in Table V.

A solution of 117 mg of **6** in 5 mL of acetone was treated with 43 mg of $AgPF_6$. After precipitated AgBr was filtered off (29.6 mg, 93%), the NMR showed only PMe_3 signals and ethyl *trans*-cinnamate. Evaporation and extraction with hexane gave 8.8 mg of the latter (30%).

Bromo(1-(carboethoxy)ethyl)carbonylchlorobis(trimethylphosphine)iridium(III) (8a). A solution of 45 mg of racemic **7** in 1 mL of CH_2Cl_2 was added to 100 mg of **1a**; a colorless solution resulted after 15 s. Evaporation and trituration with hexane gave **8a** as a white powder (78 mg, 54%) which was recrystallized from CH_2Cl_2–ligroin as colorless plates: mp 106–110 °C; IR 2020 (C=O), 1700 (ester C=O), 314 cm^{-1} (Ir–Cl); ^1H NMR ($CDCl_3$) δ 1.27 (d, J = 7.1 Hz, CH_3CH), 1.28 (t, J = 7.3 Hz, CH_3CH_2), 1.84 (m, PCH_3), 3.37 (tq, J_{HH} = 7.1 Hz, J_{PH} = 1.3 Hz, IrCH), 4.12 (m, OCH_2CH_3); ^{13}P NMR, AB quartet pattern at −38.2 ppm (relative to external H_3PO_4). Anal.

(37) (a) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 604–607 (1967); (b) A. J. Deeming and B. L. Shaw, *ibid.*, 1887–1889 (1968).
(38) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89**, 844–851 (1967).
(39) J. A. Labinger and J. A. Osborn, *Inorg. Synth.*, **18**, 62–65 (1978).
(40) J. Y. Chen and J. Halpern, *J. Am. Chem. Soc.*, **93**, 4939–4940 (1971).
(41) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610–3618 (1966).
(42) R. R. Schrock, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1971.
(43) E. Bergmann, *J. Chem. Soc.*, 402–411 (1936).
(44) W. Gerrard, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 153–158 (1937).
(45) W. Gerrard and M. J. Richmond, *J. Chem. Soc.*, 853–857 (1945).
(46) (a) L. Ramberg, *Justus Liebigs Ann. Chem.*, **349**, 324 (1906); (b) J. W. Walker, *J. Chem. Soc.*, 914–925 (1895).
(47) (a) A. Bowers, L. C. Ibanez, E. Denot, and R. Becerra, *J. Am. Chem. Soc.*, **82**, 4001–4007 (1960); (b) G. Wittig and U. Mayer, *Chem. Ber.*, **96**, 329–341 (1963).
(48) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 6319–6332 (1979).

Calcd for $C_{12}H_{27}BrClIrO_3P_2$: C, 24.43; H, 4.61; Br, 13.55; Cl, 6.01. Found: C, 24.57; H, 4.30; Br, 12.80; Cl, 5.68.

Bromo(1-(carboethoxy)ethyl)carbonylchlorobis(dimethylphenylphosphine)iridium(III) (8b) was prepared similarly from **7** and **1b** (reaction time 15 min) as a white powder (70%): IR 2050, 2040 (C≡O), 1695 (ester C≡O), 310 cm^{-1} (Ir–Cl); ^1H NMR ($CDCl_3$) δ 0.80 (d, J = 7.4 Hz, CH_3CH), 0.87 (t, J = 7.0 Hz, CH_3CH_2), 2.18 (m, PCH_3), 3.08 (tq, J_{HH} = 7.4 Hz, J_{PH} = 1.5 Hz, IrCH), 3.57 (m, OCH_2CH_3), 7.2 (m, C_6H_5). Anal. Calcd for $C_{22}H_{31}BrClIrO_3P_2$: C, 37.06; H, 4.38; Br, 11.21; Cl, 4.97. Found: C, 37.44; H, 4.23; Br, 10.06; Cl, 4.25.

Bromo(1-(carboethoxy)ethyl)carbonylchlorobis(methyldiphenylphosphine)iridium(III) (8a) was prepared similarly from **7** and **1c** (reaction time 36 h) as a white powder (65%): mp 159–161 °C; IR 2032 (C≡O), 1700 (ester C≡O), 304 cm^{-1} (Ir–Cl); ^1H NMR ($CDCl_3$) δ 0.63 (d, J = 7.0 Hz, CH_3CH), 0.98 (t, J = 7.2 Hz, CH_3CH_2), 2.55 (m, PCH_3), 3.51 (tq, J_{HH} = 7.0 Hz, J_{PH} = 1.5 Hz, IrCH), 3.55 (m, OCH_2CH_3), 7.2 (m, C_6H_5). Anal. Calcd for $C_{32}H_{38}BrClIrO_3P_2$: C, 45.91; H, 4.21; Br, 9.55; Cl, 4.23. Found: C, 45.92; H, 4.11; Br, 9.75; Cl, 4.43.

Adducts **8a–c** prepared from optically active **7** were isolated similarly and dissolved in CH_2Cl_2 for determination of specific rotation. For the reactions carried out in high-boiling polar solvents, equimolar amounts of reactants were used, and the entire reaction mixture was diluted with CH_2Cl_2 to the desired concentration. Reaction mixtures containing added galvinoxyl were first treated with activated charcoal to decolorize them sufficiently for readings to be made on the polarimeter.

(1-(Carboethoxy)ethyl)methyldiphenylphosphonium Hexafluorophosphate. Equimolar amounts of (*R*)-(+)-**7** and $PMePh_2$ were mixed in benzene solution; the colorless oil which separated was triturated with ether, dissolved in methanol–water, treated with KPF_6, and concentrated. A colorless oil separated which was extracted into CH_2Cl_2, dried with Na_2SO_4, and then concentrated. ^1H NMR ($CDCl_3$) δ 1.04 (t, J = 7 Hz, CH_3CH_2), 1.52 (dd, J_{HH} = 7 Hz, J_{PH} = 18 Hz, CH_3CHP), 2.58 (d, J_{PH} = 13 Hz, PCH_3), 4.2 (m, $PCHCH_3$ plus OCH_2CH_3), 7.6 (m, C_6H_5). The product showed no optical activity. When prepared in a similar manner but with use of CH_3OD as solvent, the resulting product had a simple doublet at δ 1.52 and a simple quartet (J = 7 Hz) at δ 4.2, indicating complete deuteration at the α position.

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Registry No. **1a**, 21209-86-9; **1b**, 21209-82-5; **1c**, 15318-32-8; **1e**, 21209-84-7; **2a**, 51422-74-3; **2b**, 17170-96-6; **3a**, 1786-36-3; **3b**, 74498-76-3; **3c**, 74498-77-4; **4a**, 74559-73-2; **4b**, 74511-92-5; **4c**, 74559-74-3; **5a**, 50996-50-4; **5b**, 74498-78-5; **6a**, 74559-75-4; **6b**, 74608-56-3; **7**, 51063-99-1; **7** (racemic), 41978-69-2; **8a**, 74511-93-6; **8b**, 74511-94-7; **8c**, 74559-76-5; $IrClBr(CH(CO_2Et)CHFPh)(CO)(PMe_2Ph)_2$, 74511-95-8; $IrClBr(CH(CO_2Et)CHFPh)(CO)(AsMe_2Ph)_2$, 74524-98-4; $IrClBr(CH(CO_2Et)CHFPh)(CO)(PMePh_2)_2$, 4511-96-9; $IrClBr(Z\text{-}FC_6H_{10})(CO)(PMe_3)_2$, 74559-77-6; (1-(carboethoxy)ethyl)methyldiphenylphosphonium hexafluorophosphate, 74498-80-9; *cis*-styrene-*d*, 21370-59-2; *trans*-styrene-*d*, 6911-31-5; phenylacetylene-*d*, 3240-11-7; phenylacetylene, 536-74-3.

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Mechanistic Studies of Oxidative Addition to Low-Valent Metal Complexes. 7.[1] Mechanisms for Addition of Alkyl Halides to Iridium(I)

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Studies on the oxidative addition of a variety of alkyl halides to complexes *trans*-carbonylchlorobis(tertiary phosphine)iridium(I) indicate the existence of two different mechanistic patterns. One, exhibited with unactivated (saturated) alkyl halides (except methyl), vinyl and aryl halides, and α-halo esters, shows characteristics consistent with a radical chain pathway. These include sensitivity to radical initiators and inhibitors, structural effects upon reactivity (tertiary > secondary > primary alkyl halide), trapping of intermediate alkyl radicals by acrylonitrile, and complete absence of stereospecificity at the reacting carbon atom. Methyl, benzyl, and allyl halides and α-halo ethers show no effect of inhibitors and hence react by a completely different mechanism or mechanisms. Irradiation by near-ultraviolet light substantially accelerates many of these reactions. The relation of these findings to systems involving other metal complexes is discussed.

Introduction

We have demonstrated[1] that oxidative addition of several classes of alkyl halide to *trans*-$IrCl(CO)(PR_3)_2$ proceeds with complete loss of stereochemistry at carbon. On the other hand, kinetic studies on reactions of methyl iodide and benzyl halides with the same complex appear much more consistent with a nucleophilic pathway,[5,6] which would lead to prediction of inversion at carbon. Indeed, an elegant study on a different metal system (Pd(0)) using optically active benzyl-α-*d* chloride found predominant inversion.[7] These results suggest two key questions: what is the nature of the mechanism responsible for the nonstereospecific reactions, and, if more than one mechanism is operating, what factors determine which is followed in any given case? In this paper we shall attempt to answer these questions for a single type of complex, *trans*-$IrCl(CO)(PR_3)_2$ (**1**), and a wide range of alkyl halides.

Results and Discussion

Preliminary Findings. Initial studies involved reactions of *trans*-$IrCl(CO)(PMe_3)_2$ (**1a**) with excess alkyl halide, in solution degassed by brief purging, carried out in serum-capped vials, with samples periodically withdrawn by syringe for monitoring by IR methods. Under these conditions, many of the reactions proceeded in erratic and unreproducible fashion with regard to rate, although the expected adducts $IrClXR(CO)(PMe_3)_2$ (**2**) were eventually obtained in all cases. For example, the time required for completion of reaction of **1a**

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(5) (a) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511–3514 (1966); (b) J. Halpern and P. B. Chock, *Proc. Int. Conf. Coord. Chem., 10th*, 135 (1967).
(6) M. Kubota, G. O. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, **7**, 195–202 (1973).
(7) (a) K. S. Y. Lau, P. K. Wong, and J. K. Stille, *J. Am. Chem. Soc.* **98**, 5832–5840 (1976); (b) Y. Becker and J. K. Stille, *ibid.*, **100**, 838–844 (1978).

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