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); ^{1}H 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); ^{1}H 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. ^{1}H 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-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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(1) Part 6: J. A. Labinger and J. A. Osborn, *Inorg. Chem.*, preceding paper in this issue.

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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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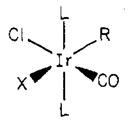
Table I. Effect of Initiation on Reactions of RX with $IrCl(CO)(PMe_3)_2$[a]

RX (concn, M)	initiator (concn, M)	temp, °C	time	deg of reacn,[b] %
trans-$C_6H_{10}FBr$	none	65	18 h	15
(0.3)	none	80	18 h	17
	AIBN (0.012)	65	18 h	50
	BZP (0.006)	80	18 h	52
$PhCHFCH_2Br$	none	65	100 min	11
(0.25)	AIBN (0.01)	65	100 min	34
	none	68	46 h	36
	AIBN (0.0075)	68	46 h	100
	BZP (0.004)	68	46 h	100
$PhCH_2CH_2Br$	none	60	18 h	22
(0.8)	AIBN (0.006)	60	18 h	88

[a] All reactions, 0.075 M in Ir complex, run in benzene in sealed tubes (see the Experimental Section for details). Entries grouped together were run with the *same* sample of alkyl halide. [b] Percent of Ir(I) complex converted to alkyl halide adduct (as shown by infrared).

with *trans*-2-bromofluorocyclohexane varied by a factor of 5 or more for a series of experiments carried out under apparently identical conditions. (Indeed, another group reported that this system does not react at all,[8] although we have been able to isolate and fully characterize the adduct.[1]) This extreme variability suggested to us that a radical chain mechanism might be involved, and subsequent experiments were designed to test for this possibility.

In general, reactions were followed by the disappearance of the IR peak at ca. 1950 cm^{-1}, due to iridium(I) complex **1**, and growth of a product peak at ca. 2030 cm^{-1}. In all cases the products were isolated as white, air-stable crystalline solids, which were fully characterized by elemental analysis, IR, and NMR spectroscopic data. Except where noted otherwise, no products containing Ir other than **2** could be detected spectroscopically. For all adducts **2** the geometry appears to be



resulting from net trans addition to **1**, similar to related earlier studies.[9] This is established by the ^1H NMR, which shows a triplet for the phosphine methyl protons, resulting from so-called virtual coupling,[10] indicative of trans phosphine ligands,[11] and a triplet for the α protons of R (when this signal is not obscured by that from the phosphine methyls), indicating R is cis to both phosphines. Also an IR peak in the region 300–320 cm^{-1} is observed for all adducts, indicating that the Cl is trans to CO.[12]

(a) Effect of Radical Initiators and Inhibitors. Reactions of **1a** with simple alkyl bromides were carried out in sealed tubes, with either benzoyl peroxide (BZP) or azobis(isobutyronitrile) (AIBN) added as initiator, and compared to samples prepared identically but without any additive. No difference was found for room-temperature reactions, but at 60–80 °C[13] the presence of initiator caused a pronounced increase in degree of reaction (Table I). This cannot result from a direct interaction of initiator with **1a**, since an equimolar mixture of AIBN and **1a** (note: initiation experiments used only 5–15 mol % initiator on the basis of Ir) showed no spectral changes after 5 days at 67 °C. (BZP reacts with **1a**, even at room temperature, to give a product with a strong CO stretch at 2070 cm^{-1}, but this product does not appear to effect any initiation.[14]) In several cases the products of reactions with initiator were isolated and found to be indistinguishable from those prepared without added initiator.

Table II. Effect of Inhibitor on Reactions of RX with IrCl(CO)L with $IrCl(CO)L_2$[a]

RX (concn, M)	Ir complex (concn, M)	inhibitor[b] (concn, M)	time	deg of reacn, %
trans-$C_6H_{10}FBr$	**1a** (0.15)		66 h	11
(1.2)[c]	**1a** (0.15)	DQ (0.015)	66 h	3
$PhCHFCH_2Br$	**1a** (0.15)		66 h	74
(1.0)[c]	**1a** (0.15)	DQ (0.015)	66 h	6
$CH_3CHBrCO_2Et$	**1a** (0.04)		5 min	85
(0.05)	**1a** (0.04)	G (0.009)	5 min	0
$CH_3CHBrCO_2Et$	**1c** (0.06)		90 min	43
(1.1)	**1c** (0.06)	G (0.021)	90 min	0
$PhCHFCHBrCO_2Et$	**1a** (0.04)		5 min	42[d]
(0.044)	**1a** (0.04)	DQ (0.026)	5 min	34[d]
	1a (0.04)	DQ (0.067)	5 min	14[d]
	1a (0.04)	G (0.005)	5 min	19
$PhCHFCHBrCO_2Et$	**1c** (0.06)		90 min	21
(1.0)	**1c** (0.06)	G (0.022)	90 min	3

[a] Except where indicated, in CH_2Cl_2 at ambient temperature. [b] DQ = duroquinone; G = galvinoxyl. [c] In benzene. [d] At 0 °C.

Both galvinoxyl and duroquinone were examined as inhibitors;[16] the former proved to be much more efficient. For simple alkyl bromides and α-bromo esters, substantial (sometimes total) retardation was observed (Table II). Again, this is not due to reaction or complexation of the iridium complex with the inhibitor: the most reactive complex **1a** shows no change in IR spectrum on treatment with equimolar amounts of either inhibitor; also, the intense galvinoxyl absorption at 425 nm[17] remains in the visible spectrum. On the other hand, several alkyl halides such as methyl iodide and benzyl bromide showed no effect at all of added inhibitor; this differing behavior is typified by Figure 1. This is the first strong indication that more than one pathway is involved in these systems.

(b) Effect of Dioxygen. A reasonable cause for the observed variability of reaction rates is the presence of small but variable amounts of dioxygen, which could function as either initiator or inhibitor in a radical chain process.[18] We found that if more rigorous methods for degassing were used, reactions proceeded more slowly and could be accelerated by addition of small amounts of O_2. A typical example: a solution of **1a** and *trans*-2-bromofluorocyclohexane in CH_2Cl_2, degassed by repeated freeze–thaw cycles on a vacuum line, gave no significant reaction over 5 h. At that point O_2 (20 mol % on the basis of Ir) was injected; after 2 h more the reaction was 80% complete. Similar behavior was noted for other simple alkyl bromides with **1a**. (Dioxygen is not the only factor, however;

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(8) F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.*, **93**, 6339–6340 (1971).

(9) J. P. Collman and W. R. Roper, *Chem. Commun.*, 244–245 (1966).

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

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

(12) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335–422 (1973).

(13) BZP and AIBN have a half-life of 1 h at 95 and 85 °C, respectively: W. A. Pryor, "Free Radicals", McGraw-Hill, New York, 1966, p 59.

(14) Small amounts of this product (by IR spectra) are observed in BZP-initiated reactions. Similar behavior (initiation and competing adduct formation) was found for *tert*-butyl hydroperoxide as well; the reaction of the latter with **1d** has been reported.[15]

(15) B. L. Booth, R. N. Haszeldine, and G. R. H. Neuss, *J. Chem. Soc., Chem. Commun.*, 1074–1075 (1972).

(16) Hydroquinone and chloranil also show some inhibitor effect, but these do appear to react fairly readily with Ir(I) and hence were not used further.

(17) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435–1438 (1957).

(18) For example, radical chain hydrogenolysis of alkyl halides by trialkyltin hydride is accelerated by small amounts of O_2 but retarded by larger amounts: H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, **28**, 2165 (1963).

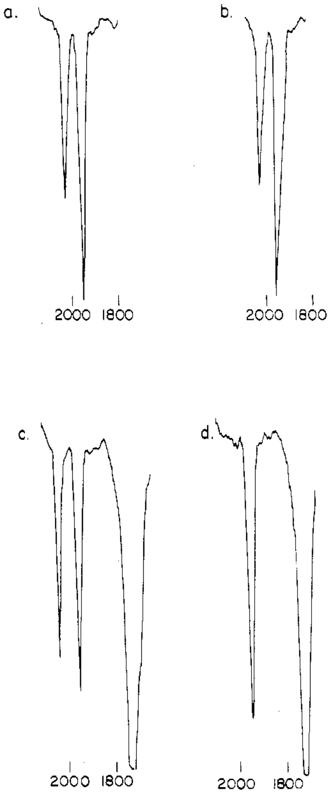

Figure 1. IR spectra of the reaction mixtures: (a) 0.01 M $Ir(PMePh_2)_2COCl$ + 0.07 M CH_3I in CH_2Cl_2 after 90 s at 25 °C; (b) same as a + 0.0076 M galvinoxyl; (c) 0.062 M $Ir(PMePh_2)_2COCl$ + 1.07 M $CH_3CHBrCO_2Et$ in CH_2Cl_2 after 90 min at 25 °C; (d) same as c + 0.021 M galvinoxyl.

even well-degassed systems showed irreproducibility for different samples of reactant or solvent, indicating that initiating and/or inhibiting impurities are present in the latter as well.)

At least three mechanisms for the effect of O_2 can readily be formulated:

(i) O_2 could react with an organic component (alkyl halide or solvent) to yield small amounts of an intermediate which is decomposed to radicals by the metal complex, providing chain initiators. Such a mechanism has been proposed for the autoxidation of olefins by metal complexes, including *trans*-$IrCl(CO)(PPh_3)_2$ (**1d**);[19] however, direct interaction of O_2 with either the alkyl halides or solvents used here appears unlikely.

(ii) O_2 could react with **1a** to give some phosphine oxide and 3-coordinate, 14-electron IrCl(CO)L, which might be expected to be considerably more reactive than **1a** by either a radical[20] or nonradical[21] pathway.

(iii) O_2 could add to **1a** to give $IrCl(CO)(PMe_3)_2(O_2)$ (**3a**), the analogues of which are known for other phosphine ligands;[22] **3a** would then react further to generate radicals which act as initiators.

We find that brief exposure of **1a** to O_2 leads to a new IR peak at 2010 cm^{-1} (CH_2Cl_2), assigned to the C=O stretch of **3a**.[23] More prolonged exposure gives rise to a dark blue color, an IR peak at 2050 cm^{-1}, and a new NMR signal (δ 1.54, d, J_{PH} = 12 Hz) resulting from Me_3PO, plus a broad multiplet at ca. δ 1.6. In O_2-catalyzed reactions of **1a** with alkyl halides, on the other hand, the peak at 2010 cm^{-1} appears initially but then disappears as the peak at 2030 cm^{-1} (product **2**) grows up. None of the spectral signals or blue color associated with prolonged reaction with O_2 ever appears. Furthermore, the oxygen-induced acceleration can be suppressed by radical inhibitors. Thus a reaction mixture of **1a** plus $PhCHFCH_2Br$, with 5% O_2 added, reacted to 75% completion in 15 min (a similar reaction without added O_2 was much slower), while the same mixture, with 10% duroquinone added in addition to O_2, gave 5% reaction over 30 min.

Table III. Relative Reactivities of Alkyl Bromides

RX	toward 1a	toward Bu_3SnH[a]
n-BuBr	1.0 (defined)	1.0 (defined)
$C_6H_{11}Br$	1.25	1.46
cis-$C_6H_{10}FBr$	4.2	
$PhCH_2CH_2Br$	5.25	
s-BuBr	5.4	2.99
t-BuBr	6.75[b]	7
trans-$C_6H_{10}FBr$	7.8	
$BrCH_2CH_2CO_2Et$	8.3	
$PhCHFCH_2Br$	27.5	

[a] Reference 24. [b] Product is not *tert*-butyl adduct but $IrClBr_2(CO)(PMe_3)_2$ (IR peak at 2065 cm^{-1}), presumably formed via β-hydride elimination and reaction with excess *t*-BuBr.

These observations support alternative iii above, in which **1a** reacts with O_2 to give **3a**, which subsequently reacts to give initiators. It may be noted that, even when large doses of O_2 were added, high yields of **2** could still be obtained; this indicates that the reaction of **3a** eventually leads back to an oxygen-free Ir species capable of forming the normal addition product. Also, although **3a** eventually gives some phosphine oxide in the absence of alkyl halide, formation of Me_3PO does not appear to be involved in the accelerating effect of O_2.

(c) Structural Effects upon Reactivity. Competitive Experiments. Relative reactivities of alkyl halides with **1a** could not be obtained reliably from direct kinetic studies, either because of irreproducibility or, in some cases, because reactions were too fast to measure by IR or NMR methods. Two competitive techniques were evolved to circumvent these problems. Relative reactivities of simple alkyl bromides were determined by reacting mixtures of a given alkyl bromide plus $BrCH_2CH_2CO_2Et$ with an insufficient amount of **1a**; the relative amounts of the two possible products is given by the ratio of intensities of the IR peaks at 2030 (due to both adducts) and 1730 cm^{-1} (due to the adduct of the β-bromo ester only). (For details of this method, see the Experimental Section.) Results are shown in Table III, along with a comparison with certain results found for the hydrogenolysis of alkyl bromides by tributyltin hydride, a reaction known to proceed via a radical chain mechanism.[24] The general trend of primary < secondary < tertiary alkyl group, as well as the acceleration by β substituents such as F, Ph, or CO_2Et, is consistent with a mechanism involving the generation of alkyl radicals in a rate-determining step (and quite inconsistent with an S_N2 type of mechanism).

As noted earlier, certain more reactive alkyl halides (MeI, $PhCH_2Br$) showed no effect of added galvinoxyl in reactions with **1**, suggesting a nonradical chain path; however, for such fast reactions this negative evidence may be open to question.

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[19] (a) E. W. Stern, *Chem. Commun.*, 736 (1970); (b) L. W. Fine, M. Grayson, and V. H. Suggs, *J. Organomet. Chem.*, **22**, 219–226 (1970); (c) A. Fusi, R. Ugo, F. Fox, A. Pasini, and S. Cenini, *ibid.* **26**, 417–430 (1971).

[20] A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7145–7147 (1974).

[21] Acceleration of reactions of $RhCl(PPh_3)_3$ by O_2 have been attributed to such a process: B. J. James, "Homogeneous Hydrogenation", Wiley, New York, 1973, pp 237–238, and references cited therein.

[22] (a) L. Vaska, *Science*, **140**, 809 (1963); (b) M. S. Weininger, I. F. Taylor, and E. L. Amma, *Chem. Commun.*, 1172–1173 (1971); (c) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128–1134 (1969).

[23] Although an analytically pure sample of **3a** was not obtained, the IR data (1990 (C=O), 840 cm^{-1} (O–O) in Nujol) and subsequent decomposition to blue species and phosphine oxide are very similar to the behavior observed for the PMe_2Ph analogue.[22c]

[24] L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047–3051 (1964).

Table IV. Effect of Inhibition on Competition between MeI and RX for $IrCl(CO)(PMe_3)_2$

RX	% MeI adduct	
	no inhibitor	with inhibitor[a]
EtI	63 ± 6	100
$PhCH_2Br$	54 ± 5	51 ± 5
$CH_2=CHCH_2Cl$	17 ± 3	18 ± 3
CH_3OCH_2Cl	53 ± 5	53 ± 5
$CH_3CHBrCO_2Et$	50 ± 8	100

[a] Galvinoxyl (10–20%, on the basis of Ir) added to reaction.

Table V. Relative Reactivities of Alkyl Halides toward $IrCl(CO)(PMe_3)_2$

MeI	1.0 (defined)	$PhCH_2Cl$	0.02
$PhCH_2Br$	0.93 ± 0.07	$CH_2=CHCH_2Cl$	5.2 ± 1.9
$CH_2=CHCH_2Br$	12.7 ± 2.2	CH_3OCH_2Cl	0.39 ± 0.01

Hence the following competitive technique was used: a mixture of MeI and a second reactive alkyl halide was reacted with **1a**, both with and without added galvinoxyl. On the assumption that MeI does indeed react by a nonchain path, if the second alkyl halide follows the same path, there should be no difference in product distribution for these two runs. In contrast, if the second alkyl halide does react by a chain path, much more of the MeI adduct should form in the reaction with galvinoxyl. Results are shown in Table IV; it appears clear that a chain path is followed for ethyl iodide and α-bromo ester but not for benzyl bromide, allyl chloride, or chloromethyl methyl ether.

Vinyl and aryl halides also appear to react by a radical path: both β-bromostyrene and iodobenzene react with **1a** (several days at room temperature) to give adducts; these reactions are inhibited by galvinoxyl. Both *cis*- and *trans*-1,2-dichloroethylene react with **1a** to give the *same* isomeric mixture of $IrCl_2$(*cis*- or *trans*-CH=CHCl)$(CO)(PMe_3)_2$. This is in sharp contrast to the reaction of these same chloro olefins with $Pd(PPh_3)_4$, which gives complete retention of configuration in the vinylic group.[25]

(d) Effect of Halide Leaving Group. Reactions involving halogen atom abstraction are generally characterized by a very large dependence of rate on the halogen (much greater than for the S_N2 reactions); for example, reactions of $Co(CN)_5^{3-}$ with alkyl halides show differences of 10^3 or more in going from RI to RBr or RBr to RCl.[26] Those alkyl halides which, according to the above experiments, follow a radical chain pathway, show similar trends. For example, at room temperature simple alkyl iodides (ethyl, isopropyl) react to completion with **1a** in seconds, whereas the corresponding bromides require several days and the chlorides are inert. Similarly $CH_3CHBrCO_2Et$ adds rapidly to **1a**, while $CH_3CHClCO_2Et$ requires prolonged irradiation (see below).

In contrast, those alkyl halides which show no effect of inhibitor also exhibit much more modest dependence on halide; limited data obtained from competitive experiments described earlier are listed in Table V. Both MeI and MeBr react completely with **1a** in less than 1 min, although MeCl is considerably slower. Methyl tosylate also reacts with **1a**, at a rate roughly comparable to that of MeCl. This fact tends to suggest a nucleophilic path rather than a radical mechanism. It may be noted that Pearson has suggested that the relative reactivities of methyl halides and methyl tosylate with a given nucleophile may be correlated with the softness or hardness of the nucleophile;[27] if these reactions of **1a** with methyl compounds are indeed nucleophilic, these results suggest that Ir(I) behaves as an exceptionally soft nucleophile. Such a finding is not unexpected for highly electron-rich, low-valent metal centers.

Table VI. Reactivity of Halomethanes with *trans*-$IrCl(CO)(PMe_3)_2$[a]

alkyl halide	reacn time[b]	alkyl halide	reacn time[b]
CH_3Cl[c]	2 days	CH_2Br_2	2 h
CH_2Cl_2	no reacn	$CHBr_3$	instantaneous
$CHCl_3$	10 min	CH_3I	<10 s
CCl_4[d]	instantaneous	CH_2I_2	instantaneous
CH_3Br	<15 s		

[a] Unless otherwise indicated, reactions carried out in CH_2Cl_2 with several-fold excess of alkyl halide. [b] Time required for complete disappearance of yellow color. [c] In neat MeCl. [d] Product not identified.

Table VII. Effect of Phosphine Ligand on Reactions of Alkyl Halides with $IrCl(CO)L_2$

L	reacn with $PhCHFCH_2Br$[a]	reacn with MeI[b]
PMe_3	100 (<30 min)	
PMe_2Ph	100 (5 h)	5.0×10^{-2}
$PMePh_2$	10 (1 week)	1.6×10^{-2}
PPh_3	0 (1 week)	3.5×10^{-3}

[a] Degree of reaction (%) after stated time, in benzene with added AIBN at 65 °C. [b] Second-order rate constant ($M^{-1}\ s^{-1}$) in benzene at 25 °C; reference 6.

Polyhalomethanes CH_nX_{4-n} show increased reactivity toward **1a**, again in agreement with expectations for a radical pathway.[28] Relative reactivities are summarized in Table VI; reactivity increases with the number of halogen atoms *except* for CH_3X, which is in all cases more reactive than this trend alone would predict. Again, this points to the existence of two different mechanisms, with simple methyl halides following a nonradical pathway.

(e) Effect of Positive Ligands. Reactions proceeding by the radical chain path are more sensitive to changes in the phosphine ligand than reactions of methyl halides. For example, when the same mixture of MeI and $CH_3CHBrCO_2Et$ was reacted with $IrCl(CO)L_2$, the amount of bromo ester adduct was found to be 55% for L = PMe_3 (**1a**), 10% for L = PMe_2Ph (**1b**), and <3% for L = $PMePh_2$ (**1c**). MeI and EtI react with **1a** at about the same rate, whereas EtI is at least 2 orders of magnitude less reactive toward **1b** than MeI. A similar sharp falloff is observed for alkyl bromides, which contrasts with the much smaller range reported for methyl iodide (Table VII). Whether these trends are electronic or steric in origin is unclear; it might be noted that all of the alkyl halides which follow the radical path are sterically larger than methyl halides and hence might be expected to show greater sensitivity to increasing bulk of ligands as methyls are replaced by phenyls.

(f) Radical Trapping. Instead of using spin traps, which are liable to react with metal complex reactants and/or products,[29] we attempted to trap intermediate alkyl radicals by using acrylonitrile as solvent; formation of such radicals should lead to polymerization of acrylonitrile. In pure acrylonitrile, **1a** exists entirely as the π complex, $IrCl(CO)(PMe_3)_2(CH_2CHCN)$; addition of isopropyl iodide to this solution caused gradual disappearance of the IR peaks of this adduct (2005, 2205 cm^{-1}) and formation of Ir(III) products (broad IR peak centered ca. 2045 cm^{-1}). The normal *i*-PrI adduct **2** comprises only about 5% of these (by NMR). Addition of methanol to the reaction mixtures precipitates up to 10 equiv/Ir of poly(acrylonitrile). Completely analogous

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[25] P. Fitton and J. E. McKeon, *Chem. Commun.*, 4–6 (1968).
[26] J. Halpern and J. P. Maher, *J. Am. Chem. Soc.*, **87**, 5361–5366 (1965).
[27] R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827–1836 (1967).
[28] For example, relative rates for reaction with Bu_3SnH are as follows (n-BuBr = 1): CH_2ClBr, 26; $CHCl_2Br$, 112; CCl_3Br, 226.[24]

behavior was found for α-bromo esters but *not* for methyl iodide; the latter reacts slowly with **1a** in CH_2CHCN to give the normal adduct in high yield and no methanol-insoluble polymeric material at all.

Reactions of $RCO(CH_2)_3I$ (R = Me, Ph) with **1a** were examined for possible radical rearrangement. $PhCO(CH_2)_3$ is known to cyclize to $\mathrm{Ph\overline{C(CH_2)_3O}}$ (although the rate is not known precisely)[24] and the Ir adduct of the resulting radical should be readily detectable by NMR. However, in both cases the normal adducts of the unrearranged alkyl group were the only products detected. Note, however, that rearrangement products are detected in certain Pt(0) reactions.[44]

(g) Photochemical Effects. Irradiation of reaction mixtures of **1a** or **1c** with a variety of alkyl halides leads to marked acceleration of the oxidative addition process. In many cases (especially **1a**), products identical with those obtained by the much slower thermal process were obtained. For example, in eq 1, irradiation (Rayonet Reactor, 25 °C) yielded quantitatively the product in 1 h; the corresponding thermal reaction is less than 5% complete in 24 h. The reaction was followed by infrared spectroscopy, and the required adduct was isolated and fully characterized immediately when the reaction was seen to be complete. However, if irradiation was continued beyond this point, further photochemical processes were observed (vide infra). *n*-BuBr (C_6H_6, 4 h) added similarly to **1a**, but no reaction was found with *n*-BuCl.

$$\mathbf{1a} + \mathrm{EtBr} \xrightarrow[h\nu]{C_6H_6} \mathrm{IrClBr(Et)(CO)(PMe_3)_2} \qquad (1)$$

Oxidative addition may occur photochemically where the thermal reaction has not been observed, i.e., eq 2. In many of these reactions, irradiation after completion of addition leads to further products. This is well illustrated by reaction of **1c** with C_2H_5I in benzene. Good yields of the expected adduct are obtained after 20 min, but, if irradiation is continued, the original adduct gradually disappears. Analysis of the ^1H NMR of the resultant solution shows the absence of C_2H_5Ir but the presence of PMe_3, C_2H_4, and several metal hydride species (between δ −9 to −16 ppm). If the adduct is isolated after 20 min, redissolved in C_6H_6 and irradiated further (75 min), again C_2H_4 and two metal hydrides are produced. Further irradiation produces additional metal hydride species. Hence not only is oxidative addition accelerated photochemically but so are retroinsertion and isomerization processes, viz., eq 3. In some cases the expected adduct is not observed, possibly because the sequential photochemical processes are too rapid. For example, prolonged irradiation of **1c** with CH_2Cl_2 (3 days) slowly leads to the product $IrCl_2H(CO)(PMe_2Ph)_2$, identical with that produced by thermal addition of HCl to **1c**. Interestingly, such a product would result from an α elimination of hydride from the expected oxidative addition product. Addition of $CH_3CHBrCOOEt$ to **1c** (C_6H_6, $h\nu$, 2 h) gave a quantitative yield of $IrClBr_2(CO)(PMePh_2)_2$. Note the thermal reaction took 36 h to go to completion.

$$\mathbf{1a} + \mathrm{CH_2Cl_2} \xrightarrow[1\ h]{h\nu} \mathrm{IrCl_2(CH_2Cl)(CO)(PMe_3)_2} \qquad (2)$$

$$\begin{aligned}&\mathrm{IrClI(C_2H_5)(CO)(PMePh_2)_2} \xrightarrow{h\nu}\\ &\qquad \underset{\text{(2 isomers)}}{\mathrm{IrClIH(CO)(PMePh_2)_2}} + \mathrm{C_2H_4} \xrightarrow{h\nu} \text{isomerization} \qquad (3)\end{aligned}$$

Two other observations merit note. The photochemical reactions of **1c** with EtI are greatly accelerated by the addition of phosphine. Hence under otherwise identical conditions, the addition of 0, 1, and 20 mol of $PMePh_2$ to the reaction (**1c**:EtI = 1:10) leads to times for complete reaction of 20, 5, and <1 min, respectively. We note that the corresponding thermal reaction is also accelerated by addition of phosphine,[30] although the effects here are considerably greater. It is not clear at present the origin of the acceleration by phosphine, but we have shown that **1c** does not react under photochemical conditions rapidly with either PMe_2Ph or $PMeEtPh_2{}^+I^-$.

The second observation concerns the possible mechanism of these reactions. With use of filtered irradiation (436 nm), the reaction of **1c** with EtI proceeds normally, yielding the expected adduct in good yield. Note therefore, since EtI absorbs at <370 nm,[34] photochemical activation of the alkyl halide is not possible. This is also supported by the additions involving CH_2Cl_2 which is transparent until the far-UV region. However, in a measure of the quantum yield at 366 nm (using ferrioxalate actinometry), using **1c** and EtI in C_6H_6, we find that the reaction was >90% complete after 145 min. Whereas if a quantum yield = 1 is assumed, total reaction should take 500 min. Hence we suggest tentatively that this reaction also proceeds by a radical chain mechanism.

In concluding this section, this cursory study shows that oxidative addition can be greatly accelerated by irradiation, which may be of great synthetic utility. However, since other processes (α and β elimination) are also photochemically accelerated, care must be taken in its use.

Radical Chain Mechanism. For simple (unactivated) alkyl halides (except methyl), vinyl and aryl halides, and α-halo esters, all of the evidence presented in this and in the preceding paper[1] supports a mechanism for oxidative addition involving a radical chain pathway. This includes the effects of radical initiators and inhibitors, the structure-reactivity relationships, the trapping of radicals by acrylonitrile, and the complete nonstereospecificity at the reacting carbon atom. An attractive mechanism for propagation of the radical chain can be based upon the known reactions of Co(II) complexes with alkyl halides[35] (eq 4). The two propagation steps consist of addition of alkyl radical to Ir(I), generating RIr^{II} which, like Co(II), can then abstract a halogen atom from RX, regenerating R·. The latter step must be rate determining to account for the strong dependence of rate on X; this is quite reasonable, since reactions involving addition of radicals to unsaturated metal centers are much faster than abstraction of halide by species such as Co(II).[36] Such an abstraction of halide from RX may proceed via an electron-transfer step similar to that proposed[40] recently for reaction of Ni(0) via eq 5. Such an electron transfer is, however, considerably more difficult for alkyl compared with aryl halides but may occur because of the instability of Ir(II) with respect to Ir(III). A rough estimate for the rate of capture of R· by **1a** can be obtained from the experiment in acrylonitrile (see the Experimental Section) and

$$\begin{gathered}\mathrm{R\cdot + Ir^{I} \rightarrow R\text{–}Ir^{II} \qquad R\text{–}Ir^{II} + RX \rightarrow R\text{–}Ir\text{–}X + R\cdot}\\ \text{overall}\quad \mathrm{RX + Ir^{I} \rightarrow R\text{–}Ir\text{–}X}\end{gathered} \qquad (4)$$

$$[\mathrm{R\text{–}Ir^{II}\cdots X\text{–}R}] \rightarrow [\mathrm{R\text{–}Ir^{III}\cdots X\text{–}R^{-}\cdot}] \rightarrow [\mathrm{R\text{–}Ir^{III}\cdots X^{-}\cdots R\cdot}] \rightarrow \mathrm{R\text{–}Ir^{III}\text{–}X + R\cdot} \qquad (5)$$

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(29) J. K. Stille and K. S. Y. Lau, *J. Am. Chem. Soc.*, **98**, 5841–5849 (1976).

(30) Both $IrCl(CO)(PMe_2Ph)_3$[31] and $IrCl(CO)(PMePh_2)_3$[32] have been reported; **1a** reacts with PMe_3 to give $Ir(CO)(PMe_3)_4{}^+Cl^-$.[33]

(31) J. Y. Chen and J. Halpern, *J. Am. Chem. Soc.*, **93**, 4939–4940 (1971).

(32) J. Y. Chen, J. Halpern, and J. Mown-Case, *J. Coord. Chem.*, **2**, 239 (1973).

(33) J. A. Labinger and J. A. Osborn, *Inorg. Synth.* **18**, 62–65 (1978).

(34) See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966.

(35) J. Halpern, *Acc. Chem. Res.*, **3**, 386–392 (1970).

(36) For example: capture of R· (by pulse radiolysis) by Cr^{2+}, $k_2 = 10^7$–10^8 $M^{-1}\ s^{-1}$;[37] addition of I· to Pt(II), $k_2 = 10^9\ M^{-1}\ s^{-1}$.[38] In contrast, for reactions of $Co(CN)_5{}^{3-}$ with alkyl iodides, $k_2 = 10^{-1}\ M^{-1}\ s^{-1}$.[26,39]

(37) H. Cohen and D. Meyerstein, *J. Chem. Soc., Chem. Commun.*, 320–321 (1972).

(38) D. Hopgood and R. A. Jenkins, *J. Am. Chem. Soc.*, **95**, 4461–4463 (1973).

(39) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **91**, 582–588 (1969).

(40) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 6319–6332 (1979).

gives a value of ca. 4×10^7 M^{-1} s^{-1}, comparable to results obtained for other systems.[36] Because reproducible kinetic data were not obtained, meaningful estimates of the rate constant for halogen abstraction cannot be made. This step must be faster than the corresponding reaction of $Co(CN)_5^{3-}$, however: the rate constant for the latter plus EtI is 6×10^{-2} M^{-1} s^{-1},[26] whereas **1a** reacts to completion with EtI in seconds. This increased kinetic reactivity may be related to the much greater thermodynamic tendency of Ir to be oxidized than Co. The initiation of this chain process in the absence of deliberately added initiators (e.g., AIBN) is unresolved. The effect of molecular oxygen has been previously discussed and it would appear that initiation here results from transformation 6 where

$$Ir^IO_2 \rightarrow Ir^{II} + O_2^{-}\cdot \qquad (6)$$

Ir(II) can further react with RX to yield R·. In the absence of oxygen we find that the reaction still proceeds, albeit much more slowly, and two explanations come to mind: (a) trace quantities of Ir(II) or Ir(0) in the starting material could be responsible, or (b) a reaction directly analogous to that proposed on Ni(0) may be slowly occurring, i.e., eq 7, where either

$$Ir^I + RX \rightarrow [Ir^{II}\text{–}X\text{–}R^{-}\cdot] \rightarrow Ir^{II}\text{–}X + R\cdot \qquad (7)$$

IrII–X or R· may serve as initiator. Note, however, this process (in contrast to Ni(0)) must be very slow compared with the chain propagation. We have no evidence concerning termination of the chain, although the dimerization/disproportionation of the R· radicals no doubt is involved.

Other Mechanisms. Reactions of methyl, allyl, and benzyl halides, as well as chloromethyl methyl ether, are not subject to inhibition and hence cannot follow the same mechanism. Although a nonchain path involving radicals is not excluded by this result, the failure to induce polymerization of acrylonitrile and the modest halide dependence do not support such a path. As noted earlier, other workers have supported an S_N2-type path for reactions of methyl and benzyl halides with Ir(I) (by kinetic studies) and, even more convincingly, for benzyl halides with Pd(0) (by stereochemical studies). While we cannot draw definite conclusions from our work, such a pathway appears entirely consistent with our findings, particularly the reaction (albeit relatively slow) of **1a** with methyl tosylate.

For allyl halides, the extremely low sensitivity of reactivity to halide (Table V) suggests the possibility of initial interaction between the metal and the olefinic double bond, followed by elimination of halide and rearrangement. This may be considered essentially an S_N2'-type of mechanism and is consistent with the ready formation of olefin complexes by **1a**. Such a mechanism was previously proposed to account for the formation of allenyl complexes in oxidative addition of propargylic halides to Ir(I) and Pt(0).[41] A related process apparently does not occur in reactions in vinylic halides, since configuration is not retained, in contrast to systems involving d^{10} metal centers (see below).

Choice of Mechanism. It is rather surprising that for this system alkyl halides may be clearly divided into two classes of mechanism, with no example which apparently reacts by a mixture of both mechanisms. Activated alkyl halides (benzyl, allyl, α-halo esters) might be expected to be activated for either mechanism;[42] yet no trace of inhibition was detected for the first two, and no trace of stereospecificity was detected at carbon for the last.[1] Equally striking is the sharp difference between methyl and ethyl halides: under ordinary conditions addition of EtBr to **1a** is about 10^4 times slower than that of MeBr and can be slowed another order of magnitude by added inhibitor. This implies that the hypothetical nonradical reaction of EtBr with **1a** is at least 10^5 times slower than that of MeBr. In contrast, in S_N2 reactions with Co(I) nucleophiles, the relative reactivity of methyl and ethyl halides is only 10^2.[43] If the alternate (nonradical chain) mechanism for Ir(I) is indeed nucleophilic, it must be much more sensitive to structural changes in the alkyl halide than are reactions of other transition-metal nucleophiles; it is not at all clear why such a difference should exist.

Relation to Other Metal Systems. Two other systems (apart from the Ni(0))[40] which have received extensive mechanistic study involve d^{10} complexes of Pd(0) and Pt(0). Reactions of the latter exhibit the same mechanistic duality—a radical chain and a nonchain path (or paths)—found here.[20] Furthermore, the demonstration of inversion at carbon for reaction of benzylic halides with Pd(0)[7] allows formulation of a nonchain path with considerable confidence as S_N2-like. These systems exhibit substantially greater complexity, however. In particular, in certain cases dihalide products are formed, which we have attributed to direct abstraction of halogen by Pt(0)[44] (see eq 8). Evidently, such a mechanism agrees well with that

$$\begin{gathered} Pt^0 + RX \rightarrow Pt^I\text{–}X + R\cdot \\ Pt^I\text{–}X + RX \rightarrow Pt^{II}X_2 + R\cdot \end{gathered} \qquad (8)$$

proposed for Ni(0), but we defer further discussion for a later paper. This process cannot be competitive for Ir(I), since detectable quantities of the analogous products $IrClX_2(CO)L_2$ were never observed (except in some photochemical experiments and with *tert*-butyl bromide). It is possible, however, that this reaction might contribute to chain initiation, and if the chain lengths were long, the amount of dihalide adduct might still be too small to detect.[45]

Another pronounced difference between these d^{10} systems and the d^8 Ir(I) complexes is found in reactions of aryl and vinyl halides, which follow the chain path for the latter[47] but not for the former.[20] A reasonable explanation for this difference lies in the greater tendency of the d^{10} complexes to undergo ligand dissociation, generating 14-electron centers; these could coordinate a double bond of the unsaturated group and still be coordinatively unsaturated, allowing an intramolecular process leading to net oxidative addition. In contrast, coordination of a double bond to Ir(I) (as in the case of CHCl=CHCl) leads to a saturated center which cannot react

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(41) J. P. Collman, J. N. Cawse, and J. W. Kang, *Inorg. Chem.*, **8**, 2574–2579 (1969).

(42) It has been suggested that α-halo esters will be particularly reactive only toward anionic nucleophiles; for example, the relative reactivity of XCH_2CO_2Et compared to $XCH_2CH_2CH_3$ is 1600 for I^- but only 60–80 for pyridine: A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, 1962, pp 2–34.

(43) G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91**, 3341–3350 (1969).

(44) A. V. Kramer and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7832–7833 (1974).

(45) It has been suggested that this direct halogen atom abstraction, followed by radical pair collapse, is a mechanism leading to oxidative addition for the reactions of Pt(0) with MeI, EtI, and $PhCH_2Br$; this proposal was based on spin-trapping experiments.[46] While the significance of the trapping results is questionable,[29] it is difficult to completely exclude *any* participation of this mechanism; although it is clearly not the predominant mechanism; EtI reacts mainly by the chain mechanism with both Pt(0)[20] and Ir(I); benzyl halides give inversion with Pd(0).[7] It was noted that the stereospecificity of addition of optically active benzyl bromide to $Pd(PEt_3)_3$ was lower than other Pd systems studied; the authors proposed some contribution from this *nonchain* radical pathway to account for this result.[7b]

(46) M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 948–949 (1973).

(47) A nonradical path has been proposed for the addition of aryl iodides to **1d** (L = tri*aryl*phosphine); this reaction occurs only at 150 °C: R. J. Mureinik, M. Weitzberg, and J. Blum, *Inorg. Chem.*, **18**, 915 (1979). In contrast, as noted in the Experimental Section, the addition of PhI to **1a** proceeds at room temperature and shows initiation and inhibition typical of the chain process. The difference in phosphine ligand is probably the key here: the radical mechanism becomes much less favorable on going from alkyl- to arylphosphines (vide supra), allowing an alternate pathway (which becomes significant only at elevated temperatures) to take over.

further except by dissociating the olefin; hence the radical chain path (resulting in isomerization) is the only one capable of leading to product. Further details of the behavior of the d^{10} systems will be discussed in a subsequent publication.

Experimental Section

Materials and Apparatus. Organic reagents and solvents were commercial samples used as received except where indicated otherwise. Iridium(I) complexes were prepared as described in the preceding paper;[1] all reactions involving Ir(I) were carried out under inert atmosphere. Details of instruments used, melting point determination, and elemental analyses may also be found in the preceding paper.[1] A number of samples containing two different halogens gave poor analytical results for the two halogens, but analyses for other elements were completely acceptable, suggesting that these discrepancies result from the analytical procedures rather than impurity of the compounds.

Bromocarbonylchloro(2-phenylethyl)bis(trimethylphosphine)iridium(III). *trans*-$IrCl(CO)(PMe_3)_2$ (**1a**) (200 mg) was placed in a Carius tube along with 2 mg of AIBN. A solution of 250 mg of $PhCH_2CH_2Br$ in 1 mL of benzene was placed in a side arm above the tube on a vacuum line. The solution was degassed by several freeze–pump–thaw cycles and added to the tube, which was sealed under vacuum and heated at 65 °C until all yellow color had faded (about 16 h). The tube was opened, solvent evaporated, and excess alkyl halide removed by trituration with hexane, giving a white powder (270 mg, 93%). Recrystallization from CH_2Cl_2–hexane gave colorless prisms: mp 157–160 °C; IR (Nujol) 2012 (C=O), 316 cm^{-1} (Ir–Cl); ^1H NMR ($CDCl_3$) δ 1.8 (PCH_3 plus $IrCH_2CH_2Ph$), 2.79 (m, $IrCH_2CH_2Ph$), 7.2 (m, C_6H_5). Anal. Calcd for $C_{15}H_{27}BrClIrCP_2$: C, 30.39; H, 4.59; Cl, 5.98; Br, 13.48. Found: C, 30.48; H, 5.03; Cl, 4.43; Br, 14.92.

Bromocarbonylchloro(2-(carboethoxy)ethyl)bis(trimethylphosphine)iridium(III) was prepared similarly from $BrCH_2CH_2CO_2Et$: mp 144–146 °C dec; IR 2022 (C=O), 312 cm^{-1} (Ir–Cl). Anal. Calcd for $C_{12}H_{27}BrClIrO_3P_2$: C, 24.43; H, 4.61; Br, 13.55; Cl, 6.01. Found: C, 23.67; H, 4.40; Br, 14.36; Cl, 6.37.

Carbonylchloromethyl(*p*-tolylsulfonato)bis(trimethylphosphine)iridium(III). A solution of 52 mg of methyl tosylate in 1 mL of CH_2Cl_2 was added to 100 mg of **1a** and the reaction followed by IR methods; after 1 day it was about 75% complete. After 5 days, evaporation and trituration with hexane gave a white powder (100 mg, 67%) which was recrystallized from CH_2Cl_2–hexane as colorless prisms: mp 222–226 °C dec; IR 2040 (C=O), 1245, 1110, 1022 (SO_2), 302 cm^{-1} (Ir–Cl); ^1H NMR δ 0.85 (t, J_{PH} = 5.4 Hz, $IrCH_3$), 1.72 (t, PCH_3), 2.39 (s, tosyl CH_3), 7.2 (m, C_6H_4). Analytical data suggest the presence of $^1/_4$ mol of CH_2Cl_2 solvate. Anal. Calcd for $C_{15}H_{28}ClIrO_4P_2S\cdot{}^1/_4CH_2Cl_2$: C, 29.76; H, 4.67; Cl, 8.64; S, 5.20. Found: C, 30.22; H, 4.82; Cl, 8.82; S, 4.92.

Analogues $IrClXMe(CO)(PMe_3)_2$ (X = Br, I) were prepared similarly except that the reaction was complete within seconds; for X = Cl, **1a** reacts with neat MeCl in a sealed tube for 2 days at room temperature. All showed closely similar spectral properties.

Bromo(bromomethyl)carbonylchlorobis(trimethylphosphine)iridium(III). A total of 50 mg of **1a** was added to a solution of 45 mg of CH_2Br_2 in 1 mL of CH_2Cl_2; decolorization was complete after 3 h. Evaporation of solvent gave a yellow oil which was recrystallized from CH_2Cl_2–ligroin as slightly yellow-green prisms: mp 207–211 °C dec; IR 2038 (C=O), 310 cm^{-1} (Ir–Cl); ^1H NMR δ 1.88 (t, PCH_3), 3.55 (t, J_{PH} = 6.5 Hz, $IrCH_2Br$). Anal. Calcd for $C_8H_{20}Br_2ClIrOP_2$: C, 16.52; H, 3.47; Br, 27.48; Cl, 6.09. Found: C, 16.63; H, 3.13; Br, 26.08; Cl, 5.42.

The following were all prepared in similar fashion.

Bromocarbonylchloro(dibromomethyl)bis(trimethylphosphine)iridium(III): from **1a** and $CHBr_3$ (reaction time 10 s); IR 2040 (C=O), 314 cm^{-1} (Ir–Cl); ^1H NMR δ 1.92 (t, PCH_3), 6.38 (t, J_{PH} = 6.9 Hz, $IrCHBr_2$).

Carbonylchloroiodo(iodomethyl)bis(trimethylphosphine)iridium(III): from **1a** and CH_2I_2 (5 s); IR 2029 (C=O), 313 cm^{-1} (Ir–Cl); ^1H NMR δ 1.90 (t, PCH_3), 2.80 (t, J_{PH} = 7.0 Hz, $IrCH_2I$).

Carbonyldichloro(dichloromethyl)bis(trimethylphosphine)iridium(III): from **1a** and $CHCl_3$ (10 min); IR 2040 (C=O), 314, 258, 251 cm^{-1} (Ir–Cl); ^1H NMR δ 1.84 (t, PCH_3), 6.43 (t, J_{PH} = 5.2 Hz, $IrCHCl_2$).

Carbonylchloroiodo(trifluoromethyl)bis(trimethylphosphine)iridium(III): from **1a** and CF_3I (instantaneous); recrystallized from CH_2Cl_2–hexane as pale orange prisms; mp >200 °C dec; IR 2054, 2045 (C=O), 321 cm^{-1} (Ir–Cl); ^1H NMR δ 1.96 (t, PCH_3); ^{19}F NMR −56.6 ppm (relative to external CF_3COOH) (t, J_{PF} = 13.0 Hz). Anal. Calcd for $C_8H_{18}ClF_3IIrOP_2$: C, 15.91; H, 3.01; F, 9.44. Found: C, 16.70; H, 3.32; F, 10.02.

Carbonyldichloro(cyanomethyl)bis(trimethylphosphine)iridium(III): from **1a** and $ClCH_2CN$ (45 s); recrystallized from CH_2Cl_2 as colorless needles; mp 167–170 °C; IR 2225 (C≡N), 2040 (C=O), 312, 268 cm^{-1} (Ir–Cl); ^1H NMR δ 1.78 (t, PCH_3), 1.94 (t, J_{PH} = 5.5 Hz, $IrCH_2CN$). Anal. Calcd for $C_9H_{20}Cl_2IrNOP_2$: C, 22.36; H, 4.17; Cl, 14.67; N, 2.90. Found: C, 22.55; H, 4.25; Cl, 14.09; N, 2.57.

Carbonyldichloro(methoxymethyl)bis(trimethylphosphine)iridium(III): from **1a** and $ClCH_2OCH_3$ (10 s); IR 2034 (C=O), 306, 257 cm^{-1} (Ir–Cl); ^1H NMR δ 1.72 (t, PCH_3), 3.28 (s, CH_3O), 4.31 (t, J_{PH} = 4.6 Hz, $IrCH_2O$).

Carbonyldichloro(methoxymethyl)bis(methyldiphenylphosphine)iridium(III): from **1c** and $ClCH_2OCH_3$ (25 min); recrystallized from CH_2Cl–EtOH; IR 2022 (C=O), 308, 260 cm^{-1} (Ir–Cl); ^1H NMR δ 2.47 (t, PCH_3), 2.56 (s, CH_3O), 3.73 (t, J_{PH} = 5.5 Hz, $IrCH_2O$), 7.2 (m, C_6H_5). Anal. Calcd for $C_{29}H_{31}IrO_2P_2$: C, 47.64; H, 4.35; Cl, 9.77. Found: C, 47.28; H, 4.24; Cl, 9.63.

Carbonylchloroethyliodobis(trimethylphosphine)iridium(III): from **1a** and EtI (5 s); IR 2021 (C=O), 304 cm^{-1} (Ir–Cl); ^1H NMR δ 1.25 (t, J_{HH} = 7.4 Hz, CH_3CH_2), 1.87 (PCH_3 plus $IrCH_2CH_3$). Anal. Calcd for $C_9H_{23}ClIIrOP_2$: C, 19.17; H, 4.71; Cl, 6.29; I, 22.51. Found: C, 19.56; H, 4.03; Cl, 6.03; I, 20.90.

Carbonylchloroiodoisopropylbis(trimethylphosphine)iridium(III): from **1a** and *i*-PrI (5 s); IR 2028, 2010 (C=O), 311 cm^{-1} (Ir–Cl); ^1H NMR δ 1.44 (d, J_{HH} = 7.2 Hz, $(CH_3)_2CH$), 1.93 (t, PCH_3), 2.96 (m, $J_{PH} \leq 0.5$ Hz, $IrCHMe_2$).

Benzylcarbonyldichlorobis(trimethylphosphine)iridium(III): from **1a** and $PhCH_2Cl$ (3 h); IR 2023 (C=O), 312, 259 cm^{-1} (Ir–Cl); ^1H NMR δ 1.68 (t, PCH_3), 3.24 (t, J_{PH} = 6.0 Hz, $IrCH_2Ph$), 7.2 (m, C_6H_5).

Benzylbromocarbonylchlorobis(trimethylphosphine)iridium(III): from **1a** and $PhCH_2Br$ (5 s); IR 2029 (C=O), 309 cm^{-1} (Ir–Cl); ^1H NMR δ 1.78 (t, PCH_3), 3.30 (t, J_{PH} = 6.2 Hz, $IrCH_2Ph$), 7.2 (m, C_6H_5).

Allylcarbonyldichlorobis(trimethylphosphine)iridium(III): from **1a** and allyl chloride (5 s); IR 2025 (C=O), 1618 (C=C), 305, 255 cm^{-1} (Ir–Cl); ^1H NMR δ 1.60 (t, PCH_3), 2.46 (ddt, J_{PH} = 6.3 Hz, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.2 Hz, $IrCH_2CH{=}CH_2$), 4.59, 4.79 (two overlapping multiplets, $IrCH_2CH{=}CH_2$), 5.94 (ddt, $^3C_{HH_{cis}}$ = 9.6 Hz, $^3J_{HH_{trans}}$ = 16.5 Hz, $^3J_{HH(CH_2)}$ = 8.5 Hz, $IrCH_2CH{=}CH_2$).

Carbonylchloroiodophenylbis(trimethylphosphine)iridium(III): from **1a** and PhI (24 h); IR 2015 (C=O), 312 cm^{-1} (Ir–Cl); ^1H NMR δ 1.64 (t, PCH_3), 7.2 (m, C_6H_5). Anal. Calcd for $C_{13}H_{23}ClIIrOP_2$: C, 25.52; H, 3.79; Cl, 5.79; I, 20.74. Found: C, 25.90; H, 3.91; Cl, 4.74; I, 22.84.

Bromocarbonylchloro(2-phenylvinyl)bis(trimethylphosphine)iridium(III): from **1a** and PhCH=CHBr (3 days); recrystallized from CH_2Cl_2–EtOH; mp 256–261 °C dec; IR 2030 (C=O), 1580, 1570 cm^{-1} (C=C). This adduct was considerably less soluble than all others and useful NMR data were not obtained. Anal. Calcd for $C_{15}H_{25}BrClIrOP_2$: C, 30.48; H, 4.26; Br, 13.52; Cl, 6.01. Found: C, 31.29; H, 4.62; Br, 12.24; Cl, 5.43.

Carbonyldichloro(2-chlorovinyl)bis(trimethylphosphine)iridium(III): Excess *cis*- or *trans*-1,2-dichloroethylene was condensed into a Carius tube containing **1a**; the resulting solution was colorless in either case, indicating virtually complete formation of olefin adduct. The tube was sealed, heated at 60 °C for 3 days, and then opened, and the volatiles were removed. ^1H NMR spectra of the reaction mixture showed that reaction was complete and, furthermore, either isomer of starting halide gave the same product spectrum. The product was recrystallized from CH_2Cl_2–hexane: mp 128–135 °C; IR 2035 (C=O), 1570 (C=C), 313, 270 cm^{-1} (Ir–Cl). The ^1H NMR showed (in addition to a complex asymmetric signal for PCH_3) the following for the $IrCH_a{=}CH_bCl$ group: for the minor isomer (40%), δ (H_a) 6.69 and δ (H_b) 7.10 (J_{HH} = 6.3, J_{PH_a} = 4.0, J_{PH_b} = 5.7 Hz); for the major isomer (60%), δ (H_a) 5.45 and δ (H_b) 6.93 (J_{HH} = 14.0, J_{PH_a} = 3.5, J_{PH_b} = 4.5 Hz). These isomers were assigned cis and trans geometry, respectively, on the basis of J_{HH} as well as comparison to analogous palladium complexes.[25] Anal. Calcd for $C_9H_{20}Cl_3IrOP_2$: C, 21.41; H, 3.99; Cl, 21.07. Found: C, 21.27; H, 3.89; Cl, 20.06.

Preparation and characterization of adducts of α-bromo esters and β-fluoroalkyl halides was described in the preceding paper.[1]

Relative Reactivities. A solution containing known concentrations of $BrCH_2CH_2CO_2Et$ plus another alkyl bromide in benzene was added to an insufficient amount of **1a** in a Carius tube, also containing 5–10% AIBN. The sealed tube was heated at 60 °C until the solution was colorless; the product mixture was isolated by evaporation of volatiles, dried (50 °C (10^{-6} torr), 18 h) to ensure removal of all unreacted alkyl halide, and then dissolved in $\mathrm{CH_2Cl_2}$, and the ratio of absorbances at 2030 and 1730 $\mathrm{cm^{-1}}$ was determined. From this ratio and the corresponding value for a similarly purified sample of $\mathrm{IrClBr(CH_2CH_2CO_2Et)(CO)(PMe_3)_2}$ alone, the composition of product was calculated; this value and the initial concentrations were then used to calculate relative reactivities by the method of Ingold and Shaw.[48]

Radical Trapping by Acrylonitrile. A 0.1 M solution of **1a** in freshly distilled, degassed acrylonitrile was treated with a slight excess of isopropyl iodide. After 18 h the solution had become very cloudy, and IR data showed no remaining Ir(I). Addition of excess MeOH precipitated fluffy white poly(acrylonitrile) (IR 2240 $\mathrm{cm^{-1}}$ (C≡N)); up to 10 equiv per Ir were obtained on filtration. Evaporation of the filtrate gave a white solid whose IR and ^{1}H NMR spectra ($\mathrm{PCH_3}$ signal) were typical of Ir(III) adducts; however, from the intensity of the signal at δ 1.44, only 5% of the total (on a molar basis) is the *i*-PrI adduct. In contrast, a similar reaction with MeI gave no clouding, complete reaction after 3 h, nearly quantitative yield of MeI adduct, and no precipitate on addition of MeOH.

In neat acrylonitrile, nearly all Ir(I) is present as the π adduct of **1a** (IR 2205 (C≡N), 2005 $\mathrm{cm^{-1}}$ (C≡O)). Evaporation of acrylonitrile from this solution gives a solid which shows only these bands; on redissolving in $\mathrm{CH_2Cl_2}$, however, peaks due to free **1a** are also observed. From the relative intensities of the peaks at 2005 and 1945 $\mathrm{cm^{-1}}$, it was estimated that a solution 0.016 M in Ir contains about 64% **1a**·$\mathrm{CH_2CHCN}$ and 36% free **1a**, giving a formation constant for the π complex of 300 $\mathrm{M^{-1}}$.[49] The rate of capture of R· by Ir(I) was estimated by assuming that only free **1a** is reactive; in neat acrylonitrile (about 15 M), the concentration of free **1a** in the above solution (0.1 M total Ir) will be 2×10^{-5} M. The rate of capture of R· by acrylonitrile is on the order of $10^3\ \mathrm{M^{-1}\ s^{-1}}$;[51] since about 5% of isopropyl radicals are captured by **1a**, the rate constant for this capture is $(10^3\ \mathrm{M^{-1}\ s^{-1}}) \times ({}^{15}/_{2} \times 10^5) \times 0.05 \simeq 4 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$.

Attempted Radical Rearrangement. 5-Iodo-2-pentanone was prepared by literature methods;[52] it reacts with **1a** (30 min) to give the normal adduct $\mathrm{IrClI((CH_2)_3COCH_3)(CO)(PMe_3)_2}$: mp 158–161 °C; IR 2026 (C≡O), 1710 (ketone C=O), 306 $\mathrm{cm^{-1}}$ (Ir–Cl); ^{1}H NMR δ 1.80 ($\mathrm{PC}H_3$ plus $\mathrm{Ir(C}H_2\mathrm{)_2CH_2COCH_3}$), 2.06 (s, $\mathrm{COCH_3}$), 2.42 (m, $\mathrm{C}H_2\mathrm{COCH_3}$). Anal. Calcd for $\mathrm{C_{12}H_{27}ClIIrO_2P_2}$: C, 23.25; H, 4.39. Found: C, 23.60; H, 4.25.

4-Iodobutyrophenone was prepared from the chloride by exchange with NaI in acetone and recrystallized from hexane: mp 52–53 °C; ^{1}H NMR δ 2.16 (m, $\mathrm{PhCOCH_2C}H_2\mathrm{CH_2I}$), 3.12 (t, $\mathrm{PhCOC}H_2\mathrm{CH_2CH_2I}$), 3.32 (t, $\mathrm{PhCOCH_2CH_2C}H_2\mathrm{I}$), 7.2 (m, $\mathrm{C_6H_5}$). Anal. Calcd for $\mathrm{C_{10}H_{11}IO}$: C, 43.82; H, 4.02. Found: C, 44.45; H, 3.94. This reacted with **1a** just as above to give the adduct: mp 152–155 °C; IR 2012 (C≡O), 1680 (ketone, C=O), 307 $\mathrm{cm^{-1}}$ (Ir–Cl); ^{1}H NMR δ 1.86 ($\mathrm{PC}H_3$ plus $\mathrm{Ir(C}H_2\mathrm{)_2CH_2COPh}$), 3.03 (t, $\mathrm{Ir(CH_2)_2C}H_2\mathrm{COPh}$), 7.2 (m, $\mathrm{C_6H_5}$). Anal. Calcd for $\mathrm{C_{17}H_{29}ClIrO_2P_2}$: C, 29.94; H, 4.29. Found: C, 30.29; H, 4.27.

In neither of these two reactions was any evidence for rearrangement (^{1}H NMR signal at δ 3.5–4.5 for protons α to oxygen) observed for either the isolated product or the unpurified reaction mixture.

Photochemical Experiments. In general photolyses were carried out in a Srinivasan-Griffin Rayonet photochemical reactor with RPF-3500-Å lamps as light source (~90% in the 3500-Å range, intensity ca. 24 W) in Pyrex vessels surrounded by a cooling jacket. Experiments were also carried out at 436 and 366 nm with use of the appropriate filters. Quantum yields were calculated by using ferrioxalate actinometry. Products were identified by isolation and conventional methods (when new) or, when known, identified by IR and NMR data (^{1}H, ^{31}P) by comparison with authentic samples.

Bromocarbonylchloroethylbis(trimethylphosphine)iridium(III). A solution of 75 mg of **1a** and 1 mL of EtBr in 15 mL of benzene was irradiated (Rayonet photochemical apparatus) for 1 h; IR spectra showed complete disappearance of **1a**. Evaporation of solvent and recrystallization from $\mathrm{CH_2Cl_2}$–hexane gave the product: mp 138 °C dec; IR ($\mathrm{CH_2Cl_2}$) 2035 $\mathrm{cm^{-1}}$ (C≡O); ^{1}H NMR δ 1.43 (t, $J_{\mathrm{HH}} = 7.5$ Hz, $\mathrm{IrCH_2C}H_3$), 1.78 ($\mathrm{PC}H_3$ plus $\mathrm{IrC}H_2\mathrm{CH_3}$). Anal. Calcd for $\mathrm{C_9H_{23}BrClIrOP_2}$: C, 20.92; H, 4.49; P, 11.99. Found: C, 21.40; H, 4.50; P, 11.90.

The following were prepared similarly.

Bromobutylcarbonylchlorobis(trimethylphosphine)iridium(III): from **1a** and BuBr; mp 105–108 °C; IR 2035 $\mathrm{cm^{-1}}$ (C≡O); ^{1}H NMR δ 0.93 (t, $J_{\mathrm{HH}} = 7.5$ Hz, $\mathrm{Ir(CH_2)_3C}H_3$), 1.77 ($\mathrm{PC}H_3$ plus $\mathrm{Ir(C}H_2\mathrm{)_3CH_3}$). Anal. Calcd for $\mathrm{C_{11}H_{27}BrClIrOP_2}$: C, 24.25; H, 5.00; P, 11.37. Found: C, 24.06; H, 5.13; P, 11.32.

Carbonyldichloro(chloromethyl)bis(trimethylphosphine)iridium(III): from **1a** in neat $\mathrm{CH_2Cl_2}$; IR 2050 $\mathrm{cm^{-1}}$ (C≡O); ^{1}H NMR δ 1.78 (t, $\mathrm{PCH_3}$), 3.95 (t, $J_{\mathrm{PH}} = 5.5$ Hz, $\mathrm{IrCH_2Cl}$). Anal. Calcd for $\mathrm{C_8H_{20}Cl_3IrOP_3}$: C, 19.50; H, 4.09; Cl, 21.59; P, 12.57. Found: C, 18.97; H, 3.89; Cl, 21.66; P, 12.61.

Reaction of 1c with $\mathbf{C_2H_5I}$. A solution of **1c** (100 mg) and EtI (1.5 mL) in benzene (18 mL) was irradiated for 20 min when the reaction was seen to be completed by infrared spectra (ν_{CO} at 2040 $\mathrm{cm^{-1}}$). The solution was divided into two parts. From one portion, the solvent was removed, the solid was dissolved in $\mathrm{C_6H_6}$ (1.5 mL), and hexane was added to yield cream colored crystals (IR 2040 $\mathrm{cm^{-1}}$ (ν_{CO}); ^{1}H NMR δ 0.78 (t, $\mathrm{CH_2C}H_3$), 1.53 (q, $\mathrm{C}H_2\mathrm{CH_3}$, $J_{\mathrm{H-H}} = 7$ Hz), 2.44 (PMe), which agrees with authentic samples of $\mathrm{IrClI(C_2H_5)(CO)(PMePh_2)_2}$). Irradiation of this product in $\mathrm{C_6H_6}$ in a sealed NMR tube for 1 h further leads to disappearance of the adduct. The NMR of this solution shows the presence of $\mathrm{C_2H_4}$ and two iridium hydrido species (^{1}H NMR δ −16.28 (t, $J_{\mathrm{P-H}} = 11$ Hz), 2.61 (PMe); −9.1 (t, $J_{\mathrm{P-H}} = 15$ Hz), 2.17 (PMe)). Further hydrido species are produced if irradiation is continued. Such species are also detected if the second portion is irradiated, the only difference being also the formation of $\mathrm{IrClI_2(CO)(PMe_2Ph)_2}$.

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Registry No. **1a**, 21209-86-9; **1a**·$\mathrm{CH_2CHCN}$, 74511-64-1; **1c**, 15318-32-8; **2** (X = Br, R = $\mathrm{CH_2CH_2Ph}$), 74511-65-2; **2** (X = Br, R = $\mathrm{CH_2CH_2CO_2Et}$), 74511-66-3; **2** (X = Cl, R = $\mathrm{CH_2Cl}$), 74511-67-4; **2** (X = Br, R = Me), 74511-68-5; **2** (X = I, R = Me), 74524-96-2; **2** (X = Br, R = $\mathrm{CH_2Br}$), 74511-69-6; **2** (X = Br, R = $\mathrm{CHBr_2}$), 74511-70-9; **2** (X = I, R = $\mathrm{CH_2I}$), 74511-71-0; **2** (X = Cl, R = $\mathrm{CHCl_2}$), 74511-72-1; **2** (X = I, R = $\mathrm{CF_3}$), 74511-73-2; **2** (X = Cl, R = $\mathrm{CH_2CN}$), 74511-74-3; **2** (X = Cl, R = $\mathrm{CH_2OCH_3}$), 74511-75-4; **2** (X = I, R = Et), 74511-76-5; **2** (X = I, R = *i*-Pr), 74511-77-6; **2** (X = Cl, R = $\mathrm{CH_2Ph}$), 74524-97-3; **2** (X = Br, R = $\mathrm{CH_2Ph}$), 74511-78-7; **2** (X = Cl, R = allyl), 74511-79-8; **2** (X = I, R = Ph), 74511-80-1; **2** (X = Br, R = CH=CHPh), 74511-81-2; **2** (X = Cl, R = *cis*-2-chlorovinyl), 74511-82-3; **2** (X = Cl, R = *trans*-2-chlorovinyl), 74559-72-1; **2** (X = I, R = $\mathrm{(CH_2)_3COCH_3}$), 74511-83-4; **2** (X = I, R = $\mathrm{(CH_2)_3COPh}$), 74511-84-5; **2** (X = Br, R = Et), 74511-85-6; **2** (X = Br, R = Bu), 74511-86-7; **2** (X = *p*-tolylsulfonato, R = Me), 74511-87-8; $\mathrm{IrCl_2(CH_2OCH_3)(CO)(PMePh_2)_2}$, 74511-88-9; $\mathrm{IrClI(C_2H_5)(CO)(PMePh_2)_2}$, 74511-89-0; $\mathrm{PhCH_2CH_2Br}$, 103-63-9; $\mathrm{BrCH_2CH_2CO_2Et}$, 539-74-2; methyl tosylate, 80-48-8; MeI, 74-88-4; MeCl, 74-87-3; $\mathrm{ClCH_2CN}$, 107-14-2; $\mathrm{ClCH_2OCH_3}$, 107-30-2; *trans*-$\mathrm{C_6H_{10}FBr}$, 17170-96-6; EtI, 75-03-6; *i*-PrI, 75-30-9; $\mathrm{PhCH_2Cl}$, 100-44-7; $\mathrm{PhCH_2Br}$, 100-39-0; allyl chloride, 107-05-1; PhI, 591-50-4; PhCH=CHBr, 103-64-0; *cis*-1,2-dichloroethylene, 156-59-2; *trans*-1,2-dichloroethylene, 156-60-5; 5-iodo-2-pentanone, 3695-29-2; 4-iodobutyrophenone, 65488-05-3; EtBr, 74-96-4; BuBr, 109-65-9; $\mathrm{CH_2Cl_2}$, 75-09-2; $\mathrm{CH_2Br_2}$, 74-95-3; $\mathrm{CHBr_3}$, 75-25-2; $\mathrm{CH_2I_2}$, 75-11-6; $\mathrm{CHCl_3}$, 67-66-3; $\mathrm{CF_3I}$, 2314-97-8; **1b**, 21209-82-5; $\mathrm{PhCHFCH_2Br}$, 1786-36-3; $\mathrm{CH_3CHBrCO_2Et}$, 535-11-5; $\mathrm{PhCHFCHBrCO_2Et}$, 716-59-6; $\mathrm{C_6H_{11}Br}$, 108-85-0; *cis*-$\mathrm{C_6H_{10}FBr}$, 51422-74-3; *s*-BuBr, 78-76-2; *t*-BuBr, 507-19-7; $\mathrm{CH_2{=}CHCH_2Br}$, 106-95-6; $\mathrm{CCl_4}$, 56-23-5; $\mathrm{CH_3Br}$, 74-83-9; $\mathrm{CH_3I}$, 74-88-4.

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