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Kinetics of Reactions of Methyl Iodide with Four-Coordinated Iridium(I) Complexes

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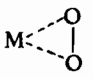
The rates of reactions of methyl iodide with four-coordinated iridium(I) complexes, IrL_2XY with X = Cl, and Y = CO, generally increase with increasing basicity of L such as $P(OPh)_3 < PPh_3 < P(p\text{-}tolyl)_3 < PMePh_2 < PEt_3 < PMe_2Ph$. Triphenylarsine iridium(I) complexes react faster with methyl iodide than the corresponding triphenylphosphine complexes. The rates for the iridium complexes with L_2 and X=Cl increase as Y is $CO < PPh_3 < N_2$. The rates for the complexes with Y = CO and L = PPh_3, AsPh, $P(p\text{-}tolyl)_3$, or PMe_2Ph increase as X is $I < Br < Cl$, and reasons for the increasing rates with decreasing basicity or decreasing tendency of the iridium complex to undergo oxidative addition upon variation of X have been suggested. The rates for the complexes with X = CO and L = PPh_3 and $AsPh_3$ increase as X is $NCS < NCO < NNN$. The dependence of the rates on L and X are compared with data for reactions of iridium(I) complexes with oxygen and hydrogen, and mechanistic implications are discussed.

Introduction

Considerable interest has been recently focused on oxidative-addition reactions of iridium(I) complexes, especially *trans*-$Ir(CO)Cl(PPh_3)_2$, *1* because of the relevance of these reactions to fundamental processes involved in reactions which are homogeneously catalyzed by transition metal complexes. Most of the earlier investigations have dealt with the characterization and structures of the products of the oxidative-addition reactions,[1,2] and more recently attention has been directed to the mechanisms of such reactions.[3] The kinetics and mechanisms of the oxidative addition reactions of *1* with hydrogen, oxygen, and methyl iodide were first reported by Chock and Halpern.[4] Kinetic data for reactions of *1* with O_2, CO, C_2H_4, SO_2 and H_2 have been discussed by Vaska.[2] Strohmeier and co-workers reported kinetic studies of reactions of hydrogen and various phosphine and halogen substituted derivatives of *1*.[5] Other kinetic studies include reactions of *1* with organoazides,[6] 2-chloroacetylenes,[7] *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene[8] and benzenethiol.[9] Kinetic studies of oxidative addition reactions of related iridium(I) complexes with substituted silanes[10] and methyl iodide[11] have also been reported. The kinetics of reactions of methyl iodide with complexes of rhodium(I) have been reported.[12] There is clear evidence from the above studies that oxidative addition reactions are first order in both metal complex and oxidant, but important finer details of the mechanisms of these reactions remain to be elucidated.

A perplexing mechanistic consideration is whether oxidative-addition reactions proceed via a transition state involving a concerted three-center interaction of metal and oxidant atoms such as *2*,*3* or *4*, or a transition state involving a two-center interaction of metal and oxidant atoms such as *5* or *6*. A biphilic[13] reaction involving transfer of a pair of electrons to the antibonding molecular orbital of one oxygen atom leading to *6*, followed by a rapid nucleophilic attack by the other oxygen atom leading to *2*, may be difficult to differentiate kinetically from a concerted interaction of three atoms such as in *2*. Kinetic data published thus far are suggestive of two distinct mechanistic types. The activation parameters for the reactions of *trans*-$Ir(CO)X(PPh_3)_2$ with hydrogen and oxy-



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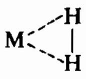

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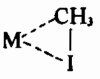

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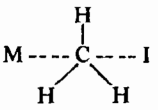

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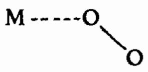

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Table I. Analytical Data[a]

		C	H	N	Other	M.p.[g]
ID	$Ir(CO)[P(C_6H_5)_3]_2NCO$	58.01 (58.07)	3.84 (3.96)	1.78 (1.76)	7.87[b] (7.80)	250-253
IE	$Ir(CO)[P(C_6H_5)_3]_2N_3$	56.44 (56.21)	3.84 (3.90)	5.34 (5.43)	7.87[b] (7.85)	186-191
IF	$Ir(CO)[P(C_6H_5)_3]_2NCS$	56.87 (56.66)	3.76 (3.66)	1.74 (1.70)		201-204
IG	$Ir(CO)[P(C_6H_5)_3]_2F$	58.2 (60.4)	3.96 (4.19)		2.49 (2.31)[f]	
IIA	$Ir(CO)[P(p\text{-}CH_3C_6H_4)_3]_2Cl$	59.76 (59.63)	4.94 (4.71)		4.11[c] (4.11)	194-238
IIB	$Ir(CO)[P(p\text{-}CH_3C_6H_4)_3]_2Br$	56.8 (57.9)	4.66 (4.66)		8.79[d] (8.82)	232
IIC	$Ir(CO)[P(p\text{-}CH_3C_6H_4)_3]_2I$	54.0 (56.3)	4.42 (4.70)		13.3[e] (13.6)	156
IIIA	$Ir(CO)[PCH_3(C_6H_5)_2]_2Cl$	49.43 (49.25)	3.99 (3.94)		9.42[b] (9.22)	147-151
IIIB	$Ir(CO)[PCH_3(C_6H_5)_2]_2Br$	46.3 (46.2)	3.74 (3.73)		11.4[d] (11.3)	
IIIC	$Ir(CO)[PCH_3(C_6H_5)_2]_2I$	43.4 (43.2)	3.51 (3.48)		17.0[e] (17.5)	
IIID	$Ir(CO)[PCH_3(C_6H_5)_2]_2NCO$	50.7 (50.6)	3.96 (3.88)	2.11 (1.82)		
IV	$Ir(CO)[P(C_2H_5)_3]_2Cl$	31.7 (30.7)	6.14 (6.02)		6.14 (7.03)[c]	63
VA	$Ir(CO)[P(CH_3)_2C_6H_5]_2Cl$	37.80 (38.39)	4.17 (3.91)			113-115
VIA	$Ir(CO)[P(OC_6H_5)_3]_2Cl$	52.33 (51.32)	3.33 (3.46)			157-160
VIIA	$Ir(CO)[As(C_6H_5)_3]_2Cl$	51.19 (51.04)	3.48 (3.30)		4.08[c] (4.45)	198-235
VIIB	$Ir(CO)[As(C_6H_5)_3]_2Br$	48.7 (49.2)	3.31 (3.30)		8.76[d] (8.64)	
VIIC	$Ir(CO)[As(C_5H_5)_3]_2I$	46.2 (46.5)	3.15 (3.15)		13.2[e] (13.1)	
VIID	$Ir(CO)[As(C_6H_5)_3]_2NCO$	52.19 (52.20)	3.45 (3.50)	1.60 (1.87)		
VIIE	$Ir(CO)[As(C_6H_5)_3]_2N_3$	51.06 (51.11)	3.47 (3.53)	4.83 (4.90)		161-163
VIIF	$Ir(CO)[As(C_6H_5)_3]_2NCS$	51.25 (50.51)	3.39 (3.39)	1.57 (1.55)		181

[a] First line, calculated, Second line, found; [b] Analysis for P; [c] Analysis for Cl; [d] Analysis for Br; [e] Analysis for I; [f] Analysis for F; [g] Decomposes upon melting.

gen in benzene were in the range $\Delta H^* = 10.8$ to 13.1 Kcal/mole and $\Delta S^* = -14$ to -24 eu.[4] Transition states involving interaction of atoms *2* and *3* have been proposed.[4] The activation parameters for the reactions of $Ir(CO)X(PPh_3)_2$ with methyl iodide were in the range $\Delta H^* = 5.6$ to 8.8 kcal/mole and $\Delta S^* = -43$ to -51 eu. The marked solvent dependency of the reaction proceeds through interaction of atoms in the intermediate such as *5* analgous to that for the Menschutkin reaction.[4] Further support for this proposal comes from studies of the pressure dependence of the reaction of methyl iodide with *1*, which show characteristics similar to those of the Menschutkin reaction.[14] Stereochemical studies of the oxidative addition of alkyl halides to Ir^I complexes have not clearly established whether the reaction is similar to S_N2 nucleophilic displacements. While inversion of configuration at carbon has been reported in the addition of *trans*-1-bromo-2-fluorocyclohexane to $Ir(CO)Cl[P(CH_3)_3]_2$,[15] this finding could not be verified.[16] More recently, the addition of $C_5H_5CH(F)CH(Br)CO_2C_2H_5$ to $Ir(CO)Cl[P(CH_3)_3]_2$ has been shown to proceed with inversion of configuration at carbon.[17] Evidence for retention of configuration at carbon has been reported for the reaction of optically active $CH_3CHBrCOOC_2H_5$ with *trans*-$Ir(CO)Cl[P(CH_3)Ph_2]_2$ and the proposal for a transition state involving three atoms such as *4* has been advanced.[18] Some problems regarding interpretation of this latter report remain to be resolved.[19] Recently, it has been demonstrated that an alternate pathway, a free-radical process may be operative for oxidative addition of certain alkyl bromides.[20]

The rates of reaction of oxygen and hydrogen with *trans*-$Ir(CO)X(PPh_3)_2$ increase as the halogen X is varied: Cl<Br<I. This is the order corresponding to increasing basicity or nucleophilicity of the metal and the tendency of such complexes to undergo oxi-

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Table II. Rates of reactions of methyl iodide with complexes orIridium(I) in benzene solution at 25°C.

ID $\mathrm{Ir(PPh_3)_2(CO)NCO}$ [d]

$[\mathrm{CH_3I}]$ M	$10^4k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.260	2.90	1.11
0.400	6.70	1.00
0.600	6.70	1.12
0.800	7.69	1.00

$k_2 = 1.06 \times 10^{-3}$

IE $\mathrm{Ir(PPh_3)_2(CO)N_3}$

$[\mathrm{CH_3I}]$ M	$10^4k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.190	0.66	3.45
0.400	1.43	3.58
0.600	2.15	3.59
0.800	2.94	3.67

$k_2 = 3.57 \times 10^{-3}$

IF $\mathrm{Ir(PPh_3)_2(CO)NCS}$

$[\mathrm{CH_3I}]$ M	$10^4k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.200	2.79	1.40
0.400	7.84	1.96
0.600	12.5	2.08
0.800	19.1	2.16

$k_2 = 1.90 \times 10^{-4}$

IG $\mathrm{Ir(PPh_3)_2(CO)F}$

$[\mathrm{CH_3I}]$ M	$10^4k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.130	2.49	1.92
0.145	3.71	2.58
0.213	4.67	2.19
0.329	6.57	2.01
0.337	8.26	2.45
0.459	10.0	2.18
0.536	10.4	1.94

$k_2 = 2.18 \times 10^{-2}$

IIA $\mathrm{Ir[P(}p\text{-}\mathrm{tolyl)_3]_2(CO)Cl}$

$[\mathrm{CH_3I}]$ M	$10^4k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.100	8.5	8.5
0.198	17.2	8.7
0.200	17.8	10.0
0.401	47.0	11.6

$k_2 = 1.00 \times 10^{-2}$

IIB $\mathrm{Ir[P(}p\text{-}\mathrm{tolyl)_3]_2(CO)Br}$

$[\mathrm{CH_3I}]$ M	$10^5k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.176	1.10	6.3
0.176	1.09	6.2
0.178	1.21	6.8
0.334	1.85	5.5
0.346	1.92	5.6

$k_2 = 6.0 \times 10^{-3}$

IIC $\mathrm{Ir[P(}p\text{-}\mathrm{tolyl)_3]_2(CO)I}$

$[\mathrm{CH_3I}]$ M	$10^5k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.307	1.78	5.8
0.395	1.29	3.2
0.401	1.98	5.3
0.404	1.94	4.8

$k_2 = 4.8 \times 10^{-3}$

IIIA $\mathrm{Ir[PCH_3(PPh_3)_2]_2(CO)Cl}$

$[\mathrm{CH_3I}]$ M	$10^3k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.0180	3.21	1.8
0.0651	10.6	1.6
0.0685	9.64	1.4
0.404	67.6	1.7
1.185	176.0	1.5

$k_2 = 1.6 \times 10^{-2}$

IIIB $\mathrm{Ir[PCH_3(PPh_3)_2]_2(CO)Br}$

$[\mathrm{CH_3I}]$ M	$10^3k(\mathrm{obsd})$ sec^{-1}	10^3k_2 $M^{-1}\mathrm{sec}^{-1}$
0.0100	1.26	1.3
0.135	2.07	1.5
0.138	2.17	1.6
0.141	2.09	1.4
0.146	2.19	1.5
0.149	2.09	1.5

$k_2 = 1.5 \times 10^{-2}$

IIIC $\mathrm{Ir(PCH_3(PPh_3)_2]_2(CO)I}$

$[\mathrm{CH_3I}]$ M	$10^3k(\mathrm{obsd})$ sec^{-1}	10^4k_2 $M^{-1}\mathrm{sec}^{-1}$
0.110	1.23	1.1
0.175	1.70	1.0

$k_2 = 1.1 \times 10^{-2}$

IVA $\mathrm{Ir[P(C_2H_5)_3]_2(CO)Cl}$

$[\mathrm{CH_3I}]$ M	$10^3k(\mathrm{obsd})$ sec^{-1}	10^4k_2 $M^{-1}\mathrm{sec}^{-1}$
0.0656	2.07	3.2
0.0753	2.34	3.1
0.0961	2.82	2.9
0.0985	3.05	3.1
0.152	4.72	3.1
0.270	7.71	2.9
0.319	8.28	2.6

$k_2 = 2.9 \times 10^{-2}$

VA $\mathrm{Ir[P(CH_3)_2PPh_3]_2(CO)Cl}$

$[\mathrm{CH_3I}]$ M	$10^3k(\mathrm{obsd})$ sec^{-1}	10^4k_2 $M^{-1}\mathrm{sec}^{-1}$
0.050	2.56	5.1 [d]
0.099	4.85	4.9 [d]
0.150	8.18	5.5 [d]
0.197	8.75	4.4 [d]

$k_2 = 5.0 \times 10^{-2}$

Table IX. (Continued)

VIA Ir[P(OPh)$_3$]$_2$(CO)Cl

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
0.80	1.3	1.6
1.50	2.6	1.8
3.00	4.8	1.6

$k_2 = 1.7 \times 10^{-5}$

VIA Ir[P(OPh)$_3$]$_2$(CO)Cl[a]

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
1.00	2.6	2.6
1.51	3.5	2.3
2.00	5.8	2.9[d]
2.00	5.5	2.8[b]
2.00	5.5	2.8[c]
2.50	7.1	2.8

$k_2 = 2.7 \times 10^{-4}$

VIIA Ir[As(Ph)$_3$]$_2$(CO)Cl

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
0.050	2.29	4.6
0.099	4.76	4.8
0.200	10.7	5.3
0.400	24.6	6.2
0.602	38.0	6.3

$k_2 = 5.4 \times 10^{-3}$

VIIB Ir[As(Ph)$_3$]$_2$(CO)Br

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
0.168	0.77	4.8
0.234	1.15	4.9
0.261	1.34	5.1
0.391	1.98	5.1
0.538	2.59	4.8

$k_2 = 4.9 \times 10^{-3}$

VIIC Ir[As(Ph)$_3$]$_2$(CO)I

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
0.190	0.83	4.4
0.379	1.53	4.0
0.516	2.14	4.1
0.698	2.67	3.8

$k_2 = 4.1 \times 10^{-3}$

VIIE Ir[As(Ph)$_3$]$_2$(CO)NCO

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
0.602	1.6	2.7[d]
0.801	3.4	4.2[d]
0.399	1.3	3.3[d]
0.598	2.1	3.5[d]

$k_2 = 3.4 \times 10^{-3}$

VIIF Ir[As(Ph)$_3$]$_2$(CO)NCS

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	10^{2}k$_2$ M^{-1}sec^{-1}
0.209	1.0	4.9
0.303	1.7	5.7
0.338	1.9	4.1
0.482	3.0	6.3
0.516	3.0	5.8
0.631	4.01	6.4
0.789	3.67	4.6

$k_2 = 5.2 \times 10^{-4}$

VIIIA Ir[PPh$_3$]$_3$Cl

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	k$_2$ M^{-1}sec^{-1}
0.0216	7.8	0.19
0.0239	7.9	0.18
0.0298	7.2	0.12
0.0312	7.1	0.12
0.0335	9.8	0.19
0.0382	10.1	0.17

$k_2 = 0.16$

IXA Ir[PPh$_3$]$_2$(N$_2$)Cl

[CH$_3$I] M	10^{3}k(obsd) sec^{-1}	k$_2$ M^{-1}sec^{-1}
0.0110	3.25	0.24
0.0205	5.58	0.24
0.0249	5.71	0.21
0.0256	6.72	0.24
0.0328	7.08	0.20
0.0379	8.31	0.20
0.0424	12.4	0.28

$k_2 = 0.23$

[a] in dichloromethane solution at 25°C; [b] from appearance of product using ir; [c] from disappearance of iriduim(I) carbonyl using ir; [d] Guggenheim treatment.

dative addition reactions.[1a,21] On the other hand, the rate of addition of methyl iodide to *trans*-IrX(CO)(PPh$_3$)$_2$ has the inverse rate dependence, namely Cl > Br > I. This observed decrease in the rates of the nucleophilic addition reaction with methyl iodide with apparent enhanced basicity of the iridium atom remains to be explained. To elucidate factors contributing to this apparent anomaly, and to obtain further general information on the placement of reactant fragments on metal sites, we have studied the kine-

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tics of reactions of methyl iodide with various four-coordinated iridium(I) complexes, IrL_2XY, where L is triaryl or alkyl phosphine or arsine, X is CO, N_2 or PPh_3 and Y is halogen or pseudohalogen.

Experimental Section

Materials. Reagent grade benzene was redistilled and stored over molecular sieves. All solvents were de-oxygenated with dry argon or nitrogen which was passed through Alfa de-oxo catalyst. Reagent grade methyl iodide was treated with an aqueous solution of sodium thiosulfate, dried over molecular sieves, distilled and stored over clean mercury.

The complexes $Ir(PPh_3)_3Cl$ and $Ir(N_2)(PPh_3)_2Cl$ were freshly prepared prior to kinetic studies using the method described by Collman and co-workers.[6] The iridium(I) complexes were prepared by previously described methods.[6] The purity of the iridium complexes were checked by noting the absence of extraneous bands in the 2000-2200 cm^{-1} region as well as

Table III. Comparison of rates of reactions of methyl iodide with Iridium(I) complexes at 25°C and spectral data.

			Rate $M^{-1}sec^{-1}$	$\nu(CO)$ ^{a} cm^{-1}	Visible max nm
A. Dependence on Phosphine					
VIA	$Ir[P(OPh)_3]_2(CO)Cl$	1.7×10^{-5}	2000	466	390
IA	$Ir[PPh_3]_2(CO)Cl$ ^{c}	3.5×10^{-3}	1957	440	388
IIA	$Ir[P(p\text{-totyl})_3]_2(CO)Cl$	1.0×10^{-2}	1958	442	388
IIIA	$Ir[P(CH_3)Ph_2](CO)Cl$	1.6×10^{-2}	1957	434	383
IVA	$Ir[P(C_2H_5)_3]_2(CO)Cl$	2.9×10^{-2}	1938	434	377
VA	$Ir[P(CH_3)_2Ph]_2(CO)Cl$	5.0×10^{-2}	1953	428	376
B. Comparison of Phosphine and Arsine Complexes					
IA	$Ir[PPh_3]_2(CO)Cl$ ^{c}	3.5×10^{-3}	1957	440	388
VIIA	$Ir[AsPh_3]_2(CO)Cl$	5.4×10^{-3}	1955	436	389
IB	$Ir[PPh_3]_2(CO)Br$ ^{c}	1.6×10^{-3}	1961	445	392
VIIB	$Ir[AsPh_3]_2(CO)Br$	4.9×10^{-3}	1960	440	392
ID	$Ir[PPh_3]_2(CO)N_3$	3.6×10^{-3}	1959	444	392
VIID	$Ir[AsPh_3]_2(CO)N_3$	6.7×10^{-3}	1954	445	393
IE	$Ir[PPh_3]_2(CO)NCO$	1.1×10^{-3}	1962	440	383
VIIE	$Ir[AsPh_3]_2(CO)NCO$	3.4×10^{-3}	1960	439	386
IF	$Ir[PPh_3]_2(CO)NCS$	2.0×10^{-4}	1973	450	397
VIIF	$Ir[AsPh_3]_2(CO)NCS$	5.2×10^{-4}	1968	448	396
35.09 (36.64).					
IA	$Ir[PPh_3]_2Cl(CO)$ ^{c}	3.5×10^{-3}		440	388
VIIIA	$Ir[PPh_3]_2Cl(PPh_3)$	0.16		^{b}	
IXA	$Ir[PPh_3]_2Cl(N_2)$	0.23		416	373
D. Dependence on halogen or pseudohalogen					
1. Triphenylphosphine complexes					
IG	$Ir[PPh_3]_2(CO)F$	2.0×10^{-2}	1955	434	385
IA	$Ir[PPh_3]_2(CO)Cl$ ^{c}	3.5×10^{-3}	1957	440	388
IB	$Ir(PPh_3)_2(CO)Br$ ^{c}	1.6×10^{-3}	1961	445	392
IC	$Ir(PPh_3)_2(CO)I$ ^{c}	0.9×10^{-1}	1963	452	397
ID	$Ir(PPh_3)_2(CO)N_3$	3.6×10^{-3}	1959	444	392
IE	$Ir(PPh_3)_2(CO)NCO$	1.1×10^{-3}	1962	440	383
IF	$Ir(PPh_3)_2(CO)NCS$	0.2×10^{-3}	1973	450	397
2. Tri(*p*-tolyl)phosphine Complexes					
IIA	$Ir[P(p\text{-tolyl})_3]_2(CO)Cl$	9.9×10^{-3}	1958	442	388
IIB	$Ir[P(p\text{-tolyl})_3]_2(CO)Br$	6.4×10^{-3}	1960	441	389
IIC	$Ir[P(p\text{-tolyl})_3]_2(CO)I$	4.7×10^{-3}	1963	450	396
3. Methyldiphenylphosphine Complexes					
IIIA	$Ir[P(CH_3)Ph_2]_2(CO)Cl$	1.6×10^{-2}	1957	434	383
IIIB	$Ir[P(CH_3)Ph_2]_2(CO)Br$	1.5×10^{-2}	1961	439	384
IIIC	$Ir[P(CH_3)Ph_2]_2(CO)I$	1.1×10^{-2}	1963	450	392
4. Triphenylarsine Complexes					
VIIA	$Ir(AsPh_3)_2(CO)Cl$	5.4×10^{-3}	1955	436	389
VIIB	$Ir(AsPh_3)_2(CO)Br$	4.9×10^{-3}	1958	440	392
VIIC	$Ir(AsPh_3)_2(CO)I$	4.1×10^{-3}	1960	448	398
VIID	$Ir(AsPh_3)_2(CO)N_3$	6.7×10^{-3}	1954	445	393
VIIE	$Ir(AsPh_3)_2(CO)NCO$	3.4×10^{-3}	1960	439	386
VIIF	$Ir(AsPh_3)_2(CO)NCS$	5.2×10^{-4}	1968	448	396

[a] Spectra in chloroform. [b] No maxima in this region, kinetics followed at 440 or 410 nm. [c] Data from reference 6.

bands at 850 cm^{-1} due to IrO_2 absorption. Analytical data for the compounds are given in Table I.

Kinetic Measurements. The reactions were followed spectrophotometrically using either a Cary 16K or Cary 13 recording spectrophotometer outfitted with thermostated cell compartments. The rates of disappearance of bands shown in Table III were followed to obtain kinetic data. These systems were shown by us and others[4] to obey Beer's Law. The initial concentrations of the iridium(I) complexes were in the range 2×10^{-4} to 5×10^{-3} *M* and the concentration of methyl iodide was in at least 20-fold excess. Special precautions were taken to reduce losses of methyl iodide by evaporation and to exclude oxygen by using argon and serum cap techniques. A Perkin-Elmer Model 621 was used to record infrared data. Microanalyses were performed by Chemalytics, Inc., Tempe, Arizona and Dr. F. Pascher, Bonn, Germany.

Results and Discussion

The kinetics of the reactions of methyl iodide with iridium(I) complexes, IrL_2XY were studied by following the disappearance of the iridium complex by measuring the decay of the absorption band in the 374-392 nm region (see Table III). Pseudo-first order rate constants were obtained from linear plots of ln (A_t - A_∞) vs time for solutions containing an excess of methyl iodide. The second order rate constants (k_2) calculated from the methyl iodide concentrations are given in Table II and confirm the rate law (1).

$$-d[IrL_2XY]/dt = k_2[IrL_2XY][CH_3I] \qquad (1)$$

There was some scatter for certain systems especially for those with low methyl iodide concentrations and for those which react rapidly with oxygen. While most of the systems examined in this study showed good conformity to this rate law, deviation from linearity of plots of ln (A_t - A_∞) vs. time was observed after one-half life for certain systems such as complexes which reacted with a small k_2, e.g. $Ir(PPh_3)_2(CO)NCS$ or $Ir[P(OPh)_3]_2(CO)Cl$. This deviation was also more prominent for those solutions containing larger concentrations of methyl iodide. The absorbance readings for these systems changed appreciably with time even after 10 half-lives due to a second slower reaction of the iridium complex with methyl iodide. The A_∞ values for these systems were thus taken when the absorbance readings reached a relatively constant value, which in some cases corresponded to periods of over 30 half-lives of the first reaction. Plots of ln (A_t - A_∞) vs time (cf. Figure 1) gave indication of two consecutive first order reactions, the second generally having a rate constant 100 times smaller than the first.

The Guggenheim method[22] was thus used to determine the rate constants for the first of these two reactions which is for example:

$$Ir(CO)Cl[P(OPh)_3]_2 + CH_3I \rightarrow Ir(CO)Cl[P(OPh)_3]_2(CH_3)I \qquad (2)$$

7 *8*

That the rate constants obtained by the Guggenheim treatment of the rate data during the initial stages of the reaction corresponds to reaction (2) was verified by measuring the rates of disappearance of *7* and appearance of *8* by monitoring the intensities of infrared absorption at 1997 and 2064 cm^{-1} respectively. The rate constant 2.9×10^{-4} M^{-1}-sec^{-1} obtained by the Guggenheim tretatment of the visible absorption data compared favorably with the values 2.8×10^{-4} M^{-1}--sec^{-1} and 2.8×10^{-4} M^{-1}-sec^{-1} obtained by monitoring the disappearance of *7* and the appearance of *8* using the infrared data. The values of k_2 obtained by the Guggenheim treatment of the visible spectral data also compared favorably with the values calculated from plots of ln (A_t - A_∞) vs t when A_t after 10 half-lives was taken as A_∞. Accordingly, where it is not indicated in Table I, this latter method was used to obtain rate constants.

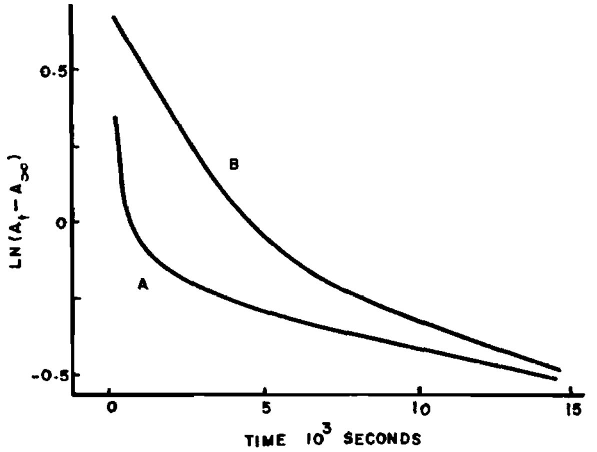

Figure 1. Kinetic plots showing deviation from linearity for first order single reaction and subsequent reaction (A) Ir-$(PPh)_3)_2(CO)Cl$ in 0.80 *M* CH_3I; (B) $Ir(PPh_3)_2(CO)NCO$ in 0.40 *M* CH_3I. Rate constant for the first reaction is $1.00 \times 10^{-3} M^{-1}$sec^{-1} and for the subsequent reaction it is $7.5 \times 10^{-5} M^{-1}$sec^{-1} .

The second reaction which is much slower than the first reaction is presumed to be due to the substitution reaction (3). While we have not succeeded in

$$Ir(CO)Cl[P(OPh)_3]_2(CH_3)I + CH_3I \rightarrow$$

9

$$Ir(CO)I[P(OPh)_3]_2(CH_3)I + CH_3Cl \qquad (3)$$

10

isolating pure samples of the diiodide *10*, we note that analyses of the methyl iodide adducts *9* are often characterized by high iodide content. The second reaction does not lead to marked changes in the infrared spectrum of *9* in the CO stretching region, an observation which would be expected for a reaction involving a halogen exchange. This second reaction was also more prominent in systems in which the pseudohalogen was more labile. Thus the rates of the second reaction were faster for X = NCO or Cl compared to X = Br. As we are primarily concerned with the details of the first reaction, careful quanti-

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(22) E.A. Guggenheim, *Phil. Mag.*, *2*, 538 (1926).

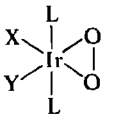
tative assessment of the second reaction was not persued. While the reaction of methyl iodide with $IrClPPh_3P)_3 \cdot 2CH_3I$,[23] it is likely that the product is $Ir(PPh_3)_2(CH_3)I_2$ analogous to the isomorphous $Rh(PPh_3)_2(CH_3)I_2$, the structure of which has been determined.[24] The reaction leading to the formation of $Ir(Ph_3P)_2(CH_3)I_2$ is thus analogous to the reaction of the iridium complex with a second molecule of methyl iodide suggested earlier. The reaction of $IrCl(PPh_3)_2N_2$ with methyl iodide leads to the same product, $Ir(PPh_3)_3(CH_3)I_2$.

Initial determinations of the rate constants for the reaction of $Ir(PPh_3)_3Cl$ and methyl iodide gave considerable scatter. Measurements of the absorption spectrum of $Ir(PPh_3)_3Cl$ in benzene in the absence of methyl iodide revealed that the compound was disappearing by a reaction such as the insertion of the iridium atom into the aromatic carbon-hydrogen bond[23,25] or reaction of the compound with residual oxygen. The rate of this background disappearance of $Ir(PPh_3)_3Cl$ was observed to follow first order kinetics with a rate constant $3.6 \pm 0.4 \times 10^{-3}$ sec^{-1}, which is much faster than the rate of appearance of the product of the insertion reaction measured by Bennett and Milner.[25] Brief exposure of the solutions to atmospheric oxygen led to acceleration of the rate of disappearance of $Ir(PPh_3)_3Cl$. The pseudo-first order rate constant observed for the reaction of $Ir(PPh_3)_3Cl$ with excess methyl iodide determined by monitoring the disappearance of $Ir(PPh_3)_3Cl$ is thus the sum of the first order rate constants for the parallel reactions, namely 3.6×10^{-3} sec^{-1} and k_1, the pseudo-first order rate constant for the reaction with methyl iodide. The second order rate constants for the reaction of methyl iodide with $Ir(PPh_3)_3Cl$ can then be calculated from k_1 and are shown in Table II. Similarly, $Ir(PPh_3)_2ClN_2$ in benzene was observed to decompose with a rate constant of 6.0×10^{-4} sec^{-1} and the second order rate constant for the reaction of methyl iodide with $Ir(PPh_3)_2ClN_2$ was calculated using the procedure outlined above for the reaction with $Ir(PPh_3)_3Cl$.

The rate data are organized and summarized in Table III to facilitate comparison and discussion. The tendency for iridium(I) complexes to undergo oxidative addition reactions has frequently been related to the basicity of the iridium(I) atom as affected by the attached ligands.[1,2,26,27] The basicity of the iridium atom has been determined by measuring the extent of protonation of the complexes $Ir(CO)L_2X$ by benzoic acid.[21] The more basic phosphines were observed to enhance the basicity of the iridium complex. It can be seen from Table III that the rates of the reactions of methyl iodide are faster for the iridium complexes containing the more basic phosphines. Thus the dimethylphenyl phosphine complex VA reacts 2000 times faster than the triphenylphosphite complex VIA. The complexes of triphenylarsine react at faster rates than the corresponding triphenylphosphine complexes. The triphenylarsine complexes have a greater affinity for protons than the triphenylphosphine complexes.[21]

The dependence of the rates of reaction of methyl iodide on the halogen attached to the iridium if F$\gg$Cl$>$Br$>$I, a trend which is opposite to that observed for the rates of reaction of iridium complexes with oxygen,[2,4] hydrogen,[2,4] chloroacetylenes,[7] benzenethiols,[9] and organo azides.[6] The reversal of the rate dependence also extends to the pseudohalogens. For example, the rate of reaction of methyl iodide with $Ir(CO)(PPh_3)_2NCO$ is faster than with $Ir(CO)(PPh_3)_2NCS$, but the rate of reaction of hydrogen with $Ir(CO)(PPh_3)_2NCS$ is faster than with $Ir(CO)(PPh_3)_2NCO$.[27] The extent of protonation of complexes $Ir(CO)(PPhMe_2)_2X$ by benzoic acid, and thus the order of increasing basicity is Cl$<$Br$<$I.[21] The iodine atom which is the most polarizable and least electronegative is expected to release the largest amount of electron density to the iridium atom. The decreasing rates of reactions of methyl iodide with increasing basicity of the iridium complexes by the variation of the halogen ligand is thus unexpected. The difference in rates with variation of halogen is much smaller than the difference with variation of phosphine, but the definite consistent differences in the trends of the rates of reactions of the iridium complexes with methyl iodide as contrasted with hydrogen, oxygen, chloroacetylenes, benzenethiols, and organo azides is noteworthy. We suggest that the difference in the trend of rates is due to distinct differences in the geometries or the electronic properties of the activated complex.

The proposed transition states for the reactions of $Ir(CO)XL_2$ with oxygen and with methyl iodide are *11* and *12*. The most significant differences between *11* and *12* are (a) that the iridium atom in *11* is six-coordinated and the bonding may involve interaction of π orbitals of Ir and π* orbitals of O_2; (b) that the iridium atom in *12* is five-coordinated and the bonding of Ir-C is mostly σ in character. In a subsequent step, the iodide ion is released and re-attached at a position *trans* to the methyl group.[28] Stabilization of the transition states *11* and *12*, hence enhancement of the relative rates of reactions, may be electronically and sterically affected by substituents L and X in a different way. The rates of all reactions of iridium(I) complexes which proceed via a six-coordinated transition state may be expected to have the same type of dependency on L and X substituents.



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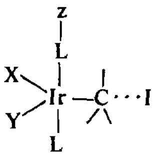

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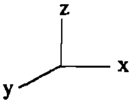

The inductive release of electrons from the more basic phosphines and the arsines enhances the nucleophilicity of the iridium atom in *11* and *12*. Similarly, from a consideration of polarizabilities and electronegativities of the halogen atom, the nucleophilicity of the iridium atom would be enhanced to a greater degree by an attached iodine atom than a chlorine

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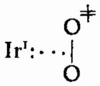
(23) M.A. Bennett and D.L. Milner, *Chem. Comm.*, 581 (1967).
(24) P.G.H. Troughton and A.C. Skapski, *ibid.*, 575 (1968).
(25) M.A. Bennett and D.L. Milner, *J. Amer. Chem. Soc.*, *91*, 6983 (1969).
(26) L. Vaska, L.S. Chen, and C.V. Senoff, *Science*, *174*, 587 (1971).
(27) L. Vaska and M.F. Werneke, *Trans. N. Y. Acad. Sci.*, 33, 70 (1971).
(28) A.J. Deeming and B.L. Shaw, *J. Chem. Soc. (A)*, 1128 (1969).

atom. Thus, the dependency of X where I>Br>Cl is observed in reactions with biphiles[13] such as oxygen, hydrogen, acetylenes, benzenethiols and organo azides. These reactions probably proceed by transition states in which these molecules occupy two coordination sites on the transition state.

Another significant way in which the transition states may differ is the extent to which the electron pair is transferred from the iridium atom to the substrate. This may be depicted, for example, by *13* and *14*, where the Ir-C bond in the activated complex *14* more closely resembles the product than the reactant.



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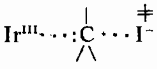

14

The high solvent dependency of rates of reactions of methyl iodide lends support to the significance of a transition state characterized by *14* in which the electron pair is more closely associated with the carbon atom that the iridium atom, which thereby has the oxidation number III.

This difference in the transition states provides a reasonable explanation for the reversal of the rate dependence on the halogen in reactions of IrL_2XY with oxygen and methyl iodide. It has recently been reported that iridium(I) binds fluorine more strongly than iodine, whereas iridium(III) binds iodine more strongly than fluorine.[29] Using a model similar to that proposed by Zumdahl and Drago,[30] we suggest that the carbon atom in *12* will share the same p_x and p_y orbitals as the ligands X and Y. Good utilization of p_x and p_y orbitals for strong Ir-X and Ir-Y bonding would lead to poor Ir-C σ-orbital overlap and consequently a raising of the energy of the transition state *12* and a slower rate of reaction. Since the methyl group would share the same p_x and p_y orbitals as the ligands X and Y, good overlap of orbitals of the ligands X and Y with Ir would lead to decreasing rates. Good overlap of orbitals of L with Ir would involve p_z orbitals of Ir, thus would contribute to increased rates due to the inductive release of electrons mentioned earlier. Reactions of methyl iodide with complexes with X = I which form a stronger bond with Ir^{III} in *12* would lead to a slower rate than reactions with complexes with X = F. The slower rate of reaction of methyl iodide with $Ir(PPh_3)_2ClCO$ than with $Ir(PPh_3)_2ClN_2$ and with $Ir(PPh_3)_3Cl$ is also consistent with the model since CO forms a stronger bond with iridium than N_2 or Ph_3P.[6] From a consideration of inductive effects, it is unexpected that the rate of reaction of methyl iodide with $Ir(PPh_3)_3Cl$ is slightly slower than the rate observed with $Ir(PPh_3)_2ClN_2$. This result may be due to steric factors such as deformation of $Ir(PPh_3)_3Cl$ from a square planar structure as reported for $Rh(PPh_3)_3Cl$.[31]

Correlation of rates to electronic and infrared spectra. Four-coordinated iridium(I) complexes can be readily distinguished from five-coordinated complexes by the presence of low energy d-d bands in the visible spectra in the four-coordinated complexes.[32] The extent of protonation of iridium complexes $IrCl(CO)L_2$ was found to be *greater* as the wavelengths of the electronic absorption band in the 430-445 nm region appeared at *lower* wavelengths.[21] Specifically, as L was varied, the extent of protonation decreased as $PMe_3(431) > PMe_2Ph(432) > PMePh_2(437) > PPh_3(440)$ and $AsPh_3(438) > PPh_3(440)$. (The numbers given in parenthesis refer to the wavelength maxima in nm of the lowest excitation band). On the other hand, the extent of protonation of complexes $Ir(CO)(PPh_2Me)_2X$ was found to be *less* as the wavelength of the maxima appeared at *lower* wavelengths. viz. I(445)>Br(437)>Cl(432). A similar linear relationship between the excitation energy and the free energy of oxygenation of $Ir(CO)(PPh_3)_2X$ has been reported.[26]

Examination of the data in Table III reveals that the rates of reactions of methyl iodide with $Ir(CO)ClL_2$ are generally faster for those complexes which have maxima at lower wavelengths as L is varied. A notable exception to the trend is the complex $IrCO(P(OPh)_3)_2Cl$. The variation of rates with halogen in $Ir(CO)L_2X$ follows the same order, namely faster rates with those complexes with maxima at lower wavelengths. A model relating the structure of the excited electronic state, the structure of the activated complex and the thermodynamics of the reactions remains to be explored.

The CO stretching frequencies in the infrared spectra of the iridium(I) carbonyls which generally reflect the amount of back-bonding from the metal to CO has been related to the reactivity of these compounds with hydrogen.[5] In can be observed in Table III that the rates of reactions of a related series of compounds can be related to the CO stretching frequencies. Those compounds with higher CO frequencies react with methyl iodide at a slower rate than those with lower CO frequencies. The high CO frequencies and low rates of reaction of $Ir(CO)[P(OPh)_3]_2Cl$ and the thiocyanato derivatives stand out in this regard. Complexes of triphenylphosphine have CO stretching frequencies which are slightly higher than those of the corresponding triphenylarsine complexes, and the triphenylphosphine complexes react at a slower rate than the triphenylarsine complexes. The CO stretching frequencies in the halide and pseudo halide complexes increase in the order Cl<Br<I and N_3<NCO<NCS and the rates of reaction with methyl iodide decrease in the order Cl>Br>I and N_3>NCO>NCS. The complexes with the more basic phosphines which have low CO frequencies react at a faster rate with methyl iodide.

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(31) P.B. Hitchcock, M. McPartlin, and R. Mason, *Chem. Comm.*, 1367 (1969).

(32) K.A. Taylor in «Homogeneous Catalysis», B.J. Luberoff, Ed. Advances in Chemistry Series, No. 70, American Chemical Society, Washington, D. C. (1968). Chapter 10.