Preparation of (η-Cyclo-octa-1,5-diene)halogenohydridobis(phosphine)-iridium(III) Salts and Kinetic Study of the Oxidative-addition Reactions of (η-Cyclo-octa-1,5-diene)bis(phosphine)iridium(I) Salts with Hydrohalogenic Acids: Evidence for Anionic Intermediates

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The complexes $[IrH(X)(cod)L_2][PF_6]$ [cod = cyclo-octa-1,5-diene, X = Cl, Br, or I, L = $PPh_2(OMe)$ or $PMePh_2$; X = Cl or Br, L = $PEtPh_2$] and $[IrHX_2(cod)L]$ (X = Br or I, L = $PMePh_2$ or $PEtPh_2$) have been synthesised from HX (X = Cl, Br, or I) and the salts $[Ir(cod)L_2][PF_6]$ [L = $PPh_2(OMe)$, $PMePh_2$, or $PEtPh_2$]. The equilibrium (i)

$$[Ir(cod)L_2]^+ + Cl^- \rightleftharpoons [IrCl(cod)L] + L \qquad (i)$$

exists due to steric crowding, and explains the presence of the second chloride in the end product. Kinetic studies on both the oxidative-addition reactions of $[Ir(cod)L_2]^+$ and $[IrCl(cod)L]$ with HCl have revealed that the nucleophilic attack of Cl^- precedes the protonation of the complexes.

FROM extensive mechanistic studies on oxidative-addition reactions of alkyl halides there has recently appeared [1] convincing evidence that the mechanistic path involves rate-determining nucleophilic attack by a metal complex on the alkyl group of the alkyl halide. This may be represented diagrammatically as:

$$\overset{\delta-}{L_xM}\text{---}\overset{\delta+}{R}\text{—}\overset{\delta-}{X}$$

A polar transition state was earlier inferred [2] from the large negative $\Delta S^\ddagger$ values obtained during a kinetic study of the addition of MeI to $[IrCl(CO)(PPh_3)_2]$ and from increases in rate constants with increasing polarity of the solvents used.[3] The isolation of *trans*-alkylchlororhodium complexes from the interaction of a rhodium macrocycle with butyl bromide in the presence of LiCl has been cited [4] as evidence for the cationic nature of the intermediate in the oxidative-addition mechanism, and further kinetic evidence for this proposal came from the observations [5-7] that additions of HCl to $[PtR_2(PEt_3)_2]$ [R = Ph or C_6H_4Y (Y = *p*-MeO, *p*-Me, *p*-F, or *m*-F)] showed a linear dependence on $[H^+]$ and an independence of $[Cl^-]$ of the pseudo-first-order rate constants.

Recently, however, halide ions have been shown to exert a powerful catalytic effect on the oxidative-addition of MeI to $[RhCl(CO)L_2]$ (L = $AsPh_3$ or $SbPh_3$) [8] and $[Ir(cod)(bipy)]^+$ (cod = cyclo-octa-1,5-diene, bipy = 2,2′-bipyridyl) [9] and anionic species, formed by exchange of a neutral group with a halide ion, were proposed as the reactive intermediates.[8] It is significant that, from the limited data presented for the reaction of BuBr with the rhodium macrocycle,[4] an anionic intermediate formed from initial interaction of Cl^- with the rhodium metal centre would also be consistent with the product obtained.

During our studies on the reaction of HX (X = halide) with the cations $[Ir(cod)L_2]^+$ (L = phosphine or phosphinite) neutral products of formula $[IrHX_2(cod)L]$ were formed and which required at some stage the introduction of a second halide into the metal co-ordination sphere. We have now fully investigated these reactions with HX (X = Cl, Br, or I) and have studied reaction (1) for L = PPh_3 (n = 1) and $PEtPh_2$, $PMePh_2$,

$$[Ir(cod)L_2]^+ + HCl \xrightarrow{MeOH} [IrHCl_{(3-n)}(cod)L_n] \qquad (1)$$

or $PPh_2(OMe)$ (n = 2) by stopped-flow techniques with the aims of (*i*) further distinguishing between the three possible oxidative-addition mechanisms proposed (polar transition state,[1,2] concerted mechanism,[10] and, although highly unlikely for HCl, the radical mechanism [11]), (*ii*) if a polar transition state is involved to see whether the intermediate is formed *via* electrophilic attack of the proton or nucleophilic attack of the chloride on the metal-atom centre, and (*iii*) to try to determine the effect, if any, of ligand size on the formation of the oxidised product.

RESULTS

Preparation and Characterisation of Complexes.—Treatment of an acetone solution of $[Ir(cod)L_2][PF_6]$ [12] [1; L = $PPh_2(OMe)$] with an excess of HX (X = Cl, Br, or I) produced $[IrH(X)(cod)L_2][PF_6]$ [2; L = $PPh_2(OMe)$] in high yield. The analogous salts (2; X = Cl, L = $PMePh_2$ or $PEtPh_2$) were obtained from (1) and an excess of HCl, but corresponding bromo- and iodo-derivatives (L = $PMePh_2$) were only formed by use of stoicheiometric

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additions of HX. Although (2; X = Br, L = $PEtPh_2$) formed on stoicheiometric addition of HBr, corresponding reactions with HI produced only the neutral complex $[IrHI_2(cod)(PEtPh_2)]$. When an excess of HX (X = Br or I) was used on (1; L = $PMePh_2$) the neutral complexes $[IrHX_2(cod)L]$ (3; L = $PMePh_2$) readily formed in high yield. Reaction of (1; L = PPh_3) with stoicheiometric amounts of HX gave mixtures of starting material and (3; X = Cl, Br, and I; L = PPh_3),[13] a total conversion into (3) being effected only by addition of excess of acid.

TABLE 1

Melting points and analytical data

Complex	M.p. (θ_C/°C)	Analysis (%) *		
		C	H	Cl, Br, or I
$[IrH(Cl)(cod)(PMePh_2)_2][PF_6]$	197—198	46.6 (46.3)	4.4 (4.45)	4.6 (4.0)
$[IrH(Br)(cod)(PMePh_2)_2][PF_6]$	198	43.9 (43.0)	4.25 (4.25)	10.15 (9.55)
$[IrH(I)(cod)(PMePh_2)_2][PF_6]$	193—194	41.45 (41.95)	4.1 (4.05)	13.5 (13.0)
$[IrHBr_2(cod)(PMePh_2)]$	267	37.8 (38.1)	3.65 (3.95)	24.75 (24.2)
$[IrHI_2(cod)(PMePh_2)]$	190	33.5 (33.4)	3.5 (3.45)	33.05 (33.65)
$[IrH(Cl)(cod)\{PPh_2(OMe)\}_2][PF_6]$	169	44.5 (44.65)	4.15 (4.3)	4.3 (3.9)
$[IrH(Br)(cod)\{PPh_2(OMe)\}_2][PF_6]$	173	42.0 (42.6)	3.95 (4.1)	8.75 (8.35)
$[IrH(I)(cod)\{PPh_2(OMe)\}_2][PF_6]$	164—166	40.25 (40.6)	3.75 (3.9)	13.2 (12.6)
$[IrH(Cl)(cod)(PEtPh_2)_2][BPh_4]$	105—110	65.75 (66.45)	5.6 (5.85)	4.05 (3.25)
$[IrH(Br)(cod)(PEtPh_2)_2][PF_6]$	123—127	45.7 (45.3)	4.7 (4.55)	8.75 (8.35)
$[IrHI_2(cod)(PEtPh_2)]$	152—160	34.45 (34.35)	3.55 (3.65)	32.55 (33.0)
$[IrCl(cod)(PMePh_2)]$	142—144	46.55 (47.05)	4.6 (4.7)	6.6 (6.6)
$[IrCl(cod)(PEtPh_2)]$	135—139	47.7 (48.05)	4.95 (4.95)	6.75 (6.45)

* Calculated values are given in parentheses.

TABLE 2

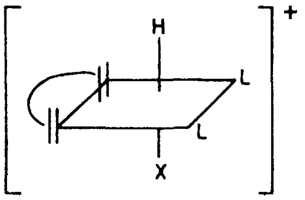
Infrared [a] and ^1H n.m.r.[b] data

Complex	ν(Ir–H) ±5 cm^{-1}	^1H N.m.r.		
		Methyl	Hydride	Diene [c]
$[IrH(Cl)(cod)(PMePh_2)_2][PF_6]$	2 250	7.92 (pt) (11)	24.95 (t) (20)	5.2, 5.6, 7.35
$[IrH(Br)(cod)(PMePh_2)_2][PF_6]$	2 250	7.92 (pt) (10)	24.21 (t) (20)	5.2, 5.5, 6.8—7.8, 8.45
$[IrH(I)(cod)(PMePh_2)_2][PF_6]$	2 240	7.84 (pt) (10)	22.86 (t) (20)	5.3, 6.7—8.4
$[IrHBr_2(cod)(PMePh_2)]$	2 233	7.4 (d) (11.5)	23.0 (d) (10)	obscured
$[IrHI_2(cod)(PMePh_2)]$	2 260	7.02 (d) (10)	22.32 (d) (8)	4.53, 6.2, 6.4—7.8, 8.45
$[IrH(Cl)(cod)\{PPh_2(OMe)\}_2][PF_6]$	2 250	6.74 (pt) (12)	24.65 (t) (22)	4.57, 5.17, 7.29, 7.64
$[IrH(Br)(cod)\{PPh_2(OMe)\}_2][PF_6]$	2 250	6.72 (pt) (12)	23.93 (t) (25)	4.8, 5.1, 7.27, 7.47, 7.65
$[IrH(I)(cod)\{PPh_2(OMe)\}_2][PF_6]$	2 230	6.69 (pt) (12)	22.90 (t) (24)	5, 7.26
$[IrH(Cl)(cod)(PEtPh_2)_2][BPh_4]$	2 260			
$[IrH(Br)(cod)(PEtPh_2)_2][PF_6]$	2 260 [d]			
$[IrHI_2(cod)(PEtPh_2)]$	2 260			

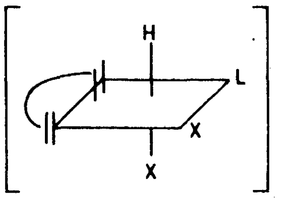
[a] Nujol. [b] In τ; the separation of the outer peaks (J/Hz) is given in parentheses. All the spectra were recorded in CD_2Cl_2. d = 1 : 1 doublet, t = 1 : 2 : 1 triplet, pt = partial triplet. [c] All the diene resonances were observed as broad peaks. [d] Resonances were broad and unresolved possibly due to exchange occurring in solution. No hydride resonances were observed.

Melting points and analytical data for all the new complexes prepared are given in Table 1. Complexes (2) were all characterised as salts from the strong vibration in the i.r. spectra at 840 cm^{-1}, characteristic of the $[PF_6]^-$ anion. ν(M–H) stretching frequencies for both (2) and (3) were observed in the 2 150—2 260 cm^{-1} region and are characteristic of a hydride ligand *trans* to a halide group. The methyl resonances of (2) were observed as partial triplets in their ^1H n.m.r. spectra, indicative[12] of *cis* couplings. The ^{31}P–^{31}P *trans* couplings observed to date in iridium(III) systems have all been strong, giving easily identifiable first-order patterns.[14] The hydride resonances for (2) occurred as symmetrical 1 : 2 : 1 triplets from the couplings of two magnetically equivalent ^{31}P nuclei, and the decrease in their τ values along the series Cl > Br > I (see Table 1) was consistent with variations in chemical shift corresponding to the *trans* activation of these ligands. A doublet hydride resonance was recorded for (3).

From these data we have assigned the following configurations for (2) and (3).



(2)



(3)

Kinetics.—Equilibrium (2) (too fast to measure kinetically by the stopped-flow technique) was observed by utilising

$$[Ir(cod)L_2]^+ + Cl^- \underset{\text{methanol}}{\overset{K_1}{\rightleftharpoons}} [IrCl(cod)L] + L \qquad (2)$$

the distinct u.v.–visible peaks (Table 5) of the two metal complexes. The neutral products [IrCl(cod)L] (L = PPh_3, $PEtPh_2$, or $PMePh_2$) were characterised from bridge-fission reactions of $[\{IrCl(cod)\}_2]$ and L. Values of the equilibrium constant K_1 of 2×10^{-2}, 4×10^{-4}, and 10^{-5}—10^{-6} were obtained for L = PPh_3, $PEtPh_2$, and $PMePh_2$ respectively

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from static measurements. For L = $PPh_2(OMe)$, [IrCl(cod)L] could not be isolated and the equilibrium constant

TABLE 3

Values of $k_{obs.}$ for the reactions $[Ir(cod)L_2]^+ + HCl \longrightarrow [IrHCl(cod)L_2]^+$ and $[IrCl(cod)L] + HCl \longrightarrow [IrHCl_2(cod)L]$ at 25 °C and I = 1 mol dm^{-3} in MeOH

Complex	[HCl]	$[HClO_4]$	[LiCl]	$k_{obs.}$
	mol dm^{-3}			s^{-1}
$[Ir(cod)(PPh_3)_2]^+$	0.05			0.350
	0.1			0.48
	0.2			0.89
	0.4			2.37
	0.6			4.28
	0.8			6.73
	1.0			10.0
	0.2 [a]			1.07
	0.2 [b]			0.86
	0.2 [c]			0.59
	0.2 [d]			0.49
	0.2 [e]			0.42
	0.2 [f]			0.32
$[IrCl(cod)(PPh_3)]$	0.05			0.44
	0.1			0.72
	0.2			1.50
	0.4			2.77
	0.5			4.28
	0.6			5.13
	0.8			9.0
	1.0			11.0
	0.1	0.0		0.69
	0.1	0.05		0.83
	0.1	0.1		0.99
	0.1	0.25		1.37
	0.1	0.35		1.44
	0.1	0.5		1.78
	0.1	0.65		2.17
	0.1	0.75		2.57
	0.1	0.85		2.89
	0.1		0.0	0.68
	0.1		0.05	0.81
	0.1		0.1	0.99
	0.1		0.2	1.26
	0.1		0.25	1.31
	0.1		0.3	1.51
	0.1		0.4	1.78
	0.1		0.5	1.93
	0.1		0.75	2.72
$[Ir(cod)\{PPh_2(OMe)\}_2]^+$	0.05			0.05
(fast reaction)	0.1			0.06
	0.2			0.10
	0.4			0.20
	0.5			0.28
	0.6			0.41
	0.8			0.59
	1.0			1.12
	0.2	0.0		0.080
	0.2	0.05		0.078
	0.2	0.1		0.074
	0.2	0.2		0.073
	0.2	0.4		0.072
	0.2	0.6		0.071
	0.2	0.8		0.071
	0.2		0.0	0.089
	0.2		0.1	0.12
	0.2		0.2	0.16
	0.2		0.4	0.28
	0.2		0.5	0.39
	0.2		0.6	0.46
	0.2		0.8	0.78
(slow reaction)	0.1			0.002 3
	0.2			0.007 5
	0.4			0.023
	0.5			0.035
	0.6			0.053
	0.8			0.09
	0.2		0.0	0.008 3
	0.2		0.1	0.011
	0.2		0.2	0.013
	0.2		0.4	0.016
	0.2		0.5	0.018
	0.2		0.6	0.02
	0.2		0.8	0.022
	0.2	0.0		0.008 3
	0.2	0.1		0.018
	0.2	0.2		0.025
	0.2	0.4		0.03
	0.2	0.5		0.036
	0.2	0.6		0.041
	0.2	0.8		0.053
$[Ir(cod)(PMePh_2)_2]^+$				
(fast reaction)	0.1			0.07
	0.2			0.48
	0.4			4.18
	0.5			7.62
	0.6			12.83
	0.8			27.72
	1.0			56.34
	0.2		0.0	1.33
	0.2		0.05	1.78
	0.2		0.1	2.78
	0.2		0.2	4.62
	0.2		0.4	11.18
	0.2		0.5	12.83
	0.2		0.6	18.24
	0.2		0.8	31.50
	0.2	0.05		1.18
	0.2	0.1		1.33
	0.2	0.2		1.78
	0.2	0.4		2.67
	0.2	0.5		2.89
	0.2	0.6		2.89
	0.2	0.8		3.01
	0.2	1.0		3.01
(slow reaction)	0.1			0.059
	0.2			0.124
	0.4			0.267
	0.6			0.465
	0.8			0.55
	0.2	0.1		0.11
	0.2	0.2		0.11
	0.2	0.4		0.12
	0.2	0.5		0.10
	0.2	0.6		0.11
	0.2	0.8		0.12
	0.2		0.0	0.084
	0.2		0.1	0.114
	0.2		0.2	0.124
	0.2		0.4	0.154
	0.2		0.5	0.169
$[IrCl(cod)(PMePh_2)]$	0.05			1.36
	0.1			4.81
	0.2			19.25
	0.4			44.14
	0.5			76.15
	0.6			93.02
	0.8			133.26
	1.0			187.3
$[Ir(cod)(PEtPh_2)_2]^+$				
(fast reaction)	0.05			0.3
	0.1			0.924
	0.2			5.29
	0.4			24.93
	0.5			38.08
	0.6			57.27
	0.8			93.65
	1.0			138.6
	0.2	0.0		14.14
	0.2	0.05		20.38

TABLE 3 (*Continued*)

Complex	[HCl]	[HClO$_4$]	[LiCl]	$k_{obs.}$
		mol dm^{-3}		s^{-1}
	0.2	0.1		21.66
	0.2	0.2		24.80
	0.2	0.4		31.50
	0.2	0.5		32.08
	0.2	0.6		33.0
	0.2	0.8		32.08
	0.2		0.0	14.14
	0.2		0.05	17.33
	0.2		0.1	23.90
	0.2		0.2	34.65
	0.2		0.4	55.89
	0.2		0.5	66.63
	0.2		0.6	78.75
	0.2		0.8	108.28
[IrCl(cod)(PEtPh$_2$)]	0.05			0.98
	0.1			4.2
	0.2			14.74
	0.4			37.26
	0.6			68.89
	0.8			103.43
	1.0			156.87

[a] [L] = 0 mol dm^{-3}. [b] [L] = 0.5×10^{-3} mol dm^{-3}. [c] [L] = 2.5×10^{-3} mol dm^{-3}. [d] [L] = 5×10^{-3} mol dm^{-3}. [e] [L] = 1×10^{-2} mol dm^{-3}. [f] [L] = 2×10^{-2} mol dm^{-3}.

K_1 is estimated to be $<10^{-5}$. Equilibrium (2) thus lies quite far to the left-hand side for the last three phosphines.

TABLE 4

Rate and equilibrium constants for the reactions in scheme (6) at 25 °C and I = 1 mol dm^{-3} in MeOH

Complex	From gradient	From intercept	Plot	Equation
[Ir(cod)(PPh$_3$)$_2$]$^+$	k_3K_2 = 16.8 dm^6 mol^{-2} s^{-1}	k_3K_2 = 18.5 dm^6 mol^{-2} s^{-1}	$(1/k_{obs.}) - k_{-3}$ against [L]	(11)
	k_3K_2 = 10.0 dm^6 mol^{-2} s^{-1}	k_{-3} = 0.49 s^{-1}	$k_{obs.}$ against [HCl]$_0^2$	(9)
[IrCl(cod)(PPh$_3$)]	k_3K_2 = 13.0 dm^6 mol^{-2} s^{-1}	k_{-3} = 0.69 s^{-1}	$k_{obs.}$ against [HCl]$_0^2$	(9)
	k_3K_2 = 24.4 dm^6 mol^{-2} s^{-1}	k_{-3} = 0.44 s^{-1}	$k_{obs.}$ against [H$^+$]	(9)
	k_3K_2 = 26.0 dm^6 mol^{-2} s^{-1}	k_{-3} = 0.42 s^{-1}	$k_{obs.}$ against [Cl$^-$]	(9)
[Ir(cod){PPh$_2$(OMe)}$_2$]$^+$	k_2K_1/[L] = 1.03 dm^6 mol^{-3} s^{-1}	k_{-2} = 0.028 s^{-1}	$k_{obs.}$ against [HCl]$_0^2$	(24)
(fast reaction)	k_2K_1/[L] = 0.7 dm^6 mol^{-3} s^{-1}	k_{-2} = 0.04 s^{-1}	$\frac{[Cl^-]}{k_{obs.} - k_2}$ against $\frac{1}{[Cl^-]}$	(23)
(slow reaction)	k_5K_4 = 0.139 dm^6 mol^{-2} s^{-1}		$k_{obs.}$ against [HCl]$_0^2$	(29)
	k_5K_4 = 0.28 dm^6 mol^{-2} s^{-1}		$k_{obs.}$ against [H$^+$]	(29)
	k_5K_4 = 0.22 dm^6 mol^{-2} s^{-1}		$1/k_{obs.}$ against 1/[Cl$^-$]	(28)
[Ir(cod)(PMePh$_2$)$_2$]$^+$	$k_3K_1K_2$/[L] = 73 dm^9 mol^{-3} s^{-1}	[L]/k_2K_1 = 0.006 mol^2 dm^{-6} s	[HCl]$_0^2$ /$k_{obs.}$ against 1/[HCl]$_0$	(20)
(fast reaction)	$k_3K_1K_2$/[L] = 150 dm^9 mol^{-3} s^{-1}		$k_{obs.}$ against [Cl$^-$]^2	(21)
	$k_3K_1K_2$/[L] = 140 dm^9 mol^{-3} s^{-1}	[L]/k_2K_1 = 0.005 2 mol^2 dm^{-6} s	$1/k_{obs.}$ against 1/[H$^+$]	(19)
(slow reaction)	k_4 = 0.74 dm^3 mol^{-1} s^{-1}		$k_{obs.}$ against [HCl]$_0$	(27)
	k_4 = 0.63 dm^3 mol^{-1} s^{-1}	K_1/k_4[L] = 3.75 s	$1/k_{obs.}$ against 1/[Cl$^-$]	(26)
[IrCl(cod)(PMePh$_2$)]	k_3K_2 = 600 dm^6 mol^{-2} s^{-1}	k_2 = 250 dm^3 mol^{-1} s^{-1}	[HCl]$_0$/$k_{obs.}$ against 1/[HCl]$_0$	(13)
[Ir(cod)(PEtPh$_2$)$_2$]$^+$	k_3K_2 = 526 dm^6 mol^{-2} s^{-1}	$k_3K_1K_2$/[L] = 1 298 dm^9 mol^{-3} s^{-1}	$\frac{[HCl]_0^2}{k_{obs.}} - \frac{[HCl]_0}{k_2}$ against $\frac{1}{[HCl]_0}$	(16)
	$k_3K_1K_2$/[L] = 3 571 dm^9 mol^{-3} s^{-1}	[L]/k_2K_1 = 0.000 8 mol^2 dm^{-6} s	$1/k_{obs.}$ against 1/[H$^+$]	(7)
	$k_3K_1K_2$/[L] = 3 846 dm^9 mol^{-3} s^{-1}	k_3K_2 = 610 dm^6 mol^{-2} s^{-1}	[Cl$^-$]/$k_{obs.}$ against 1/[Cl$^-$]^1	(18)
[IrCl(cod)(PEtPh$_2$)]	k_3K_2 = 476 dm^6 mol^{-2} s^{-1}	k_2 = 250 dm^3 mol^{-1} s^{-1}	[HCl]$_0$/$k_{obs.}$ against 1/[HCl]$_0$	(13)

Because of this equilibrium it is possible that any oxidative-addition involving the cations [Ir(cod)L$_2$]$^+$ may in fact occur *via* the neutral product [IrCl(cod)L] {explaining the formation of [IrHX$_2$(cod)L]} and hence reactions (3) were

$$[\mathrm{IrCl(cod)L}] + \mathrm{HCl} \xrightarrow{\text{methanol}} \tag{3}$$
$$(\mathrm{L} = \mathrm{PPh_3},\ \mathrm{PEtPh_2},\ \text{or}\ \mathrm{PMePh_2})$$

also studied. For L = PPh$_3$, reaction (3) produced a mixture of the starting material and the oxidised product [IrHCl$_2$(cod)(PPh$_3$)] indicating that these two species are in equilibrium. For L = PMePh$_2$ and PEtPh$_2$ the end products are presumably [IrHCl$_2$(cod)L], but they could not be isolated. For the oxidative-addition reaction (4)

$$[\mathrm{Ir(cod)L_2}]^+ + \mathrm{HCl} \xrightarrow{\text{methanol}} \tag{4}$$

when L = PPh$_3$ the end products were once again a mixture of [IrCl(cod)(PPh$_3$)] and [IrHCl$_2$(cod)(PPh$_3$)] and the empirical rate law is identical with that found for reaction (3). From this we imply that reaction (4) proceeds predominantly through [IrCl(cod)(PPh$_3$)]. When L = PEtPh$_2$, PMePh$_2$, or PPh$_2$(OMe) reaction (4) produced the salts [IrH(Cl)(cod)L$_2$]$^+$ and for the latter two ligands two consecutive reactions were observed. The observed rate constants and calculated rate and equilibrium constants are given in Tables 3 and 4 respectively and the empirical rate laws for all the reactions are given in Table 6.

The notation [HCl]$_0$ will be used throughout for the hydrogen-ion concentration in the absence of added LiCl or HClO$_4$. Since conductivity measurements have shown HCl to be extensively dissociated under the conditions used (HCl and HClO$_4$ reaction solutions were made up from aqueous Merck solutions, causing *ca.* 2% water to enter the reaction solutions), [H$^+$] = [Cl$^-$] $\simeq$ [HCl]$_0$. When LiCl or HClO$_4$ is added to the reaction solutions in order to vary [Cl$^-$] and [H$^+$] independently of one another the notations [H$^+$] ([Cl$^-$] constant) and [Cl$^-$] ([H$^+$] constant) will be used. In these cases [H$^+$] $\simeq$ [HCl] + [HClO$_4$], [Cl$^-$] $\simeq$ [HCl] + [LiCl], and therefore [H$^+$] $\neq$ [Cl$^-$] {under anaerobic conditions no reaction was observed between [Ir(cod)L$_2$]$^+$ or [IrCl(cod)L] and HClO$_4$}.

DISCUSSION

From the kinetic results two mechanisms can be ruled out. First, the absence of any variations in the rates of reactions on adding the radical trap hydroquinone precludes the highly improbable possibility of radical intermediates. Secondly, if HCl was added to the complex as a molecule the dependences of the reaction rate on [H$^+$]

TABLE 5

Visible peaks (λ/nm [a]) monitored during kinetic runs in methanol

Complex	L: PPh$_3$	PEtPh$_2$	PMePh$_2$	PPh$_2$(OMe)
[IrCl(cod)L]	444	442	442	*b*
	(1 740)	(907)	(1 393)	
[Ir(cod)L$_2$]$^+$	491	492	493	492
	(1 967)	(2 108)	(2 540)	(2 945)
[IrH(Cl)(cod)L$_2$]$^+$	*b*	*c*	*c*	*c*
[IrHCl$_2$(cod)L]	*c*	*b*	*b*	*b*

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] This complex could not be isolated. [c] Characterless visible spectrum.

and [Cl⁻] would be exactly the same, as variations in either [H⁺] or [Cl⁻] will vary [HCl] *via* equilibrium (5).

$$\mathrm{H}^+ + \mathrm{Cl}^- \rightleftharpoons \mathrm{HCl} \qquad (5)$$

Thus the difference in dependences on [H⁺] and on [Cl⁻] observed (Table 6) cannot be explained by a one-step concerted HCl addition. In fact the independence of [H⁺] points to a mechanism involving initial Cl⁻ attack on the iridium, and all the observed data could be explained by this mechanism taking into account equilibrium (2).

The following reaction scheme can be envisaged:

$$\begin{tikzcd}
{[\mathrm{Ir(cod)L_2}]^+ + \mathrm{Cl}^-} \arrow[r, shift left, "K_1"] \arrow[d, shift right, "{K_4,\mathrm{Cl}^-}"'] & {[\mathrm{IrCl(cod)L}] + \mathrm{L}} \arrow[l, shift left, "\mathrm{fast}"] \arrow[d, shift right, "{K_2,\mathrm{Cl}^-}"'] \\
{[\mathrm{IrCl(cod)L_2}]} \arrow[u, shift right, "-\mathrm{Cl}^-"'] \arrow[d, "\mathrm{H}^+"', "k_5"] & {[\mathrm{IrCl_2(cod)L}]^-} \arrow[u, shift right, "-\mathrm{Cl}^-"'] \arrow[d, shift right, "{k_3,\mathrm{H}^+}"'] \\
{[\mathrm{IrH(Cl)(cod)L_2}]^+} & {[\mathrm{IrHCl_2(cod)L}]} \arrow[u, shift right, "{-\mathrm{H}^+, k_{-3}}"']
\end{tikzcd} \qquad (6)$$

When L = PPh₃ only one reaction is observed and the only product isolated is [IrHCl₂(cod)(PPh₃)] and hence the reaction most probably proceeds through the paths described by K_1, K_2, and k_3. For L = PMePh₂ and PPh₂(OMe) two reactions are observed but the only products isolated are the salts containing the cations $[\mathrm{IrH(Cl)(cod)L_2}]^+$. It is possible in these cases that the initial formation of the kinetically favoured [IrHCl₂(cod)L] product is followed by a slower second reaction to the thermodynamically more favoured $[\mathrm{IrH(Cl)(cod)L_2}]^+$ *via* paths described by K_4 and k_5. Since the magnitude of the optical-density change of this second reaction decreases with increasing [HCl], an equilibrium (K_3) is probably established from the first reaction [K_1 and K_2, scheme (6)] causing some $[\mathrm{Ir(cod)L_2}]^+$ to be left in solution. Even though this equilibrium (K_3) lies well over to [IrHCl₂(cod)L], we were still able to detect the second reaction because of the very large absorption coefficients of the visible peaks of $[\mathrm{Ir(cod)L_2}]^+$ (see Table 5). With L = PEtPh₂ only one reaction is observed and the only product isolated is a salt containing the cation $[\mathrm{IrH(Cl)(cod)(PEtPh_2)_2}]^+$. It is hence necessary to assume that the equilibrium (K_3) for the oxidative-addition reaction involving this ligand lies so far over to [IrHCl₂(cod)(PEtPh₂)] that the second reaction is not observed because [IrHCl₂(cod)L] is colourless. With this approach it is now possible to explain all the observed data. However, due to the complexity of the data all the reactions studied will be discussed separately.

TABLE 6

Empirical rate equations established for reactions (1) and (3) with variation of [HCl], [Cl⁻], and [H⁺]

		L			
Complex	Substrate parameter varied	PPh₃	PEtPh₂	PMePh₂	PPh₂(OMe)
$[\mathrm{Ir(cod)L_2}]^+$ (fast reaction)	$[\mathrm{HCl}]_0$	$k_{\mathrm{obs.}} = C_1 + C_2[\mathrm{HCl}]_0^2$	$\frac{[\mathrm{HCl}]_0^2}{k_{\mathrm{obs.}}} - \frac{[\mathrm{HCl}]_0}{C_{14}} = C_{15} + \frac{C_{16}}{[\mathrm{HCl}]_0}$	$\frac{[\mathrm{HCl}]_0^2}{k_{\mathrm{obs.}}} = C_7 + \frac{C_8}{[\mathrm{HCl}]_0}$	$k_{\mathrm{obs.}} = C_{12} + C_{13}[\mathrm{HCl}]_0^2$
	[H⁺] (HClO₄ added)		$\frac{1}{k_{\mathrm{obs.}}} = C_{19} + \frac{C_{20}}{[\mathrm{H}^+]}$	$\frac{1}{k_{\mathrm{obs.}}} = C_{10} + \frac{C_{11}}{[\mathrm{H}^+]}$	independent
	[Cl⁻] (LiCl added)		$\frac{[\mathrm{Cl}^-]}{k_{\mathrm{obs.}}} = C_{17} + \frac{C_{18}}{[\mathrm{Cl}^-]}$	$k_{\mathrm{obs.}}\cdot\ C_9\,[\mathrm{Cl}^-]^2$	$\frac{[\mathrm{Cl}^-]}{k_{\mathrm{obs.}} - C_{12}} = \frac{1}{C_{13}[\mathrm{Cl}^-]}$
	[L]	$\frac{1}{k_{\mathrm{obs.}} - C_1} = C_4 + C_5[\mathrm{L}]$			
(slow reaction)	$[\mathrm{HCl}]_0$			$k_{\mathrm{obs.}} = C_{21}[\mathrm{HCl}]_0$	$k_{\mathrm{obs.}} = C_{23}[\mathrm{HCl}]_0^2$
	[H⁺] (HClO₄ added)			independent	$k_{\mathrm{obs.}} = C_{26}[\mathrm{H}^+]$
	[Cl⁻] (LiCl added)			$\frac{1}{k_{\mathrm{obs.}}} = C_{22} + \frac{1}{C_{21}[\mathrm{Cl}^-]}$	$\frac{1}{k_{\mathrm{obs.}}} = C_{24} + \frac{C_{25}}{[\mathrm{Cl}^-]}$
[IrCl(cod)L]	$[\mathrm{HCl}]_0$	$k_{\mathrm{obs.}} = C_1 + C_2[\mathrm{HCl}]_0^2$	$\frac{[\mathrm{HCl}]_0}{k_{\mathrm{obs.}}} = \frac{1}{C_{14}} + \frac{C_{29}}{[\mathrm{HCl}]_0}$	$\frac{[\mathrm{HCl}]_0}{k_{\mathrm{obs.}}} = C_{27} + \frac{C_{28}}{[\mathrm{HCl}]_0}$	
	[H⁺] (HClO₄ added)	$k_{\mathrm{obs.}} = C_1 + C_3[\mathrm{H}^+]$			
	[Cl⁻] (LiCl added)	$k_{\mathrm{obs.}} = C_1 + C_3[\mathrm{Cl}^-]$			

C is a constant.

(1) *The Addition of* HCl *to* $[\mathrm{Ir(cod)(PPh_3)_2}]^+$ *and* [IrCl(cod)(PPh₃)].—Since [IrCl(cod)(PPh₃)] and [IrHCl₂(cod)(PPh₃)] are in equilibrium and only one reaction is observed the reaction scheme (7) is proposed. The rate equation for this reaction scheme is (8) and, since $K_2 = 2 \times 10^{-2}$, $K_2[\mathrm{Cl}^-] \ll 1$, which simplifies (8) to (9).

$$[\mathrm{IrCl(cod)(PPh_3)}] \underset{-\mathrm{Cl}^-}{\overset{K_2,\,\mathrm{Cl}^-}{\rightleftharpoons}} [\mathrm{IrCl_2(cod)(PPh_3)}]^- \underset{k_{-3},\,-\mathrm{H}^+}{\overset{k_3,\,\mathrm{H}^+}{\rightleftharpoons}} [\mathrm{IrHCl_2(cod)(PPh_3)}] \qquad (7)$$

$$k_{\mathrm{obs.}} = \frac{k_3K_2[\mathrm{H}^+][\mathrm{Cl}^-]}{1 + K_2[\mathrm{Cl}^-]} + k_{-3} \qquad (8)$$

$$k_{\mathrm{obs.}} = k_3K_2[\mathrm{H}^+][\mathrm{Cl}^-] + k_{-3} \qquad (9)$$

In the absence of LiCl or HClO₄ in the reaction solution when $[\mathrm{HCl}]_0 \simeq [\mathrm{H}^+] = [\mathrm{Cl}^-]$, or on adding either LiCl or HClO₄ when $[\mathrm{H}^+] \neq [\mathrm{Cl}^-]$, equation (9) can explain both the second-order dependence on $[\mathrm{HCl}]_0$ in the first case and the linear dependence on [H⁺] and [Cl⁻] in the second (Table 6). The k_3K_2 and k_{-3} values calculated from the different kinetic plots are in relatively good agreement (Table 4).

When $[\mathrm{Ir(cod)(PPh_3)_2}]^+$ is used as the starting complex in solution, equilibrium (2) has to be added to scheme (7) as a pre-equilibrium, and the rate equation now becomes (10). Assuming that the term $K_1K_2[\mathrm{Cl^-}]^2$ is very small,

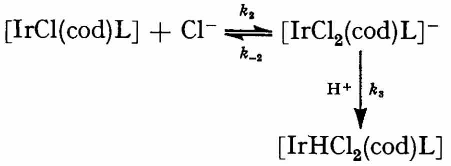
$$k_{\mathrm{obs.}} = \frac{k_3K_1K_2[\mathrm{H^+}][\mathrm{Cl^-}]^2}{[\mathrm{PPh_3}] + K_1[\mathrm{Cl^-}] + K_1K_2[\mathrm{Cl^-}]^2} + k_{-3} \quad (10)$$

$$\frac{1}{k_{\mathrm{obs.}} - k_{-3}} = \frac{[\mathrm{PPh_3}]}{k_3K_1K_2[\mathrm{H^+}][\mathrm{Cl^-}]} + \frac{1}{k_3K_2[\mathrm{H^+}][\mathrm{Cl^-}]} \quad (11)$$

(10) can be rewritten as (11) which, in the case of the reaction performed with $\mathrm{PPh_3}$ added to the reaction solution, fits the empirical rate equation (Table 6). Now, using the known constants k_{-3} and K_1 the calculation of k_3K_2 is in agreement within experimental error with values previously calculated (Table 4). In the absence of added $\mathrm{PPh_3}$ and thus with $[\mathrm{PPh_3}] \ll K_1[\mathrm{Cl^-}]$, equation (10) simplifies to (9), once again accounting for the observed $[\mathrm{HCl}]_0^2$ dependence.

It is also possible to explain the above results by a mechanism whereby the $\mathrm{H^+}$ attack precedes the $\mathrm{Cl^-}$ addition and by treating the intermediate $[\mathrm{IrH(Cl)(cod)(PPh_3)}]^+$ as a steady state. However, since it can be shown that for all the other phosphines used in this study that $\mathrm{Cl^-}$ addition precedes the $\mathrm{H^+}$ oxidation, we assume that this is also the case for $\mathrm{PPh_3}$.

(2) *The Reaction of* $[\mathrm{IrCl(cod)L}]$ ($\mathrm{L = PMePh_2}$ *or* $\mathrm{PEtPh_2}$) *with Hydrochloric Acid.*—As can be seen from the empirical rate equations in Table 6, the complexes containing either $\mathrm{PMePh_2}$ or $\mathrm{PEtPh_2}$ displayed the same behaviour. This can be accommodated by the reaction scheme (12) if $[\mathrm{IrCl_2(cod)L}]^-$ is considered to be in a steady state. The rate equation derived from this scheme is (13), and since $[\mathrm{HCl}]_0 \simeq [\mathrm{H^+}] = [\mathrm{Cl^-}]$ it is in



$$\begin{tikzcd}
{[\mathrm{IrCl(cod)L}] + \mathrm{Cl^-}} \arrow[r, shift left, "k_2"] & {[\mathrm{IrCl_2(cod)L}]^-} \arrow[l, shift left, "k_{-2}"] \arrow[d, "\mathrm{H^+}"', "k_3"] \\
 & {[\mathrm{IrHCl_2(cod)L}]}
\end{tikzcd}$$

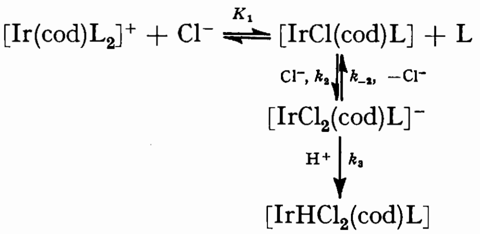
(12)

$$k_{\mathrm{obs.}} = \frac{k_2k_3[\mathrm{H^+}][\mathrm{Cl^-}]}{k_{-2} + k_3[\mathrm{H^+}]} \quad (13)$$

perfect agreement with the empirical rate equation (Table 6).

These limiting $[\mathrm{H^+}]$ and linear $[\mathrm{Cl^-}]$ dependences also conform with a reaction scheme in which $\mathrm{H^+}$ oxidises $[\mathrm{IrCl(cod)L}]$ to establish an equilibrium between $[\mathrm{IrCl(cod)L}]$ and $[\mathrm{IrH(Cl)(cod)L}]^+$ {which must be saturated towards $[\mathrm{IrH(Cl)(cod)L}]^+$ at high $[\mathrm{H^+}]$ in order to yield a limiting dependence on $[\mathrm{H^+}]$} followed by the $\mathrm{Cl^-}$ addition. However, since $\mathrm{HClO_4}$ does not react with $[\mathrm{IrCl(cod)L}]$ this possibility can be discarded. Also, it is not very likely that a stable five-co-ordinate iridium(III) complex will exist in large quantities in solution.

(3) *Oxidative-addition Reactions of* $[\mathrm{Ir(cod)L_2}]^+$ [$\mathrm{L} = \mathrm{PEtPh_2}$, $\mathrm{PMePh_2}$, *or* $\mathrm{PPh_2(OMe)}$] *with Hydrochloric Acid.*—(*a*) *The fast reaction.* (*i*) *For* $\mathrm{L = PEtPh_2}$. If it is assumed that two reactions occur, with the second slow one not detectable and the observed reaction the same as the fast reaction observed for $\mathrm{L = PMePh_2}$ and $\mathrm{PPh_2(OMe)}$, then the data obtained for the fast reaction can be explained by the reaction scheme (14). The rate equation derived from this scheme, taking into account that $[\mathrm{IrCl_2(cod)L}]^-$ is in a steady state, is (15) and can be



$$\begin{tikzcd}
{[\mathrm{Ir(cod)L_2}]^+ + \mathrm{Cl^-}} \arrow[r, shift left, "K_1"] & {[\mathrm{IrCl(cod)L}] + \mathrm{L}} \arrow[l, shift left] \arrow[d, shift right, "\mathrm{Cl^-},\ k_2"'] \\
 & {[\mathrm{IrCl_2(cod)L}]^-} \arrow[u, shift right, "k_{-2},\ -\mathrm{Cl^-}"'] \arrow[d, "\mathrm{H^+}"', "k_3"] \\
 & {[\mathrm{IrHCl_2(cod)L}]}
\end{tikzcd}$$

(14)

$$k_{\mathrm{obs.}} = \frac{k_2k_3K_1[\mathrm{H^+}][\mathrm{Cl^-}]^2}{(k_3[\mathrm{H^+}] + k_{-2})([\mathrm{L}] + K_1[\mathrm{Cl^-}])} \quad (15)$$

approximated to a form that fits all the empirical rate equations (Table 6). For instance, with HCl additions alone to $[\mathrm{Ir(cod)L_2}]^+$, because $[\mathrm{HCl}]_0 \simeq [\mathrm{H^+}] = [\mathrm{Cl^-}]$, equation (15) reduces to (16) which now fits the empirical

$$\frac{[\mathrm{HCl}]_0^2}{k_{\mathrm{obs.}}} - \frac{[\mathrm{HCl}]_0}{k_2} = \frac{[\mathrm{L}]}{k_3K_1K_2[\mathrm{HCl}]_0} + \frac{1}{k_3K_2} + \frac{[\mathrm{L}]}{k_2K_1} \quad (16)$$

rate equation in Table 6. When $\mathrm{HClO_4}$ is added to the reaction solution with [HCl] constant at 0.02 mol dm^{-3} then $[\mathrm{L}] \gg K_1[\mathrm{Cl^-}]$ in the term $([\mathrm{L}] + K_1[\mathrm{Cl^-}])$ from (15) and hence equation (15) reduces to (17) giving the

$$\frac{1}{k_{\mathrm{obs.}}} = \frac{[\mathrm{L}]}{K_2K_1[\mathrm{Cl^-}]^2} + \frac{[\mathrm{L}]}{k_3K_2K_1[\mathrm{H^+}][\mathrm{Cl^-}]^2} \quad (17)$$

empirical rate equation in Table 6. In the case of addition of LiCl in the absence of $\mathrm{HClO_4}$ the $K_1[\mathrm{Cl^-}]$ value now contributes more to the $([\mathrm{L}] + K_1[\mathrm{Cl^-}])$ term in equation (15) but at the lower $[\mathrm{H^+}]$ it appears that $k_3[\mathrm{H^+}] \ll k_{-2}$ and equation (15) becomes (18), explaining

$$\frac{[\mathrm{Cl^-}]}{k_{\mathrm{obs.}}} = \frac{[\mathrm{L}]}{k_3K_1K_2[\mathrm{H^+}][\mathrm{Cl^-}]} + \frac{1}{k_3K_2[\mathrm{H^+}]} \quad (18)$$

the observed empirical rate law. The combinations of rate and equilibrium constants that were calculated from the data in Table 3 are, considering the complexity of the system, in relatively good agreement not only with the values from addition reactions of $[\mathrm{Ir(cod)(PEtPh_2)_2}]^+$ but also with the constants calculated from results obtained with $[\mathrm{IrCl(cod)(PEtPh_2)}]$ as starting material. Furthermore, the k_2 value obtained from the reactions of $[\mathrm{IrCl(cod)(PEtPh_2)}]$, when used to plot a graph of $([\mathrm{HCl}]_0^2/k_{\mathrm{obs.}} - [\mathrm{HCl}]_0/k_2)$ against $1/[\mathrm{HCl}]_0$, yielded comparable values for the relevant combinations of constants in Table 4. This thus confirms the proposed mechanisms for the first fast reaction as being the formation of $[\mathrm{IrHCl_2(cod)(PEtPh_2)}]$.

(*ii*) *For* $L = PMePh_2$. Once again reaction scheme (14) can explain all the observed data by approximating equation (15). The equilibrium constant K_1 for reaction (2) ($L = PMePh_2$) is *ca.* 10^{-5}, therefore $[IrCl(cod)L][L]/[Ir(cod)L_2^+][Cl^-] = 10^{-5}$ and, since $[IrCl(cod)L] = [L]$, then $[L]^2 = 10^{-5}[Ir(cod)L_2^+][Cl^-]$; $[Ir(cod)L_2^+] \simeq 5 \times 10^{-3}$ mol dm^{-3} and the highest $[Cl^-] = 1$ mol dm^{-3}, therefore $[L] \simeq 2.2 \times 10^{-4}$ mol dm^{-3} while $K_1[Cl^-]$ is at the most 10^{-5} mol dm^{-3}. The approximation that $[L] \gg K_1[Cl^-]$ can thus be employed for equation (15) which then becomes (19) or (20). With

$$k_{obs.} = \frac{k_2k_3K_1[H^+][Cl^-]^2}{k_3[H^+][L] + k_{-2}[L]} \tag{19}$$

$$\frac{[Cl^-]^2}{k_{obs.}} = \frac{[L]}{k_2K_1} + \frac{[L]}{k_3K_1K_2[H^+]} \tag{20}$$

only HCl present in solution, $[HCl]_0 \simeq [H^+] = [Cl^-]$ and equation (20) can explain the empirical rate equation in Table 6. The limiting dependence of $[H^+]$ (when $HClO_4$ is added) implies that, at low $[H^+]$, $k_3[H^+][L] \ll k_{-2}[L]$ and therefore a linear dependence on $[H^+]$ is found, whereas, at high $[H^+]$, $k_3[H^+][L] \gg k_{-2}[L]$ and the rate is independent of $[H^+]$. With added LiCl $\{[H^+]$ is thus low making $k_3[H^+][L] \ll k_{-2}[L]\}$ rate equation (15) becomes (21), which fits the empirical rate

$$k_{obs.} = k_3K_1K_2[H^+][Cl^-]^2/[L] \tag{21}$$

equation in Table 6. The constants calculated from the data in Table 3 using equations (19)—(21) are in good agreement (Table 4).

(*iii*) *For* $L = PPh_2(OMe)$. If one assumes in this case that $k_3[H^+] \gg k_{-2}$ [equation (15)], the rate equation (22) can be derived from reaction scheme (14) (for the reaction in equilibrium). Since K_1 is apparently

$$k_{obs.} = \frac{k_2K_1[Cl^-]^2}{[L] + K_1[Cl^-]} + k_{-2} \tag{22}$$

slightly larger than that for $L = PMePh_2$, the value for the $K_1[Cl^-]$ term becomes comparable with the [L] term, especially when LiCl is added, and equation (22) can be written as (23) which conforms to the limiting

$$\frac{[Cl^-]}{k_{obs.} - k_{-2}} = \frac{[L]}{k_2K_1[Cl^-]} + \frac{1}{k_2} \tag{23}$$

dependence found for $[Cl^-]$ (Table 6). At higher $[H^+]$ or $[HCl]_0$ values the equilibria in scheme (14) will lie further to the right-hand side and therefore [L] will increase so that $[L] \gg K_1[Cl^-]$ (especially when no LiCl is added). Equation (22) can then be simplified to (24)

$$k_{obs.} = \frac{k_2K_1[Cl^-]^2}{[L]} + k_{-2} \tag{24}$$

which explains the second-order dependence on $[HCl]_0$ when no $HClO_4$ or LiCl is added ($[HCl]_0 \simeq [H^+] = [Cl^-]$), as well as the independence of $[H^+]$. The calcuated values for the combination of constants given in Table 4 are in reasonable agreement.

Once again the data for $L = PEtPh_2$, $PMePh_2$, and $PPh_2(OMe)$ can be explained by a pre-equilibrium between $[IrCl(cod)L]$ and $[IrH(Cl)(cod)L]^+$ followed by Cl^- addition, but since $HClO_4$ does not react with $[IrCl(cod)L]$ this is no longer a possibility.

(*b*) *Slow reaction.* (*i*) *For* $L = PMePh_2$. This second slow reaction is most probably the reverse of the kinetically favoured first fast reaction resulting in the slower formation of the thermodynamically more stable $[IrH(Cl)(cod)L_2]^+$ product, *e.g.* as in (25). Because there

$$\begin{tikzcd}
{[IrHCl_2(cod)L]} \arrow[r, shift left, "K_2K_3"] & {[IrCl(cod)L]} \arrow[l, shift left, "+H^+ + Cl^-"] \arrow[r, shift left, "+L"] & {[Ir(cod)L_2]^+ + Cl^-} \arrow[l, shift left, "-L, K_1"] \arrow[d, shift right, "Cl^-, k_4"'] & (25) \\
& {[IrH(Cl)(cod)L_2]^+} & {[IrCl(cod)L_2]} \arrow[l, "k_5", "H^+"'] \arrow[u, shift right, "k_{-4}, -Cl^-"'] &
\end{tikzcd}$$

is no $[H^+]$ dependence in this case, one can assume that k_5 is large and k_4 is the rate-determining step. Since K_2 will be very small, the terms containing this constant can be neglected in the rate equation derived from this reaction scheme. This will then approximate to (26)

$$k_{obs.} = \frac{k_4[L][Cl^-]}{K_1[Cl^-] + [L]} \tag{26}$$

$$k_{obs.} = k_4[Cl^-] \tag{27}$$

and, since $K_1[Cl^-] \ll [L]$, (26) will approximate to (27) which explains the empirical rate equation (Table 6) ($[HCl]_0 \simeq [Cl^-] = [H^+]$ with no added LiCl or $HClO_4$), as well as the independence of $[H^+]$ (when $HClO_4$ is added). When LiCl is added to the reaction solution the $[H^+]$ is low and the equilibrium in scheme (14) does not lie as far over to the right-hand side, resulting in a smaller [L], and therefore the approximation $K_1[Cl^-] \ll [L]$ is most probably no longer valid. Equation (26) can thus explain the limiting dependence on $[Cl^-]$ in Table 6. The k_4 values of 0.74 and 0.63 dm^3 mol^{-1} s^{-1} are within experimental error (Table 4).

(*ii*) *For* $L = PPh_2(OMe)$. The rate equation (28) can

$$k_{obs.} = \frac{k_5K_4[H^+][Cl^-][L]}{K_1[Cl^-] + [L]} \tag{28}$$

be derived from reaction scheme (25) if route k_5 is taken as the rate-determining step. As was the case with the fast reaction for $PPh_2(OMe)$, [L] becomes much larger than $K_1[Cl^-]$ at high $[H^+]$ and therefore equation (28) simplifies to (29), explaining the $[HCl]_0{}^2$ dependence

$$k_{obs.} = k_5K_4[H^+][Cl^-] \tag{29}$$

($[H^+] = [Cl^-] \simeq [HCl]_0$) and direct $[H^+]$ dependence ($[H^+] \neq [Cl^-]$) of the empirical rate equation in Table 6. At lower $[H^+]$ the rate equation (28) does not simplify to (29) but fully conforms with the observed rate law shown in Table 6 for the $[Cl^-]$ dependence when LiCl is added.

Conclusions.—From the data presented here it appears that the oxidative-addition of HCl to [IrCl(cod)L] and $[Ir(cod)L_2]^+$ complies with a mechanism whereby the chloride ion first attacks the metal-atom centre and this is followed by rapid protonation of the resulting five-co-ordinate intermediate. It is significant that halide attack occurs on both the cationic and neutral iridium(I) complexes and it hence seems unlikely that this mechanistic route is controlled simply by the charge on the iridium in the cationic complexes used here. This is in complete contrast to the findings from HCl additions to *cis*-$[PtR_2(PEt_3)_2]$ and for the proposals for the systems $ML_4 + HCl$ (M = Ni [7] or Pt,[6] L = one of a series of phosphines). It is of interest to note that the supposition [8] that anionic species formed as intermediates in the catalytic reaction involving halide ions, MeI, and $[RhCl(CO)L_2]$ *via* neutral ligand displacement could more reasonably be formed as the five-co-ordinate anions $[RhCl_2(CO)L_2]^-$. This would greatly increase the nucleophilic character of the metal atom, facilitating a more rapid attack on the methyl of the MeI, and would also account for the total absence of *trans*-bromo-complexes from oxidative-addition reactions of BuBr with rhodium macrocycles performed in the presence of LiCl.[4] It is also pertinent to note that increases in the rate constants observed [3] on increasing the polarity of the solvent in reactions of MeI with $[PtPh_2(bipy)]$ may be explained by a greater tendency to form intermediate five-co-ordinate solvolysed species as the donor properties of the solvent are increased. Finally, the formation of the salts [2; L = $PPh_2(OMe)$, $PMePh_2$, or $PEtPh_2$] and the neutral product (3; L = PPh_3) by stoicheiometric additions of HX (X = Cl, Br, or I) to (1) can only be interpreted in terms of ligand-size effects controlling the composition of the product formed and not the electronic properties of the ligands involved. Also, we feel that the formation of the products (3; L = $PMePh_2$ or $PEtPh_2$) with an excess of HX (X = Br or I) is a function of the size of X^- rather than its electronic properties.

EXPERIMENTAL

The ^1H n.m.r. spectra were recorded on a Varian A60 and the i.r. spectra on a Perkin-Elmer 457 grating spectrophotometer. Melting points were determined on a Kofler hot-stage apparatus and are corrected. All the ligands were obtained commercially. The reactions were carried out at room temperature in acetone solutions (15 cm^3). The solution was concentrated under reduced pressure, ethanol added, and the resulting precipitate recrystallised from dichloromethane–ethanol to give the required products. All the complexes reported were prepared in this manner unless otherwise stated. The yields were all greater than 50%.

The kinetic runs were carried out on a Durrum stopped-flow apparatus by following the disappearance of the visible peaks of the $[Ir(cod)L_2]^+$ or [IrCl(cod)L] complexes. These peaks and their absorption coefficients are given in Table 5. The reactions were run under pseudo-zero-order conditions with respect to HCl and the ionic strength was maintained constant with $Li[ClO_4]$. The $[Cl^-]$ and $[H^+]$ were varied by addition of LiCl and $HClO_4$ respectively. No reaction, other than the formation of [IrCl(cod)L], was observed on adding LiCl or $HClO_4$ to solutions containing $[Ir(cod)L_2]^+$. The reactions were studied under nitrogen because the complexes were sensitive to air. AnalaR methanol (E. Merck), and hydrochloric and perchloric acid solutions (Titrisol) were used.

Preparation of Complexes.—*Chloro*(η-*cyclo-octa*-1,5-*diene*)-*hydridobis*(*methoxydiphenylphosphine*)*iridium*(III) *hexafluorophosphate*. This complex was prepared as white prisms by treating $[Ir(cod)\{PPh_2(OMe)\}_2][PF_6]$ (0.8 g) with excess of HCl (32%, 0.6 cm^3). Similarly prepared from their appropriate salts and concentrated acids were $[IrHBr(cod)\{PPh_2(OMe)\}_2][PF_6]$, $[IrH(I)(cod)\{PPh_2(OMe)\}_2][PF_6]$, $[IrH(Cl)(cod)(PMePh_2)_2][PF_6]$, $[IrH(Cl)(cod)(PEtPh_2)_2][BPh_4]$, and $[IrH(Br)(cod)(PEtPh_2)_2][PF_6]$.

Bromo(η-*cyclo-octa*-1,5-*diene*)*hydridobis*(*methyldiphenylphosphine*)*iridium*(III) *hexafluorophosphate*. This complex was prepared as white needles by dropwise addition of a solution of HBr (48%, 0.5 cm^3) in ethanol (30 cm^3) to $[Ir(cod)(PMePh_2)_2][PF_6]$ (0.8 g) until the solution changed from red to colourless. Similarly prepared was $[IrH(I)(cod)(PMePh_2)_2][PF_6]$ from $[Ir(cod)(PMePh_2)_2][PF_6]$ and a solution of HI (67%) in ethanol.

Dibromo(η-*cyclo-octa*-1,5-*diene*)*hydrido*(*methyldiphenylphosphine*)*iridium*(III). This complex was prepared as off-white prisms from $[Ir(cod)(PMePh_2)_2][PF_6]$ (0.8 g) and excess of HBr (48%, 0.6 cm^3). Similarly prepared were $[IrHI_2(cod)(PMePh_2)]$, $[IrHCl_2(cod)(PPh_3)]$, $[IrHBr_2(cod)(PPh_3)]$, $[IrHI_2(cod)(PPh_3)]$, and $[IrHI_2(cod)(PEtPh_2)]$.

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