Kinetic and Other Studies on Oxidative Addition Reactions of Iridium Phosphine Complexes of the Type *trans*-$[IrCl(CO)(PMe_2R)_2]$ (R = Ph, *o*-$MeO{\cdot}C_6H_4$, or *p*-$MeO{\cdot}C_6H_4$)

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Oxidative addition reactions of the new complexes *trans*-$[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$ and *trans*-$[IrCl(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$ have been compared with those of *trans*-$[IrCl(CO)(PMe_2Ph)_2]$; the $PMe_2(o\text{-}MeOC_6H_4)$ complex reacted much faster than the other two. Activation parameters have been calculated from kinetic studies of the reactions of the three complexes with methyl iodide in toluene. All three complexes give similarly large negative $\Delta S^{\ddagger}$ values and the $\Delta H^{\ddagger}$ value for the $PMe_2(o\text{-}MeOC_6H_4)$ complex is considerably less by (18·8 kJ mol^{-1}) than that for the PMe_2Ph complex. This difference is interpreted in terms of a direct electronic interaction between the methoxyl oxygen and the iridium; this type of electronic effect has not been observed previously in oxidative addition reactions. The reactions of the three complexes with acetic acid and with benzoic acid have been compared. N.m.r. and i.r. data are given.

OXIDATIVE addition reactions are important in transition metal chemistry and catalysis; in this connection complexes of the type *trans*-$[IrCl(CO)L_2]$ (L = tertiary phosphine or tertiary arsine) have been extensively studied.[1-4] Although the electronic and steric factors which influence the reactivity of compounds of this type

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† No reprints available.

[1] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.

[2] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335.

[3] J. Halpern, *Accounts Chem. Res.*, 1968, **3**, 386.

[4] B. L. Shaw and R. E. Stainbank, *J. Chem. Soc.* (*A*), 1971, 3716, and references therein.

are not completely understood it is known that the iridium acts as a nucleophile and that the tendency to undergo oxidative addition is enhanced by (i) decreasing the bulk of the ligand L and (ii) increasing the donor power of L (and thereby increasing the electron density on the iridium). Thus with bulky ligands such as PBu_2^tEt or PBu_2^tPh, steric factors are dominant and these give very inert complexes.[4,5] With a series of *para*-substituted phenylphosphine ligands, $P(p\text{-}ZC_6H_4)_3$, the steric effects are presumably similar and differences in reactivity will be due almost entirely to electronic factors. Thus for the addition of methyl iodide to *trans*-$[IrCl(CO)\{P(p\text{-}ZC_6H_4)_3\}_2]$ the rates increase in the order Z = Cl < H < Me < OMe, which is the expected order of increasing donor power of the ligands $P(p\text{-}ZC_6H_4)_3$ to the iridium.[6] Similarly for the addition of methyl iodide to *trans*-$[RhCl(CO)\{P(p\text{-}ZC_6H_4)_3\}_2]$, giving $[RhICl(Me)CO\{P(p\text{-}ZC_6H_4)_3\}_2]$, the relative rate constants for Z = F, H, and OMe are 1·2, 5·5, and 44·3, respectively.[7] In most other cases the relative importance of steric and electronic effects on reactivity is not known; *e.g.* PMe_2Ph complexes are much more reactive than PPh_3 complexes because PMe_2Ph is both a better donor and less bulky than PPh_3.[8,9]

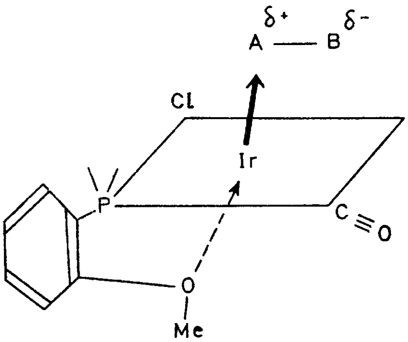


FIGURE 1 Showing how electron donation from the methoxyl oxygen would increase the nucleophilicity of the iridium and hence lower the activation energy of an oxidative addition reaction

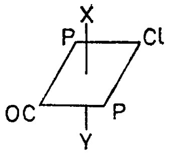
In all systems studied hitherto electronic effects of the tertiary phosphine on the reactivity of the iridium have operated *via* the phosphorus ligand atom. It occurred to us, however, that with a ligand such as *ortho*-methoxyphenyl(dimethyl)phosphine the ether oxygen would interact directly with the iridium and by electron donation lower the activation energy required for an oxidative addition reaction. Such donation and activation is shown schematically in Figure 1. An *X*-ray structural study of $[RhCl_3\{AsMe_2(o\text{-}MeOC_6H_4)\}_2]$ [10] has shown that the oxygen of an *ortho*-methoxy-group is co-ordinated to the rhodium. One would expect the interaction of an ether oxygen and iridium(I) to be weak but it should become stronger during the formation of the highly polar intermediates[11] believed to be involved in many oxidative addition reactions.

We have therefore made and studied the reactivity of *trans*-$[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$. An *ortho*-methoxy-group could increase electron density on the iridium *via* the phosphorus atom and also reduce reactivity by a steric effect. We have therefore also studied *trans*-$[IrCl(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$ and compared the reactivities of both complexes with that of *trans*-$[IrCl(CO)(PMe_2Ph)_2]$.

RESULTS AND DISCUSSION

The methods used to synthesise *o*- and *p*-methoxyphenyl(dimethyl)phosphine were based on standard procedures (see Experimental section). These phosphines were characterized as the quaternary salts with methyl iodide. *trans*-$[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$ was prepared *via* $[IrHCl_2(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$ in an analogous manner to the PMe_2Ph complexes.[7] We were unable to induce $[IrHCl_2(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$ to crystallize from a solution prepared by treating chloroiridic acid in ethanol with carbon monoxide and subsequent addition of the phosphine; however, further treatment of this solution with sodium methoxide readily gave the required *trans*-$[IrCl(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$. This with hydrochloric acid gave $[IrHCl_2(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$, configuration (I; X = H, Y = Cl). The configurations of the complexes follow from i.r. and ^1H n.m.r. data (see Tables 1 and 2).

As mentioned above we thought there might be enhanced reactivity of *trans*-$[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$ towards oxidative addition because of direct interaction between the oxygen of the *ortho*-methoxy-group and the iridium. Steric hindrance by the *ortho*-methoxy-group could also be important and cause formation of products of unusual stereochemistry. We therefore investigated oxidative addition towards a representative selection of electrophiles (X–Y), namely MeI, MeCOCl, PhCOCl, and $CH_2{:}CH{\cdot}CH_2Cl$, but found in all cases that an adduct of the usual type (I) formed readily. Thus with such



(I)

electrophiles *trans*-$[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$ and *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ give adducts of analogous stereochemistry. However from the rate of disappearance of the yellow colour of the iridium(I) species we observed qualitatively that the $PMe_2(o\text{-}MeOC_6H_4)$ complex reacted much faster than the PMe_2Ph complex.

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[5] B. L. Shaw and R. E. Stainbank, *J.C.S. Dalton*, 1972, 223.

[6] R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Amer. Chem. Soc.*, 1972, **94**, 7364.

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[9] M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, 1973, **7**, 195.

[10] R. Grazianai, G. Bombieri, L. Volponi, C. Panatteni, and R. J. H. Clark, *J. Chem. Soc.* (*A*), 1969, 1236.

[11] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.

The various adducts of configuration (I) were characterized by microanalyses and by i.r. and ^1H n.m.r. spectroscopy (see Experimental section and Tables). We also investigated by ^1H n.m.r. spectroscopy the addition of methyl iodide to *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ and to *trans*-$[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$. In both cases the addition went cleanly to give $[IrClI(Me)(CO)L_2]$ of configuration (I) only. In contrast *trans*-$[IrCl(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$ reacted rapidly with methyl iodide, allyl chloride, benzoyl chloride, and carbon tetrachloride in benzene or toluene to produce colourless solutions from which only oils could be isolated. The complexity of the ^1H n.m.r. spectra of these oils indicated that mixtures were present. Thus an ^1H n.m.r. study of the products from methyl iodide in benzene showed the major component (*ca.* 80%) to have two PMe 1 : 2 : 1 triplets, an IrMe 1 : 2 : 1 triplet, and an OMe singlet (Table 2), but a second IrMe resonance was also visible. The τ and *J* values indicated that the major component was probably $[IrClI(Me)(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2]$ of con-

TABLE 1

Configuration, % yield, m.p., microanalytical (%) (calc. values in parentheses), and i.r. (cm^{-1}) data for complexes of types *trans*-$[IrX(CO)L_2]$ and $[IrXYCl(CO)L_2]$, configuration (I)

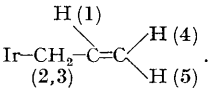
			Analysis				ν(CO)		ν(Ir–Cl)		
Complex [a]	Yield	M.p.(t/°C)	C	H	Cl	I	(in $CHCl_3$)	(in Nujol)	*trans*-CO	*trans*-X	Other bands (Nujol)
$[IrCl(CO)L_2]$	79	152—164 [b]	38·35 (38·55)	4·25 (4·45)	5·80 (6·00)		1940	1946	310		
$[IrHCl_2(CO)L_2]$	74	180—185 [b]	36·10 (36·2)	4·20 (4·35)	11·05 (11·25)		2036	2039 2020sh	302	255	ν(Ir–H) [c] 2188
$[IrClMe(CO)L_2],\frac{1}{2}C_6H_6$	90	220—230	35·70 (35·75)	4·10 (4·20)	4·65 (4·60)	16·65 (16·40)	2030	2035 2000sh	295		
$[IrCl_2(MeCO)(CO)L_2]$	76	189—210 [b]	37·85 (37·6)	4·45 (4·35)	10·70 (10·55)		2060	2045	311	232	ν(CO)acyl 1630
$[IrCl_2(PhCO)(CO)L_2]$	86	202—207 [b]	43·00 (42·6)	4·20 (4·25)	9·40 (9·70)		2060	2042	305	230 244	ν(CO)acyl 1622
$[IrCl_2(\sigma\text{-}C_3H_5)(CO)L_2]$	76	169—175 [b]	39·80 (39·5)	4·65 (4·65)	10·65 (10·60)		2030	2025	297	249	ν(C=C) 1620
$[IrCl(CO)L'_2]$	76	161—165 [b]	38·70 (38·55)	4·35 (4·45)	6·05 (6·00)		1930 [d]	1930 1892sh	307		
$[IrHCl_2(CO)L'_2]$	86	116—120 [b]	36·45 (36·1)	4·30 (4·20)	10·80 (11·05)		2035 [d]	2040 1990sh	302	258	ν(Ir–H) [d] 2180
$[IrI(CO)L'_2]$	91	108—112 [b]	33·60 (33·4)	3·90 (3·85)		18·45 (18·55)	1945 [d]	1932 1910sh			
$[IrI_2Me(CO)L'_2]$	75	168—171 [b]	29·40 (29·1)	3·45 (3·55)		30·50 (30·75)	2030 2040	2025 2035			

[a] L = $Me_2(o\text{-}MeO{\cdot}C_6H_4)P$, L′ = $Me_2(p\text{-}MeO{\cdot}C_6H_4)P$. [b] Decomp. [c] In chloroform. [d] In benzene.

TABLE 2

^1H N.m.r. data for complexes in $CDCl_3$ at 34° and 60 MHz, unless stated otherwise; τ values ±0·02 p.p.m., *J* values ±0·2 Hz; s = singlet, m = multiplet, t = 1 : 2 : 1 triplet, dd = double doublet, ddt = double doublet of triplets

	PMe_2		OMe	Other resonances		
Complex [a]	τ	$\lvert {}^2J(P\text{–}H) + {}^4J(P\text{–}H)\rvert$	τ	τ	*J*	Assignment [d]
$[IrCl(CO)L_2]$ [b]	7·92t	7·3	6·52s			
$[IrHCl_2(CO)L_2]$	7·88t	8·7	6·07s	27·14t	$^2J(P\text{–}H)$ 12·7	Ir–H
$[IrICl(Me)(CO)L_2],\frac{1}{2}C_6H_6$	7·62t	8·0		2·73s		C_6H_6
	7·87t	8·6	6·13s	9·49t	$^3J(P\text{–}H)$ 5·7	Ir–Me
$[IrCl_2(MeCO)(CO)L_2]$	7·85t	9·3	6·15s	8·68s		Ir–COMe
	7·92t	9·3				
$[IrCl_2(PhCO)(CO)L_2]$	7·81t	9·2	6·40s			
	7·98t	9·6				
$[IrCl_2(\sigma\text{-}C_3H_5)(CO)L_2]$ [c]	7·84t	8·5	6·16s	4·41m	$J_{1,5}$ 16·4	1
	7·97t	8·5		5·74dd	$J_{1,4}$ 9·8	4
					$J_{4,5}$ 2·5	
				5·91ddt	$J_{(2,3)5}$ 1·5	5
				7·85 [e]		2,3
$[IrCl(CO)L'_2]$ [b]	8·25t	7·0	6·77s			
$[IrHCl_2(CO)L'_2]$	7·97t	8·2	6·22s	26·7t	$^2J(P\text{–}H)$ 11·7	Ir–H
$[IrI(CO)L'_2]$ [b]	8·10t		6·79s			
$[IrI_2(Me)(CO)L'_2]$ [b]	7·65t	7·5	6·8s	8·9t	$^3J(P\text{–}H)$ 5·3	Ir–Me
	7·95t	8·4				
$[IrICl(Me)(CO)L'_2]$ [f]	7·86t	8·0	6·8s	9·0 [g]		Ir–Me [h]
	8·11t	8·1		9·15t	$^3J(P\text{–}H)$ 5·5	

[a] L = $Me_2(o\text{-}MeO{\cdot}C_6H_4)P$, L′ = $Me_2(p\text{-}MeO{\cdot}C_6H_4)P$. [b] In benzene. [c] At 90 MHz. [d] Labelling scheme  .

[e] Determined by double irradiation. [f] Prepared *in situ* by addition of MeI to a benzene solution of Ir^I complex. [g] Overlapping resonance at τ 9·15 [h] Due to two isomers.

figuration (I), and it seems likely that the second component was an isomer. Addition of a polar solvent such as deuteriochloroform or methanol to the reaction mixture caused conversion into the isomer of configuration (I); no other product was detected by ^1H n.m.r. spectroscopy. Treatment of *trans*-[IrI(CO)-$\{PMe_2(p\text{-}MeOC_6H_4)\}_2$] with methyl iodide followed by addition of a polar solvent (methanol or chloroform) gave [$IrI_2Me(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2$] of configuration (I).

TABLE 3

Summary of kinetic data for the addition of MeI to [$IrCl(CO)(PMe_2Ph)_2$]

Temp. (t/°C)	Initial concns.		10^3k_{obs}/ s^{-1}
	10[MeI]/ mol l^{-1}	$10^4[Ir^I]$/ mol l^{-1}	
1·4	3·07	2·5	2·61
	2·89	2·45	2·37
	2·18	2·53	1·86
	2·02	2·48	1·78
	1·10	2·53	0·99
	1·04	2·52	0·98
	0·00	2·54	0·05
15·7	2·87	2·46	6·80
	0·47	2·59	1·14
	1·37	2·52	3·46
	1·85	2·47	4·58
	2·57	2·49	6·26
	2·24	2·44	5·44
	0·00	2·46	0·08
25·3	0·00	2·63	0·14
	0·68	2·63	3·31
	0·31	2·70	1·60
	0·48	2·60	2·44
	0·45	2·58	2·27
	0·93	2·54	4·43
	1·08	2·47	5·05

TABLE 4

Summary of kinetic data for the addition of MeI to [$IrCl(CO)\{PMe_2(o\text{-}MeC_6H_4)\}_2$]

Temp. (°C)	Initial concns.		10^3k_{obs}/ s^{-1}
	10^3[MeI]/ mol l^{-1}	$10^4[Ir^I]$/ mol l^{-1}	
1·4	2·03	1·49	3·79
	2·03	2·48	3·50
	2·03	0·52	3·75
4·6	0·00	1·49	0·14
	3·00	1·50	6·70
	3·01	1·99	6·92
	2·00	2·01	4·26
	1·98	2·00	4·22
	2·50	1·98	5·37
	2·49	2·00	5·85
	1·50	1·51	3·45
15·7	0·00	1·01	0·23
	1·73	1·44	6·97
	1·82	1·50	7·03
	2·69	1·52	10·40
	1·46	1·51	5·39
	0·96	1·01	3·70
	1·69	1·50	6·05
	1·26	1·02	4·86
	2·07	1·47	7·37
	0·49	0·74	2·15
25·3	0·00	1·46	0·39
	1·42	1·60	7·74
	1·75	1·43	9·43
	1·02	1·02	5·35
	0·75	1·00	4·02
	1·24	1·01	6·60
	1·94	0·97	10·60
	0·46	0·70	3·16
	1·48	1·46	8·28

As mentioned above, methyl iodide was observed to add much faster to *trans*-[$IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2$] than to *trans*-[$IrCl(CO)(PMe_2Ph)_2$]. In an attempt to determine the factors responsible for this we have investigated the kinetics of these additions in toluene solution. The disappearance of the iridium(I) species was followed spectrophotometrically by observing the absorption maximum at *ca.* 430 nm (see Experimental section). If at least a 10-fold excess of methyl iodide was used, first-order plots of $\log(O.D_t - O.D_\infty)$ *vs.* time (t) were linear to more than 80% conversion (O.D = optical density). The reactions were first order in iridium(I) concentration, *i.e.* $-d[IrCl(CO)L_2]/dt = k_{obs}[IrCl(CO)L_2]$ where k_{obs} gives a good fit to the expression $k_{obs} = k_1 + k_2[MeI]$. Values of k_{obs} at temperatures in the range 1—26° are listed in the Tables and a typical dependence on methyl iodide concentration is illustrated in Figure 2. The rate constant k_1 for the process independent of methyl iodide contributed very little to k_{obs}, usually less than 3%. It may represent loss of iridium(I) species by reaction with traces of dissolved oxygen. Some oxidative additions to iridium(I) species seem to be radical in nature and are inhibited by radical scavengers.[12] We find however that the rate of addition of methyl iodide to *trans*-[$IrCl(CO)(PMe_2Ph)_2$] at 25·3° in the presence of *p*-t-butylcatechol (10 times the concentration of the complex) was the same (±5%) as in the absence of this efficient radical scavenger. We have also found that the addition of methyl iodide to *trans*-[$IrCl(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2$] is first-order in iridium complex concentration and $k_{obs} = k_1 + k_2[MeI]$ even though the major

TABLE 5

Summary of kinetic data for the addition of MeI to [$IrCl(CO)\{PMe_2(p\text{-}MeOC_6H_4)\}_2$]

Temp. (°C)	Initial concns.		10^3k_{obs}/ s^{-1}
	10^2[MeI]/ mol l^{-1}	$10^4[Ir^I]$/ mol l^{-1}	
25·3	7·97	2·50	5·47
	12·7	2·51	8·35
	5·60	2·50	3·93
	1·73	2·49	1·40
	0·00	2·49	0·14
1·40	20·4	2·51	3·45
	26·7	2·50	4·19
	35·4	2·49	5·52
	8·82	2·49	1·33
	40·0	2·51	6·50

TABLE 6

Data for addition of MeI to [$IrCl(CO)(X)_2$] in toluene at 25·3 °C

X	10^2k_2/ l mol^{-1} s^{-1}	$\Delta H_2^{\ddagger}$/ kJ mol^{-1}	$\Delta S_2^{\ddagger}$/ J K^{-1} mol^{-1}
PMe_2Ph	4·7 ± 0·15	46·4 ± 0·8	−114 ± 3
$PMe_2(o\text{-}MeOC_6H_4)$	530 ± 25	27·6 ± 0·8	−133 ± 3
$PMe_2(p\text{-}MeOC_6H_4)$ [a]	6·75 ± 0·2	38·1 ± 7·5	−138 ± 25

[a] Data computed from runs at two temperatures only.

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[12] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043.

product is accompanied by another product. Activation parameters, and values of k_1 and k_2 were calculated from k_{obs} and [MeI] by using a non-linear least squares programme.[13] Values are listed in Table 6.

It seems likely that our measured values of k_2, $\Delta H^‡$, and $\Delta S^‡$ for *trans*-[IrCl(CO){PMe$_2$(*p*-MeOC$_6$H$_4$)}$_2$] will be close to the true values for the formation of [IrClI(Me)(CO){PMe$_2$(*p*-MeOC$_6$H$_4$)}$_2$] of configuration (I), since our n.m.r. studies suggested that this was the major product (*ca.* 80%). As can be seen, the PMe$_2$(*o*-MeOC$_6$H$_4$) complex reacts about 100 times faster than the other two complexes at 25°. All three reactions show a large negative entropy of activation presumably associated with a highly polar transition state similar to that postulated for the reaction between *trans*-[IrCl(CO)(PPh$_3$)$_2$] [11] and methyl iodide and since found for other oxidative addition reactions.[7,14,15] We consider that the decrease in $\Delta H^‡$ of 8·3 kJ mol^{-1} in going from the PMe$_2$Ph to the PMe$_2$(*p*-MeOC$_6$H$_4$) complex is caused by electron donation from the *para*-methoxyphenyl group to the iridium. The effect on the rate is in part compensated for by an increase in the negative value of $\Delta S^‡$ from -114 to -138 J K^{-1} mol^{-1} so that at 25° the ratio of the k_2 values is only 1·5. A small difference in $\Delta H^‡$ (4·6 kJ mol^{-1} was similarly observed for the reactions of methyl iodide with [RhCl(CO)(PPh$_3$)$_2$] and [RhCl(CO){P(*p*-MeOC$_6$H$_4$)$_3$}$_2$].[7] The high reactivity of the PMe$_2$(*o*-MeOC$_6$H$_4$) complex is a consequence of the small enthalpy of activation (a reduction of 18·8 kJ mol^{-1} from the PMe$_2$Ph complex). We suggest that in this PMe$_2$(*o*-MeOC$_6$H$_4$) complex the dominant effect increasing the nucleophilic power of the iridium over that observed for the other two complexes is a direct interaction with a methoxy-group as shown in Figure 1. An electronic effect acting through the phosphorus would be expected to be greater for the *p*-methoxyphenyl(dimethyl)phosphine since *o*-methoxybenzoic acid is a stronger acid than benzoic acid, which is in turn stronger than *p*-methoxybenzoic acid, *i.e.* for an *ortho*-position the electron-attracting power of a methoxy-group by induction can be greater than its electron-donating power by mesomerism. *o*-Methoxyphenylphosphines are quaternized much faster than the corresponding *p*-methoxyphenylphosphines. This has been explained in terms of a direct interaction between a lone pair on the methoxyl oxygen and phosphorus 3*d*-orbitals.[16,17,*]

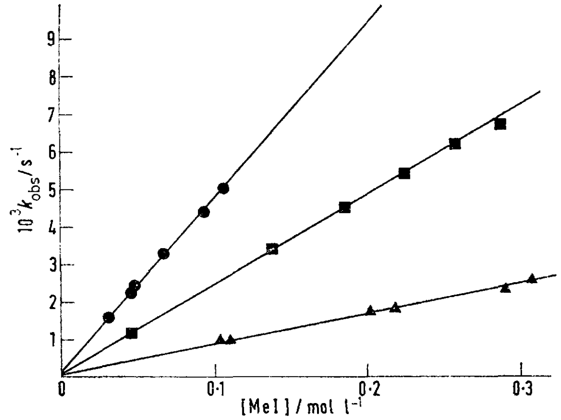

FIGURE 2 k_{obs} as a function of [MeI] for [IrCl(CO)(PMe$_2$Ph)$_2$] at 1·4 (▲), 15·7 (■), and 25·3 °C (●)

Affinities of the Complexes trans-[IrCl(CO){PMe$_2$(MeOC$_6$H$_4$)}$_2$] *for Acetic and Benzoic Acids.*—We have shown previously that the affinities of complexes of the types *trans*-[IrX(CO)L$_2$] for benzoic and acetic acids correlate well with their tendencies to undergo oxidative addition reactions.[8] The ratios of Ir^{III} to Ir^{I} at equilibrium were determined spectrophotometrically. We have done similar studies on our new methoxyphenyl complexes. The concentration of the iridium(I) complex decreased rapidly (within a few seconds) on mixing its solution with the organic acid and this was followed by a slow secondary process corresponding to a few percent change after 30 min. This secondary process may be due to a disproportionation reaction since when glacial acetic acid was added to *trans*-[IrCl(CO){PMe$_2$(*o*-MeOC$_6$H$_4$)}$_2$] some [IrHCl$_2$(CO){PMe$_2$(*o*-MeOC$_6$H$_4$)}$_2$] could be isolated after several hours.

TABLE 7

Ratio [Ir^{III}] : [Ir^{I}] obtained on treatment of complexes of the type *trans*-[IrCl(CO)L$_2$] with benzoic acid or acetic acid in benzene at 25°. Total [iridium] 10^{-3}M, total [benzoic acid + benzoate] 2×10^{-2}M, total [acetic acid + acetate] 0·1M

[IrCl(CO)L$_2$]	[Ir^{III}]/[Ir^{I}] [a]	
L	Benzoic acid	Acetic acid
PMe$_2$Ph	2·0 [b]	0·95
PMe$_2$(*p*-MeOC$_6$H$_4$)	3·25	1·45
PMe$_2$(*o*-MeOC$_6$H$_4$)	2·5	2·0

[a] Obtained from plots of the changes in optical density at the $\lambda_{max.}$ of the Ir^{I} complex (see Experimental section) *vs.* time and extrapolations to zero time as described previously. [b] From ref. 8.

The ratios of iridium(III) to iridium(I) are similar for all three complexes (Table 7). For the addition of acetic acid the order of increasing affinities is the same as the order of increasing rate constants, but for benzoic acid the relative positions of the *ortho*- and *para*-methoxy-complexes is reversed. This reversal may be due to an increased steric interaction between the *ortho*-methoxy-group and benzoate. The closely similar 'equilibrium' values for all three complexes give some indirect support to our explanation for the greatly enhanced rates of oxidative addition of the *ortho*-

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[*] We are grateful to a referee for drawing our attention to this work.

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methoxy-complex in terms of the direct interaction shown in Figure 1. This interaction could increase the rates of both the forward and the reverse reaction and not markedly affect the stability of the iridium(III) adduct, *i.e.* the equilibrium constant.

EXPERIMENTAL

All preparations were carried out in an argon atmosphere. The phosphines and phosphonium iodides were prepared by a method analogous to that reported[18] for dichloro-(1-naphthyl)phosphine, dimethyl-(1-naphthyl)phosphine, and trimethyl-(1-naphthyl)phosphonium iodide: dichloro-(*o*-methoxyphenyl)phosphine, yield 58%, b.p. 110—114° at 0·2 mmHg, τ (neat liquid) 6·1 (s, OMe); dichloro-(*p*-methoxyphenyl)phosphine, yield 57%, b.p. 102—105° at 0·07 mmHg, τ (C_6H_6) 6·84 (s, OMe); *o*-methoxyphenyl-(dimethyl)phosphine, yield 90%, b.p. 124—125° at 70 mmHg, τ (neat liquid) 6·2 (s, OMe), 8·7 (d, PMe), *J*(P–Me) 3·5 Hz; *p*-methoxyphenyl(dimethyl)phosphine, 80·5%, b.p. 112—114° at 69 mmHg, τ (neat liquid) 6·44 (s, OMe), 8·83 (d, PMe), *J*(P–Me) 3·2 Hz; *o-methoxyphenyl(trimethyl)phosphonium iodide* crystallized as white prisms (87%) (Found: C, 38·55; H, 5·15; I, 40·5. $C_{10}H_{16}IOP$ requires C, 38·75; H, 5·2; I, 40·9%); *p-methoxyphenyl(trimethyl)phosphonium iodide* was isolated as white prisms (90%) (Found: C, 38·85; H, 5·1; I, 41·25. $C_{10}H_{16}IOP$ requires C, 38·75; H, 5·2; I, 40·9%).

The two following complexes were prepared using the methods described for the dimethylphenylphosphine complexes:[19] *carbonyl(dichloro)hydridobis-{o-methoxyphenyl(dimethyl)phosphine}iridium*(III), white prisms (7·4%) (from ethanol); *carbonyl(chloro)bis-{o-methoxyphenyl(dimethyl)phosphine}iridium*(I), yellow prisms (79%) (from methanol).

σ-Allyl(carbonyl)dichlorobis-{o-methoxyphenyl(dimethyl)phosphine}iridium(III).— Carbonyl(chloro)bis-{*o*-methoxyphenyl(dimethyl)phosphine}iridium(I) (0·20 g, 0·34 mmol) was dissolved in a mixture of allyl chloride (0·3 ml, 3·6 mmol) and ethanol (2 ml). The product separated as white prisms (0·170 g, 0·26 mmol).

Acetyl(carbonyl)dichlorobis-{o-methoxyphenyl(dimethyl)phosphine}iridium(III).—Acetyl chloride (0·5 ml, 7·03 mmol) was added to a solution of carbonyl(chloro)bis-{*o*-methoxyphenyl(dimethyl)phosphine}iridium(I) (0·20 g, 0·34 mmol) in benzene (1 ml). Diethyl ether (1 ml) was added to the resultant colourless solution, and on cooling to 0° the product separated as white *prisms* (0·167 g, 0·26 mmol).

Benzoyl(carbonyl)dichlorobis-{o-methoxyphenyl(dimethyl)phosphine}iridium(III) was prepared similarly as white *prisms* (86%).

Carbonyl(chloro)iodobis-{o-methoxyphenyl(dimethyl)phosphine}(methyl)iridium(III).—Methyl iodide (0·31 ml, 5 mmol) was added to a solution of carbonyl(chloro)bis-{*o*-methoxyphenyl(dimethyl)phosphine}iridium(I) (0·30 g, 0·51 mmol) in benzene (1 ml). The product separated immediately as white plates (0·35 g, 0·45 mmol).

Carbonyl(chloro)bis-{p-methoxyphenyl(dimethyl)phosphine}iridium(I).—A solution of chloroiridic acid (1·66 g, 3·6 mg-atom of iridium) in ethanol (25 ml) was refluxed in a stream of carbon monoxide for 18 h. *p*-Methoxyphenyl-(dimethyl)phosphine (1·21 g, 7·2 mmol) was added to the resultant yellow solution at *ca.* 60° in an atmosphere of nitrogen and refluxing was continued for 2 min. A solution of sodium methoxide in methanol (4 ml; 0·87M) was added to the resultant pale yellow solution. The orange solution formed was refluxed for a further 5 min and then cooled to 0°. The product formed as yellow *prisms* (1·63 g, 2·75 mmol).

Carbonyl(dichloro)hydridobis-{p-methoxyphenyl(dimethyl)phosphine}iridium(III).—Hydrochloric acid (0·2 ml; 8M) was added to a suspension of carbonyl(chloro)bis-{*p*-methoxyphenyl(dimethyl)phosphine}iridium(I) (0·245 g, 0·42 mmol) in ethanol (2 ml). The resultant solution was heated to boiling for 1 min, then cooled to 0°. The product separated as white *prisms* (0·223 g, 0·36 mmol).

Carbonylbis-{p-methoxyphenyl(dimethyl)phosphine}iodoiridium(I).—Sodium iodide (0·12 g, 0·8 mmol) was added to a solution of carbonyl(dichloro)hydridobis-{*p*-methoxyphenyl(dimethyl)phosphine}iridium(III) (0·21 g, 0·33 mmol) in ethanol (3 ml). The resultant yellow solution was treated with sodium methoxide in methanol (0·5 ml; 0·87M). The product separated as yellow *plates* (0·20 g, 0·3 mmol).

Carbonyldi-iodomethylbis-{p-methoxyphenyl(dimethyl)phosphine}iridium(III).— Carbonyl(iodo)bis-{*p*-methoxyphenyl-(dimethyl)phosphine}iridium(I) (0·12 g, 0·176 mmol) was treated with methyl iodide (1 ml). The resultant mixture was heated to boiling for 1 min. Methanol (0·5 ml) was added to the brown solution and the required product crystallized as pale yellow prisms (0·11 g, 0·133 mmol).

Kinetic Measurements.—Carbonyl(chloro)bis(dimethylphenylphosphine)iridium(I) was prepared as described previously.[19] The complexes $[IrCl(CO)L_2]$ [L = PMe_2Ph, $PMe_2(o\text{-}MeOC_6H_4)$, or $PMe_2(p\text{-}MeOC_6H_4)$] were successively recrystallized to give a constant absorbance value at *ca.* 430 nm.

Methyl iodide puriss (assay ⩾99% by g.l.c.) (Koch–Light) was used. Benzene was distilled from sodium; toluene was dried over sodium. Before use, these solvents were deoxygenated with nitrogen.

The reactions were followed spectrophotometrically by observation of the absorption maxima: $[IrCl(CO)(PMe_2Ph)_2]$ 432 nm (ε 598 l mol^{-1} cm^{-1}); $[IrCl(CO)\{PMe_2(o\text{-}MeOC_6H_4)\}_2]$ 430 nm (ε 560); $[IrCl(CO)PMe_2\{(p\text{-}MeOC_6H_4)\}_2]$ 432 nm (ε 621).

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