Kinetics of Addition of Dihydrogen to *trans*-Carbonylchlorobis(dimethylphenylphosphine)iridium(I) and *trans*-Carbonylchlorobis[(2-methoxyphenyl)dimethylphosphine]iridium(I)

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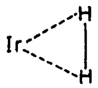
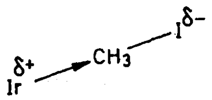
Rate constants and activation parameters have been calculated from kinetic studies of the reactions of the two title complexes with hydrogen in toluene. The values are similar for the two complexes and therefore neighbouring-group participation by the 2-methoxy-group is not an important effect. This is in contrast to the addition of methyl iodide where the (2-methoxyphenyl)dimethylphosphine complex was previously shown to react more than 100 times faster than the dimethylphenylphosphine complex.

THERE have been several kinetic studies on the addition of dihydrogen to complexes of the type *trans*-$[IrX(CO)L_2]$ (X = halogen, L = tertiary phosphine).[1-6] Sometimes the addition is readily reversible and equilibrium constants have also been determined.[1,2] It is generally thought that the addition of dihydrogen to these iridium(I) complexes is concerted involving a relatively non-polar transition state with an interaction depicted as in (I). The evidence supporting this proposed mechanism is (*i*) the addition is stereospecifically *cis*,[7-9] (*ii*) the entropies of activation are only moderately large negative numbers, *e.g.* for the addition of dihydrogen to *trans*-$[IrCl(CO)(PPh_3)_2]$ in benzene $\Delta S^\ddagger = -96$ J K^{-1} mol^{-1},[3] and (*iii*) the small kinetic deuterium-isotope effect, k_H/k_D,[3] suggests that Ir–H bond formation is more important than H–H bond breaking in the activated complex. In contrast the addition of methyl iodide to complexes of the type *trans*-$[IrX(CO)L_2]$ is stereospecifically *trans* and involves a highly polar transition state, such as (II), and is promoted by polar solvents and shows a large negative entropy of activation, *e.g.* for the



(I)



(II)

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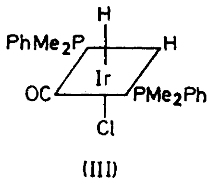
addition of methyl iodide to *trans*-$[IrCl(CO)(PPh_3)_2]$ in benzene $\Delta S^‡ = -213$ J K^{-1} mol^{-1}.[3]

The steric and electronic influences of the tertiary phosphines, L, on the rate of addition of dihydrogen to *trans*-$[IrCl(CO)L_2]$ are not well understood. Thus Strohmeier and Onoda [10] found that the rates increased in the order $L = P(C_6H_{11})_3 < PPr^i_3 < P(OPh)_3 < PBu^n_3 < PPh_3 < P(CH_2Ph)_3 < P(C_6H_4Me\text{-}o)_3$. Electronic effects seem to be small, *e.g.* there is only a slight increase in the rates of addition of dihydrogen to *trans*-$[IrCl(CO)\{P(C_6H_4Z\text{-}4)_3\}_2]$ with increasing donor power of the phosphine ligand, *i.e.* k increases from 0·21 to only 0·67 l mol^{-1} s^{-1} along the series Z = Cl, F, H, Me, and OMe. The corresponding increase in rates of addition of methyl iodide are far greater ($k = 3{\cdot}7 \times 10^{-5}$—$3{\cdot}5 \times 10^{-2}$ l mol^{-1} s^{-1}).[3,4]

We have shown that the addition of methyl iodide to *trans*-$[IrCl(CO)\{PMe_2(C_6H_4OMe\text{-}2)\}_2]$ in toluene at 298 K is more than 100 times faster than the addition to *trans*-$[IrCl(CO)(PMe_2Ph)_2]$. This large increase of rate was interpreted in terms of a direct interaction between the iridium and the *ortho*-methoxy-group in the polar transition state, *i.e.* the effect is one of neighbouring-group participation (also called the anchimeric effect or intramolecular catalysis).[11] We have now studied the kinetics of addition of dihydrogen to *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ and to *trans*-$[IrCl(CO)\{PMe_2(C_6H_4OMe\text{-}2)\}_2]$ in toluene to see if neighbouring-group participation by the methoxy-group is an important effect. There is currently considerable interest in 2-methoxyphenylphosphinerhodium complexes as hydrogenation catalysts due to the important work of Knowles, who has shown, for example, that a $Rh\text{-}PMe(C_6H_{11})(C_6H_4OMe\text{-}2)$ system can effect highly stereoselective hydrogenation of double bonds, including a synthesis of the drug L-3,4-dihydroxyphenylalanine (L-dopa).[12] In Knowles' work the 2-methoxy-group was introduced to interact with the substrate by hydrogen bonding and not to promote the addition of dihydrogen to the rhodium.

RESULTS AND DISCUSSION

The iridium(I) complexes were prepared as described previously.[13,14] The PMe_2Ph complex has been previously shown to react readily with dihydrogen giving $[Ir(H)_2Cl(CO)(PMe_2Ph)_2]$, (III), isolated as an oil.[7]



(III)

We have similarly prepared the complex $[Ir(H)_2Cl(CO)\{PMe_2(C_6H_4OMe\text{-}2)\}_2]$ by treating a benzene solution of the corresponding iridium(I) complex with 1 atm of hydrogen. The dihydride was isolated as a colourless oil, which rapidly became yellow. The complex $[Ir(H)_2Cl(CO)\{PMe_2(C_6H_4OMe\text{-}2)\}_2]$ was also assigned the configuration (III) on the basis of its ^1H n.m.r. spectrum, which showed a singlet at τ 6·62 (OMe) and a triplet at τ 7·91 with $|^4J(P\text{-}H) + {}^2J(P\text{-}H)|$ 8 Hz for the *trans*-(2-methoxyphenyl)dimethylphosphine ligands. At high field, two doublets of triplets at τ 17·75 [$^2J(P\text{-}H_b)$ 20·1, $^2J(H_a\text{-}H_b)$ 5 Hz] and 28·75 [$^2J(P\text{-}H_a)$ 14·4 Hz] indicate that each hydride is *cis* to the two phosphorus nuclei and is coupled to the other hydride.

The addition of dihydrogen to *trans*-$[IrCl(CO)L_2]$ was followed by observing the rate of uptake of gas at constant pressure. As the concentration of dihydrogen in solution remained constant throughout each experiment, first-order plots of log $(V_\infty - V_t)$ against time (t) were linear to 90% conversion (V = volume taken up). The reactions were first order in iridium(I) concentration and a first-order dependence on $[H_2]$ was assumed such that $-d[IrCl(CO)L_2]/dt = k_{obs.}[IrCl(CO)L_2]$ where $k_{obs.} = k_1[H_2]$. Values of $k_{obs.}$ at temperatures in the range 30—45 °C are listed in Tables 1 and 2. Activation parameters, and values of k_1 (listed in Table 3) were calculated from $k_{obs.}$ and $[H_2]$ using a non-linear least-squares program.[15]

TABLE 1

Summary of kinetic data for addition of H_2 to $[IrCl(CO)(PMe_2Ph)_2]$

	Initial concentrations		
	$10^3[H_2]$ *	$10^3[Ir]$	
θ_c/°C	mol l^{-1}		$10^3k_{obs.}/s^{-1}$
30·2	2·87	5·45	0·821
30·1	2·89	4·48	0·774
34·7	2·95	5·18	1·10
34·8	2·89	5·53	1·18
39·5	2·97	4·76	1·63
39·5	2·97	5·20	1·50
39·5	2·95	4·78	1·48
43·5	2·90	3·32	1·83
43·1	2·90	1·39	1·70

* Calculated using the atmospheric pressure and temperature and the formula and tables in ref. 16.

TABLE 2

Summary of kinetic data for the addition of H_2 to $[IrCl(CO)_2\{PMe_2(C_6H_4OMe\text{-}2)\}_2]$

θ_c/°C	$10^3[H_2]$/ mol l^{-1}	$10^3[Ir]$/ mol l^{-1}	$10^3k_{obs.}$/ s^{-1}
30·1	2·90	5·20	0·556
30·2	2·87	5·34	0·606
30·1	2·89	4·80	0·592
34·8	2·89	5·60	0·737
35·1	2·94	5·15	0·794
39·5	2·95	5·85	1·18
39·5	2·95	4·26	1·17
43·9	2·90	3·52	1·35
43·3	2·90	4·04	1·40

The reactivities of *trans*-$[IrCl(CO)L_2]$ [$L = PMe_2Ph$ and $PMe_2(C_6H_4OMe\text{-}2)$] towards hydrogen are very similar and contrast with their relative reactivities towards MeI. The $\Delta H^‡$ and $\Delta S^‡$ values for these re-

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TABLE 3

Rate constants (at 30·2 °C) and activation parameters for the addition of H_2 to [IrCl(CO)(X)$_2$] in toluene

X	10^2k_1/ l mol^{-1} s^{-1}	$\Delta H_1^\ddagger$/ kJ mol^{-1}	$\Delta S_1^\ddagger$/ J K^{-1} mol^{-1}
PMe_2Ph	28·0 ± 1	46 ± 3	−105 ± 9
$PMe_2(C_6H_4OMe\text{-}2)$	20·0 ± 0·9	50 ± 3	−94 ± 9

actions (Table 3) are similar to those reported for the addition of dihydrogen to *trans*-[IrCl(CO)(PPh$_3$)$_2$] in benzene at 25 °C,[3] *viz.* $10^2k = 67$ l mol^{-1} s^{-1}, $\Delta H^\ddagger = 45$ kJ mol^{-1}, and $\Delta S^\ddagger = -96$ J K^{-1} mol^{-1}. Thus our results show that an *ortho*-methoxy-group on the phosphine does not have an important accelerating effect on the addition of dihydrogen to iridium(I), whereas it has a very large (>100 times) accelerating effect on the addition of methyl iodide.[14] This difference probably reflects the much lower polarity of the transition state (I) involved in the dihydrogen addition compared with methyl iodide addition (II).

EXPERIMENTAL

Kinetic studies were carried out in a two-necked Pyrex flask (50 cm^3). One neck was sealed with a rubber syrum cap, the other was connected to a gas burette (10 cm^3). Toluene (20 cm^3) was placed in the flask and this was stirred with a 1 cm Teflon-coated magnet driven by an external motor so that it operated at the gas–liquid interface. The iridium(I) complex was placed in a small ' cup ' which could be controlled by a thin wire through the syrum cap. The apparatus was evacuated and then filled with hydrogen gas (this operation was repeated three times). It was then heated to the temperature required and left for *ca.* 20 min in order to equilibrate. The iridium(I) complex was then added to the toluene solution. The volume of hydrogen in the burette was measured at regular intervals by levelling the water level in the burette with that in an external reservoir. The partial pressure of the hydrogen was determined from the atmospheric pressure and the vapour pressure of toluene at the temperature used and the corresponding concentrations in solution computed from solubility data in the literature.[16]

Carbonylchlorodihydridobis[(2-*methoxylphenyl*)*dimethylphosphine*]*iridium*(III).—A solution of carbonylchlorobis-[(2-methoxyphenyl)dimethylphosphine]iridium(I) (0·10 g, 0·19 mmol) in benzene (10 cm^3) was stirred in 1 atm of hydrogen for *ca.* 45 min. The resulting colourless solution was evaporated to dryness under reduced pressure to give the product as a white oil which was characterised by its ^{1}H n.m.r. spectrum.

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