# Mechanism of the Reaction of Hydrogen and Phenylacetylene with $IrH(CO)(PPh_3)_3$. Kinetic Evidence for the Co-ordinatively Unsaturated $IrH(CO)(PPh_3)$ Species in Solution as Reactive Intermediates and for the Reaction of Hydrogen with the Co-ordinatively Saturated $IrH(CO)(PPh_3)_3$ Species

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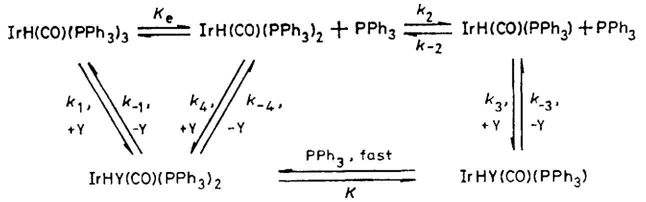
A kinetic study of the reaction between $IrH(CO)(PPh_3)_3$ and $H_2$ or PhCCH provided evidence for the existence of the co-ordinatively unsaturated intermediate $IrH(CO)(PPh_3)$ in solution, as well as a direct attack of hydrogen on the co-ordinatively saturated $IrH(CO)(PPh_3)_3$.

The oxidative addition of hydrogen and addition of acetylenes and olefins to low-valent transition-metal complexes are important reaction steps in the homogeneous catalytic hydrogenation and hydroformylation of unsaturated hydrocarbons.[1] Although hydrogen,[2] acetylenes,[3] and olefins,[3] are believed to be inert towards co-ordinatively saturated complexes, an associative mechanism [*i.e.* addition of olefin to the assumed key intermediate $HRh(CO)_2(PPh_3)_2$] for the $RhCl(PPh_3)_3$-catalysed hydroformylation of olefins has been postulated.[4] On the other hand, Halpern[5] obtained kinetic evidence for the existence of the very reactive 14-electron species $RhCl(PPh_3)_2$ in benzene solution, inferring its importance in the $RhCl(PPh_3)_3$-catalysed hydrogenation of olefins and related reactions. We have now investigated

$$IrH(CO)(PPh_3)_3 + Y \rightarrow IrYH(CO)(PPh_3)_2 + PPh_3 \quad (1)$$

reaction (1) kinetically (Y = $H_2$ or PhCCH) since we believed that the controversial *trans*-oxidative addition of $H_2$ to $IrH(CO)(PPh_3)_3$ observed by Harrod[6] could be due to the very reactive three-co-ordinate $IrH(CO)(PPh_3)$ intermediate in solution.

Our kinetic measurements on reaction (1) were performed in dioxygen-free benzene solutions at 25 ± 0·05 °C. The rates of reaction (1) were determined spectrophotometrically (Cary 210) by monitoring the decay of the absorption due to $IrH(CO)(PPh_3)_3$ at 330 nm. The hydrido-acetylene product of reaction (1) (Y = PhCCH) further reacts to insert the $\pi$-bonded acetylene into the Ir–H bond, giving a four-co-



**Scheme 1**

ordinated vinyl complex which subsequently reacts with a second molecule of acetylene.[7] The latter two reactions are fast, however, and could not be detected kinetically. The kinetic measurements encompassed the concentration ranges (a) (Y = $H_2$) [$H_2$] = $3{\cdot}5 \times 10^{-4}$ to $2{\cdot}8 \times 10^{-3}$ mol dm$^{-3}$, [$PPh_3$] = $5 \times 10^{-6}$ to $5{\cdot}5 \times 10^{-2}$ mol dm$^{-3}$, [$IrH(CO)(PPh_3)_3$] = $6{\cdot}3 \times 10^{-5}$ to $4{\cdot}1 \times 10^{-5}$ mol dm$^{-3}$: (b) (Y = PhCCH) [PhCCH] = $5{\cdot}9 \times 10^{-3}$ to $2{\cdot}45 \times 10^{-1}$ mol dm$^{-3}$, [$PPh_3$] = $1{\cdot}1 \times 10^{-4}$ to $2{\cdot}78 \times 10^{-4}$ mol dm$^{-3}$, [$IrH(CO)(PPh_3)_3$] (constant) = $1{\cdot}05 \times 10^{-4}$ mol dm$^{-3}$.

The kinetic data can only be accommodated by the reactions in Scheme 1, with minor simplifications depending on the incoming group Y. Dimer formation can be excluded since the reaction rate has a first-order dependence on complex concentration.

Application of the steady-state approximation to $IrH(CO)(PPh_3)$ yields the rate law described by equation (2), which on

$$k_{obs} = \frac{k_1[PPh_3][Y]}{([PPh_3] + K_e)} + \frac{k_4K_e[Y]}{([PPh_3] + K_e)} + \frac{k_2k_3K_e[Y]}{(k_{-2}[PPh_3] + k_3[Y])([PPh_3] + K_e)} + \frac{k_{-1}[PPh_3]^2}{(K + [PPh_3])} + \frac{k_{-4}[PPh_3]}{(K + [PPh_3])} + \frac{k_{-2}k_{-3}K[PPh_3]}{([PPh_3] + K)(k_3[Y] + k_{-2}[PPh_3])} \quad (2)$$

application of the SPSS programme[8] was found to fit our kinetic data accurately for the following values.

(a) Reaction (1), Y = $H_2$; $k_1 = (4{\cdot}47 \pm 0{\cdot}18) \times 10^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$, $k_2K_e = (2{\cdot}61 \pm 0{\cdot}07) \times 10^{-8}$ s$^{-1}$, $k_{-2}/k_3 = 104 \pm 8$, $k_4K_e$ = *ca.* 0, $k_{-4} = (1{\cdot}61 \pm 0{\cdot}24) \times 10^{-4}$ s$^{-1}$, $k_{-1}$ = *ca.* 0, $k_{-3}K$ = *ca.* 0. The values of the rate constants $k_1$, $k_2$, $k_2K_e$, $k_{-2}/k_3$, and $k_{-4}$ obtained from the SPSS programme with rate law (2) as the model are almost identical with those obtained when the terms containing $k_4K_e$, $k_{-1}$, and $k_{-3}K$ are omitted, indicating that the reaction paths described by $k_{-1}$, $k_4$, and $k_{-3}$ do not contribute significantly to the overall reaction. For all [$PPh_3$] used $K_e \ll [PPh_3]$ and $K \ll [PPh_3]$ so that rate law (2) simplifies to equation (3).

$$k_{obs} = k_1[H_2] + \frac{k_2k_3K_e[H_2]}{k_{-2}[PPh_3]^2 + k_3[H_2][PPh_3]} + k_{-4} \quad (3)$$

These results thus imply a direct attack of hydrogen on the five-co-ordinate complex $IrH(CO)(PPh_3)_3$, and the existence of a very reactive fourteen-electron species $IrH(CO)(PPh_3)$. Surprisingly, the kinetic contribution from the four-co-ordinate complex $IrH(CO)(PPh_3)_2$ is negligible. From the kinetic data it also follows that the reverse process mainly is described by $k_{-4}$, with no significant contribution from paths $k_{-1}$ and $k_{-3}K$. The intimate mechanism of attack of hydrogen on the five-co-ordinate complex $IrH(CO)(PPh_3)_3$ and subsequent dissociation of a triphenylphosphine molecule with simultaneous formation of two iridium–hydride bonds is not clear, but a radical mechanism appears to be inoperative, since no change in reaction rate was observed on addition of the radical scavenger galvinoxyl.

*trans*-Addition of hydrogen is not expected to occur through the reaction path $k_1$, but attack of hydrogen on the three-co-ordinated species $IrH(CO)(PPh_3)$ could initially form a trigonal bipyramidal intermediate with a *cis*-$H_2$ arrangement, followed by the fast bonding of a second triphenylphosphine ligand, resulting in both the *cis*- and *trans*-isomers of $IrH_3(CO)(PPh_3)_2$.

(b) Reaction (1), Y = PhCCH: $k_4K_e = (6{\cdot}72 \pm 0{\cdot}13) \times 10^{-7}$ s$^{-1}$, $k_2K_e = (3{\cdot}62 \pm 0{\cdot}21) \times 10^{-8}$ s$^{-1}$, $k_{-2}/k_3 = -7 \pm 15$, $k_1$ = *ca.* 0, $k_{-1}$ = 0, $k_{-4}$ = *ca.* 0, $k_{-3}K$ = *ca.* 0. Once again, the values of the constants $k_4K_e$ and $k_2K_e$ obtained from the SPSS programme by omitting the terms containing all the other constants from the model equation (thus using rate law 4) are almost identical with the above values. From these values it can be seen that the equilibrium constant $K_e$ must be very small (of the order of $10^{-6}$ dm$^3$ mol$^{-1}$ s$^{-1}$). The negative $k_{-2}/k_3$ value indicates that under the reaction conditions used ([PhC≡CH] $\gg$ [$PPh_3$]), these rate constants do not play any significant role in the rate law, implying that $k_{-2}[PPh_3] \ll k_3[PhCCH]$. This causes rate law (2) to simplify to rate law (4).

$$k_{obs} = k_4K_e[PhCCH]/[PPh_3] + k_2K_e/[PPh_3] \quad (4)$$

It can also be inferred from this that $IrH(CO)(PPh_3)$ is much more reactive than the four-co-ordinate intermediate $IrH(CO)(PPh_3)_2$, similar to what was found[5] for $RhCl(PPh_3)_3$, therefore explaining why the $k_4$ path could not be detected for reaction (1) (Y = $H_2$).

A prerequisite for the validity of rate laws (3) and (4), and therefore the reactions in Scheme 1, is that the $k_2K_e$ values obtained for both Y = $H_2$ and PhCCH should be comparable, which can be seen to be the case.

This represents the first evidence obtained for (a) a 14-electron species as an intermediate in reactions involving $IrH(CO)(PPh_3)_3$ and its probable importance in catalytic cycles of this complex; (b) direct hydrogen attack on a co-ordinatively saturated d$^8$ metal complex.

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