Intermediates or Their Analogues in Hydroformylation of Alkenes Catalysed by Hydridocarbonyltris(triphenylphosphine)rhodium(I)

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Summary The characterisation of rhodium or iridium compounds as models for intermediates in hydroformylation of alkenes is reported.

IN the hydroformylation[1,2] of alkenes by $\text{RhH(CO)(PPh}_3)_3$ various square and 5-co-ordinate alkyl and acyl intermediates have been suggested: the final step involves oxidative addition of molecular hydrogen to a square acyl, followed by reductive elimination of aldehyde from the rhodium(III) complex. We report the isolation[3] or spectroscopic characterisation of intermediates of the required types or analogues for them with Ir or with more stable organic groups.

Using alk-1-enes no intermediate alkyl can be even detected by i.r. or n.m.r. methods. However, tetrafluoroethylene (5 atm.) and $\text{RhH(CO)(PPh}_3)_3$ give the stable square alkyl *trans*-$\text{Rh(C}_2\text{F}_4\text{H)(CO)(PPh}_3)_2$ (ν_{CO} 1990 cm.$^{-1}$). This compound dissociates extensively in solution, unlike *trans*-$\text{RhCl(CO)(PPh}_3)_2$ and the resulting formally 3-co-ordinate species $\text{Rh(C}_2\text{F}_4\text{H)(CO)(PPh}_3)$ acts as a catalyst for hydrogenation and hydroisomerisation of alk-1-enes [*cf.* $\text{RhCl(PPh}_3)_2$[4]]. The complex undergoes oxidative additions, *e.g.*, HCl gives at $-70°$ the unstable $\text{Rh(C}_2\text{F}_4\text{H)HCl(CO)(PPh}_3)_2$ (ν_{RhH} 2155; ν_{CO} 2090 cm.$^{-1}$; τ 22·6) which at 25° decomposes to $\text{RhCl(CO)(PPh}_3)_2$ and 1,1,2,2-tetrafluoroethane. With H_2(50°, 70 atm.) in presence of an excess of PPh_3 quantitative conversion into $\text{RhH(CO)(PPh}_3)_3$ and $\text{C}_2\text{F}_4\text{H}_2$ occurs. Reversible addition of neutral ligands also occurs in solution. Thus SO_2 gives $\text{Rh(C}_2\text{F}_4\text{H)(SO}_2\text{)(CO)(PPh}_3)_2$ (ν_{CO} 2060 cm.$^{-1}$) and with CO there are successive additions to give (a) $\text{Rh(C}_2\text{F}_4\text{H)(CO)}_2\text{(PPh}_3)_2$ (ν_{CO} 2003, 1957 cm.$^{-1}$), which is extensively dissociated in solution to $\text{Rh(C}_2\text{F}_4\text{H)(CO)}_2\text{(PPh}_3)$, and (b) $\text{Rh(C}_2\text{F}_4\text{H)(CO)}_3\text{(PPh}_3)$ (ν_{CO} 2075, 2015 cm.$^{-1}$). N.m.r. spectra show that intermolecular exchange occurs between these species.

Although spectroscopic evidence can be obtained for the presence of acyl intermediates in the reaction of $\text{RhH(CO)(PPh}_3)_3$ with CO and a liquid alk-1-ene such as hexene, the interpretation of both i.r. and n.m.r. data is easier when ethylene is used. Complete conversion into the 5-co-ordinate $\text{Rh(COEt)(CO)}_2\text{(PPh}_3)_2$($\nu_{CO}$ 1990, 1943; ν_{acyl} 1650 cm.$^{-1}$) occurs at 1 atm. (1 : 1 mixture of CO + C_2H_4). This species, which is stable in solution only in presence of CO, reacts with H_2 (1 atm.) losing CO to give $\text{RhH(CO)(PPh}_3)_3$ and propionaldehyde, while with HCl it gives CO,$\text{RhCl(CO)(PPh}_3)_2$ and $\text{C}_2\text{H}_5\text{CHO}$: both reactions are strongly inhibited by high partial pressures of CO suggesting that dissociation to give the square acyl, which then undergoes oxidative addition, is operative. Further evidence is provided by the more stable iridium complexes. $\text{IrH(CO)}_2\text{(PPh}_3)_2$[5] reacts with C_2H_4 (10 atm.) alone to give a mixture of ethyl and propionyl species; at $-70°$, unstable $\text{Ir(COEt)(CO)(PPh}_3)_2$ can be isolated (ν_{CO} 1955, ν_{acyl} 1635 cm.$^{-1}$) With C_2H_4 + CO (30 atm.), the very stable $\text{Ir(COEt)(CO)}_2\text{(PPh}_3)_2$ is obtained. This reacts much more slowly than its rhodium analogue with H_2 to give $\text{C}_2\text{H}_5\text{CHO}$ and $\text{IrH(CO)}_2\text{(PPh}_3)_2$; although no intermediate dihydrido-species could be isolated the corresponding chloride, $\text{Ir(COEt)HCl(CO)(PPh}_3)_2$, was formed by HCl, and this decomposes to $\text{C}_2\text{H}_5\text{CHO}$ and $\text{IrCl(CO)(PPh}_3)_2$. The action of CO (1 atm.) on solutions of $\text{M(COEt)(CO)}_2\text{(PPh}_3)_2$ (M = Rh and Ir) causes partial conversion into $\text{M(COEt)(CO)}_3\text{(PPh}_3)$.

Similar but more stable aryl species can also be made. Thus, interaction of $\text{IrCl(CO)(PPh}_3)_2$ with phenyl-lithium in ether gives the square phenyl $\mathrm{IrPh(CO)(PPh_3)_2}$ (ν_{CO} 1940 cm.$^{-1}$) which on treatment with CO gives successively $\mathrm{IrPh(CO)_2(PPh_3)_2}$ (ν_{CO} 1980, 1940 cm.$^{-1}$), $\mathrm{Ir(COPh)(CO)_2(PPh_3)_2}$ (ν_{CO} 1984, 1930; ν_{acyl} 1608 cm.$^{-1}$) and $\mathrm{Ir(COPh)(CO)_3(PPh_3)}$ (ν_{CO} 2059, 1998; ν_{acyl} 1637 cm.$^{-1}$). On treating the complex,[6] $\mathrm{RhPh(PPh_3)_3}$, with CO similar rhodium species are formed, and in this case interaction of the benzoyl complex with H_2 (1 atm.) gives $\mathrm{C_6H_5CHO}$ and $\mathrm{RhH(CO)(PPh_3)_3}$.

In view of the ready dissociation or displacement by CO of $\mathrm{PPh_3}$ for some of the species, it now seems clear that the very high phosphine-to-rhodium ratios needed[2] to ensure high specificity for straight-chain aldehyde formation are required to suppress dissociation and to maintain the bis-(triphenylphosphine) species where the steric interaction is greatest[1,7]; under such conditions the associative mechanism[1] is most likely.

(*Received, September 5th,* 1969; *Com.* 1346.)

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