

## Hydride Intermediates in Homogeneous Hydrogenation Reactions of Olefins and Acetylenes using Rhodium Catalysts

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SPECIES with transition-metal-to-hydrogen bonds have often been postulated as intermediates in the catalytic hydrogenation of unsaturated compounds in both homogeneous and heterogeneous systems. While on the one hand it is well known that hydride complexes can add olefins giving alkyl-metal complexes<sup>1</sup> and, on the other, that a hydride species is present in the rather complicated cobalt(II)-cyanide systems which act as homogeneous hydrogenation catalysts, there has been no case where the growth and subsequent decay of a hydridic species during the conversion of olefin

to paraffin with molecular hydrogen could be observed.

We have demonstrated the connection between hydride formation and homogeneous hydrogenation by using a new compound, tris(triphenylphosphine)chlororhodium(I),<sup>2</sup> which, in ethanol-benzene solutions at *ca.*  $5 \times 10^{-3}$  M concentration and at 25° and pressures  $\leq 1$  atm., is an exceedingly rapid catalyst for reduction of compounds containing double or triple bonds.

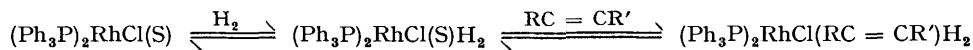
A solution of  $(\text{Ph}_3\text{P})_3\text{RhCl}$  in benzene or deuteriochloroform takes up molecular hydrogen<sup>3</sup> and the

<sup>1</sup> *E.g.* F. Hein and R. Weiss, *Z. anorg. Chem.*, 1958, **295**, 145; J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

<sup>2</sup> Obtained as red-purple crystals by the interaction of ethanolic solutions of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  with a 6-fold molar excess of triphenylphosphine acting as complexing and reducing agent and a suppressor of dissociation. This compound and the corresponding bromide and iodide have also been obtained by M. A. Bennett, University College, London (personal communication).

<sup>3</sup> In ethyl acetate and acetic acid, one mole of hydrogen per mole of complex is absorbed.

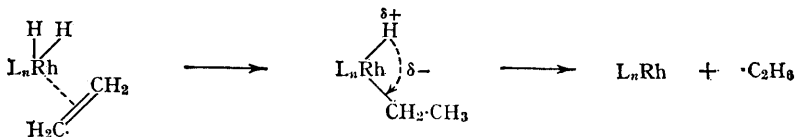
n.m.r. spectrum shows high-field lines at  $\tau$  28.2, 27.4, 21.5 and 18.8; this multiplicity indicates the presence of isomeric species, as does the multiplicity of Rh-H stretches (*ca.* 2000  $\text{cm}^{-1}$ ) of isolated crystalline adducts. Addition of an olefin such as



hex-1-ene causes instantaneous disappearance of the high-field lines, and n.m.r. spectra or gas-liquid chromatography show the presence of paraffin. Re-saturation of the solution with hydrogen again develops the high-field signals.

While details of the mechanism remain to be elucidated, the following points are significant:

(i)  $(\text{Ph}_3\text{P})_3\text{RhCl}$  dissociates in solvents (S), according to molecular-weight studies, to give  $\text{Ph}_3\text{P}$  and a solvated species, generally  $(\text{Ph}_3\text{P})_2\text{RhCl}(\text{S})$ ,<sup>4</sup>



so that a site for olefin or acetylene co-ordination is provided by displacement of solvent; at higher temperatures, *e.g.*, in boiling benzene, sparingly-soluble bridged halide complexes are formed.

(ii) The hydride species must be in equilibrium

with dissolved hydrogen. Thus the high-field lines disappear when argon is bubbled through the solutions and can be regenerated by hydrogen. The principal active species,  $(\text{Ph}_3\text{P})_2\text{RhCl}(\text{S})$ , will hence be involved in labile equilibria of the type:

The rate of hydrogenation appears to fall with increasing basicity of the co-solvent with benzene.

(iii) The precise way in which hydrogen is transferred to olefin is uncertain, although it seems most likely that it occurs at a single metal atom in this system. Using ethylene, we have been unable to obtain n.m.r. evidence for an alkyl intermediate,  $\text{Rh}-\text{C}_2\text{H}_5$ , although such a species could be present in kinetically significant amounts, so that hydrogenation could proceed:

Alternatively, when excess of olefin is present, as in the catalytic systems, the hydrogen could merely be polarized  $\overset{\delta+}{\text{H}}-\overset{\delta-}{\text{H}}$  at the metal site and add directly to the weakly co-ordinated olefin.

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<sup>4</sup> Axial solvation to give  $(\text{Ph}_3\text{P})_2\text{RhCl}(\text{S})_3$  is actually more likely. The lability of one triphenylphosphine is also shown by the immediate reaction of the solutions with carbon monoxide to give  $(\text{Ph}_3\text{P})_2\text{RhCl}(\text{CO})$ ; the latter is a very slow homogeneous hydrogenation catalyst.