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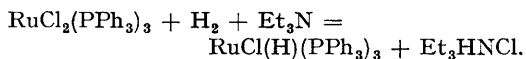
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## Selective Catalytic Homogeneous Hydrogenation of Terminal Olefins using Tris(triphenylphosphine)hydridochlororuthenium(II); Hydrogen Transfer in Exchange and Isomerisation Reactions of Olefins

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WE have shown<sup>1</sup> that tris(triphenylphosphine)-dichlororuthenium,<sup>2</sup>  $\text{RuCl}_2(\text{PPh}_3)_3$ , in benzene-ethanol, may be as effective an homogeneous hydrogenation catalyst as  $\text{RhCl}(\text{PPh}_3)_3$ ,<sup>3</sup> however the interpretation of kinetic measurements in such mixed solvents has presented difficulties.

The active ruthenium catalyst species, tris(triphenylphosphine)hydridochlororuthenium(II),  $\text{RuCl}(\text{H})(\text{PPh}_3)_3$ , can be prepared *in situ* in pure benzene by a quantitative base-promoted hydrogenolysis at 25° and 1 atm. pressure using solid bases such as sodium phenoxide, or, more conveniently, organic bases such as triethylamine:



The red-violet crystalline hydrido-complex, m.p., 95–96°, which analyses correctly, can be readily isolated; its n.m.r. spectrum shows a well resolved quartet centred at  $\tau$  27.8 confirming the presence of three equivalent phosphorus atoms mutually *cis* to the hydrido-ligand, and implying either a trigonal-bipyramidal structure with axial phosphine groups, or a pseudo-octahedral one with a solvent-occupied site.<sup>4</sup>

The new complex is remarkable in that it is highly selective for the catalytic hydrogenation of terminal olefins, differing in this respect from the rhodium system.<sup>3</sup> Furthermore, for such olefins it is considerably more active than either

$\text{RhCl}(\text{PPh}_3)_3$  in benzene (Table) or of  $\text{RuCl}_2(\text{PPh}_3)_3$  in ethanol-benzene,<sup>1</sup> thus rates of hydrogen absorption of over 100 ml. min.<sup>-1</sup> with catalyst concentrations  $8.3 \times 10^{-4}\text{M}$  and pressure sub-atmospheric have been recorded.<sup>5</sup> Some typical rates are given in the Table; the utility of such a selective catalyst in organic chemistry is obvious.

Other studies on  $\text{RuCl}(\text{H})(\text{PPh}_3)_3$  and on  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ <sup>6</sup> [which is dissociated in solution to  $\text{RhH}(\text{CO})(\text{PPh}_3)_2$ ], have been made with regard to (a) hydrogen atom exchange and (b) isomerisation reactions, with olefins.

The exchange studies were made by observing the growth of the high-field proton resonances when the deuterio-complexes  $\text{RhD}(\text{CO})(\text{PPh}_3)_3$  and  $\text{RuCl}(\text{D})(\text{PPh}_3)_3$  are treated with olefins.

(i) The ruthenium complex catalyses exchange not only with terminal olefins ( $t_{\frac{1}{2}}$  ca. 30 sec.) but with internal olefins ( $t_{\frac{1}{2}}$  ca. 5 min.) even though the latter cannot be readily hydrogenated. Isomerisation of olefins, *e.g.*, the conversion of *cis*-hept-2-ene into the *trans*-isomer, or hex-1-ene into hex-2-ene is non-detectable in 24 hr.

(ii) The rhodium complex catalyses exchange of terminal olefins exceedingly rapidly, *e.g.*, for pent-1-ene,  $t_{\frac{1}{2}}$  ca. 20 sec., whereas internal olefins are very slow, *e.g.*, *cis*-pent-2-ene,  $t_{\frac{1}{2}}$  ca. 60 min. Further, using  $10^{-2}\text{M}$ -catalyst and 2M-olefin in benzene at 25°, pent-1-ene gives a 50% conversion into a mixture of *cis*- and *trans*-pent-2-enes within

TABLE

*Homogeneous catalytic hydrogenation of olefins: RuCl(H)(PPh<sub>3</sub>)<sub>3</sub>, 5 × 10<sup>-5</sup> moles, olefin, 7.1 × 10<sup>-2</sup> moles in benzene to total volume 60 ml. Rate at 50 cm. partial pressure hydrogen at 25°*

Substrate	Rate (ml. min. <sup>-1</sup> )	Product
Pent-1-ene .. ..	99	Pentane
Hex-1-ene .. ..	109	Hexane
Hex-2-ene .. ..	0.1	—
Hept-1-ene .. ..	69 <sup>a</sup>	Heptane
Hept-3-ene .. ..	0.1	—
Oct-2-ene .. ..	0.1 <sup>b</sup>	—
Dec-1-ene .. ..	86	Decane
Cyclohexene .. ..	0.3	—
Penta-1,3-diene .. ..	3	Pent-2-ene

<sup>a</sup> Under same conditions, RhCl(PPh<sub>3</sub>)<sub>3</sub> gives 14 ml. min.<sup>-1</sup>.

<sup>b</sup> Non-competitive to hept-1-ene at same concentration.

an hour. Both these exchange and isomerisation processes are inhibited by an excess of PPh<sub>3</sub> which competitively blocks the co-ordination site.

The isomerisation of olefins by rhodium chloro-complexes has been postulated to require hydrido-intermediates, but these could not be detected,<sup>7</sup>

while from studies on iridium complexes at elevated temperatures it was concluded that "a preformed hydride assists the olefin isomerisation but it is not necessarily essential".<sup>8</sup> The present experiments clearly show the direct involvement of a transition-metal-hydrogen bond in exchange and isomerisation reactions, which must proceed *via* the reversible formation of an alkyl intermediate. For the ruthenium complex, n.m.r. spectra show the reversible formation of a Ru-C<sub>2</sub>H<sub>5</sub> bond under ethylene pressure at 25°.

Since RuCl(H)(PPh<sub>3</sub>)<sub>3</sub> readily exchanges with internal olefins, the failure to hydrogenate readily may be attributed to steric hindrance in the hydrogenolysis of the metal-to-carbon bond in the alkyl intermediate.

It may also be noted that RhH(CO)(PPh<sub>3</sub>)<sub>3</sub> is considerably more effective than RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub><sup>3</sup> as a hydroformylation catalyst; even at 25° with 50 atm. each of CO and H<sub>2</sub> in benzene, a 20% conversion of pent-1-ene into aldehyde occurs in a few hours.

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<sup>1</sup> D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, 1965, **208**, 1203.

<sup>2</sup> T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

<sup>3</sup> J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 1711.

<sup>4</sup> Cf. The structure of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> by S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778, where the octahedral site is occupied by an  $\alpha$ -hydrogen of a phenyl group.

<sup>5</sup> Cf. The rates of <0.1 ml. min.<sup>-1</sup> quoted by I. Jardine and F. J. McQuillan, *Tetrahedron Letters*, 1966, 4871, in the application of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> in benzene for hydrogenation of various substrates.

<sup>6</sup> S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500. An improved procedure is the hydrogenolysis of RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub> in presence of PPh<sub>3</sub> and NEt<sub>3</sub> under hydrogen pressure, but even better is the interaction of RhCl(CO)(PPh<sub>3</sub>)<sub>2</sub>, PPh<sub>3</sub>, and NaBH<sub>4</sub> in ethanol from which the product crystallises in high yields.

<sup>7</sup> R. D. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272.

<sup>8</sup> R. S. Coffey, *Tetrahedron Letters*, 1965, 3809.