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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[1] that tris(triphenylphosphine)-dichlororuthenium,[2] $RuCl_2(PPh_3)_3$, in benzene–ethanol, may be as effective an homogeneous hydrogenation catalyst as $RhCl(PPh_3)_3$;[3] however the interpretation of kinetic measurements in such mixed solvents has presented difficulties.

The active ruthenium catalyst species, tris-(triphenylphosphine)hydridochlororuthenium(II), $RuCl(H)(PPh_3)_3$, 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:

$$RuCl_2(PPh_3)_3 + H_2 + Et_3N = RuCl(H)(PPh_3)_3 + Et_3HNCl.$$

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 τ 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.[4]

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.[3] Furthermore, for such olefins it is considerably more active than either $RhCl(PPh_3)_3$ in benzene (Table) or of $RuCl_2(PPh_3)_3$ in ethanol–benzene;[1] thus rates of hydrogen absorption of over 100 ml. min.$^{-1}$ with catalyst concentrations $8·3 \times 10^{-4}$M and pressure sub-atmospheric have been recorded.[5] Some typical rates are given in the Table; the utility of such a selective catalyst in organic chemistry is obvious.

Other studies on $RuCl(H)(PPh_3)_3$ and on $RhH(CO)(PPh_3)_3$[6] [which is dissociated in solution to $RhH(CO)(PPh_3)_2$], 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 deutero-complexes $RhD(CO)(PPh_3)_3$ and $RuCl(D)(PPh_3)_3$ 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}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: $RuCl(H)(PPh_3)_3$, 5×10^{-5} *moles, olefin,* $7{\cdot}1 \times 10^{-2}$ *moles in benzene to total volume* 60 *ml. Rate at* 50 *cm. partial pressure hydrogen at* 25°

Substrate	Rate (ml. min.$^{-1}$)	Product
Pent-1-ene	99	Pentane
Hex-1-ene	109	Hexane
Hex-2-ene	0·1	—
Hept-1-ene	69[a]	Heptane
Hept-3-ene	0·1	—
Oct-2-ene	0·1[b]	—
Dec-1-ene	86	Decane
Cyclohexene	0·3	—
Penta-1,3-diene ..	3	Pent-2-ene

[a] Under same conditions, $RhCl(PPh_3)_3$ gives 14 ml. min.$^{-1}$.

[b] Non-competitive to hept-1-ene at same concentration.

an hour. Both these exchange and isomerisation processes are inhibited by an excess of PPh_3 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,[7] 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".[8] 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 $Ru–C_2H_5$ bond under ethylene pressure at 25°.

Since $RuCl(H)(PPh_3)_3$ 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 $RhH(CO)(PPh_3)_3$ is considerably more effective than $RhCl(CO)(PPh_3)_2$[3] as a hydroformylation catalyst; even at 25° with 50 atm. each of CO and H_2 in benzene, a 20% conversion of pent-1-ene into aldehyde occurs in a few hours.

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[1] D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, 1965, **208**, 1203.

[2] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

[3] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[4] *Cf.* The structure of $RuCl_2(PPh_3)_3$ by S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778, where the octahedral site is occupied by an α-hydrogen of a phenyl group.

[5] *Cf.* The rates of $<0{\cdot}1$ ml. min.$^{-1}$ quoted by I. Jardine and F. J. McQuillan, *Tetrahedron Letters*, 1966, 4871, in the application of $RuCl_2(PPh_3)_3$ in benzene for hydrogenation of various substrates.

[6] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500. An improved procedure is the hydrogenolysis of $RhCl(CO)(PPh_3)_2$ in presence of PPh_3 and NEt_3 under hydrogen pressure, but even better is the interaction of $RhCl(CO)(PPh_3)_2$, PPh_3, and $NaBH_4$ in ethanol from which the product crystallises in high yields.

[7] R. D. Cramer, *J. Amer. Chem. Soc.*, 1966, **88**, 2272.

[8] R. S. Coffey, *Tetrahedron Letters*, 1965, 3809.