Homogeneous Hydrogenation of α-Olefins using Hydridocarbonyltris(triphenylphosphine)rhodium(I)

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CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I) is a useful catalyst for the homogeneous hydrogenation of a variety of olefins and acetylenes[1] and dichlorotris(triphenylphosphine)ruthenium(II), when activated by a base, is even more effective, though selective for terminal olefins.[2]

We now report that hydridocarbonyltris(triphenylphosphine)rhodium(I),[3] $RhH(CO)(PPh_3)_3$, is also an effective actalyst in benzene solutions, but again highly selective for terminal olefins. This complex is also an efficient hydroformylation catalyst.[2]

With hex-1-ene, no isomerisation could be detected at sub-atmospheric pressures of hydrogen. Kinetic studies led to a rate expression similar to that found for $RhCl(PPh_3)_3$[1] for reduction to n-hexane, over a catalyst-concentration range 0·105 to 5·00 mM, hexene concentrations 0·28—1·8 M, hydrogen partial pressures 20—60 cm. and temperatures 15—30°. From the data we obtain the values $\Delta H\ddagger = 10{\cdot}1$ k.cal.mole^{-1}, $\Delta S\ddagger$, $-7{\cdot}3$ e.u., which can be compared with 18·6 k.cal.mole^{-1} and $+1{\cdot}1$ e.u., for hexene using $RhCl(PPh_3)_3$. At 25° and 50 cm.$^{-1}$ pressure using 1·25 mM catalyst concentration, $k'_H/k'_D = 1{\cdot}47$. There is no detectable hydrogenation using cyclohexene, *cis*-4-methylpent-2-ene, penta-1,3-diene, or similar olefins.[4]

The mechanism of hydrogenation is quite different from that with $RhCl(PPh_3)_3$ and proceeds *via* an alkyl intermediate which undergoes hydrogenolysis. This is supported by the fact[2] that $RhD(CO)(PPh_3)_3$ undergoes hydride transfers rapidly with α-olefins whereas exchange with internal olefins is slower by a factor of at least 10^3. The rate-determining step in the hydrogenation and exchange reactions is presumably displacement, by olefin, of a solvent molecule (S) in the dissociated species $RhH(CO)(PPh_3)_2(S)$.

In its catalytic properties, $RhH(CO)(PPh_3)_3$ is similar to $CoH(CO)_4$, although more stable and amenable to study. The system is still a complicated and labile one; of the principle reactions (1—4), which proceed at 25° and 1 atmos., only the dissociation step has been noted previously.[3] The solvent may be benzene, toluene, or dichloromethane.

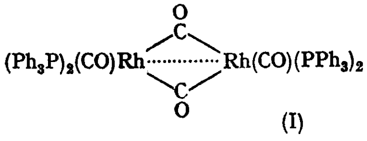
$$RhH(CO)(PPh_3)_3 \underset{}{\overset{+S}{\rightleftharpoons}} RhH(CO)(PPh_3)_2(S) + PPh_3 \qquad (1)$$

$$RhH(CO)(PPh_3)_2(S) \underset{+H_2}{\overset{+CO}{\rightleftharpoons}} RhH(CO)_2(PPh_3)_2(S) \qquad (2)$$

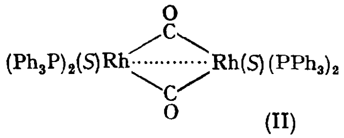
$$2RhH(CO)_2(PPh_3)_2(S) \underset{+H_2}{\overset{+CO}{\rightleftharpoons}} [Rh(CO)_2(PPh_3)_2]_2 \qquad (3)$$

$$[Rh(CO)_2(PPh_3)_2]_2 \underset{+CO}{\overset{S+N_2}{\rightleftharpoons}} [Rh(CO)(PPh_3)_2S]_2 \qquad (4)$$

The changes can be followed by analysis of i.r. and n.m.r. spectra of hydrido- and deuterido-species under differing conditions of temperature, gas atmosphere, and solvent. The initial reactive species $RhH(CO)(PPh_3)_2(S)$ is clearly involved in hydrogenation, exchange, and isomerisation processes, while $RhH(CO)_2(PPh_3)_2(S)$ is involved in hydroformylation. The unstable yellow dimer obtained in (3) can be isolated (ν_{CO} 2017, 1992, 1800, and 1770 cm.$^{-1}$) and formulated as (I) [isoelectronic with $Co_2(CO)_8$]. The red solvated dimer, isolated as crystalline solvates (*e.g.* $S = CH_2Cl_2$) has ν_{CO} 1739 cm.$^{-1}$ and is formulated as (II). The species $RhH(CO)_2(PPh_3)_2(S)$, which is in equilibrium with other species has $\nu_{Rh\text{-}H}$ 2050, τ *ca.* 19·1 br,† ν_{CO} 1980, 1942 cm.$^{-1}$. The spectroscopic analysis has been assisted by the complete spectral characterisation of the closely related but much more stable new iridium species, $IrH(CO)_2L_2$ ($L = PPh_3$ and $AsPh_3$), which are obtained by borohydride reduction of *trans*-$IrCl(CO)L_2$ in presence of CO in tetrahydrofuran solution.



(I)



(II)

(*Received, February* 21*st*, 1968; *Com.* 211.)

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† Solutions of $RhH(Co)(PPh_3)_3$ at 25° have τ 19·27 br but below −10° show a 1:3:3:1 quartet, J (P–H) 14 c./sec., due to the undissociated trigonal bipyramidal species.

[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), **1966**, 1711; F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), **1967**, 1574; S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), **1968**, 1054.

[2] P. S. Hallman, D. Evans, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1967, 305.

[3] S. S. Bath and L. Vaska, *J. Amer. Chem. Soc.*, 1963, **85**, 3500.

[4] L. Vaska, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 89, reports qualitative observations that ethylene is hydrogenated by $RhH(CO)(PPh_3)_3$.