

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

By CHARMIAN O'CONNOR, G. YAGUPSKY, D. EVANS, and G. WILKINSON*

(Inorganic Chemistry Laboratories, Imperial College, London, S.W.7)

CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I) is a useful catalyst for the homogeneous hydrogenation of a variety of olefins and acetylenes¹ 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 $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, is also an effective catalyst in benzene solutions, but again highly selective for terminal olefins. This

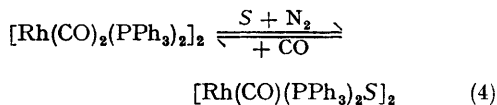
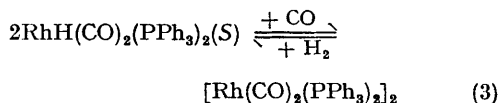
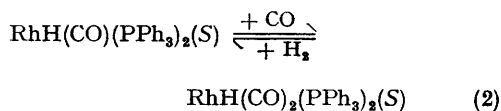
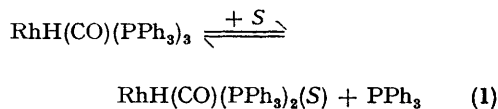
complex is also an efficient hydroformylation catalyst.²

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 $\text{RhCl}(\text{PPh}_3)_3$ 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

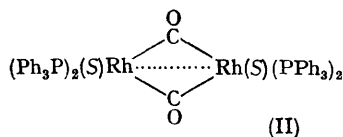
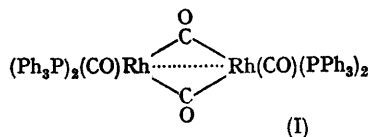
values $\Delta H^\ddagger = 10.1$ k.cal.mole⁻¹, ΔS^\ddagger , -7.3 e.u., which can be compared with 18.6 k.cal.mole⁻¹ and $+1.1$ e.u., for hexene using $\text{RhCl}(\text{PPh}_3)_3$. At 25° and 50 cm.⁻¹ pressure using 1.25 mm catalyst concentration, $k'_H/k'_D = 1.47$. There is no detectable hydrogenation 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 $\text{RhCl}(\text{PPh}_3)_3$ and proceeds *via* an alkyl intermediate which undergoes hydrogenolysis. This is supported by the fact² that $\text{RhD}(\text{CO})(\text{PPh}_3)_3$ undergoes hydride transfers rapidly with α -olefins whereas exchange with internal olefins is slower by a factor of at least 10³. The rate-determining step in the hydrogenation and exchange reactions is presumably displacement, by olefin, of a solvent molecule (S) in the dissociated species $\text{RhH}(\text{CO})(\text{PPh}_3)_2(\text{S})$.

In its catalytic properties, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ is similar to $\text{CoH}(\text{CO})_4$, 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.



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 $\text{RhH}(\text{CO})(\text{PPh}_3)_2(\text{S})$ is clearly involved in



hydrogenation, exchange, and isomerisation processes, while $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2(\text{S})$ 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 $\text{Co}_2(\text{CO})_8$]. The red solvated dimer, isolated as crystalline solvates (*e.g.* $S = \text{CH}_2\text{Cl}_2$) has ν_{CO} 1739 cm.⁻¹ and is formulated as (II). The species $\text{RhH}(\text{CO})_2(\text{PPh}_3)_2(\text{S})$, which is in equilibrium with other species has $\nu_{\text{Rh-H}}$ 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, $\text{IrH}(\text{CO})_2\text{L}_2$ ($L = \text{PPh}_3$ and AsPh_3), which are obtained by borohydride reduction of *trans*- $\text{IrCl}(\text{CO})\text{L}_2$ in presence of CO in tetrahydrofuran solution.

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† Solutions of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ at 25° have τ 19.27 br but below -10° show a 1:3:3:1 quartet, $J(\text{P-H})$ 14 c./sec., due to the undissociated trigonal bipyramidal species.

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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 $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.