Molecular Hydrogen Complexes in Catalysis: Highly Efficient Hydrogen Production from Alcoholic Substrates catalysed by Ruthenium Complexes

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The complex [RuH$_2$(N$_2$)(PPh$_3$)$_3$] catalyses the thermal production of hydrogen from a range of different alcoholic substrates with rates corresponding to up to >1000 catalyst turnover h^{-1}; the mechanism of the reaction is discussed and possible reasons for the high efficiency of this catalyst including the fact that loss of hydrogen occurs from a molecular hydrogen complex, are explored.

We have recently reported that sustained hydrogen production can be achieved from ethanol[1] or secondary alcohols[2] at rates corresponding to *ca.* 100 catalyst turnovers per hour in reactions catalysed by various rhodium complexes. We now report that hydrogen production from a wide range of alcoholic substrates can be achieved at rates up to an order of magnitude higher if [RuH$_2$(N$_2$)(PPh$_3$)$_3$] is employed as the catalyst.

Table 1 shows the rates of hydrogen production from various substrates catalysed by [RuH$_2$(N$_2$)(PPh$_3$)$_3$], as well as those for reactions catalysed by [RuH$_2$(PPh$_3$)$_4$] and [Rh(bipy)$_2$]Cl (bipy = bipyridine), the best of the rhodium catalysts that we have studied. In almost every case, the rate of hydrogen production using [RuH$_2$(N$_2$)(PPh$_3$)$_3$] is significantly higher than when using the other catalysts (although it should be noted that a higher temperature is employed for the

Table 1. Rates of hydrogen production (catalyst turnovers h^{-1}) from alcohols catalysed by Group VIII metal complexes in the presence of sodium hydroxide.[a]

Catalyst	MeOH	EtOH	PrOH	Substrate BuOH	$(CH_2OH)_2$	$(MeCHOH)_2$	$(CH_2OH)_2CHOH$
$RuH_2(N_2)(PPh_3)_3$	6.4	148.1[b]	191.0	523.5	515.9	217.5	12.4
$RuH_2(N_2)(PPh_3)_3 + h\nu$	37.3	210.2	238.1	458.0	1185.3		37.6
$RuH_2(PPh_3)_4$	7.5	23.8	66.1	526.5	149.3		18.4
$RuH_2(PPh_3)_4 + h\nu$	27.7	138.7	161.3	455.9	431.0		22.3
$[Rh(bipy)_2]Cl$[c]	7.5	120.3	96.9	87.5	43.8	184.6	21.3

[a] Conditions: [catalyst] = 1—5 × 10^{-4} mol dm^{-3}; [NaOH] = 1 mol dm^{-3}, 150 °C, 5 cm^3, 2 h, ±5%. [b] The rate was 97.6 h^{-1} over the next 17 h. [c] 120 °C.

Table 2. Rates of hydrogen production [n = catalyst turnovers h^{-1} (±5%)] from propan-2-ol catalysed by various ruthenium complexes at 150 °C.

| Complex	Concentration /10^{-4} mol dm^{-3}	n/h^{-1}
$RuH_2(N)_2(PPh_3)_3$	1.96	330
$K[RuH_3(PPh_3)_3]$[a]	3.2	344
$[RuH_4(PPh_3)_3]$	4.7	317

[a] Contaminated with small amounts of $[RuH_4(PPh_3)_3]$.

ruthenium catalyst) and illumination† increases the rate of hydrogen production still further. The maximum rate is observed using ethane-1,2-diol under illumination and corresponds to ca. 5 litres of hydrogen per litre of catalyst solution per hour. Base is required to make these reactions proceed, suggesting that the first step of the reaction might involve attack of alkoxide ion on the ruthenium complex to give an anionic species from which aldehyde is lost to give the known[3] $[RuH_3(PPh_3)_3]^-$.

Halpern has recently demonstrated[4] that this anionic complex is an efficient ketone hydrogenation catalyst precursor, but that the reaction involves initial protonation by product alcohol to give the known $[RuH_4(PPh_3)_3]$ which is the active catalytic species. This latter complex contains molecular hydrogen,[5] which is readily replaced[5] by neutral or anionic donors to release H_2.

A possible mechanism for the dehydrogenation of alcohols, based on similar reactions is shown in Scheme 1. Consistent with this scheme, Table 2 shows that the rate of hydrogen production from propan-2-ol, a substrate for which decarbonylation of the alcohol is unlikely to occur, is the same for reactions catalysed by $[RuH_2(N_2)(PPh_3)_3]$, $[RuH_4(PPh_3)_3]$, or $K[RuH_3(PPh_3)_3]$, suggesting that they at least form a common intermediate. Furthermore, reaction of a saturated solution of $K[RuH_3(PPh_3)_3]$ in tetrahydrofuran (THF) with excess NaOH in propan-2-ol (0.25 mol dm^{-3}) leads quantitatively to $[RuH_4(PPh_3)_3]$, which precipitates, thus indicating the very high basicity of the ruthenium anion. Similarly, $[RuH_4(PPh_3)_3]$ is formed quantitatively on warming a THF solution of $[RuH_2(N_2)(PPh_3)_3]$ with excess NaOH in propan-2-ol under argon. These stoicheiometric reactions are entirely consistent with the mechanism of the scheme and suggest that loss of H_2 from $[RuH_4(PPh_3)_3]$ is rate determining.

The very rapid rates of hydrogen production in the reactions catalysed by $[RuH_2(N_2)(PPh_3)_3]$ can then be attributed to: (i) the facile formation of the alkoxide complex on account of the lability of the N_2 molecule; (ii) the facile protonation of the
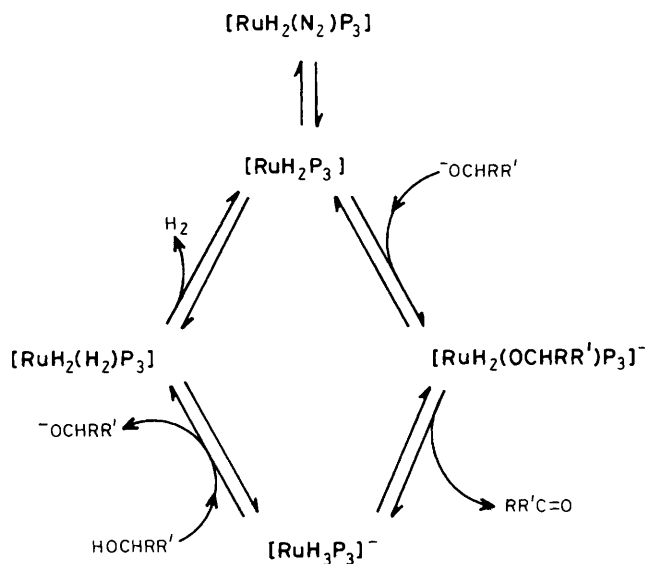
Scheme 1. Mechanism for the production of hydrogen from alcohols catalysed by $[RuH_2(N_2)(PPh_3)_3]$.

trihydrido species under basic conditions, on account of its negative charge; (iii) the lability of H_2 in $[RuH_4(PPh_3)_3]$ on account of its being present as co-ordinated dihydrogen {hydrogen is lost much more slowly from the all hydride containing $[RuH_3(PPh_3)_3]^-$}.[4] We believe that this is the first example of a catalytic reaction in which the importance of co-ordinated molecular hydrogen has been demonstrated (in this case as a good leaving group).

$[RuH_4(PPh_3)_3]$ and related complexes are known[6] to decarbonylate alcohols readily to give $[RuH_2(CO)(PPh_3)_3]$, and indeed, quantitites of this material can be recovered after catalytic dehydrogenation reactions, e.g. of ethanol or butanol. However, this too is an active dehydrogenation catalyst [62 turnover h^{-1} for ethanol containing NaOH (1 mol dm^{-3}) at 150 °C]. The increase in rate on illumination may arise because of photochemical enhancement of the rate of H_2 evolution from $[RuH_4(PPh_3)_3]$,‡ although it is also possible that light increases the rate of the reaction catalysed by $[RuH_2(CO)(PPh_3)_3]$ formed in situ and hence the apparent overall rate of H_2 production.

The very high rate of hydrogen production from ethane-1,2-diol may be attributable to the much higher acidity of this alcohol, or it may indicate chelate binding of the substrate.

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† Light from a 500 W tungsten–halogen lamp was focused on to the sample.

‡ Although photochemical loss of H_2 from $[RuH_4(PPh_3)_3]$ does not appear to have been studied, photochemical loss of H_2 from related complexes, including $[RuH_2(CO)(PPh_3)_3]$ is well known.[7]

Consistent with the latter suggestion would be the observation that efficient hydrogen production is found for butane-2,3-diol, which could also form a 5-membered chelate ring, but that hydrogen production from propane-1,2,3-triol, which is a stronger acid than ethane-1,2-diol,[8] is less efficient. In the last case, a 5-membered ring can also be formed but the presence of an extra CH_2OH group is likely to make this a sterically rather congested mode of bonding.

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