Sulphur-containing Dinuclear Rhodium Complexes as Catalyst Precursors for the Selective Hydroformylation of Alkenes

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Dinuclear thiolato bridged complexes, particularly $[\mathrm{Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2}]$, catalyse the hydroformylation of hex-1-ene at low pressure and temperature to afford selectively and with high turnover rates the corresponding aldehydes.

In catalysis, sulphur or sulphur compounds are normally considered to be poisons, particularly for oxo processes with rhodium catalysts since the rhodium concentration is usually maintained at a low level and no recycling takes place.[1]

There has been much recent interest in the catalytic activity of various dinuclear rhodium(I) complexes such as $[\mathrm{Rh_2(\mu\text{-}H)_2\{P(OPr^i)_3\}_4}]$[2] or $[\mathrm{Rh_2(\mu\text{-}SR)_2\{P(OR')_3\}_4}]$[3] in hydrogenation. We have examined the activity of dinuclear thiolato bridged rhodium complexes for hydroformylation and compared their activity with that of the mononuclear $[\mathrm{RhH(CO)(PPh_3)_3}]$ complex[4] under the same conditions.

$[\mathrm{Rh_2(\mu\text{-}SBu^t)_2\{P(OMe)_3\}_4}]$

(1)

$[\mathrm{Rh_2(\mu\text{-}SBu^t)_2(CO)_2\{P(OMe)_3\}_2}]$

(2)

$[\mathrm{RhH(CO)(PPh_3)_3}]$

(3)

$[\mathrm{RhCl(CO)\{P(OMe)_3\}_2}]$

(4)

$[\mathrm{(H)_2\{P(OMe)_3\}(CO)Rh^{III}(\mu\text{-}SBu^t)_2Rh^I(CO)\{P(OMe)_3\}}]$

(5)

We have studied the activity of the complexes **(1)** and **(2)** which are very soluble in common solvents (even alkanes), under low pressure (5 bar) and low temperature (80 °C) conditions, with a mixture (1 : 1) of H_2 and CO, for the conversion of hex-1-ene into the corresponding aldehydes, *i.e.* heptanal and 2-methylhexanal.

As shown in Figure 1, complex **(1)** showed a very modest catalytic performance when compared with $[\mathrm{RhH(CO)(PPh_3)_3}]$[4] **(3)**. Complex **(3)**, used without excess of triphenylphosphine, led to a good initial rate which rapidly decreased, however, and for the complete conversion of hex-1-ene the reaction required 16 h. Complex **(2)** showed a short induction period after which the rate rapidly increased to *ca.* 2.4 mmol min^{-1}, *i.e.*, a turnover rate[†] of *ca.* 4.4 min^{-1} (Figure 2). Under the conditions in Figures 1 and 2, at least 90% conversion was attained in less than 1 h.

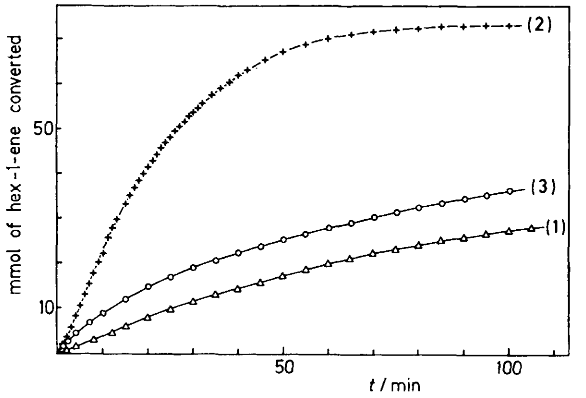

Figure 1. Conversion of hex-1-ene using the complexes **(1)**—**(3)**: P = 5 bar; T = 80 °C; 10 cm^3 of hex-1-ene in 40 cm^3 of toluene; 0.55 × 10^{-3} g-atom of rhodium.

Finally, although the rate decreased at the end of the reaction (Figure 2) the addition of fresh alkene caused the reaction to start immediately again with a rate comparable to that initially observed. Thus, the catalytic species is not, or only very slightly, deactivated after reaction; this effect is presumably superimposed on the non-stationary conditions when the hex-1-ene concentration was low.

Hex-1-ene was selectively converted into heptanal (*ca.* 80%) and 2-methylhexanal (*ca.* 20%); hydrogenation or isomerisation of the double bond was not observed.

Preliminary studies on the mechanism provided some information. ^{31}P N.m.r. spectroscopy indicated that (i) no hex-1-ene co-ordination to rhodium occurred when 1 mol. equiv. of alkene was added to complex **(2)**, (ii) no stable nor isolable hydride species was formed when complex **(2)** was heated at 80 °C in an atmosphere of hydrogen, (iii) complex **(2)** remained unchanged when heated at 80 °C in the presence of a mixture of hydrogen and carbon monoxide (*ca.* 1 : 1), (iv)

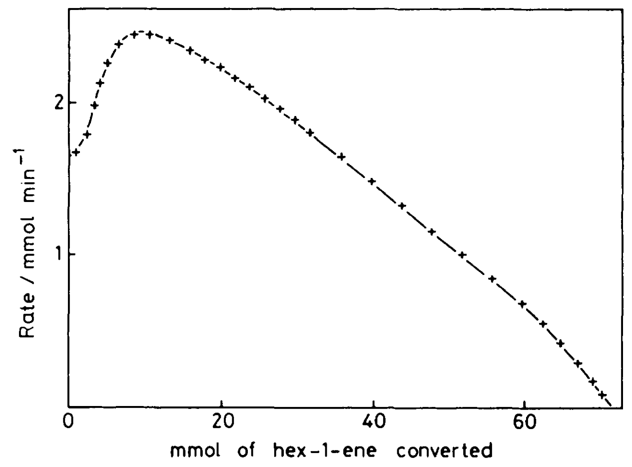

Figure 2. Rate of the reaction of **(2)** as a function of the conversion of hex-1-ene.

[†] The turnover rate is defined here as the number of molecules of substrate converted per g-atom of rhodium per unit time. In this case (5 bar; 80 °C), the initial turnover rate, obtained from Figure 2, as the ordinate at time t = 0, is 6 min^{-1}. However, if we consider that the complex acts as a dinuclear entity (although no catalytic cycle can be presently shown) each molecule of complex activates one molecule of dihydrogen, one molecule of carbon monoxide, and one molecule of hex-1-ene: thus, the turnover rate would be 12 min^{-1}.

when experiment (iii) was performed with 1 equiv. of hex-1-ene a small amount of a new complex appeared, this complex, as in (ii), having no hydrido ligands on rhodium. Moreover the ^{31}P n.m.r. spectra recorded after catalysis starting from complex (**2**) or from complex (**2**) including two extra trimethyl phosphite ligands were the same except for the presence in the latter case of free ligand.

The complex [RhCl(CO){P(OMe)$_3$}$_2$]^5 (**4**) was prepared and treated with 1 equiv. of LiSBu^t; solution ^{1}H and ^{31}P n.m.r. spectra as well as analysis of the product obtained after crystallization were in agreement with the presence of complex (**2**). No equilibrium between complex (**2**) and a mononuclear species was detected in solution. Thus we believe that the catalytic cycle involves dinuclear species. Since experiment (i) shows that no co-ordination of hex-1-ene occurs, a mixed complex (**5**) could be formed in an early step. Complex (**5**) is reminiscent of the intermediate species [(H)$_2${P(*o*-tolyl)$_3$}$_2$-Rh(μ-Cl)$_2$Rh{P(*o*-tolyl)$_3$}$_2$] proposed by Tolman *et al.*[6] and an analogous complex isolated by Muetterties *et al.*[7] in obtaining [H$_2${P(OPr^i)$_3$}$_2$Rh(μ-H)$_2$Rh{P(OPr^i)$_3$}$_2$] from [Rh$_2$(μ-H$_2$)-{P(OPr^i)$_3$}$_4$].

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