

Preliminary communication

Novel active dirhodium complexes for the low pressure hydroformylation reaction. Unexpected inhibiting effect of high partial pressures of hydrogen

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(Received June 13, 1991)

Abstract

The complex $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ was shown to be an active precursor for the low pressure hydroformylation of terminal alkenes in the presence of an excess of triphenylphosphine. Preliminary kinetic studies have shown that as usual has CO an inhibiting effect, but unexpectedly the reaction was also inhibited by high H_2/CO ratios.

It was previously shown that the dinuclear μ -thiolato rhodium complexes with phosphite ligands $[\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2\text{L}_2]$ were active and selective for the hydroformylation of hex-1-ene at 0.5 MPa and 80°C [1,2]. However our first experiments with complexes with $\text{L} = \text{PPh}_3$ showed low conversion rates [3]. Analyses of the complex after reaction revealed the presence of $[\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_4]$, which was shown independently to be inactive. We also observed [4] that addition of thiol to the $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ complex led to $[\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2(\text{PPh}_3)_2]$ and four equivalents of triphenylphosphine; it was shown that the two catalytic systems follow independent routes [4].

We have found that the molar phosphorus to rhodium ratio has a very large influence on the rate of the reaction. In addition, coordinating solvents such as *N,N'*-dimethylformamide reinforce this effect: for instance when $\text{P/Rh} = 6$ the turnover frequency (at $t = 10$ min) reaches 23 min^{-1} , (see Table 1). Further addition of free ligand lowers the rate slightly. The selectivity towards linear aldehyde can be significantly improved by use of high P/Rh ratios, whereas it is almost unaffected by the nature of the solvent. These studies carried out with a classical CO/H_2 syngas (1/1) show that it is necessary to have an excess of triphenylphosphine with respect to $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ in order to main-

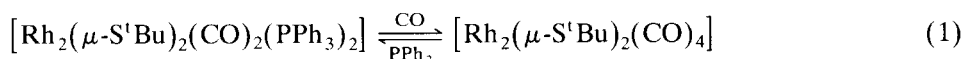
Table 1

Effect of solvent on the activity of the system $[\text{Rh}_2(\mu\text{-S}^i\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]/\text{PPh}_3^a$

Solvent	R_{max}^b ($\mu\text{mol/s}$)	Turn-over Frequency (min^{-1})	Linearity $n/(n+1)$ (%)
Toluene	46	16	76
$\text{C}_2\text{H}_4\text{Cl}_2^c$	73	26	73
DMF	65	23	76

^a $[\text{Rh}] = 1.1 \times 10^{-4}$ mol; $\text{P/Rh} = 6$; $T = 80^\circ\text{C}$; $P = 0.8$ MPa; $(\text{CO}/\text{H}_2 = 1/1)$; solvent: 25 ml; hex-1-ene: 40 mmol. ^b R_{max} corresponding to the maximum of the experimental curve. ^c Turn-over frequency determined at $t = 10$ min.

tain the integrity of the active species, that is to keep the equilibrium in eq. 1 over to the left:



A kinetic study was undertaken in order to gain more insight into the catalytic cycle. The kinetic curves (Fig. 1) appear to be particularly difficult to interpret since they shown an induction period and a very short time during which the quasi stationary state approximation applies. However, coherent conclusions were obtained from the rates calculated for 20% conversion of oct-1-ene, and the results were quite similar to those at 30% and 40% conversions *. The salient influences of the various parameters allow to the following main conclusions. The selectivity in aldehydes is usually at least 98% for H_2/CO ratios near 1/1; some isomerization to oct-2-ene was observed, but no octane or alcohols were detected except at high H_2 partial pressures. The reaction order with respect to the alkene is ca. 1. Moreover the initial concentration of alkene in toluene plays an important rôle (Fig. 2) since the rate increases, though not linearly, when the initial amount of

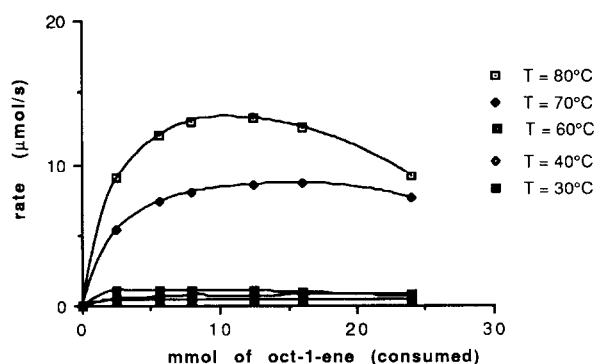


Fig. 1. Kinetic curves for the hydroformylation of oct-1-ene at 0.5 MPa of total pressure ($\text{H}_2/\text{CO} = 1/1$) at various temperatures; $[\text{Rh}_2(\mu\text{-S}^i\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2] = 1.05 \times 10^{-4}$ mol.

* Hex-1-ene or oct-1-ene gave similar results, but for analytical reasons, particularly in respect of the separation of the alkane isomers and the alkane, we preferred to use oct-1-ene.

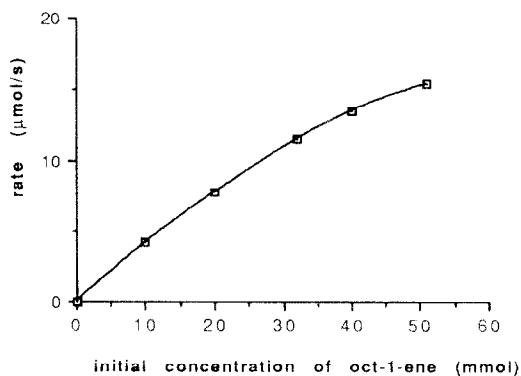


Fig. 2. Reaction rate (determined for a 20% conversion) as a function of the initial concentration in alkene; similar curves were observed for 10 or 30% conversion.

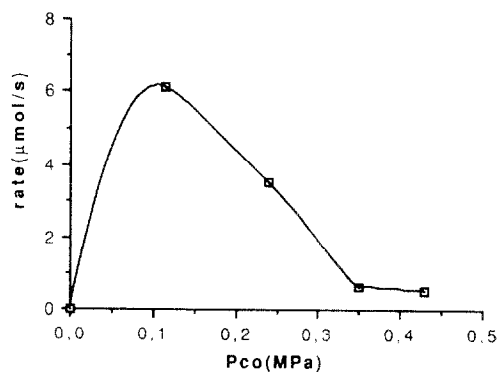


Fig. 3. Reaction rate (at 20% conversion) versus the CO partial pressure ($P(\text{H}_2)$ maintained 0.12 MPa; $T = 80^\circ\text{C}$).

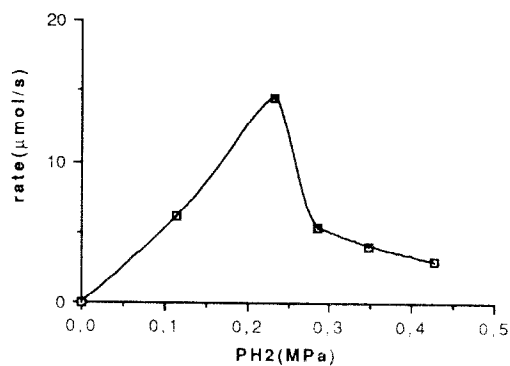


Fig. 4. Reaction rate (at 20% conversion) versus the H_2 partial pressure ($P(\text{CO})$ maintained at 0.114 MPa; $T = 80^\circ\text{C}$).

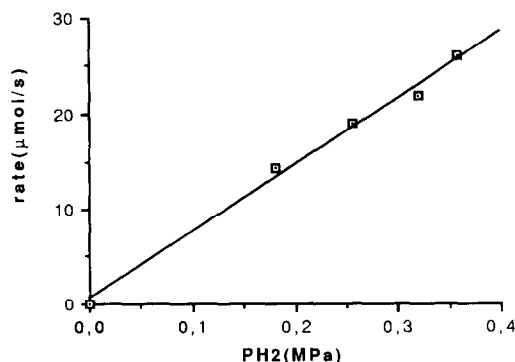
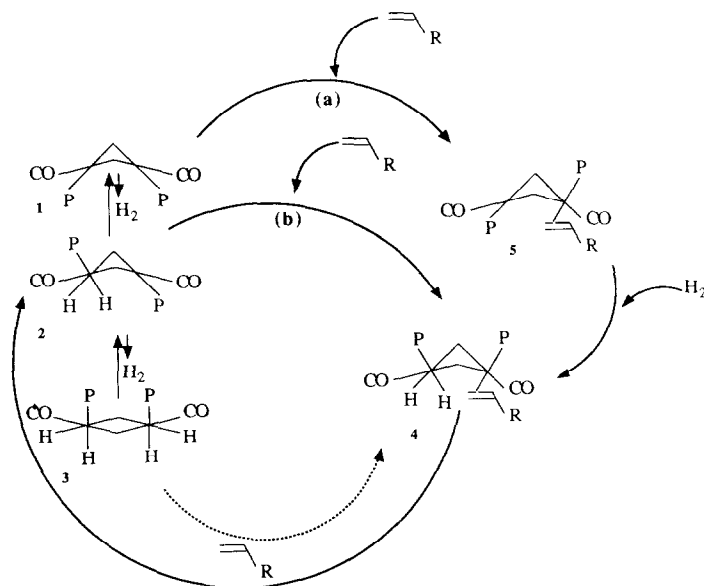


Fig. 5. Reaction rate versus the $P(H_2)$ partial pressure. Linear part of the curve of Fig. 4 checked with $P(CO)$ maintained at 0.21 MPa: $T = 80^\circ\text{C}$ (at 20% conversion).

oct-1-ene is increased. Figures 3 and 4 show the effects of the CO and H_2 partial pressures. When $P(H_2)$ was kept at 0.12 MPa, the maximum rate was found for $P(CO) = 0.12$ MPa. Above this value the rates decrease; this effect is quite usual in the rhodium-catalysed hydroformylation, in which the order with respect to CO is -1 [5] (although Chaudhari recently observed a more complex order with respect to CO for the $[HRh(CO)(PPh_3)_3]$ species [6]). However, when $P(CO)$ was maintained constant at 0.114 MPa (Fig. 4) the reaction rate was almost linearly related to $P(H_2)$ until the maximum value of $P(H_2) = 0.23$ MPa was reached. Above 0.23 MPa increase in the hydrogen partial pressure presents a marked inhibiting effect; for instance at $P(H_2) = 0.43$ MPa the reaction rate was only $3 \mu\text{mol s}^{-1}$ whereas for $P(H_2) = 0.23$ MPa it was $14.5 \mu\text{mol s}^{-1}$.



Scheme 1. Beginning of the catalytic cycle showing the alkene (a) and the hydride (b) routes; P denotes PPh_3 .

We previously proposed a catalytic cycle involving dinuclear intermediates [3], and which is partially depicted in Scheme 1. In this coordination of alkene to the active species **2** gives **4**, from which the hydride transfer to give an alkyl intermediate followed by the CO insertion will continue the catalytic cycle. In our opinion two explanations can be advanced to account for the inhibiting effect of H_2 . In the first species **2** is transformed into the tetrahydrido species **3**, which slowly gives compound **4** in the presence of alkene. In the second the fastest "alkene route" is through species **5**, which results from the initial coordination of the alkene to **1**: too high a $P(H_2)$ would result in formation of species **2** and retard the coordination of the alkene to give **4**.

It is desirable to demonstrate the presence of hydrido species as intermediates. In reaction on NMR tubes, even under low pressures (0.25 MPa) of hydrogen and carbon monoxide, such species have not been detected. Work is in progress to try to detect them under higher pressures.

Acknowledgments. E. Leandro de Oliveira thanks the University Federal of Rio Grande do Norte (Natal), Brazil, for leave of absence, spent in the Laboratoire de Chimie des Procédés. We are indebted to the comptoir Lyon-Alemand Louyot for a generous gift of rhodium salts.

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