Efficient Hydroformylation Rhodium Catalysts using Water as Solvent and Hydrogen Source

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The fast and selective conversion of alkenes into aldehydes can be achieved under mild conditions by using the CO/H_2O couple in the presence of the water-soluble complexes $Rh_2(\mu\text{-}SBu^t)_2(CO)_2(Ls)_2$, $Rh(cod)(Ls)_2^+$ (cod = cyclo-octa-1,5-diene), and $RhH(CO)(Ls)_3$, where Ls is the trisulphonated phosphine, $P(m\text{-}C_6H_4SO_3Na)$.

Recently, much effort[1] has been devoted to performing the water-gas-shift reaction (1) at low temperature using transition metal complexes as catalysts. Various applications using

$$CO + H_2O \xrightarrow{M} CO_2 + H_2 \qquad (1)$$

hydride complexes directly in reduction reactions have been shown.[2] However, although the equilibrium showed a large shift towards hydrogen production at low temperature ($K_{1073\text{ K}} = 1.105$, $K_{300\text{ K}} = 1.5 \times 10^3$), the rate remained low. We are interested in carbonylation reactions, particularly in the hydroformylation reaction, and have recently shown[3] that the dinuclear rhodium precursors $Rh_2(\mu\text{-}SR)_2(CO)_2L_2$ catalyse the conversion of alkenes into aldehydes at low temperature and pressure with high rates and complete selectivity, reaction (2).

$$R\text{–}CH{=}CH_2 + CO + H_2 \xrightarrow{M} RCH_2CH_2CHO + RCH(Me)CHO \qquad (2)$$

The use of the water-soluble phosphorus ligand $P(m\text{-}C_6H_4SO_3Na)_3$,(Ls), allowed us to obtain a high selectivity for the linear aldehyde and to solve the crucial problem of catalyst recovery since the organic products were easily separated from the catalyst phase; with propene, turnover frequencies as

Table 1. Catalytic activity of $Rh_2(\mu\text{-}SBu^t)_2(CO)_2(Ls)_2$ for the hydroformylation of hex-1-ene using the CO/H_2O couple.[a]

pH	% Yield[b]	Turnover frequency /h^{-1}	Ratio of linear : branched aldehyde
6	53	28[c]	18 : 1
4.8[d]	75	40[c]	23 : 1

[a] $T = 80\,°C$; $P_{CO} = 8 \times 10^5$ Pa; 10^{-4} at. g Rh; P : Rh 6 : 1; H_2O (25 cm^3); hex-1-ene (5 cm^3). [b] After 15 h. [c] Calculated for a dinuclear species. [d] Acetic buffer.

Table 2. Activities of various rhodium precursors for the hydroformylation of hex-1-ene using the CO/H_2O couple.[a]

Precursor	% Yield[b]	Turnover frequency/h^{-1}	Ratio of linear : branched aldehyde
$Rh_2(\mu\text{-}SBu^t)_2(CO)_2(Ls)_2$	53	28[c]	18 : 1
$Rh(cod)(Ls)_2ClO_4$	20	5,3	15.2 : 1
$RhH(CO)(Ls)_3$	25	6,6	9 : 1

[a] $T = 80\,°C$; $P_{CO} = 8 \times 10^5$ Pa; 10^{-4} at. g Rh; P : Rh 6 : 1; pH = 6; H_2O (25 cm^3); hex-1-ene (5 cm^3). [b] After 15 hours. [c] Calculated for a dinuclear species.

high as 1 s^{-1} are reached with a linear to branched aldehyde ratio of 96 : 4.[4,5] This water-soluble catalytic system prompted us to study reaction (3) as an application of the water-gas-shift reaction (1).

$$R\text{–}CH{=}CH_2 + H_2O + 2CO \xrightarrow{M} RCH_2CH_2CHO + RCH(Me)CHO + CO_2 \quad (3)$$

The ligand Ls can conveniently be used either in neutral or in acidic media. Basic conditions were avoided since Ls is oxidized to OLs. Table 1 shows some important results. High conversion rates were obtained after 15 hours, especially in acidic medium. At low pH values, the rates are slow and a small amount of the rhodium complex was found in the organic phase. High overall selectivities for aldehydes were obtained since only about 3% of the alkenes were hydrogenated. Furthermore the selectivity for linear aldehydes is similar to that observed with the classical CO/H_2 couple,[5] using the same water-soluble Ls ligand.

We have extended this study to other complexes of rhodium, *i.e.*, $Rh(cod)(Ls)_2BF_4$ and $RhH(CO)(Ls)_3$, and the catalytic activities in neutral conditions are given in Table 2. At the same rhodium concentration, the mononuclear species are significantly less active than the dinuclear precursor. Moreover, whereas the overall selectivity for aldehydes may be comparable, the linear aldehyde percentage is sensitive to the nature of the catalyst, and the complex $RhH(CO)(Ls)_3$ appears to be less selective, giving a linear : branched ratio of 9 : 1. In all these experiments the gas phase after reaction contains about 20% of hydrogen. These results confirm that all three rhodium complexes, under our mild conditions, are active catalysts for the water-gas-shift reaction (1).

In conclusion, the water-soluble ligand Ls allowed the conversion of alkenes into aldehydes in a two phase medium, with convenient rates and high selectivities, especially using the dinuclear complex $Rh_2(\mu\text{-}SBu^t)_2(CO)_2(Ls)_2$. This catalytic system is potentially very useful since it can be used with either the CO/H_2 couple or the CO/H_2O couple depending on the conditions.

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