Dinuclear rhodium(I) complexes for the selective hydroformylation of alkenes using either CO/H₂ or CO/H₂O

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Abstract - The dinuclear rhodium(I) Rh₂(μ-S-R)(CO)₂(PPh₃)₂ complexes have been designed for the low pressure hydroformylation of various alkenes. The reaction is fully selective in aldehydes and turnover frequencies as high as 1 s⁻¹ can be reached. A catalytic cycle in which all the intermediates remain dinuclear is consistent with the observed data and involves a cooperative effect between the two metal centres. The use of the water-soluble tris(m-sulphopheny1)phosphine ligand led to 96% of selectivity in linear aldehyde and solved very easily the problem of catalyst recovery by decantation; in this case the CO/H₂O and CO/H₂ couples can be undistinguishably used as feedstock.

INTRODUCTION

During the past decade a great effort has been made to solve the problem of chemoselectivity and regioselectivity in homogeneous catalysis, particularly in hydroformylation (ref. 1). The HRh(CO)(PPh₃)³ complex 1 (ref. 2) was shown to be very interesting for propene since the hydrogenation in propane was limited to 5% and a good butanal to methyl-2-propanal ratio of 92/8 was obtained provided a large excess of triphenylphosphine should be introduced. We observed that for heavy alkenes as well as allyl- or propenyl-benzenes issued from the biomass this complex is not particularly well adapted due to extensive isomerization of the reactive terminal carbon-carbon double bond (ref. 3). Hydrogenation cannot be avoided and deactivation is due to the formation of the species Rh₄(μ-PPh₂)(CO)₅(PPh₃) (ref. 4).

RESULTS AND DISCUSSION

We decided to design novel catalyst precursors in order to improve the mononuclear complex 1 and we explored various dirhodium complexes bridged by two thioato ligands with the assumption that a cooperative effect between the two metal centres could induce high selectivities and reactivities. The complexes Rh₂(μ-S-R)(CO)₂(P(OMe)₃)₂ were shown to be very active for the low pressure hydroformylation of 1-hexene (5 bar, 80°C) particularly when R = t-Bu and R' = Me or Ph (complexes 2 and 3), since a turn over frequency of 32 min⁻¹ was observed for 2 (ref. 5). This catalytic system is characterized by a full selectivity in aldehyde and no isomerization of the terminal alkene, by a modest selectivity in linear aldehyde (n/i ≈ 88/12 in the optimum conditions) and by the recovery after catalysis of the dinuclear species 2 or 3 which can convert again a new charge of 1-hexene without loss of activity (ref. 5 and 6). The complex Rh₂(μ-S-t-Bu)(CO)₂(PPh₃)₄, 4, needs, to be very active, a slight excess of triphenylphosphine in order to avoid the formation of the inactive species Rh₂(μ-S-t-Bu2)(CO)₄ 5 in the hydroformylation reaction and to shift the equilibrium 5 ⇌ 4 + (x-2)PPh₃ towards the right side. For instance, at 8 bar with a P/Rh ratio of 11, a turnover rate in the initial conditions of 53 min⁻¹ was reached (n/n+i = 78%) whereas when P/Rh = 26, T.O.R. = 32 min⁻¹ and n/n+i = 88%. Moreover in polar solvents higher rates can even be obtained : C₂H₅Cl₂, P/Rh = 10, T.O.R. = 65 min⁻¹.

In addition, we discovered that complex 4 is selectively and irreversibly formed starting from 1 by addition of one equivalent of thiol. We checked by IR and ³¹P NMR spectroscopies that the following equation is obeyed :

\[
2 \text{HRh(CO)}(\text{PPh}_3)_3 + 2 \text{t-BuSH} \rightarrow \text{Rh}_2(\mu-\text{S-t-Bu})_2(\text{CO}_2)(\text{PPh}_3)_2 + 4 \text{PPh}_3 + 2\text{H}_2
\]

This reaction is slow under the ambient conditions or in the hydroformylation conditions and the kinetic curves show that the catalytic system starts from 1 with a moderate rate to reach 4 with higher rates ; after catalysis the dinuclear species 4 is only found in the reaction mixture.

Numerous IR, ¹H and ³¹P NMR spectroscopic investigations were carried out on complexes 2 and 3 + H₂ or H₂O and in the hydroformylation conditions. We never detected any intermediate species and we only observed the presence of the starting rhodium complexes and the growing of the aldehydes. The model complex Ir₂(μ-μ-S-t-Bu)₂(CO)₂(P(OMe)₃)₂ 6 charged in a NMR tube with 1-hexene and 2.5 bar of syn-gas was slowly transformed into two species 6 and 7. Complex 6 is characterized by one ³¹P signal (δ = 96.4 ppm) and two hydrido signals (δ₁H₁ = -7.17 dd, δ₂H₂ = -15.07 dd, J₉₁H₂ = 3.6,
From the observation of the changes on the reactivity induced by varying the alkyl or aryl group of the thiolato ligand or the phosphorus ligand, on the basis of Extended Hückel calculations (ref. 6) and more recently ab initio calculations (ref. 10) on several intermediate species, we can propose a catalytic cycle in which the dinuclear core is maintained. All the steps have been presented elsewhere (ref. 6). The rate determining step is certainly that related to the activation of dihydrogen:

\[
\text{Rh}_2(\mu-\text{SR})_2(\text{CO})_2L_2 + \text{H}_2 \rightarrow \text{H}_2(\text{CO})L \text{Rh}(\mu-\text{SR})_2 \text{Rh}(\text{CO})L
\]

Three concepts give account of the peculiar reactivity presented by our dinuclear complexes: (i) the flexibility around the bridging ligands allows the transfer of an atom or a ligand from one metal centre to the other one, (ii) the σ donation of the various ligands or parts of the molecule on one metal centre, (iii) the back donation on the whole complex. These last two concepts are related to the electron density on one rhodium atom modulated by the ligands at each step (oxidative addition, coordination of the alkene, hydride transfer, CO insertion, reductive elimination). In our opinion these concepts account for the cooperative effect which takes place between the two rhodium centres and which is certainly the driving force of the selectivity and of the rate we observed for the low pressure hydroformylation reaction.

Various investigations were carried out to extend this catalytic system by varying the bridges or by introducing diphosphine ligands, some of them containing transition metals.

Preparation of \(\text{Rh}_2(\mu-X)_2(\text{CO})_2L_2\) complexes bridged by azolate ligands led to active precursors similar to complexes 2-4 for the hydroformylation of alkenes but with lower rates (ref. 11, 12). Particularly relevant was however the synthesis of the mixt complex \(\text{COD Rh}(\mu-S-t-Bu)(\mu-pz)\), COD Rh COD by reaction of COD Rh Cl (pyrazole) with COD Rh (acac) and then substitution of the C1 bridge by the S-t-Bu ligand (ref. 13). Carboxylation followed by addition of two aliquots of \(\text{P}(\text{OME})_3\), \(\text{P}(\text{OPh})_3\) or \(\text{PPH}_3\) led to the formation of the \(\text{Rh}_2(\mu-S-t-Bu)(\mu-pz)(\text{CO})_2L_2\) complexes. These species can be slowly and irreversibly formed by mixing the homo-bridged complexes. An X-ray crystal structure of 8 revealed a bent geometry, a square planar environment for each rhodium atom and a cis arrangement, the two phosphorus atoms are trans to the bridging sulphur atom. The catalytic activity is only slightly lower than that shown by \(\text{Rh}_2(\mu-S-t-Bu)(\text{CO})_2[\text{P}(\text{OME})_3]_2\); thus, presumably the P-Rh-S-Rh-P framework is responsible for the high level of catalytic activity presented by this family of complexes (ref. 13).

Whereas diphosphine ligands with a too short distance between the two phosphorus atoms, when they react with \(\text{Rh}_2(\mu-S-t-Bu)(\text{CO})_4\), give rise to a complex mixture of rather inactive mono- and di-nuclear species, the bis (diphenylphosphino)propane, dppp, and bis (diphenylphosphino)butane, dppb, ligands led to the complexes \(\text{Rh}_2(\mu-S-t-Bu)(\text{CO})_2L_2\) 9 and 10 (ref. 14, 15). Similarly the ligands 1,1'-bis (diphenylphosphino)ferrocene, dppf, and 1,1'-bis (diphenylphosphino)ruthenocene, dppr, allowed to prepare the same complexes 11 and 12 (ref. 16). By X-ray structures (ref. 17), the complexes were shown to present a bent geometry with a roughly square planar environment for the rhodium atom; the two CO ligands are in a cis arrangement and the diphosphate ligand adopts a symmetrical bridging situation. The rhodium-rhodium distances are respectively 3.039(1) A in 10 and 3.089(1) in 11 (ref. 17). All these complexes are active precursors in hydroformylation, although they present a lower level of activity than complexes 2-4. Complex 10 shows a long period of induction (turnover frequency of 0.2 min\(^{-1}\), 9 is slightly faster (2.3 min\(^{-1}\)), whereas 11, 12 and dppp + \(\text{Rh}_2(\mu-S-t-Bu)(\text{CO})_4\) are characterized by turnover frequencies of 7.7, 8.1 and 7.1 min\(^{-1}\) respectively (ref. 17). The selectivity in aldehydes is quite good; however these catalytic systems give desirably selectivities in linear compound: usually 70% except 83% for 11. Presumably the hydridic character of the hydride ligand is less pronounced than that in 2, 3 and 4 and could be due to the presence of a CO ligand in the trans-position instead of a phosphorus ligand (ref. 6).
For organic synthesis on a large scale and particularly from an industrial point of view, it is crucial to separate very easily and to recover the catalyst. With the light alkenes, the aldehydes are distilled off without any significant loss of activity for the rhodium complex (ref. 1). However, starting from terpenes or allyl-benzenes (estrargole, safrol, eugenol...) we observed that distillation induced extensive decomposition of the complexes. We investigated the immobilization of the rhodium complexes onto an insoluble support or instead of using phosphine ligands (ref. 18, 19), we grafted them through the thiolato bridges (ref. 20). Starting from Rh₂Cl₂(CO)₄ and support-SH, then by addition of two aliquots of phosphine or phosphite, we prepared the equivalents of complexes 2 or 4, i.e. Rh₂(μ-S-support)₂(CO)₂L₂. However these precursors gave poor results in catalysis and a significant loss of rhodium in solution.

In collaboration with Rhône-Poulenc, we preferred to use the water-soluble ligand tris(m-sulphophenyl)phosphine (ref. 21), or Lw, to hold the rhodium complex in the aqueous phase and to recover it by decanting. The use of this ligand in hydroformylation was shown by Rhône-Poulenc, starting from various rhodium salts (ref. 22, 23). We prepared Rh₂(μ-S-t-Bu)₂(CO)₂(Lw)₂, 13, and compared its performances with those of HRh(CO)(Lw)₃, 14, for the hydroformylation of 1-hexene at 5 bar and 80°C (ref. 24). In 65 h, 72% of the alkene were transformed with 13 and 50% with 14; in both cases the selectivity in aldehyde was 98-99%. As previously observed for the Rh-Lw systems (ref. 22, 23) and by Wilkinson and coworkers for the HRh(CO)(L₁)₃ complex containing the monosulphonated triphenylphosphine ligand (ref. 25), the selectivity in linear aldehyde was 93% for 14, 88% for 15. Adding a slight excess of Lw to 13 (P/Rh = 6) improved this selectivity to 96% (ref. 25). After separation of the organic phase, the aqueous layer can be recycled without loss of catalytic activity nor loss of rhodium (< 0.5 ppm). These performances are quite general (ref. 24, 26) and for the hydroformylation of propene at 50 bar of total pressure and 120°C, we observed a complete conversion into butanal and methyl-2 propanal in 1 hour; with a large excess of ligand, P/Rh = 50 or 100, the selectivity in butanal reached 96%. For a P/Rh ratio of 50 a turnover frequency of 28 min⁻¹ was calculated whereas, starting from Rh₂Cl₂(COD)₂ in the same conditions to generate HRh(CO)(Lw)₃, the turnover frequency was only 5 min⁻¹ (ref. 24).

Moreover, during the past decade the Water-Gas-Shift reaction (WGSR) has been largely studied in order to catalyze it at low temperature by transition metal complexes (ref. 27), the production of hydrogen being in these conditions favoured:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \quad \quad K_{400} = 1.5 \times 10^3; \quad K_{673} = 11.7
\]

In addition, with the late transition metals, the hydride intermediates can be used to catalyze various reactions. The applications of the WGSR to produce fine chemicals was recently reviewed (ref. 28). We examined the possibility to carbonylate directly the alkenes with the CO/H₂O couple. Disappointing results were obtained with HRh(CO)(PPH₃)₃ and Rh₂(μ-S-t-Bu)₂(CO)₂(PPh₃)₂, which catalyzed very slowly in ethoxyethanol the hydroformylation of 1-hexene, provided triethylamine should be added as cocatalyst: 8% of aldehyde in 18 h, P = 8 bar, t = 80°C (ref. 29). Extensive isomerization occurred and the two complexes were transformed into the inactive species PhRh(CO)(PPh₃)₂ and Rh₂(CO)₄(PPh₃)₄ (ref. 30).
Table 1. Hydroformylation of 1-hexene in neutral and acidic media catalyzed by Rh$_2$(μ-S-t-Bu)$_2$(CO)$_2$(Lw)$_2$ 13 and [Rh(COD)(Lw)$_2$]$^+$ 15

<table>
<thead>
<tr>
<th>pH</th>
<th>H$_2$ produced (%)</th>
<th>conversion into aldehydes (%)</th>
<th>Turnover frequency (h$^{-1}$)</th>
<th>n/n+i (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>15</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>12</td>
<td>53</td>
<td>28</td>
</tr>
<tr>
<td>4.8</td>
<td>21</td>
<td>nd</td>
<td>75</td>
<td>40</td>
</tr>
<tr>
<td>3.7</td>
<td>2</td>
<td>1</td>
<td>40</td>
<td>21</td>
</tr>
</tbody>
</table>

Experimental conditions: Rh $10^{-4}$ g, P/Rh = 6, 1-hexene 40 mmol, H$_2$O 20 cm$^3$, 5 cm$^3$ acetic or formic buffer, T = 80°C, P$_{CO}$ = 8 bar, t = 15 h.

However, with the Lw containing rhodium complexes, we obtained very interesting results since under mild conditions the alkenes were transformed into the corresponding aldehydes with only 2% of hydrogenation, but with selectivities into linear aldehyde of 95-96% (ref. 29):

$$ RCH = CH_2 + 2 CO + H_2O \rightarrow RCH_2CH_2CHO + CO $$

HRh(CO)(Lw)$_2$, 14, and Rh$_2$(μ-S-t-Bu)$_2$(CO)$_2$(Lw)$_2$, 13, are good catalyst precursors in basic media, 13 being two times as fast as 14, but this study was restricted to neutral or acidic conditions since we observed the fast oxidation, presumably catalyzed by the RhOH$^+$ systems, of the Lw ligand into the oxide OLw as well as the formation of heavy products.

In neutral conditions, at 80°C and 8 bar, the selectivity in aldehydes was 98%; 14 gave a turnover frequency of 6.6 min$^{-1}$ and a selectivity in heptanal of 90%, whereas the dinuclear complex 13 gave 28 min$^{-1}$ and 94.8%.

The WGSR can also be accomplished in acidic media (ref. 27, 28); Kaspar et al. have shown that the cationic species [Rh(COD)(L$_1$)$_2$]$^+$, which contains the monosulphonated triphenylphosphine ligand, was an active precursor (ref. 31). Thus we prepared the complex [Rh(COD)(Lw)$_2$]$^+$, 15. Various pH values were examined. Table 1 lists some results of interest.

For the mononuclear complex 15, the reaction rates were improved by decreasing the pH since with a formic buffer (pH = 3.7) the conversion rate was three times as fast as at pH 6. The most interesting results come from the activity of 13 at pH 4.8; indeed a turnover frequency of 40 h$^{-1}$ was obtained instead of 28 h$^{-1}$ at pH 6. The selectivities in linear aldehyde remained quite constant at 95%. The gaseous phase analyzed after the reaction contained more or less hydrogen. In order to have a quantitative measurement of the hydrogen produced and also to understand how the WGSR and the hydroformylation reaction are connected, we have carried out the WGSR alone and calculated the overall amounts of hydrogen coming from water in the two cases. The results are reported in Table 2.

Table 2. Overall H$_2$ produced by the WGSR with or without 1-hexene catalyzed by Rh$_2$(μ-S-t-Bu)$_2$(CO)$_2$(Lw)$_2$; conditions as in Table 1.

<table>
<thead>
<tr>
<th>pH</th>
<th>1-hexene (mmol)</th>
<th>H$_2$ (mmol)</th>
<th>conversion into aldehydes (%)</th>
<th>H$_2$ total (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>40</td>
<td>0</td>
<td>4.8</td>
<td>53</td>
</tr>
<tr>
<td>4.8</td>
<td>40</td>
<td>5.3</td>
<td>7.5</td>
<td>35</td>
</tr>
</tbody>
</table>

The last column of Table 2 shows that the WGSR alone produced 7 mmol of hydrogen, whereas the WGS + hydroformylation reactions required the transformation of 25 to 35 mmol of water. Thus the presence of an alkene increases significantly the production of hydrogen from water. The Water-Gas-Shift seems to be slower than the hydroformylation which utilizes, presumably directly, the hydride species generated by the first reaction.

In conclusion, the dinuclear complexes Rh$_2$(μ-SR)$_2$(CO)$_2$L$_2$ appear to be very active precursors for the selective hydroformylation of alkenes under mild conditions. The use of the water-soluble tris(m-sulphophenyl)phosphine ligand is a powerful method to produce selectively the linear aldehyde and to recover the rhodium catalyst.
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