

## Dinuclear rhodium(I) complexes for the selective hydroformylation of alkenes using either CO/H<sub>2</sub> or CO/H<sub>2</sub>O

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Abstract - The dinuclear rhodium(I) Rh<sub>2</sub>(μ-SR)<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub> 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<sup>-1</sup> 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-sulphophenyl)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/H<sub>2</sub>O and CO/H<sub>2</sub> couples can be undistinguishably used as feedstock.

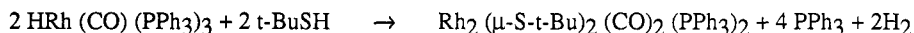
### INTRODUCTION

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)(PPh<sub>3</sub>)<sub>3</sub> 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 Rh<sub>4</sub>(μ-PPh<sub>2</sub>)<sub>4</sub>(CO)<sub>5</sub>(PPh<sub>3</sub>), (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 thiolato ligands with the assumption that a cooperative effect between the two metal centres could induce high selectivities and reactivities. The complexes Rh<sub>2</sub>(μ-SR)<sub>2</sub>(CO)<sub>2</sub>[P(OR')<sub>3</sub>]<sub>2</sub> 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<sup>-1</sup> 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 Rh<sub>2</sub>(μ-S-t-Bu)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, **4**, needs, to be very active, a slight excess of triphenylphosphine in order to avoid the formation of the inactive species Rh<sub>2</sub>(μ-S-t-Bu)<sub>2</sub>(CO)<sub>4</sub> **5** in the hydroformylation reaction and to shift the equilibrium **5** + x PPh<sub>3</sub> = **4** + (x-2)PPh<sub>3</sub> 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<sup>-1</sup> was reached (n/n+i = 78%) whereas when P/Rh = 26, T.O.R. = 32 min<sup>-1</sup> and n/n+i = 88%. Moreover in polar solvents higher rates can even be obtained : C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, P/Rh = 10, T.O.R. = 65 min<sup>-1</sup>.

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 <sup>31</sup>P NMR spectroscopies that the following equation is obeyed :



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, <sup>1</sup>H and <sup>31</sup>P NMR spectroscopic investigations were carried out on complexes **2** and **3** + H<sub>2</sub> or H<sub>2</sub>/CO 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 Ir<sub>2</sub>(μ-S-t-Bu)<sub>2</sub>(CO)<sub>2</sub>[P(OMe)<sub>3</sub>]<sub>2</sub> **5** 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 <sup>31</sup>P signal (δ = 96.4 ppm) and two hydrido signals (δ<sub>H1</sub> = -7.17 dd, δ<sub>H2</sub> = -15.07 dd, J<sub>H1H2</sub> = 3.6,

$J_{\text{PH}_1} = 17.1$ ,  $J_{\text{PH}_2} = 19.6$  Hz); these two  $J_{\text{PH}}$  coupling constants indicate (ref. 7) that the hydrido ligands are *cis* with respect to the phosphorus atom. Moreover these data are similar to those published for the complex  $[\text{COD Ir}(\mu\text{-bis}(\text{diphenylphosphino-pyrazolato})) \text{Ir H}_2 \text{COD}]^+$ , except that one hydrido is *trans* to one phosphorus ligand (ref. 8). The spectroscopic data for **6** are consistent either with  $(\text{CO})_2 \text{Ir}(\mu\text{-S-t-Bu})_2 \text{Ir}(\text{CO})\text{H}_2[\text{P}(\text{OMe})_3]$  or with a mononuclear formula  $\text{Ir H}_2(\text{CO})_2(\text{S-t-Bu})[\text{P}(\text{OMe})_3]$  bearing a terminal thiolato ligand. Concerning species **7**, an AB system in  $^{31}\text{P}$  and a doublet in  $^1\text{H}$  NMR at high field were clearly detected at 173K:  $\delta_{\text{P}_1} = 114.6$  ppm,  $\delta_{\text{P}_2} = 119.7$ ,  $\delta_{\text{H}} = -12.9$ ,  $J_{\text{P}_1\text{P}_2} = 37.3$ ,  $J_{\text{P}_1\text{H}} = 136$ ,  $J_{\text{P}_2\text{H}} = 23$ . Such values are consistent with a hydrido ligand *cis* to  $\text{P}_2$  and *trans* to  $\text{P}_1$  and not with the hypothetical  $\text{H Ir}(\text{CO})_2\text{L}_2$  previously published (ref. 9) and characterized by a triplet ( $\delta_{\text{H}} = -12.16$  ppm,  $J_{\text{PH}} = 20$  Hz, from ref. 9); a dinuclear P Ir H Ir P framework can be retained.

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:



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  $\sigma$  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  $\text{Rh}_2(\mu\text{-X})_2(\text{CO})_2\text{L}_2$  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  $\text{COD Rh}(\mu\text{-S-t-Bu})(\mu\text{-pz}) \text{Rh COD}$  by reaction of  $\text{COD Rh Cl}$  (pyrazole) with  $\text{COD Rh}(\text{acac})$  and then substitution of the Cl bridge by the S-t-Bu ligand (ref. 13). Carbonylation followed by addition of two aliquots of  $\text{P}(\text{OMe})_3$ , **8**,  $\text{P}(\text{OPh})_3$  or  $\text{PPh}_3$  led to the formation of the  $\text{Rh}_2(\mu\text{-S-t-Bu})(\mu\text{-pz})(\text{CO})_2\text{L}_2$  complexes. These species can be slowly and irreversibly formed by mixing the homobridged 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  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2[\text{P}(\text{OMe})_3]_2$ ; 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 are reacted with  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_4$ , 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  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2\text{L}_2$  **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 type of complexes **11** and **12** (ref. 16). By IR,  $^1\text{H}$ ,  $^{31}\text{P}$  NMR spectroscopies (ref. 15) and for **10** and **11** by X-ray structures (ref. 17), the complexes were shown to present a bent geometry with roughly a square planar environment for the rhodium atom; the two CO ligands are in a *cis* arrangement and the diphosphine ligand adopts a symmetrical bridging situation. The rhodium-rhodium distances are respectively 3.039(1) Å in **10** and 3.089(1) Å 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  $0.2 \text{ min}^{-1}$ ), **9** is slightly faster ( $2.3 \text{ min}^{-1}$ ), whereas **11**, **12** and *dppp* +  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_4$  are characterized by turnover frequencies of 7.7, 8.1 and  $7.1 \text{ min}^{-1}$  respectively (ref. 17). The selectivity in aldehydes is quite good; however these catalytic systems give deceiving 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).

The X-ray structure of the ferrocenyldiphosphine complex (Fig. 1) shows very clearly that the P2 phosphorus atom deviates from the square plane around the  $\text{Rh}_2$  atom so that the two phosphorus atoms are not symmetrical. As shown on Fig. 2, the  $^{31}\text{P}$  NMR spectra recorded at low temperature (240K) reveal (ref. 17) that the structure of **11** in solution is the same as in the solid state since two inequivalent phosphorus doublets are detected and split into doublets by coupling with the more distant rhodium (or phosphorus) atom. When the temperature is raised the two Rh-P situations are interchanged in the molecule by rotation of the *dppf* ligand and at 312K only one doublet is observed. For such a situation a bridge splitting mechanism could be proposed, whereas for larger diphosphine ligands (*dppb* for instance) a competitive CO/alkene coordination mechanism could give account of the observed reactivities. Here also a catalytic cycle in which all the intermediate species remain dinuclear can be proposed (ref. 17).

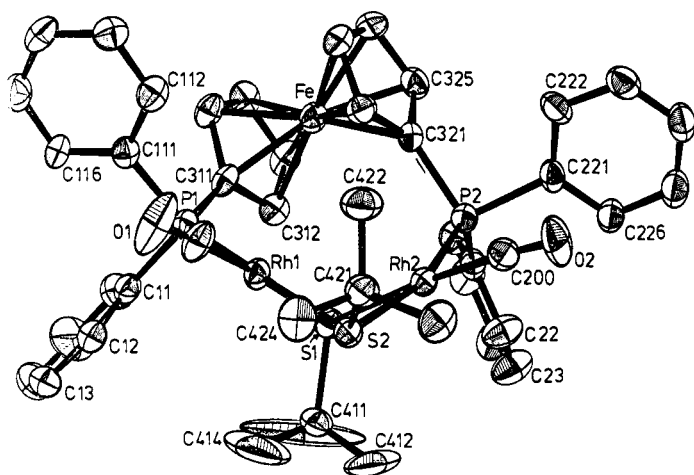


Fig. 1

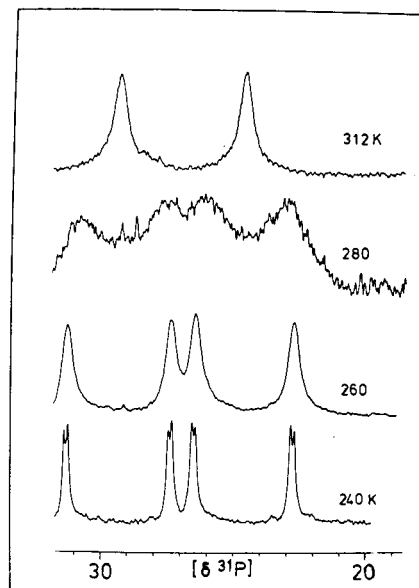
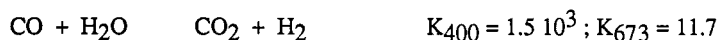


Fig. 2

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 (estragole, safrol, eugenol...) we observed that distillation induced extensive decomposition of the complexes. We investigated the immobilization of the rhodium complexes onto an insoluble support instead of using phosphine ligands (ref. 18, 19), we grafted them through the thiolato bridges (ref. 20). Starting from  $\text{Rh}_2\text{Cl}_2(\text{CO})_4$  and support-SH, then by addition of two aliquots of phosphine or phosphite, we prepared the equivalents of complexes 2 or 4, i.e.  $\text{Rh}_2(\mu\text{-S-support})_2(\text{CO})_2\text{L}_2$ . 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  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2(\text{Lw})_2$ , **13**, and compared its performances with those of  $\text{HRh}(\text{CO})(\text{Lw})_3$ , **14**, for the hydroformylation of 1-hexene at 5 bar and  $80^\circ\text{C}$  (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  $\text{HRh}(\text{CO})(\text{L}_1)_3$  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** ( $\text{P/Rh} = 6$ ) 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  $120^\circ\text{C}$ , we observed a complete conversion into butanal and methyl-2 propanal in 1 hour; with a large excess of ligand,  $\text{P/Rh} = 50$  or 100, the selectivity in butanal reached 96%. For a  $\text{P/Rh}$  ratio of 50 a turnover frequency of  $28 \text{ min}^{-1}$  was calculated whereas, starting from  $\text{Rh}_2\text{Cl}_2(\text{COD})_2$  in the same conditions to generate  $\text{HRh}(\text{CO})(\text{Lw})_3$ , the turnover frequency was only  $5 \text{ min}^{-1}$  (ref. 24).

Moreover, during the past decade the Water-Gas-Shift reaction (WGS) 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:



In addition, with the late transition metals, the hydride intermediates can be used to catalyze various reactions. The applications of the WGS to produce fine chemicals was recently reviewed (ref. 28).

We examined the possibility to carbonylate directly the alkenes with the  $\text{CO}/\text{H}_2\text{O}$  couple. Disappointing results were obtained with  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2(\text{PPh}_3)_2$ , which catalyzed very slowly in ethoxyethanol the hydroformylation of 1-hexene, provided triethylamine should be added as cocatalyst: 8% of aldehyde in 18 h,  $\text{P} = 8$  bar,  $t = 80^\circ\text{C}$  (ref. 29). Extensive isomerization occurred and the two complexes were transformed into the inactive species  $\text{PhRh}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Rh}_2(\text{CO})_4(\text{PPh}_3)_4$  (ref. 30).

**Table 1.** Hydroformylation of 1-hexene in neutral and acidic media catalyzed by  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2(\text{Lw})_2$  **13** and  $[\text{Rh}(\text{COD})(\text{Lw})_2]^+$  **15**

pH	$\text{H}_2$ produced (%)		conversion into aldehydes (%)		Turnover frequency ( $\text{h}^{-1}$ )		n/n+i (%)	
	<b>13</b>	<b>15</b>	<b>13</b>	<b>15</b>	<b>13</b>	<b>15</b>	<b>13</b>	<b>15</b>
6	19	12	53	20	28	5.3	94.8	93.8
4.8	21	nd	75	35	40	9.3	95.8	95.8
3.7	2	1	40	60	21	16	95.5	95.

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

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) :



$\text{HRh}(\text{CO})(\text{Lw})_3$ , **14**, and  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2(\text{Lw})_2$ , **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  $\text{Rh}/\text{OH}^-$  systems, of the Lw ligand into the oxide OLw as well as the formation of heavy products.

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

The WGSR can also be accomplished in acidic media (ref. 27, 28) ; Kaspar et al. have shown that the cationic species  $[\text{Rh}(\text{COD})(\text{L}_1)_2]^+$ , which contains the monosulphonated triphenylphosphine ligand, was an active precursor (ref. 31). Thus we prepared the complex  $[\text{Rh}(\text{COD})(\text{Lw})_2]^+$ , **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  $40\text{ h}^{-1}$  was obtained instead of  $28\text{ h}^{-1}$  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  $\text{H}_2$  produced by the WGSR with or without 1-hexene catalyzed by  $\text{Rh}_2(\mu\text{-S-t-Bu})_2(\text{CO})_2(\text{Lw})_2$  ; conditions as in Table 1.

pH	1-hexene (mmol)		$\text{H}_2$ (mmol)		conversion into aldehydes (%)	$\text{H}_2$ total (mmol)	
	with	without	with	without		with	without
6	40	0	4.8	6.3	53	25	6.3
	0	0	0	0			
4.8	40	0	5.3	7.5	75	35	7.5
	0	0	0	0			

The last column of Table 2 shows that the WGSR alone produced  $\approx 7\text{ mmol}$  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  $\text{Rh}_2(\mu\text{-SR})_2(\text{CO})_2\text{L}_2$  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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