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Behaviour of water-soluble dinuclear rhodium complexes in the hydroformylation reaction of oct-1-ene

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Abstract

The biphasic hydroformylation reaction of oct-1-ene, has been investigated by using the water-soluble dinuclear complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ as precursor. Addition of ethanol as a cosolvent dramatically improved the yields but the good regioselectivity in linear aldehyde observed for neat oct-1-ene–water systems (97%) decreased to 83% (for 22% ethanol w/w). It is shown that the dinuclear framework cannot be maintained, that the mononuclear complex $[RhH(CO)(TPPTS)_3]$ is formed, and that thiol and significant amounts of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ move into the organic phase. This reaction from the dinuclear species requires the simultaneous presence of water and carbon monoxide. Introduction of the water-soluble thiol $HS(CH_2)_3NMe_2$ in the bridging positions affords the complex $[Rh_2(\mu\text{-}S(CH_2)_3NHMe_2)_2(CO)_2(TPPTS)_2]Cl_2$ which can be kept in the aqueous phase but has a low level of catalytic activity.

Key words: Rhodium; Hydroformylation; Alkenes; Biphasic catalysis

1. Introduction

In homogeneous catalysis, the isolation of heavy products can make catalyst recovery very difficult. Indeed, the distillation of the organic products can induce degradation of the complex, so that the catalytic activity upon re-use, is much decreased. Several studies have been made with water-soluble ligands to retain the complex in the aqueous phase [1]. The separation of the catalyst from the organic phase then becomes a simple decantation. Two processes, namely the hydroformylation of propene [2] and the a selective 1,4-addition on a 1,3-diene [3] in which tris(3-sulphonatophenyl)phosphine (TPPTS) is utilized, are already used in industry. In particular, the hydroformylation reaction involving $[RhH(CO)(TPPTS)_3]$ appears very attractive, since facile recycling and high selectivities are gained simultaneously [4]. When compared with the precursor $[RhH(CO)(PPh_3)_3]$, the selectivity in linear aldehyde given by $n/(n+i)$ (where n is the number of moles of linear aldehyde and i that of branched aldehyde) increases from 92% to 95%, the conversion of propene in the C_4 aldehydes being in the two cases 97–98% [1(d)].

More recently, we have shown that $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ avoids the hydrogenation of the alkene, providing a complete selectivity in aldehydes [5]. Moreover, linearities higher than 97% have been achieved. These promising results prompted us to explore the reactivity of this system when heavy alkenes are considered. We selected oct-1-ene as representative of this class of compound. If the biphasic medium is convenient for catalyst recovery, the low solubility of the alkene in water should reduce the reaction rate dramatically, and special effort was devoted to improve the transfers between the organic and aqueous phases.

This paper deals with the addition of suitable cosol-

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TABLE 1. Hydroformylation of oct-1-ene catalysed by **1** in a biphasic medium: influence of the molar P:Rh ratio (**1**, 0.16 mmol; oct-1-ene, 64 mmol; H_2O, 150 ml; $P = 0.5$ MPa ($[CO]/[H_2] = 1$); $T = 80°C$; $t =$ 15 h; stirring rate, 2500 rev min^{-1})

Run	P:Rh	Conversion (%)	Selectivity in aldehydes (%)	$n/(n+i)$ (%)	Separation
1	6:1	24	100	90	difficult
2	10:1	18	100	96	easy
3	50:1	6	100	–	easy

vents, the identification of the organometallic species before and after catalysis, and the possible loss of rhodium in the organic phase. In addition, another dinuclear precursor containing a bridging aminothiolate has been explored.

2. Results and discussion

2.1. Direct hydroformylation of oct-1-ene

When neat oct-1-ene is introduced directly into the autoclave previously charged with the aqueous solution containing $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ (**1**) and an excess of TPPTS, the conversion rates remain low as shown in Table 1.

The chemoselectivity is still complete, as previously observed in the case of **1** during the hydroformylation of propene or hex-1-ene [5]. For a low molar phosphorus: rhodium ratio (6:1, first row), the regioselectivity is only 90% whereas, for higher P:Rh ratios, linearities around 96% can be reached. However, increasing the excess of phosphine reduced the rate dramatically so that, for a P:Rh ratio of 50:1, only 6% of substrate is converted and so little branched aldehyde is formed that it cannot be measured with any accuracy. Only the runs performed at the highest P:Rh ratios allowed the two phases to be easily separated.

A run carried out with hex-1-ene under the conditions of run 2 of Table 1 leads to a conversion of 81% (run 4), the selectivities being quite similar. This difference is mainly governed by the solubility of the two olefins in water. The solubility of oct-1-ene is around a twentieth of that of hex-1-ene (2.07×10^{-6} kg and 50×10^{-6} kg respectively per kilogram of water) [6]. Thus, in order to increase the concentration of alkene in water, a cosolvent was introduced into the reaction medium.

2.2. Selection of an adapted cosolvent

Previous studies on the hydrogenation of heavy alkenes in biphasic systems have shown that there are many suitable cosolvents, which increase the concentration of oct-1-ene in water and simultaneously avoid

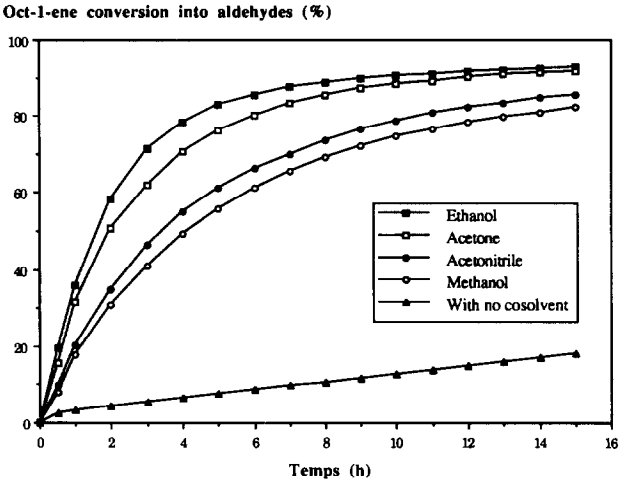


Fig. 1. Cosolvent effect on the hydroformylation reaction catalysed by **1**. (**1** 0.16 mmol; oct-1-ene, 64 mmol; TPPTS, 2.88 mmol; H_2O, 110 ml; cosolvent, 40 ml; $P = 0.5$ MPa ($[H_2]/[CO] = 1$); $T = 80°C$; $t = 15$ h; stirring rate, 2500 rev min^{-1}).

the presence of water in the organic phase [7], assuming that the water-soluble complex might also pass into the organic phase. We chose to use ethanol, methanol, acetonitrile and acetone [7]. The reaction rates are greatly enhanced compared with the run performed with no cosolvent, as shown by the four curves corresponding to 22% w/w cosolvent (Fig. 1). However, there is a loss of selectivity in each case since some isomerization of oct-1-ene occurs (5–10%). Moreover the regioselectivity decreases from 96% to about 83% (Table 2).

Addition of an organic water-miscible solvent to an aqueous solution induces a decrease in its solvophobicity parameter Sp which is directly related to the cohesion energy of the solvent [8]. The Sp values are established from the difference between free energies for the transfer of a given solute from water to another solvent. They have been expressed at 298 K relative to two fixed solvents and the range runs from 1 for water to 0 for the most hydrophobic solvent, hexadecane.

TABLE 2. Hydroformylation of oct-1-ene catalysed by **1** (**1**, 0.16 mmol; oct-1-ene, 64 mmol; TPPTS, 2.88 mmol; H_2O, 110 ml; cosolvent, 40 ml; $P = 0.5$ MPa ($[H_2]/[CO] = 1$); $T = 80°C$; $t = 15$ h; stirring rate, 2500 rev min^{-1})

Run	Cosolvent (22% w/w)	Sp	$n/(n+i)$ (%)	$\log(n/i)$
2	–	1	95.5	1.33
5	Ethanol	0.74	82.7	0.68
6	Methanol	0.84	99.6	0.94
7	Acetonitrile	–	83.8	0.71
8	Acetone	0.81	86.2	0.80

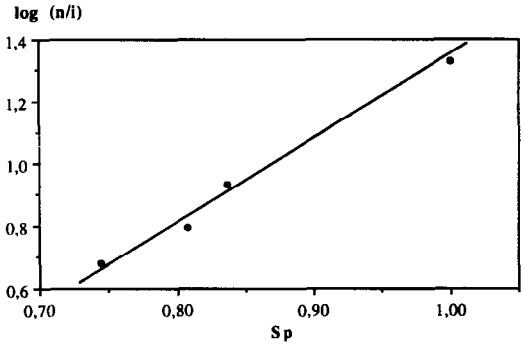


Fig. 2. $\log(n/i)$ *vs.* solvophobicity parameter Sp for the hydroformylation of oct-1-ene catalysed by **1** when different cosolvents are added to the medium. (**1**, 0.16 mmol; oct-1-ene, 64 mmol; TPPTS, 2.88 mmol; H_2O, 110 ml; cosolvent, 40 ml; $P = 0.5$ MPa ($[H_2]/[CO] = 1$); $T = 80°C$; $t = 15$ h; stirring rate, 2500 rev min^{-1}).

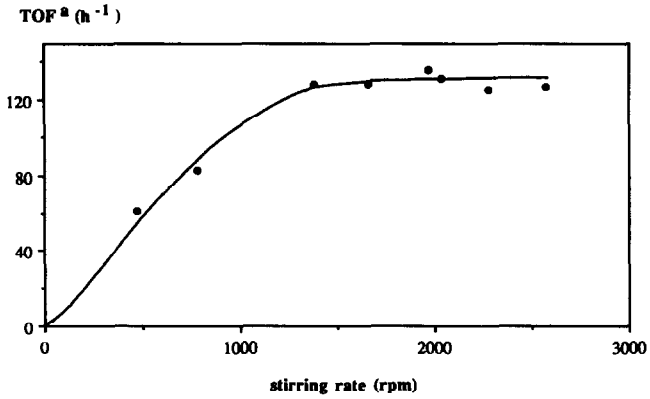


Fig. 3. Influence of the stirring rate on the turn-over frequency TOF of hydroformylation of oct-1-ene. (**1**, 0.16 mmol; oct-1-ene, 64 mmol; TPPTS, 2.88 mmol; H_2O, 110 ml; ethanol, 40 ml; $P = 0.5$ MPa ($[H_2]/[CO] = 1$); $T = 80°C$, $t = 15$ h). The turnover frequency was measured between 0.5 and 1 h.

For the Diels–Alder reaction, Braun *et al.* [9] and Schneider and Sangwan [10] observed a good correlation between log(endo/exo) values and the solvophobicity parameter. Sinou and coworkers [11] showed that there is a linear relationship between $\log(S/R)$ and Sp when they reduced dehydroaminoacids in the presence of a rhodium complex containing chiral diphosphines. In our case, provided that the formation of linear and branched aldehydes obey similar mechanisms, the n/i ratio is related directly to the rate constant ratio k_n/k_i.

Therefore, by analogy with the results observed for the Diels–Alder and the hydrogenation reactions, we explored the possibility that $\log(n/i)$ is governed by Sp. The results obtained for the hydroformylation of oct-1-ene with **1** as precursor in various media containing the four cosolvents (22% w/w) are listed in Table 2. $\log(n/i)$ shows a linear correlation with Sp (Fig. 2).

Ethanol was then selected because it leads to better conversion rates than the three other solvents. In this case we have shown that concentrations below 22% (w/w) in ethanol dramatically reduce the reaction rates. Moreover, because diffusion between the two phases can govern the kinetics, the turn-over frequency has been studied as a function of the stirring rate, in order to determine the minimum value beyond which the reaction obeys only a chemical law. As shown in Fig. 3, the stirring rate must be greater than 1300 rev min^{-1}. All further runs were carried out at 2300 rev min^{-1}.

2.3. Recycling of the aqueous phase

After a first run performed with 16% w/w of ethanol, the reaction mixture was transfered into a separatory funnel under argon. After decantation, the aqueous phase, which had changed from yellow to brown, was reintroduced into the autoclave. Table 3 shows that the conversion decreases from 87% to 81%, whereas the chemo- and regio-selectivities are not affected. A second recycling test performed under the same conditions revealed the same tendency, the conversion being 73%. The aqueous phase became deep brown, while the organic one became pale yellow. Therefore, a careful analysis of the reaction medium after a catalytic test was undertaken.

2.4. Compounds present in solution after a catalytic run

The yellow organic phase was concentrated, then analysed by IR spectroscopy. The three $\nu(CO)$ bands at 2068, 2049 and 1999 cm^{-1} belong unambiguously to the tetracarbonyl complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ (**2**). The amount of this complex was evaluated as 20% of the rhodium introduced as $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ by UV spectroscopy.

After every run, the aqueous phase was concentrated and analysed by IR and NMR spectroscopies. All the data are consistent with the presence of the mononuclear hydrido complex $[RhH(CO)(TPPTS)_3]$

TABLE 3. Recycling of the water-soluble catalyst for hydroformylation of oct-1-ene (**1**, 0.16 mmol; oct-1-ene, 64 mmol; TPPTS, 2.88 mmol; H_2O, 120 ml; ethanol, 30 ml; $P = 0.5$ MPa ($[H_2]/[CO] = 1$); $T = 80°C$; $t = 15$ h; stirring rate, 2300 rev min^{-1})

Run	Conversion (%)	Selectivity in aldehydes (%)	$n/(n+i)$ (%)	Turn-over frequency [a] (h^{-1})
9	87	89	90	58
10 [b]	81	90	90	47
11 [c]	73	90	91	17

[a] Measured between 0.5 and 1 h; [b] first recycling; [c] second recycling.

(3). The ν(CO) and ν(Rh–H) bands were found at 1922 cm^{-1} and 2003 cm^{-1} respectively. In the ^{31}P NMR spectrum a doublet was detected at 45.1 ppm ($^2J_{Rh-P}$ = 155.1 Hz) in addition to the two singlets of TPPTS (−2.9 ppm) and its oxide OTPPTS (35.8 ppm). In the ^1H NMR spectrum the hydride ligand was characterized by a quadruplet at −9.6 ppm ($^3J_{P-H}$ = 13.4 Hz). Moreover, **1** was never detected.

We suspected that water could play a special role in the transformation of **1** into **3**; so the reactivity of **1** under stoichiometric conditions was investigated. Both at room temperature and at 80°C, **1** remains unchanged when it is dissolved in water under dinitrogen, even in the presence of an excess of TPPTS (P:Rh, 10:1). However, replacing dinitrogen with carbon monoxide, at room temperature for 4 h gives **3** with about 50% yield. At higher temperatures, the conversion proceeds more rapidly, and at 80°C the reaction is complete. The simultaneous presence of CO and H_2O is necessary since **1** cannot be transformed when heated under reflux in methanol under CO. As the reaction does not require dihydrogen, the water gas shift reaction occurs to provide the rhodium hydride. When a run is carried out with no excess of TPPTS, the ligand required to form **3** is removed from **1** which changes into **2**. As this tetracarbonyl complex is not soluble in water, it was separated by filtration and identified by IR spectroscopy.

Thus, after catalysis, **1** is fully transformed into **3** which is maintained in the aqueous phase and **2** which leaks in the organic phase. In addition, the ^{t}BuSH is recovered from the organic phase. The simultaneous leak of **2** and thiol renders the reaction irreversible.

2.5. *Involvement of 1 and 3 in catalysis*

The order of reaction with respect to **1** was found to be 0.7, between the first order expected for **3** and 0.5 order for **1**. The mononuclear complex **3** was prepared according to the procedure of Hanson and coworkers [12]. We checked that it gives a kinetic order of one for the hydroformylation of oct-1-ene under the same experimental conditions. A 0.7 order could be due to the simultaneous catalytic activity of both **1** and **3**. However, we prefer to consider that this order, determined by the initial conditions, is rather the consequence of the loss of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ from the organic phase, decreasing thus the concentration of **3** for catalysis.

The PPh_3 analogue of **3** is known to form brown solutions containing carbonyl clusters very easily; they are inactive in hydroformylation [13]. We observed such brown colours and, as with $[RhH(CO)(PPh_3)_3]$, we noted that significant amounts of internal olefins are produced during the hydroformylation reaction. To prevent the deactivation of **3**, it is necessary to add a large excess of ligand [12] to the detriment of the reactivity. In order to avoid the complete transformation of **1** to a mononuclear species, we introduced a water-soluble thiolato ligand in the bridging positions between the two rhodium atoms.

2.6. *Water-soluble bridging ligands containing complexes*

Recently Bayon and coworkers [14] have published the synthesis of $[Rh_2(\mu\text{-}SR)_2(COD)_2]$, in which the dimethylaminopropylthiolate can be protonated at the nitrogen atom to produce water solubility. Carbonylation followed by addition of phosphite or triphenylphosphine afforded dinuclear precursors for hydroformylation [14].

We prepared the tetracarbonyl complex directly by adding the $Me_2N(CH_2)_3SH$ to $[RhCl_2(CO)_2]^-$ in methanol [15]. As hydrochloric acid is produced, we obtained the ionic complex $[Rh_2(\mu\text{-}SCH_2CH_2CH_2NHMe_2)(CO)_4]Cl_2$ (**4**) which was fully characterized and which shows three ν(CO) bands characteristic of a dinuclear structure at 2067 (m), 2044 (s) and 2018 (s) cm^{-1}. Addition of TPPTS to the water-soluble complex **4** in water afforded the disubstituted complex $[Rh_2(\mu\text{-}S(CH_2CH_2CH_2NHMe_2)_2(CO)_2(TPPTS)_2]Cl_2$ (**5**) which was characterized by elemental analysis, IR and ^1H, ^{13}C, ^{31}P NMR spectroscopy.

Using **5** as **1** was used in the presence of ethanol cosolvent gave disappointing results since the conversion into C_9 aldehydes is only 10% after 15 h (compare with 95% for **1**). For further identification, water was removed under reduced pressure until a brown powder was obtained. Its IR spectrum shows a single ν(CO) band at 1973 cm^{-1} and not the two bands characteristic of **3**. The ^1H NMR spectrum of the solid dissolved in D_2O shows the multiplet assigned to TPPTS, the CH_2 signals of the thiolate slightly shifted with respect to those of **5**, but does not show any hydride signal. The same IR, ^1H and ^{31}P NMR data were recorded when **5** was directly stirred in water under a $CO–H_2$ atmosphere. From the value of $^1J_{Rh-P}$ the complex under consideration is in an oxidation state I. From IR and NMR data we conclude that a fragment $Rh(CO)(S(CH_2)_3NHMe_2)(TPPTS)_x$ is present, and that presumably the complex is dinuclear. Also, as previously observed for the dinuclear complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR_3)_2]$ (R = Ph, OMe or OPh) used in classical organic solvents [16], the absence of hydrogenation and isomerization of the alkene for the run performed with **5** is characteristic of a dinuclear framework.

The absence of **3** in this system can be related to the low catalytic activity noted during the hydroformylation

reaction. Thus the hypothesis that the high catalytic activity observed for the system derived from **1** is in fact due to the mononuclear complex **3** is reinforced by these observations.

3. Experimental section

3.1. Equipment

NMR spectra were recorded on a Brüker WH 90 (^{31}P $\{^1H\}$ (36.43 MHz); external reference, H_3PO_4 85%), a Brüker AC 200 ^1H (200.13 MHz); external reference, tetramethylsilane (TMS) and a Brüker WM 250 spectrometer (^{13}C (62.90 MHz); external reference, TMS), (^{31}P (101.26 MHz); external reference, H_3PO_4 85%): s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; dm, doublet of multiplets; ddt, doublet of doublets of triplets; dtd, doublet of triplets of doublets; tdd, triplet of doublets of doublets. IR spectra were collected on a Perkin–Elmer 1710 FTIR spectrometer: m: medium; s: strong; vs: very strong. The UV–visible spectra were recorded on a Perkin–Elmer 550 spectrometer. The elemental analyses were performed by the Service Central d'Analyse du CNRS in Vernaison (France). Gas chromatography analyses were performed on a Carlo Erba HRGC 5160 instrument equipped with an Econo Cap FFAP capillary column. All the products yields were determined using anisole as the internal standard.

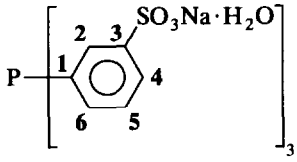
3.2. Materials

All reagents were used as supplied by the manufacturers: hex-1-ene, heptanal, octane, thiourea, 3-dimethylamino-1-propanol (Aldrich); nonanal (Janssen); oct-1-ene (Sigma); anisole (Prolabo). Argon, nitrogen, carbon monoxide and hydrogen were from Prodair (purity greater than 99%) and were used as received without purification. TPPTS was provided by Rhône-Poulenc Chimie as a solution in water. Solvents such as acetone, acetonitrile, diethylether, ethanol, methanol and toluene were obtained from SDS; they were used without further purification.

All operations involving metal species were carried out under dinitrogen or argon by standard Schlenk techniques. Reagents and solvents were degassed by bubbling nitrogen for 15 min before each use.

3.3. Full characterization of tris(3-sulphonatophenyl) phosphine

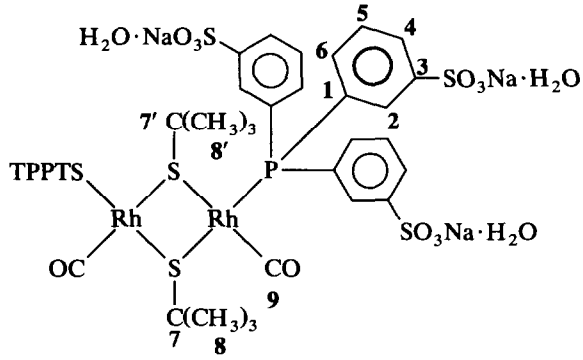
TPPTS was purified by precipitation from the aqueous solution by slow addition of ethanol. The resulting white solid was washed successively with ethanol and ether, dried under vacuum and stored under nitrogen. Judged by the elemental analysis, TPPTS is trihydrated so that a molecular weight of 622.47 g mol^{-1} was assumed.



Elemental anal. Found: C, 35.0; H, 2.7; O, 28.8. Calc. without H_2O: C, 38.5; H, 2.1; O, 25.1. Calc. with $3H_2O$: C, 35.2; H, 2.9; O, 30.6%.

3.4. $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ (1)

This complex was prepared, according to the literature [5], by the addition of 2 equivalents of TPPTS to $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ [15], in methanol.



^1H NMR (D_2O, 24°C): δ 0.70 (9H, s, $H_{8'}$); 1.70 (9H, s, H_8); 7.39 (6H, t, $J(H_6P) \approx J(H_6H_5) = 7.8$ Hz, H_6); 7.63 (6H, t, $J(H_5H_4) \approx J(H_5H_6) = 8.5$ Hz, H_5); 7.85 (6H, d, $J(H_4H_5) = 7.8$ Hz, H_4); 8.03 (6H, d, $J(H_2P) = 10.6$ Hz, H_2) ppm.

^{13}C NMR (H_2O–D_2O, 25°C): δ 36.42 (q, $J(C_8H_8) = 128.0$ Hz, CH_3); 40.22 (q, $J(C_{8'}H_{8'}) = 126.8$ Hz, CH_3); 47.50 (s, C_7); 55.13 (s, $C_{7'}$); 130.14 (dt, $J(C_4H_4) = 165.6$ Hz, C_4); 131.61 (dd, $J(C_5H_5) = 166.3$ Hz, $J(C_5P) = 10.0$ Hz, C_5); 133.34 (ddt, $J(C_6H_6) = 165.6$ Hz, $J(C_6P) = 10.0$ Hz, $J(C_6H_4) \approx J(C_6H_2) = 6.0$ Hz, C_6); 136.74 (dd, $J(C_1, P) = 43.9$ Hz, $J(C_1H_5) = 7.7$ Hz, C_1), 139.78 (ddt, $J(C_2H_2) = 164.9$ Hz, $J(C_2P) = 12.1$ Hz, $J(C_2H_4) \approx J(C_2H_6) = 7.0$ Hz, C_2); 145.45 (t, $J(C_3P) \approx J(C_3H_5) = 8.9$, C_3); 192.14 (dd, $J(C_9Rh) = 72.5$ Hz, $J(C_9P) = 14.2$ Hz, C_9) ppm.

^{31}P $\{^1H\}$ NMR (H_2O–D_2O, 36.43 MHz, 30°C): δ 39.69 (d, $J(PRh) = 152.5$ Hz) ppm.

IR (KBr): $\nu(CO)$ 1967 cm^{-1}.

Elemental anal. Found: C, 33.0; H, 2.7. Calc.: C, 32.8; H, 3.2%.

3.5. $[RhH(CO)(TPPTS)_3]$ (3)

This complex was prepared, according to the method in the literature [12].

^1H NMR (D_2O, 25°C): δ −9.5 ppm (q, $J(HP) =$

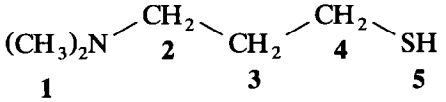
13.5 Hz 7.27 (t, $J(H_5H_4) \approx J(H_5H_6) = 7.5$ Hz, H_5); 7.51 (s, H_2); 7.54 (dd, $J(H_6H_5) = 8.5$ Hz $J(H_6P) = 7.0$ Hz, H_6); 7.71 (d, $J(H_4H_5) = 7.6$ Hz, H_4) ppm.

^{13}C NMR (H_2O–D_2O, 25°C): δ 128.68 (d, $J(C_4H_4) = 173.2$ Hz, C_4); 130.68 (dm, $J(C_5H_5) = 164.5$ Hz, C_5); 131.54 (dm, $J(C_6H_6) = 177.4$ Hz, C_6); 139.07 (dm, $J(C_2H_2) = 156.8$ Hz, $J(C_2P) = 7.0$ Hz, C_2); 140.47 (m, $J(C_1Rh) = 7.3$ Hz, $J(C_1P) = 11.7$ Hz, C_1): 144.93 (m, $J(C_3P) < 5$ Hz, $J(C_3H_5) < 5$ Hz, C_3). The signal corresponding to the carbonyl ligand was not detected.

^{31}P {^1H} NMR (H_2O–D_2O, 101.26 MHz, 25°C): δ 46.77 (d, J(PRh) = 155.8 Hz) ppm. IR (KBr): ν(CO) 1926 (m) cm^{-1}; νRh–H 2003 (s) cm^{-1}.

3.6. $Me_2NCH_2CH_2CH_2SH$

3-Dimethylamine-1-propanol (60 ml, 0.51 mol) and thiourea (46.3 g, 0.61 mol) were added to 165 ml of 48% aqueous bromhydric acid (1.53 mol) and the mixture was heated under reflux under dinitrogen for 72 h. After cooling, the solution was treated with sodium hydroxide (85.34 g, 1.52 mol) and heated under reflux under dinitrogen for 45 min in order to hydrolyse the isothiouronium salt. The organic layer was separated at around 80°C; the aqueous phase was filtered and extracted three times with 30 ml of diethyl ether. The organic fractions were combined, dried with magnesium sulphate and filtered, after which ether was removed under vacuum. After distillation under reduced dinitrogen pressure, the product was obtained as colorless liquid.



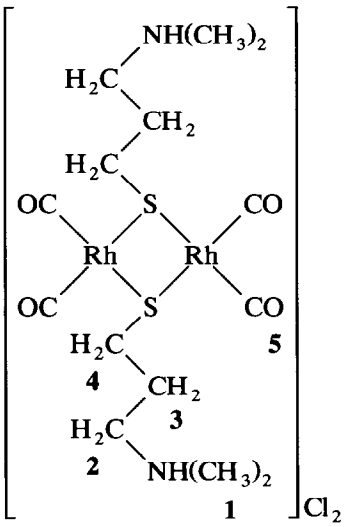
^1H NMR (C_6D_6, 24°C): δ 1.33 (1H, t, $J(H_5H_4) = 8.0$ Hz, H_5); 1.59 (2H, "quintuplet", $J(H_3H_2) = 6.8$ Hz $J(H_3H_4) = 7.0$ Hz, H_3); 2.09 (6H, s, H_1); 2.20 (2H, t, $J(H_2H_3) = 6.8$ Hz, H_2); 2.40 (2H, dt, $J(H_4H_5) = 7.8$ Hz, $J(H_4H_3) = 7.0$ Hz, H_4) ppm.

^{13}C NMR(C_6D_6, 30°C): δ 22.94 (t, $J(C_4H_4) = 139.3$ Hz, C_4); 32.52 (t, $J(C_3H_3) = 127.1$ Hz, C_3); 45.93 (q, $J(C_1H_1) = 132.3$ Hz, C_1); 58.42 (t, $J(C_2H_2) = 130.8$ Hz, C_2) ppm. Elemental anal. Found: C, 50.3; H, 11.2; N, 12.1; Calc. C, 50.4; H, 11.0; N, 11.8%.

3.7. $[Rh_2(\mu\text{-}SCH_2CH_2CH_2NHMe_2)(CO)_4]Cl_2$ (4)

Using the classical method for the syntheses of tetracarbonyl dinuclear rhodium complexes [15], a red solution of 1 g (3.8 mmol) of $RhCl_3 \cdot 3H_2O$ in 30 ml of methanol was heated under reflux with slow bubbling of CO for 20 h. The solution, which became yellow, was then slowly cooled to room temperature and treated with 500 µl (3.8 mmol) of 3-dimethylamino-1-propanethiol to give an orange precipitate of $[Rh_2(\mu\text{-}SCH_2CH_2CH_2NHMe_2)(CO)_4]Cl_2$. Further precipitation was caused by cooling the mixture at −20°C. The product (1.07 g; yield 90%) was collected by filtration, washed with diethyl ether and dried under vacuum.

Treatment of an aqueous solution of this complex with 2 equivalents of sodium hydroxide yields a brown precipitate of $[Rh_2(\mu\text{-}SCH_2CH_2CH_2NMe_2)(CO)_4]$ characterized by its heat sensitivity and its IR (hexane) spectrum (ν(CO) = 2071 (m), 2052 (s) and 2005 (s) cm^{-1}) which are consistent with the data in the literature [14].



^1H NMR (D_2O, 21°C): δ 2.13 (2H, quintuplet, $J(H_3H_2) \approx J(H_3H_4) = 7.3$ Hz, H_3); 2.82 (6H, s, H_1); 3.14 (2H, t, $J(H_{2/4}H_3) = 7.6$ Hz, $H_{2/4}$); 3.18 (2H, t, $J(H_{4/2}H_3) = 8.5$ Hz, $H_{4/2}$) ppm.

^{13}C NMR (D_2O, 30°C): δ 30.58 (t, $J(C_3H_3) = 131.4$ Hz, C_3); 34.17 (t, $J(C_4H_4) = 145.4$ Hz, C_4); 45.46 (q, $J(C_1H_1) = 143.8$ Hz, C_1); 58.57 (t, $J(C_2H_2) = 140.9$ Hz, C_2); 186.58 (d, $J(C_5Rh) = 69.7$ Hz, C_5) ppm.

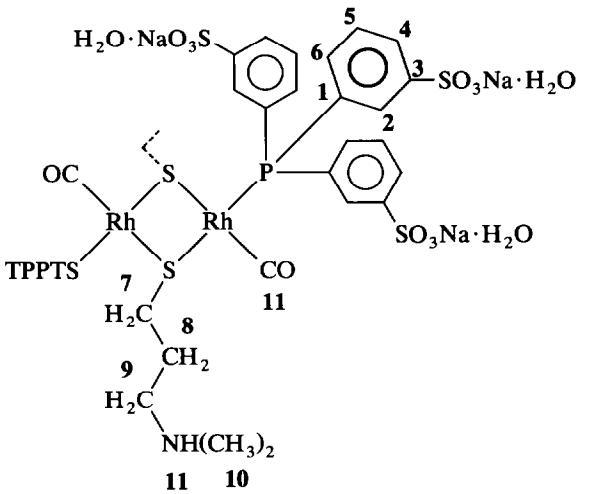
IR (KBr): ν(CO) = 2067 (m), 2044 (s), 2018 (s) cm^{-1}.

Elemental anal. Found: Rh, 29.2; C, 26.3; H, 4.4; N, 4.5; Cl, 11.7; S, 11.5. Calc. Rh, 32.8; C, 26.8; H, 4.2; N, 4.5; Cl, 11.3; S, 10.3%.

3.8. $[Rh_2(\mu\text{-}SCH_2CH_2CH_2NHMe_2)_2(CO)_2(TPPTS)_2]Cl_2$ (5)

Using the classical methods for the synthesis of disubstituted dinuclear rhodium complexes [5], a solution of 1.25 g (2 mmol) of TPPTS in 5 ml of water was added to a garnet-red solution of 0.63 g (1 mmol) of $[Rh_2(\mu\text{-}SCH_2CH_2CH_2NHMe_2)_2(CO)_4]Cl_2$ in 10 ml of water. Carbon monoxide evolved immediately while the mixture became brown. The solvent was then re-

moved under vacuum to yield the expected product as a brown powder.



11 10

^{1}H NMR (D_2O, 24°C): δ 1.69 (m, H_8); 2.46 (m, H_9); 2.60 (s, H_{10}); 2.83 (m, H_7); 7.40 (m, H_{11}); 7.57 ("t", $J(H_6P) \approx J(H_6H_5) = 7.6$ Hz, H_6); 7.86 (d, $J(H_4H_5) = 8.2$ Hz, H_4); 7.96 ("t", $J(H_5H_4) \approx J(H_5H_6) = 8.5$ Hz, H_5); 8.09 (d, $J(H_2P) = 11.8$ Hz, H_2) ppm.

^{13}C NMR (H_2O–D_2O, 25°C): δ 30.21 (t, $J(C_8H_8) = 132.2$ Hz C_8); 31.89 (t, $J(C_7H_7) = 147.4$ Hz, C_7); 45.29 (q, $J(C_{10}H_{10}) = 141.2$ Hz, C_{10}); 58.93 (t, $J(C_9H_9) = 149.2$ Hz, C_9); 130.82 (dt, $J(C_4H_4) = 163.1$ Hz C_4); 132.36 (dm, $J(C_6H_6) = 167.1$ Hz, C_6); 133.01 (dd, $J(C_5H_5) = 167.5$ Hz, $J(C_5P) < 10$ Hz, C_5); 135.51 (dd, $J(C_1P) = 46.6$ Hz, $J(C_1H_5) < 10$ Hz, C_1), 139.49 (dm, $J(C_2H_2) = 165.7$ Hz, C_2); 146.19 (dd, $J(C_3P)$ and $J(C_3H_5) < 10$ Hz, C_3); 191.21 (dd, $J(C_{11}Rh) = 56.5$ Hz, $J(C_{11}P) < 10$ Hz, C_{11}) ppm.

^{31}P {^{1}H} NMR (H_2O–D_2O, 30°C): δ 43.66 (d; $J(PRh) = 157.4$ Hz) ppm.

IR (KBr): ν(CO) 1967 (vs) cm^{-1}.

Elemental anal. Found: Rh, 11.3; C, 31.7; H, 3.4; N, 1.5; S, 14.1; Na, 7.6; Cl, 3.9; P, 3.4. Calc. Rh, 10.2; C, 31.7; H, 3.4; N, 1.5; S, 14.5; Na, 7.7; Cl, 3.9; P, 3.5%.

3.9 Hydroformylation procedure

The aqueous solution containing TPPTS, the rhodium complex and cosolvent were introduced into the reactor previously purged with dinitrogen and then with a H_2 : CO (1 : 1) mixture. The autoclave is heated to 80°C under 0.16 MPa of the H_2 : CO (1 : 1) mixture and under vigorous stirring. Then oct-1-ene is transferred from a cylinder into the reactor pressurized to 0.5 MPa. The kinetics of the reaction are followed by recording the pressure of a cylinder containing the H_2–CO mixture every 40 s. After 15 h, the autoclave is cooled to room temperature and slowly depressurized. The solution is collected in a separatory funnel. After decantation, the two phases are independently analysed.

4. Conclusion

The water-soluble complex [$Rh_2(\mu$-S^{t}Bu)$_2$(CO)$_2$(TPPTS)$_2$] reacts very quickly with CO and water to afford the mononuclear complex [RhH(CO)(TPPTS)$_3$]. Loss of the thiol ^{t}BuSH from the aqueous phase accelerates this reaction. If a water-soluble thiol is introduced, the dinuclear framework is maintained. This water-soluble dinuclear complex is a poor catalyst for the low pressure hydroformylation of oct-1-ene in a biphasic system. When the conditions lead to the irreversible formation of the complex [RhH(CO)(TPPTS)$_3$], high catalytic activities are reached. In order to improve the transfer phenomenon between the organic substrate and the aqueous phase a suitable cosolvent can be added. Ethanol, which increases the concentration of oct-1-ene in water by two orders of magnitude [7], increases the initial rate by a factor of about 25. However, the cosolvent affords reduced selectivities in the linear aldehyde. As the formation of the mononuclear complex leads to a loss of thiol and [$Rh_2(\mu$-S^{t}Bu)$_2$(CO)$_4$] in the organic phase, it would be better to introduce the precursor [RhH(CO)(TPPTS)$_3$] directly.

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