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Inter-facial catalysis using various water-compatible ligands in supramolecular systems

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Contents

Abstract

In order to hydroformylate heavy alkenes at adequate reaction rates whilst maintaining a water-compatible catalyst in the aqueous phase, we have examined the effect of the addition of small amounts of triphenylphosphine on the water-soluble complexes $[Rh_2(CO)_2(\mu\text{-}S^tBu)_2(TPPTS)_2]$ and $[HRh(CO)(TPPTS)_3]$ (TPPTS = tris(3-sulfonatophenyl)phosphine trisodium salt trihydrate). It has been demonstrated that the reaction occurs in the organic phase; an exchange of phosphine restores the starting complex to the aqueous phase but a significant leaching of rhodium into the organic phase occurs. Recycling of the aqueous phase led to a dramatic drop in catalytic activity. Similar studies have been carried out using

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supported aqueous phase catalysis which involves the immobilization of an aqueous film containing the catalyst on the surface of a hydrophilic support such as silica. We present good evidence that the catalyst operates in 'microreactors', at the interface between the aqueous film and the bulk organic phase.

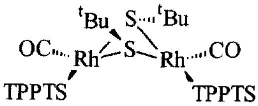
Keywords: Inter-facial catalysis; Water-soluble complexes; Supramolecular systems

1. Introduction

The search for higher activities and selectivities in the hydroformylation reaction has far from lost its interest [1]. The reaction is a unique tool in the synthesis not only of basic chemicals but also of more elaborate molecules [2–7]. Rhodium has become the metal of choice to produce highly active catalytic species under mild conditions of temperature and pressure. An intense research program has been devoted to the building of dirhodium entities in order to promote a cooperative effect between the two metal centers able to induce novel reactivities [8]. Chloro-bridged complexes have a poor reactivity, essentially due to the easy cleavage of the Cl–Rh bonds, so we have particularly explored and developed a number of thiolato-bridged complexes [9].

2. Water-soluble dinuclear rhodium catalysts

In this context, this laboratory succeeded in the elaboration of a dinuclear complex in 1983 [10] which can transform an alkene into the homologous aldehyde with very high reaction rates at 80°C and 5 bar, complete chemoselectivity in aldehyde and a regioselectivity for the *n* isomer of ca. 80–85%. These complexes, bridged by two thiolato ligands, contain two rhodium centers, each of them bound to one CO ligand and one phosphorus-containing ligand (phosphite or phosphine, including the common and inexpensive PPh_3). Their general geometry (Scheme 1), as shown by an X-ray crystal structure determination [9b], is characterized by a great flexibility around the sulfur–sulfur axis and the potential for the two rhodium centers to act in catalysis in a synergistic manner [11]. It was particularly shown, that such a dinuclear complex can react with only one equivalent of iodomethane to afford a Rh(I)Rh(III) compound [9d]. Diphosphine ligands can also be introduced [12] and, provided the distance between the two coordinating sites is large enough, the same general formula is adopted.



Scheme 1. General view of the dinuclear complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$.

While this family of complexes gives total selectivity in aldehydes, even though some of them are very active hydrogenation catalysts [13], the linearity of the resulting product still remains unsatisfactory: even in the presence of an excess of phosphine ligand the best $n/n+i$ ratios do not exceed 88%. Indeed, such values of the linearity are an intrinsic characteristic of these dinuclear complexes operating in organic solvents [14]. EHMO calculations [11] and kinetic studies [15] are consistent with a catalytic cycle in which all the intermediates remain dinuclear [16].

When the water-soluble ligand tris(3-sulfonatophenyl)phosphine trisodium salt trihydrate (TPPTS) [17] is introduced, to give $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ [18,19], the reaction clearly occurs in the aqueous phase with propene and light alkenes to afford linearities approaching 97%. This complex can perform the same hydroformylation reaction using water as the hydrogen source under acidic conditions: the same selectivities are obtained [20–22].

Regardless of the particular phosphorus ligand used, the kinetics are distinct from those of the mononuclear hydridorhodium species $HRh(CO)(PPh_3)_3$ and $HRh(CO)(TPPTS)_3$. With these latter complexes, the reaction starts immediately, whereas with the dinuclear complexes, an induction period is observed, followed by a rate of reaction faster than that of the mononuclear species [10,18]. In particular, the hydroformylation of propene occurs very quickly at 120°C and with a TPPTS/ $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ ratio of 8 the turnover frequency reaches 53 min^{-1} for a $n/n+i$ selectivity of 96%. However, due to its lower solubility in water, 1-hexene is converted more slowly and 18 h is usually required for the complete conversion of a charge at 80°C. After decantation of the two phases, the aqueous phase containing the whole rhodium complex can be recycled for three runs with no decrease of the yield nor the linearity in *n*-heptanal (96–97%). Once again, it is possible to use carbon monoxide exclusively as the gaseous reactant and to involve the water-gas-shift (WGS) reaction in producing the intermediate dihydridorhodium species, which is also an active species in the hydroformylation catalytic cycle [20]. The hydroformylation cycle was shown to be faster than the WGS cycle and, for 1-hexene at pH 4.8, a TOF of 40 h^{-1} was reached.

The chemistry of heavy alkenes has also been explored [19], but their major drawback is their dramatically reduced solubilities in water. For example, the solubility of 1-hexene in water is 50 mg l^{-1}, whereas that of 1-octene is only 2.1 mg l^{-1}: the net result is a decrease in the yield of aldehydes which falls in 15 h from 81 to 2% (linearities 97 and 96%, respectively). Thus, in this type of catalysis, the main problem to solve is to improve the contact between the substrate and the water-soluble catalyst whilst maintaining a complete absence of leaching of rhodium into the organic phase.

3. Use of co-solvent in biphasic catalysis

Previous studies of the hydrogenation of heavy alkenes in biphasic systems have shown that the use of a suitable co-solvent increases the concentration of the olefin in water while avoiding the presence of water in the organic phase [23]. A useful

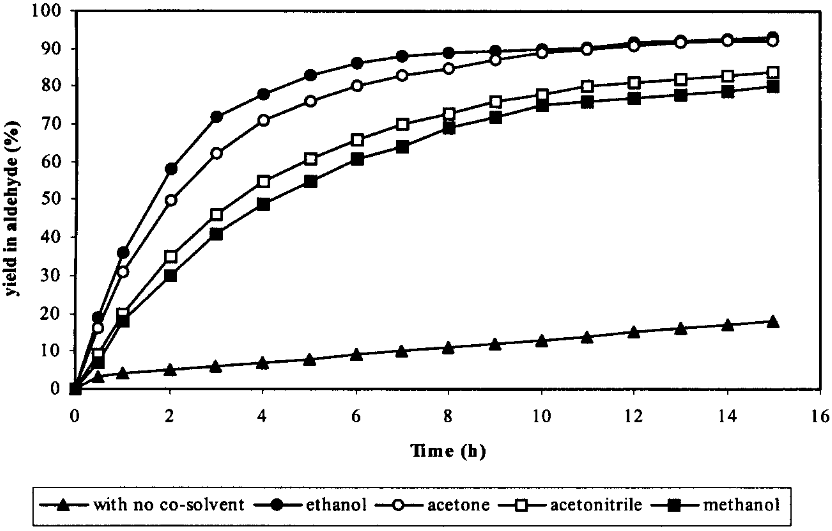


Fig. 1. Influence of the nature of the co-solvent on the yield of C_9 aldehydes vs. time.

co-solvent has to present several different properties: (i) miscibility with water; (ii) inertness toward reactants and products; and (iii) a low boiling point, so that it may be easily separated from the products. The solubility of water in the organic phase is another determining characteristic in the selection of the co-solvent. To select the best co-solvent, we used the ternary diagrams 1-octane/water/co-solvent studied by Hablot [24]. Ethanol, methanol, acetone, acetonitrile or ethylene glycol were chosen owing to their good characteristics and their inertness toward the products, except the possible formation of acetals in the case of alcohols. Ethanol was found to be the best (Fig. 1): the reaction rates are greatly increased, especially for 22% w/w co-solvent (Fig. 2), with regard to neat 1-octene. However 5–10% internal octenes are produced and the regioselectivity decreases significantly from 96 to about 83%, in proportion to the amount of ethanol in the aqueous phase. It had been shown that the linearity is directly induced by the polarity of the medium. In a non-polar solvent, because of a weaker back donation onto the carbonyl ligands, the hydrogen atom presents a more pronounced hydride nature and is preferentially added onto the carbon atom which possesses the greater residual positive charge. In fact, there is a linear correlation of $\log(n/i)$ with the solvophobicity parameter, established from the difference between free energies for the transfer of a given solute from water to another solvent [25,26]. As soon as the mass transfer reaches a sufficient efficiency, the kinetics are, as usual, first-order in the concentration of the catalyst and of the substrate, as published by Delmas [27] then Deshpande [28].

However, while the presence of a co-solvent allows a significant improvement in the transfer of the substrate to the water-rich phase, it causes the leaching of substantial amounts of catalyst into the organic phase. Thus, other methods have been explored to improve the contact between the alkene and the rhodium complex.

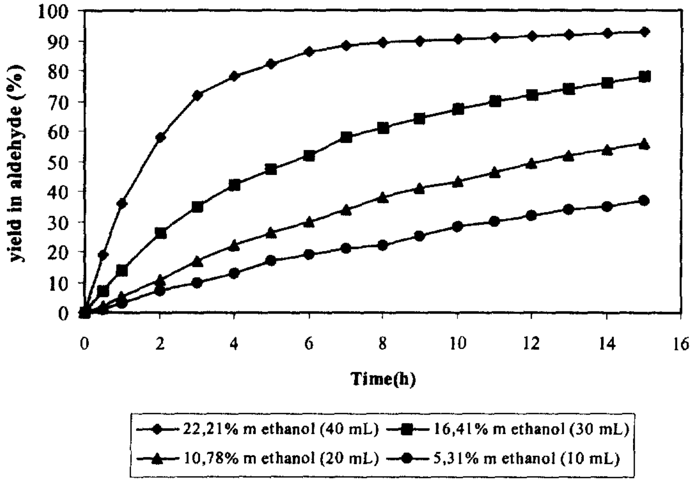


Fig. 2. Influence of the quantity of ethanol on the yield in C_9 aldehydes vs. time.

One way to meet this requirement is to increase the availability of the water-soluble catalyst which is allowed to react in the interphase area.

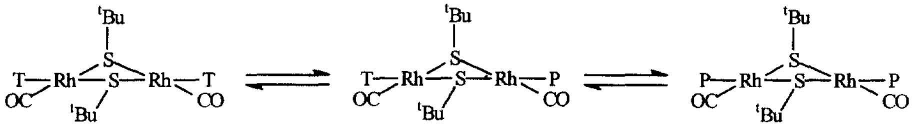
4. Interfacial catalyst through a promoting ligand

Recently, we have examined [29] the attractive method, reported by Chaudhari, Delmas and co-workers [30,31], for maintaining the water-soluble catalyst $[HRh(CO)(TPPTS)_3]$ at the interface between the aqueous and organic phase. The authors described that the addition of small quantities of PPh_3 induces an exchange phenomenon between the phosphorus ligands which allows the active mixed species to be maintained at the interface.

4.1. Interfacial catalysis with $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$

This method for improving the contact between the reactants prompted us to examine this effect on the dinuclear rhodium complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2\text{-}(TPPTS)_2]$. We examined first the hydroformylation of (*R*)-limonene as a stereotypical heavy alkene. The pure biphasic system provides a 1% conversion in 21 h showing that transfer from the organic phase is very low. Addition of 0.1 mol of PPh_3 to $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ gave a dramatic increase in the reaction rate, and the conversion of limonene was 12% in 21 h. Surprisingly, a light-yellow color appeared in the organic phase. Analysis of the organic phase by IR and ^{31}P NMR spectroscopy revealed the presence of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$; attempts to detect a mixed species in water and/or in toluene were unsuccessful.

For this reason, we have examined the effect of additional PPh_3 or TPPTS on the dinuclear framework by ^1H NMR in CD_3OD/D_2O (40:60 v/v) solution. The



T = TPPTS ; P = PPh$_3$

Fig. 3. Ligand exchange equilibria between the two phosphine ligands in the dinuclear complexes.

complex [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] presents two singlets at 0.84 ppm (9H) and 1.79 ppm (9H) for the two thiolate ligands, the complex being in a *cisoid* geometry (Fig. 3) as shown by previous studies. Addition of a large excess of triphenylphosphine ($PPh_3/Rh = 5$) to this complex resulted in the disappearance of these signals and gave rise to two intense signals (1:1 integrals) at 0.73 and 1.54 ppm and two weak peaks (1:1 integrals) at 0.77 and 1.58 ppm. The pair of signals at 0.73 and 1.54 ppm is due to the [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2$] complex and we assign the weak signals (around 10% by integration) as indicative of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)(PPh_3)$]. We tested this hypothesis by adding an excess of PPh$_3$ and TPPTS (in equimolar quantities) to the complex [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] ($PPh_3/Rh = 5$; $TPPTS/Rh = 5$). The equilibrium was reached almost immediately and ^1H NMR showed the simultaneous presence of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] and [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2$] (roughly 60:40 intensities), but not the signals at 0.77 and 1.58 ppm attributed to the mixed species. Thus, even using a suitable solvent to maintain both the organic- and water-soluble species in solution, the two equilibria in Fig. 3 are largely in favor of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] and [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2$].

Similarly, attempts to prepare the mixed complex [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)(TPPTS)$] directly by addition of one equivalent of PPh$_3$ and one equivalent of TPPTS to [$Rh_2(\mu\text{-}S^tBu)_2(CO)_4$] in a vigorously stirred toluene/water mixture resulted in the formation of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2$] and [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$]. Thus, the redistribution reaction, if it exists under these conditions, does not afford detectable amounts of the mixed species, but rather provides exclusively the two symmetrical species. Furthermore, we observed that even adding a great excess of TPPTS to [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2$] until $TPPTS/Rh = 20$ did not afford significant amounts of either the mixed species or [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$].

Since we detect only small amounts, if any, of a mixed species, we conclude that the driving force for the exchange phenomenon is not the energy of the rhodium–phosphorus bonds, either Rh–TPPTS or Rh–PPh$_3$, but rather a solvation effect. It appears that the most favorable situation, at least in bulk solution, is that in which the innermost solvation sphere is of homogeneous composition: water in the case of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$] or toluene in the case of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2$]. The formation of a heterogeneous solvation sphere, as in the case of [$Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)(PPh_3)$], seems to be disfavored. In the conditions of the biphasic catalytic tests, the concentration of any mixed species is so low that we could not detect it by NMR analysis of either phase after a catalytic run.

Addition of increasing quantities of PPh_3 to $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ resulted in increased reaction rates as shown in Fig. 4, until the PPh_3:Rh ratio reached 1. Small amounts of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ may remain in the pale-yellow aqueous solution; but the deep-yellow organic phase contains unambiguously the $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$, as shown by IR and ^{31}P NMR spectroscopy. Above a PPh_3:Rh ratio of 1, the reaction rate reached a plateau, around 70% conversion after 21 h, although for larger amounts of PPh_3 the conversion decreased slightly, due, presumably, to the classical inhibiting effect of large amounts of phosphorus ligand on the coordination of the alkene.

We have checked, in an independent experiment, that the $[Rh_2(\mu\text{-}SBu)_2(CO)_2(PPh_3)_2]$ complex requires a large excess of TPPTS in order to displace, even partially, the equilibrium toward the $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ complex: in spite of several hours' reaction at a temperature of 80°C, it was not possible to detect any complex containing TPPTS.

To make sure that the catalysis occurs in the organic phase, we examined the hydroformylation of 1-octene. As previously shown, when the catalysis occurs in the aqueous phase, the ratio of linear aldehyde to total aldehyde is around 96%, whereas when it occurs in the organic phase, this linearity is around 75% [32]. Thus, the hydroformylation of 1-octene in the presence of equimolar quantities of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ and PPh_3 gave a 75% linearity whatever the conversion rate. These results strongly indicate that the catalysis does not occur in the aqueous phase [32]. The question then arises as to whether or not the catalytic reaction occurs at the interface between the phases. If the hydroformylation reaction takes place in the aqueous side of the interphase, as supposed by Chaudhari, Delmas and co-workers, then the linearity should be near to 98%. In fact, the 75% selectivity observed is indicative of a reaction occurring in the organic side of the interphase or, in our opinion more likely, in the bulk of the organic phase. Indeed, ^{31}P NMR analyses of the yellow toluene solutions showed the presence of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$.

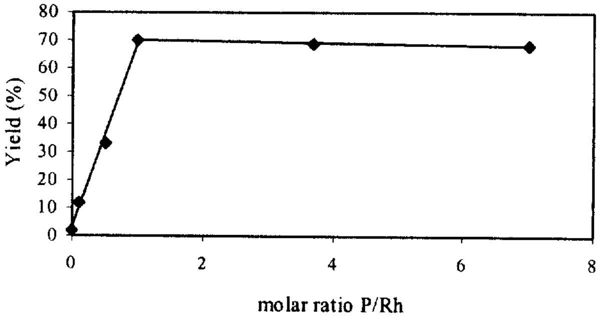


Fig. 4. Influence of added triphenylphosphine on the rate of hydroformylation with $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$.

4.2. Interfacial catalysis with $[HRh(CO)(TPPTS)_3]$

To verify whether or not this phenomenon is an intrinsic characteristic of $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$, we have also undertaken a thorough study of the $[HRh(CO)(TPPTS)_3]/[HRh(CO)(PPh_3)_3]$ system previously used by Chaudhari and Delmas [30,31] and in the same reaction of hydroformylation of 1-octene. Although these authors start from $[RhCl(cod)]_2$ and use four times the concentration of rhodium than in our experiments, we have verified from the thesis of Bhanage that we are in the same kinetic regime. We used instead $[HRh(CO)(TPPTS)_3]$ prepared ex situ by addition of TPPTS to $[Rh(CO)_2(acac)]$ under 1 bar H_2/CO (1:1) at room temperature [33]. The kinetic curve for $[HRh(CO)(TPPTS)_3]$ is classical [19] and, in the following experiments, the catalytic activity after 30 min is a significant parameter for the characterization of the system.

Addition of increasing amounts of PPh_3 resulted in an increase in the conversion as shown in Fig. 5. The curve is not linear until the PPh_3/Rh ratio reaches 3, where a plateau is reached. The tangent at the origin gives a high value of 107 h^{-1} (mol of converted 1-octene per mol of catalyst per h), which explains that the addition of small amounts of PPh_3 to $[HRh(CO)(TPPTS)_3]$ can result in a spectacular enhancement of the reaction rate. However, above a PPh_3/Rh ratio of 0.1, a distinct yellow coloration of the organic phase was noted. IR analyses of the toluene solutions confirmed the presence of the $\nu(Rh\text{–}H)$ and $\nu(C\equiv O)$ bands, at 2000 and 1920 cm^{-1}, respectively, due to $[HRh(CO)(PPh_3)_3]$ [34].

In order to determine the extent of the leaching of rhodium in the organic phase and to understand the interfacial phenomenon, an NMR study was undertaken. The complex $[HRh(CO)(TPPTS)_3]$ converts 1-octene into the corresponding aldehydes in very poor yield (roughly 1% in 30 min), the selectivity being 97% for *n*-nonanal [35]. After the run, the separation of the two phases and the evaporation of the water, a ^{31}P NMR analysis of the rhodium complex in D_2O gave a doublet at 46.3 ppm ($J_{PRh} = 155.7$ Hz) due to $[HRh(CO)(TPPTS)_3]$, a weak singlet at 37.3 ppm due to the oxidized ligand OTPPTS, and a broad signal at -2.9 ppm due to free TPPTS.

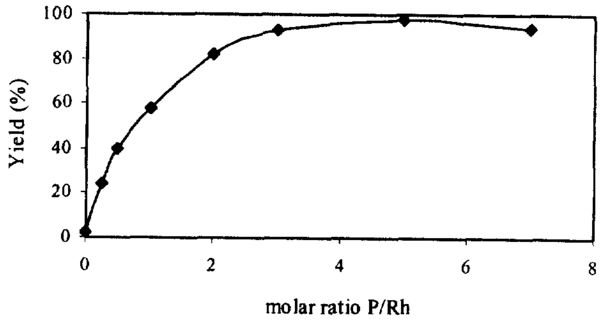


Fig. 5. Influence of added triphenylphosphine on the rate of hydroformylation with $[HRh(CO)(TPPTS)_3]$.

Using the same catalytic system, but adding 0.33 equivalents of triphenylphosphine ($[HRh(CO)(TPPTS)_3] = 0.10$ mmol/TPPTS = 0.30 mmol/$PPh_3 = 0.10$ mmol), a yield of 25% was obtained, with a selectivity in nonanal which had decreased dramatically to 75%. The ^{31}P NMR spectra of the aqueous phase (Fig. 6(a)) after the decantation showed the doublet characteristic of $[HRh(CO)(TPPTS)_3]$, and the signals of OTPPTS (roughly 20% of the intensity of the doublet) and free TPPTS. From the organic phase, the ^{31}P NMR spectra (Fig. 6(b)) revealed the presence of $[HRh(CO)(PPh_3)_3]$ at 29.5 ppm with a small J_{PRh} value strongly dependent on the

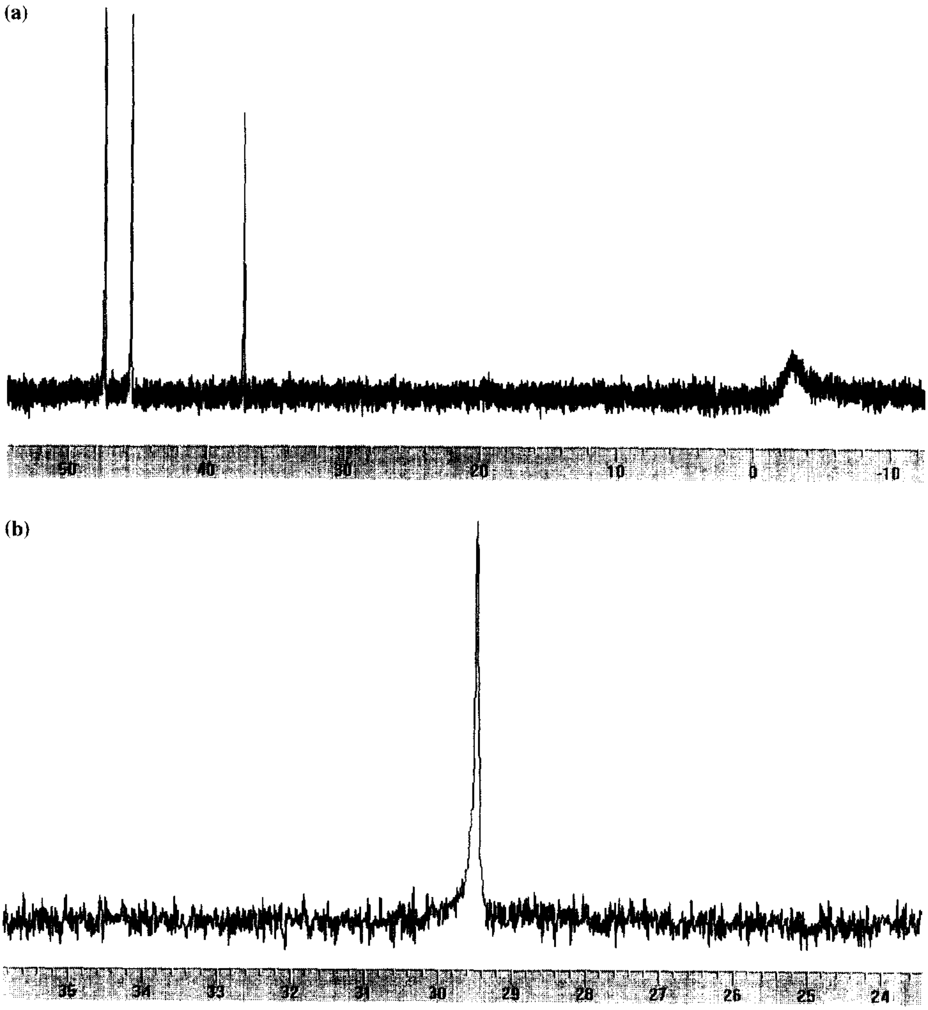


Fig. 6. (a) ^{31}P NMR spectrum of the aqueous phase after hydroformylation run of 1-octene with $HRh(CO)(TPPTS)_3$ in the presence of 0.33 equivalents of PPh_3. (b) ^{31}P NMR spectrum of the organic phase after hydroformylation run of 1-octene with $HRh(CO)(TPPTS)_3$ in the presence of 0.33 equivalents of PPh_3.

concentration of PPh_3 in the medium, characteristic of the exchange between the pentacoordinated starting complex and $[HRh(CO)(PPh_3)_2]$.

In a third experiment, a larger amount of PPh_3 was added to the system in order to reach the following starting composition: $[HRh(CO)(TPPTS)_3] = 0.10$, free TPPTS = 0.30, and $PPh_3 = 0.94$ mmol. After a 30-min run, the yield was 97% in aldehydes while the linearity remained at 75%. After work-up, the ^{31}P NMR analyses revealed the presence of large amounts of TPPTS and OTPPTS and a small quantity of $[HRh(CO)(TPPTS)_3]$ in the aqueous phase, with an OTPPTS/$[HRh(CO)(TPPTS)_3]$ ratio of roughly 6/1. The organic phase showed the signals of $[HRh(CO)(PPh_3)_3]$ at 29.0 ppm (apparent singlet) and of free PPh_3 at -5.0 ppm (broad). From the yellow colored aqueous and organic phases in these two latter experiments we did not detect any mixed species containing PPh_3 and TPPTS on the same rhodium center, which could correspond to the general formula $[HRh(CO)(TPPTS)_{3-x}(PPh_3)_x]$.

Thus, the hydroformylation experiments performed with the addition of equimolar quantities of PPh_3 or with an excess of PPh_3 showed the presence of $[HRh(CO)(TPPTS)_3]$ in the aqueous phase, and $[HRh(CO)(PPh_3)_3]$ in the toluene phase. Even when free TPPTS is clearly detected by NMR at the end of the reaction, the equilibrium is not sufficient to maintain the rhodium species exclusively in the aqueous phase. In fact, significant amounts of $[HRh(CO)(PPh_3)_3]$ are present in the organic phase and are responsible for the notable increase of activity, the yellow color of the solutions and the leaching of rhodium from the aqueous phase.

With the aim of further investigating the possible presence of mixed species, we have carried out several syntheses starting from $[Rh(acac)(CO)_2]$ in water, adding the required amounts of ligand(s) under 1 bar H_2CO. This method is known to afford the complexes $[HRh(CO)(PPh_3)_3]$ or $[HRh(CO)(TPPTS)_3]$ in high yields ($> 95\%$) [33]. Among the various experiments which have been carried out, we can report that the addition of one equivalent of TPPTS and two equivalents of PPh_3 under vigorous stirring for 6 h results, after precipitation with ethanol, in an aqueous phase containing OTPPTS exclusively. More informative is the second experiment, in which two equivalents of TPPTS and one equivalent of PPh_3 were added to $[Rh(acac)(CO)_2]$ under the same heterogeneous conditions. In this case, we observed $[HRh(CO)(TPPTS)_3]$ and OTPPTS by ^{31}P NMR, as well as a doublet of weak intensity at 34.7 ppm ($J_{PRh} = 130.2$ Hz). After washing the solution with toluene, this latter doublet disappeared. From the relative intensities of the various signals in both spectra, and as the chemical shift is the weighted mean of those of $[HRh(CO)(TPPTS)_3]$ and $[HRh(CO)(PPh_3)_3]$, we conclude that we have detected the mixed species $[HRh(CO)(TPPTS)(PPh_3)_2]$. In spite of the stoichiometry of TPPTS and PPh_3 introduced, the stability of the complex $[HRh(CO)(TPPTS)_3]$ is sufficient to consume enough TPPTS to shift the equilibrium toward the species $[HRh(CO)(TPPTS)(PPh_3)_2]$.

As for the introduction of a co-solvent in the catalytic system, we conclude that this method does not allow an adequate retention of the catalyst in the aqueous phase. In fact, in these two modes of mass transfer amelioration, an efficient anchoring of the rhodium complex is not ensured.

5. Supported aqueous phase catalysis

The supported aqueous phase catalysis (SAPC) approach has been extensively described since the pioneering work of Davis and co-workers [36], and concerns an increase of the interfacial area between the organic phase and an aqueous phase by maintaining the latter on the surface of a hydrophilic support. A great number of studies has been done with TPPTS as a water-soluble ligand. It is generally accepted that the sulfonate groups are strongly solvated by water whereas the bulk of the rest of the complex stays in the organic phase [37]. As long as the film of water is maintained on the support, the catalyst can be separated from the products by a simple filtration after the run.

The catalytic activity of supported $[Rh_2(\mu\text{-S}^tBu)_2(CO)_2(TPPTS)_2]$ has been examined in the hydroformylation of 1-octene under similar conditions to the ones described above [38]. The most direct method to prepare the catalytic system is to introduce into the autoclave, successively, the hydrophilic support, the dinuclear complex (and generally an excess of TPPTS ligand), toluene, water and 1-octene [35].

As already mentioned in the literature for the studies carried out with $[HRh(CO)(TPPTS)_3]$, we have observed that SAPC is very sensitive to the hydration level [35,38]. All our experiments used a Sipernat 22 silica that has a mean granulometry of 100 μm and a BET surface area of 162 m^2 g^{-1}. The hydration levels given in Table 1 take into account the amounts of water adsorbed on the silica (determined by thermogravimetric analysis), and the hydration of the TPPTS (one molecule of water per sulfonate group). The experiments were carried out under mild conditions (5 bar H_2/CO, 80°C, 15 h, TPPTS/Rh molar ratio = 6.0, stirring rate = 1870 rpm). Table 1 shows the results near the optimum value: the activity declines sharply on both sides. The other parameters have also been optimized, but the hydration level is the most important, and we have examined it more closely.

The scheme previously proposed by Horvath [37] for $[HRh(CO)(TPPTS)_3]$ can be summarized as the immobilization of the sulfonate groups in the aqueous phase, the

Table 1
Influence of the hydration rate on the hydroformylation of 1-octene

% H_2O	% Conversion	% Linearity
10.0	4.0	75.0
14.3	5.1	74.4
16.5	12.2	77.8
18.7	47.9	78.0
23.0	76.2	78.2
27.4	86.8	81.2
31.7	87.9	79.2
36.1	87.0	79.7
44.8	65.7	85.5

other part of the molecule emerging in the organic phase. In our experiments with $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$, the selectivity stays around 82% and this value, as we mentioned above, is strongly indicative of a catalytic reaction taking place in the organic phase. After each run, the solid was recovered by simple filtration and analyzed by NMR spectroscopy. NMR in the solid state shows the presence of TPPTS, its oxide, and a weak signal which could correspond to the complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$. Addition of an excess of water allowed the extraction of all the catalytic system, and ^{31}P NMR of this solution showed unambiguously the doublet due to $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ besides TPPTS and OTPPTS. No coloration of the organic phase was noted, and no rhodium was detected either by IR spectroscopy or by ICP analyses. Thus, Horvath's model is supported by the values of the regioselectivity of the reaction, but does not explain at all the variations in the reactivity. Indeed, the values of hydration of interest (12.4–12.9%) correspond to between one and two monolayers of a continuous film covering the silica surface. This film is not thick enough to strongly retain the catalyst on the surface to avoid its leaching. The strong affinity of water towards TPPTS, coordinated or not, is consistent with the preferential hydration of this ligand after the silica has adsorbed a monolayer of strongly bound water [39,40]. In effect, it mobilizes the required amounts of water to complete its solvation sphere.

Focusing on the fact that, at the end of the run, the catalyst appears not to be modified at all (as indicated by IR and NMR spectroscopy), the TPPTS and $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ are, during the run, in the same bulk of water: if this were not the case, the presence of CO would transform the catalyst into $[Rh_2(\mu\text{-}S^tBu)_2(CO)_4]$ [9a], which would leak into the organic phase. This co-localization is not possible with a continuous film on the silica surface. To form this environment permitting the proximity of complex and additional ligand, we propose that a small volume of water is formed immediately after the introduction of the products. Of course, such a volume would have to be large enough to contain, at the same time, the catalyst and free TPPTS. When the quantity of water introduced is less than the optimum, the availability of the catalytic system components is dramatically reduced, hampering the exchange between free and coordinated TPPTS. Addition of more water improves this availability and the optimum (12.6%) corresponds to a situation where all the $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ molecules emerge into the organic phase. When the activity begins to decrease, this corresponds to volumes of water so large that some molecules of catalyst are completely sunk into the aqueous phase. From our preliminary calculations to model this SAPC system, when the silica is hydrated at 12.6% by mass, the form and thickness of the volume is just the compromise between a good contact area and a good availability of the catalyst. Moreover, when we introduce twice the quantity of silica, with the same 12.6% hydration, keeping the other parameters unchanged, we observed a large increase in the yield (from 75.5 to 93.4%). The form of the water volume appears to be more favorable to a good mass transfer than in the first case, presumably through an appropriate rearrangement of the layers on the silica surface to provide a larger interfacial area. We can conclude that SAPC acts through 'interfacial microreactors', and we are further exploring the concept of supramolecular volumes.

6. Conclusions

The results of our recent work on improvement of the mass transfer in the biphasic hydroformylation of heavy alkenes show that two interesting approaches can be considered. Concerning interfacial catalysis, in-depth analyses of the Rh–TPPTS/PPh_3 systems are consistent with an active species containing triphenylphosphine exclusively, which works in the organic phase. From the ^{31}P NMR studies, the contribution of mixed species containing both TPPTS and PPh_3 ligands cannot exceed 5–10% of the catalytic activity. However, SAPC using various hydrophilic supports is still an attractive method to improve the contact between the substrate and the water-soluble catalyst. We confirm that the sulfonate groups anchor the catalyst in the supported aqueous film, whereas the organic part of the complex emerges into the organic phase and is responsible for the enhancement of the catalytic activity. More detailed studies are now necessary to have a good understanding of the intimate behavior of the 'microreactors', which are operating at the interface of the aqueous film and the bulk organic phase.

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