

Mechanistic approach to interfacial catalysis. Hydroformylation of heavy alkenes using tris(*m*-sodiumsulfonatophenyl)phosphine/PPh₃-containing catalysts

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Abstract

The interfacial hydroformylation of 1-octene described by Chaudhari et al. by using [HRh(CO)(TPPTS)₃] in the presence of small amounts of PPh₃ to maintain the water-soluble catalyst at the interface, has been examined in detail. NMR studies of the rhodium species present in solution clearly show that the main species responsible for the increase in the reactivity is [HRh(CO)(PPh₃)₃] which operates in the organic phase. Large amounts of tris(*m*-sodiumsulfonatophenyl)phosphine (TPPTS) do not restore the full formation of the initial complex so that significant amounts of rhodium are leached in the organic phase. A study of the behavior of [Rh₂(μ-S^tBu)₂(CO)₂(TPPTS)₂] under the same interfacial catalysis conditions has shown that the complex [Rh₂(μ-S^tBu)₂(CO)₂(PPh₃)₂] is irreversibly produced in direct proportion to the amounts of PPh₃ added to the system. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The two-phase hydroformylation of 1-propene developed by Ruhr Chemie [1], from the discovery of Rhône-Poulenc [2] on the use of a water-soluble catalyst, led to an outstanding process characterized particularly by the absence of any significant leaching of rhodium into the organic phase.

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Nevertheless, for heavy alkenes, the drawback of their very low solubility in the aqueous phase precludes their use in this process for industrial applications.

Other methods have been explored to enhance the transfer: (i) the use of a cosolvent [3–5] which improves the solubility of the organic compounds in the aqueous phase but which dramatically increases the leaching of rhodium; (ii) Supported Aqueous Phase Catalysis [6–8], which maintains the complex at the aqueous-organic interface, has been mainly studied for carbonylation reactions and seems to give very promising results; (iii) the use of β -cyclodextrins as phase transfer agents [9–21]; (iv) fluorinated phosphines in a perfluorinated solvent [22–24], which is miscible with the organic phase at high temperature but which separates from them at room temperature.

However, although each method appears to be elegant and works in one-run experiments, no definitive advance has been demonstrated yet for a preparative scale.

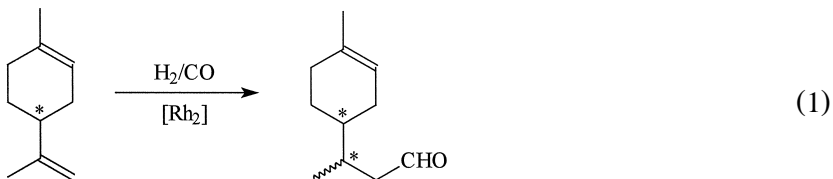
We have been interested in the concept developed by Chaudhari and Delmas [25,26] for maintaining the catalyst at the interface. We have investigated this method for the dinuclear complex used in our laboratory [3,27]; as the conclusion was negative, we have examined in more details what was proposed by these authors. We concluded that there was no detectable mixed species and that the catalysis was entirely due to the catalyst acting in the organic phase.

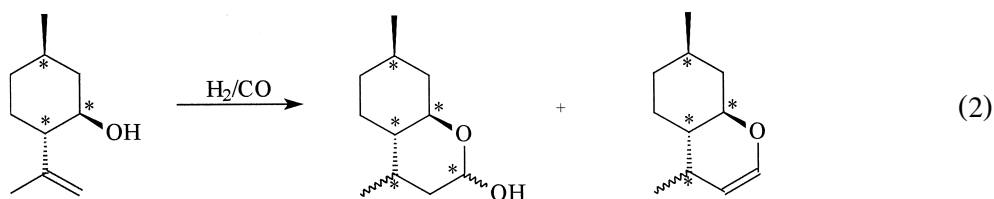
2. Results and discussion

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

The attractive results shown by Chaudhari et al. on the dramatic enhancement of the reaction rate induced by maintaining the catalyst at a close vicinity of the aqueous/organic interface [25,26] prompted us to examine this effect on the dinuclear rhodium complex which has been investigated in this laboratory for several years, containing the water-soluble ligand $P(m\text{-}SO_3Na)_3$ or tris(*m*-sodium-sulfonatophenyl)phosphine (TPPTS) [2].

Interesting results were obtained on the low pressure hydroformylation of various terpenes as heavy (C10) alkenes using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2L_2]$ complexes in toluene solution [28]. For instance, a conversion of 88% of *R*-(+)-limonene into the corresponding aldehydes was achieved with $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2\{P(OPh)_3\}_2]$ (Eq. (1)) at 5 bar, 80°C for 18 h, with a 98% selectivity into the two diastereoisomeric aldehydes. Isopulegol can be easily transformed into the corresponding chromanol (Eq. (2)) in the presence of the same catalyst at 12 bar. For this reaction of great interest in the perfumery industry, various other L_2 ligands have been examined. Independently of the enantiomeric excess which remains very modest, for *R*-(+)-limonene, $L_2 =$ bis(diphenylphosphino)propane gave 39% conversion, bis(diphenylphosphino)butane 22%, or bis(diphenylphosphino)hexane 42%.





In order to have an easy separation of the catalyst from the organic products, we were attracted by the use of the $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ complex provided the mass transfer between the two phases could be improved. Disappointing results were obtained with the use of a cosolvent like ethanol [3] since a leaching of rhodium complex was observed in the organic phase. In addition to the use of cyclodextrins and the so-called ‘Supported Aqueous Phase Catalysis’ [29] which are currently under investigation in our laboratory, we were interested in the novel method described by Chaudhari et al. [25]. Trying to adapt this ‘interfacial catalysis’ to the dinuclear water-soluble complex $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ we introduced small amounts of triphenylphosphine (TPP). The first experiment with a TPP: complex ratio of 0.1 or a TPP:TPPTS ratio of 0.05 gave a dramatic increase of the reaction rate since the conversion of limonene was 12% in 21 h as compared to around 1% in the pure biphasic system. However we were concerned by the apparition of a light yellow color of the organic phase. Infrared spectra and ^{31}P NMR analyses of the organic phase are consistent with the presence of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$; attempts to detect a mixed species in water and/or in toluene were unsuccessful.

For this reason, in independent experiments using $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ mixtures (40:60 vol:vol) as solvent we examined the effect of the addition of TPP/TPPTS ligands on the dinuclear framework by ^1H NMR. Indeed, the complex $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ presents two singlets in ^1H NMR for the two S^tBu ligands, the complex being in a cisoid geometry (Fig. 1) as shown by previous studies, at 0.84 ppm and 1.79 ppm (1:1 intensities). Addition of a large excess of triphenylphosphine ($\text{P}/\text{Rh} = 5$) to this complex resulted in the disappearance of these signals and gave rise to two intense signals (1:1 intensities) at 0.73 and 1.54 ppm and two weak peaks (1:1) at 0.77 and 1.58 ppm. The couple of signals at 0.73 and 1.54 ppm belongs to the $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ complex and we assign the weak signals (around 10% of the total intensity) as indicative of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})(\text{PPh}_3)]$. We checked this hypothesis by adding a 50:50 excess of PPh_3 and TPPTS to the complex $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ ($\text{PPh}_3/\text{Rh} = 5$; $\text{TPPTS}/\text{Rh} = 5$). The equilibrium was almost immediately reached and the ^1H NMR showed the simultaneous presence of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ and $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ (roughly 60:40 intensities) but not the two signals at 0.77 and 1.58 ppm attributed to the mixed species. Thus, even using a suitable solvent to maintain simultaneously in solution the organic- and water-soluble species, the positions of the two equilibria of Fig. 1 are largely in favor of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ and $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$. A fortiori, when using the two water and toluene solvents, as in the conditions of the

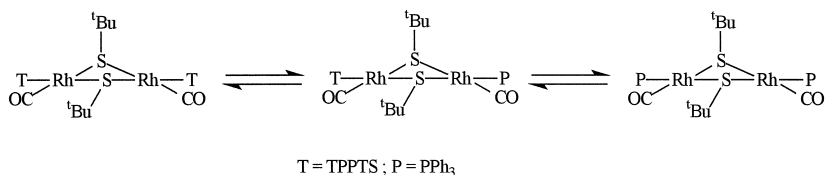


Fig. 1. TPPTS- PPh_3 exchange equilibria in the $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{L})_2]$ framework.

biphasic catalysis, the concentration of the mixed $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})(\text{PPh}_3)]$ species should be very low which explains why we did not detect it by NMR analysis of the two phases separated after a catalytic run.

Similarly, attempts to prepare directly the mixed complex $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)(\text{TPPTS})]$ by addition of 1 equivalent of TPP and 1 equivalent of TPPTS to $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_4]$ in a vigorously stirred toluene/water mixture resulted in fact in the formation of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ and $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$. Thus, the redistribution reaction, if it exists in these conditions, does not afford detectable amounts of the mixed species, but rather provides almost exclusively the two symmetrical species. Furthermore, we observed that even adding a great excess of TPPTS to $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ until TPPTS/Rh = 20 did not afford significant amounts of either the mixed species or the $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ complex.

Addition of increasing quantities of PPh_3 to $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ resulted in increased reaction rates as shown on Fig. 2, until the TPP:Rh ratio reached 1. Small amounts of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ should remain in the pale yellow aqueous solution; but the deep yellow organic phase contains unambiguously the $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ complex as shown by infrared and ^{31}P NMR spectroscopy. Above the TPP: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 $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$ complex requires a large excess of TPPTS in order to displace partially the equilibrium toward the $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ complex: in spite of a run of several hours and a temperature of 80°C , it could not be possible to detect the presence of any complex containing TPPTS.

To be sure that the catalysis occurs actually in the organic phase, we decided to change the substrate choosing 1-octene. Hydroformylation of this substrate leads to the linear aldehyde (nonanal) and to the branched isomer (2-methyl-octanal). Previous studies have shown that if the catalysis occurs in the aqueous phase, the ratio linear aldehyde/total aldehyde is around 98%, whereas when it occurs in the organic phase, this linearity is around 75% [30]. Thus, the hydroformylation of 1-octene catalyzed by $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ in presence of 1 equivalent of PPh_3 gave a 75% linearity whatever the conversion rate. These results show clearly that the catalysis does not occur in the aqueous phase [30]. The question arises if the catalysis reaction occurs at the interface. If the hydroformylation reaction takes place in the aqueous phase side of the interphase, as supposed by Chaudhari et al., then the linearity should be near to 98%. In fact, the 75% selectivity observed is relevant of a reaction occurring possibly in the organic side of the interphase but rather, in our

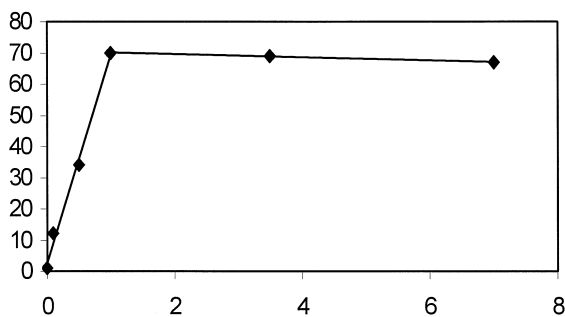


Fig. 2. Dependence of the yield on the PPh_3/Rh ratio (determined after 30 min of reaction) using $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$.

opinion, in the bulk of the organic phase. ^{31}P NMR analyses of the rhodium species contained in the yellow toluene solutions, indicated the presence of the complex $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$.

To verify that this phenomenon is not an intrinsic characteristic of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$, we have undertaken a thorough study of the $[\text{HRh}(\text{CO})(\text{TPPTS})_3]/[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ system previously used by Chaudhari and Delmas.

2.2. Interfacial catalysis with $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$

The unexpected behavior of the dinuclear complexes in biphasic system prompted us to re-examine in depth the results published by Chaudhari et al. and their research groups [25,26]. Although these authors start from $[\text{Rh}(\text{Cl})(\text{COD})]_2$ and use four times the rhodium concentrations than in our experiments, we checked from the thesis of Bhanage [26] that we are in the same kinetic regime. We directly used $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ which was prepared ex situ by addition of TPPTS to $[\text{Rh}(\text{CO})_2(\text{acac})]$ under one atmosphere of $\text{H}_2:\text{CO}$ at room temperature [8]. The kinetic curve for $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ is classical [26] and for the following experiments the catalytic activity after 30 min is a significant parameter to characterize the system.

The addition of increasing amounts of PPh_3 afforded an increase in the conversion as showed in Fig. 3. The curve is not linear until the PPh_3/Rh ratio was 3 and the plateau is reached. The tangent at the origin gives a high value of 107 (mol of converted 1-octene per mol of catalyst per hour) h^{-1} which explains that a few amounts of PPh_3 to $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ can afford a spectacular enhancement of the reaction rate. However, above a TPP/Rh ratio of 0.1 a neat coloration in yellow of the organic phase was noted. Infrared analyses of the toluene solutions confirmed the presence of the two $\nu_{\text{Rh-H}}$ and ν_{CO} bands, at 2000 and 1920 cm^{-1} , respectively, due to the $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ complex [31].

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. It can be recalled that the complex $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ converts 1-octene in very poor yield in 30 min (roughly 1%) into the corresponding aldehydes, the selectivity being 97% for nonanal [3,32]. After the run, separation of the two phases and evaporation of water, a ^{31}P NMR analysis of the rhodium complex in D_2O gave a doublet at 46.3 ppm, the $J_{\text{Rh-P}}$ coupling constant being 155.7 Hz, a weak singlet at 37.3 ppm due to the oxidized ligand OTTPPTS, and a broad signal at -2.9 ppm due to TPPTS.

Operating with the same catalytic system, but adding 0.33 equivalent of triphenylphosphine ($[\text{HRh}(\text{CO})(\text{TPPTS})_3] = 0.10$ mmol/free TPPTS = 0.30 mmol/ $\text{PPh}_3 = 0.10$ mmol) with regard to the water-soluble starting complex, a 25% yield was obtained, with a selectivity in nonanal which was dramatically decreased to 75%. The ^{31}P NMR spectra of the aqueous phase after the decantation

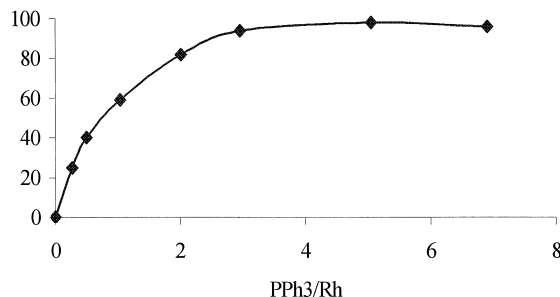


Fig. 3. Dependence of the yield on the PPh_3/Rh ratio (determined after 30 min of reaction) using $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$.

showed the doublet characteristic of $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$, and the signals of OTPPTS (roughly 20% of the intensity of the previous doublet) and TPPTS; from the organic phase, the ^{31}P NMR spectra, revealed the presence of $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ at 29.5 ppm with a small $J_{\text{Rh-P}}$ value characteristic of the exchange between the pentacoordinated starting complex and $[\text{HRh}(\text{CO})(\text{PPh}_3)_2]$, strongly dependent on the amounts of the PPh_3 concentration in the medium.

In a third experiment, a larger amount of PPh_3 was added to the system in order to reach the following starting composition: $[\text{HRh}(\text{CO})(\text{TPPTS})_3] = 0.10 \text{ mmol}/\text{free TPPTS} = 0.30 \text{ mmol}/\text{PPh}_3 = 0.94 \text{ mmol}$. After a 30-min run, the yield was 97% in aldehydes and the linearity remained at 75%. After work up the ^{31}P NMR analyses revealed the presence of large amounts of TPPTS and OTPPTS and small quantities of $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ in the aqueous phase, with a $\text{OTPPTS}/[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ ratio of roughly 6/1. The organic phase showed the signals of $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ 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 $[\text{HRh}(\text{CO})(\text{TPPTS})_{3-x}(\text{PPh}_3)_x]$.

Thus, the hydroformylation experiments performed with the addition of equivalent amounts of PPh_3 ($\text{PPh}_3/[\text{HRh}(\text{CO})(\text{TPPTS})_3] = 3$) or with an excess of PPh_3 did show the presence of $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ in the aqueous phase, and $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ in the toluene phase. Even when free TPPTS is clearly detected by NMR at the end of the reaction, the equilibrium does not fully restore the water-soluble complex to maintain the rhodium species exclusively in the aqueous phase. In fact, significant amounts of $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ 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 to investigate further the possible presence of mixed species, we have carried out several syntheses starting from $[\text{Rh}(\text{CO})_2(\text{acac})]$ in water and adding the required amounts of ligand(s) under one atmosphere of H_2/CO . This method is known to afford the complexes $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ in high yields ($> 95\%$) [8]. Among the various experiments which have been carried out, we can describe the addition of 1 equivalent of TPPTS and 2 equivalents of PPh_3 under vigorous stirring for 6 h, which resulted, after precipitation with ethanol, in exclusively OTPPTS in the aqueous phase. More informative is the second experiment, in which 2 equivalents of TPPTS and 1 equivalent of PPh_3 were added to $[\text{Rh}(\text{CO})_2(\text{acac})]$ under the same heterogeneous conditions. In this case, we observed, by ^{31}P NMR, $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$, OTPPTS and a doublet of weak intensity at 34.7 ppm ($J_{\text{Rh-P}} = 130.2 \text{ Hz}$). After washing the solution with toluene, the latter doublet at 34.7 ppm disappeared. From the relative intensities of the various signals in both spectra and as the shift at 34.7 ppm is the weighted mean of those of $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ and $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$, we can conclude that we have detected the mixed species $[\text{HRh}(\text{CO})(\text{TPPTS})(\text{PPh}_3)_2]$. In spite of the stoichiometry of TPPTS and PPh_3 introduced, the stability of the complex $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ is sufficient to consume enough TPPTS to shift the equilibrium toward the $[\text{HRh}(\text{CO})(\text{TPPTS})(\text{PPh}_3)_2]$ species.

3. Conclusion

The addition of reduced amounts of triphenylphosphine to either $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ or $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ in order to maintain the active species near the water/toluene interface to increase the yield in the hydroformylation of 1-octene has been examined. Mixed species containing simultaneously PPh_3 and TPPTS, have been observed in small quantities alongside the complexes

containing exclusively either PPh_3 or TPPTS. The notable increase in the reaction rate is, in fact, due to the activity of $[\text{HRh}(\text{CO})(\text{PPh}_3)_3]$ or $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{PPh}_3)_2]$, which are responsible for a substantial leaching of rhodium from the aqueous phase.

4. Experimental section

4.1. General comments

All syntheses were carried out under an atmosphere of nitrogen using Schlenk tube techniques. Reagents and toluene were purchased from Aldrich and used without further purification. Others solvents were purchased from SDS and used without further purification too. Rhodium trichloride trihydrate is a generous loan from Comptoir Lyon–Alemant–Louyot. TPPTS is a generous gift from Rhône-Poulenc Chimie.

4.2. Synthesis

Complexes $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$ [8] and $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$ [27] were prepared as described in the literature.

4.3. Catalytic tests

Hydroformylation experiments were carried out in a 150 ml stainless steel autoclave, equipped with mechanical stirring.

In a typical run, in a Schlenk tube, 0.2 g (0.1 mmol) of $[\text{HRh}(\text{CO})(\text{TPPTS})_3]$, or 0.05 g (0.1 mmol) of $[\text{Rh}_2(\mu\text{-S}^t\text{Bu})_2(\text{CO})_2(\text{TPPTS})_2]$, and 0.2 g (0.3 mmol) of TPPTS are dissolved in 20 ml of deaerated water, a variable amount of PPh_3 (from 0 g to 0.18 g, i.e., 0.7 mmol), 25 ml of deaerated toluene, then 2.4 g (21.4 mmol) of 1-octene, or 2.9 g of limonene (21.4 mmol), is added. The reactor is put under vacuum and the solution is introduced by suction, then the reactor is heated to 80°C (preheated oil bath) under mechanical stirring (1870 rpm). When the temperature of 80°C is reached, the autoclave is pressurized with 10 bars of an equimolar CO/H_2 mixture. During the catalytic test, the pressure is kept constant and equal to 10 bars inside the reactor. After 21 h, the gas mixture feed is stopped and the reactor is cooled to room temperature. Then the gas present inside the autoclave is evacuated. After opening the reactor, the biphasic solution is transferred by suction into a round-bottom flask and placed under nitrogen.

4.4. Analytical techniques

4.4.1. NMR spectroscopy

^{31}P NMR spectra were recorded on a Brüker AM 250 spectrometer (101.26 MHz) calibrated with H_3PO_4 as external standard. Liquid phase ^1H spectra were recorded on a Brüker AM 250 spectrometer (250.13 MHz) calibrated with TMS as external standard.

4.5. Infrared spectroscopy

Infrared manipulations were performed on a FTIR apparatus Perkin Elmer 1710.

4.5.1. GC

After catalysis the organic phases were analysed by gas phase chromatography on an Carlo Erba HRGC 5160 chromatograph equipped with a flame ionisation detector and a capillary column Alltech Econocap FFAP (30 m; 0.53 mm; 1.2 m).

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