High-Pressure $^{31}P\{^1H\}$ NMR Studies of $RhH(CO)(TPPTS)_3$ in the Presence of Methylated Cyclodextrins: New Light on Rhodium-Catalyzed Hydroformylation Reaction Assisted by Cyclodextrins

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Abstract: The effect of methylated cyclodextrins on the $RhH(CO)(TPPTS)_3$ complex in hydroformylation conditions [50 atm of CO/H_2 (1/1) and 80 °C] has been investigated by high-pressure $^{31}P\{^1H\}$ NMR spectroscopy. In the presence of methylated β-cyclodextrin, the equilibria between the rhodium species lie in favor of phosphine low-coordinated rhodium species. The formation of a stable inclusion complex between this cyclodextrin and the trisulfonated triphenylphosphine ligand (TPPTS) was found to be the key to understanding the displacement of the equilibria. Indeed, the methylated α-cyclodextrin which does not interact with the TPPTS and the methylated γ-cyclodextrin which can weakly bind to the TPPTS have no and a very low effect on the equilibria, respectively. These results explain for the first time why a decrease in the normal to branched aldehydes ratio is always observed when cyclodextrins are used as mass-transfer agents in aqueous biphasic hydroformylation processes.

Keywords: cyclodextrins; high pressure NMR; hydroformylation; phosphines; rhodium

Introduction

Long-chain olefin hydroformylation catalyzed by rhodium complexes modified by the sodium salt of the trisulfonated triphenylphosphine (TPPTS) is a potential method for the production of alcohols that are important in soap and detergent manufacture.[1] However, the solubilities of long-chain olefins in water are too low for industrially important rates to be achieved.[2] In order to circumvent this crucial problem, the use of co-solvent,[3] surfactants,[3a,4] amphiphilic phosphines[5] or cyclodextrins[6] has been reported.

Among these approaches, the use of chemically modified cyclodextrins as inverse phase-transfer agents appears to be an elegant way, which preserves some economical viability. For example, the randomly methylated-β-cyclodextrin (RAME-β-CD) that is a cheap, non-toxic and bulk commercially available compound allowed one to achieve the hydroformylation of long-chain olefins with an initial turnover frequency and aldehyde selectivity of 300 h^{-1} and 95%, respectively, while avoiding the formation of emulsions and the partition of the rhodium catalyst between the organic and aqueous phases.[7] Unfortunately, the normal to branched aldehydes ratio was always lower than that observed without a mass-transfer promoter (1.8 *vs.* 2.7 without cyclodextrin).[8] This unexpected decrease in the normal to branched aldehydes ratio is the major drawback of the cyclodextrin-based hydroformylation process as the linear aldehyde is the more desired product. The origin of this decrease is not yet elucidated. Indeed, although the β-cyclodextrin (β-CD) and RAME-β-CD can form stable inclusion complexes with the TPPTS (Scheme 1),[9] $^{31}P\{^1H\}$ NMR experiments conducted on the complex $RhH(CO)(TPPTS)_3$ under an N_2 atmosphere strongly suggest that cyclodextrins have no effect on the water-soluble organometallic complex and, consequently, on the species responsible for the formation of normal or branched aldehydes.[10] Indeed, when increasing amounts of β-CD or RAME-β-CD were added to an aqueous solution of $RhH(CO)(TPPTS)_3$ under N_2 at different temperatures, no new species were observed. Similar results were also reported by Kalck and co-workers on the water-soluble complex $[Rh_2(\mu\text{-}S\mathit{t}Bu)_2(CO)_2(TPPTS)_2]$.[11]

As the formation of new species can largely depend on the pressure of CO and H_2, we decided to reinvestigate the behavior of $RhH(CO)(TPPTS)_3$ in the presence of

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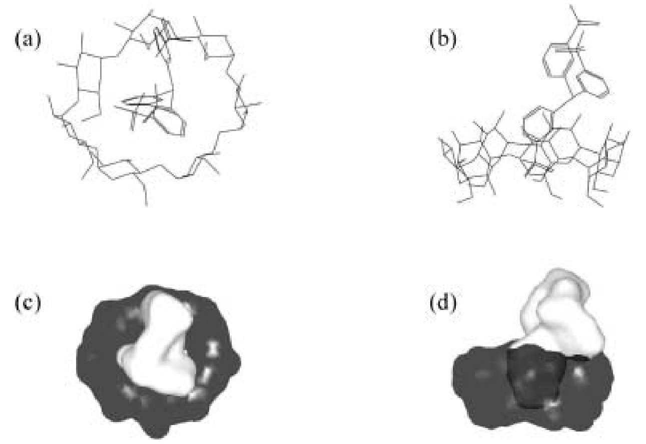


Scheme 1. Top-view **(a)** and side view **(b)** of the computer generated structures of the 1:1 inclusion complex of TPPTS with β-CD.[9b] The representations **(c)** and **(d)** indicate the Van der Waals contours of the **(a)** and **(b)** representations, respectively. Hydrogen atoms have been removed for clarity in the side view and the top view.

cyclodextrin derivatives under pressure of CO and H_2 at the reaction temperature. We report here the effect of randomly methylated α-cyclodextrin (RAME-α-CD), randomly methylated β-cyclodextrin (RAME-β-CD) and randomly methylated γ-cyclodextrin (RAME-γ-CD) on the $RhH(CO)(TPPTS)_3$ complex in conditions similar to those of the catalytic experiments [50 atm of CO/H_2 (1/1) and 80 °C].

Results and Discussion

First, we studied the stability of $[RhH(CO)(TPPTS)_3]$ (**1**) under pressure of CO and H_2 without cyclodextrin in either the absence or presence of added TPPTS. The stability study of **1** without an excess of TPPTS was performed as follows: a solution of complex **1** (0.02 M) was introduced in a 10 mm HP-NMR tube under N_2. After the $^{31}P\{^1H\}$ NMR spectrum had been recorded at room temperature (Figure 1a), the tube was pressurized with a 1:1 mixture of CO/H_2 to 50 atm and heated at 80 °C. After 1 hour, the NMR tube was cooled to room temperature and the spectrum recorded (Figure 1b).

Beside the expected doublet corresponding to **1** (44.7 ppm, $^1J_{P\text{-}Rh} = 156.0$ Hz), three new doublets and two signals corresponding to the free TPPTS (-5.7 ppm) and the phosphine oxide impurity (35.7 ppm) were clearly visible in the spectra recorded at high pressure (Figure 1b). The doublet at 37.7 ppm ($^1J_{P\text{-}Rh} = 136.3$ Hz) was attributed to $[RhH(CO)_2(TPPTS)_2]$ (**2**) by comparison with the well-known corresponding complex $[RhH(CO)_2(PPh_3)_2]$.[12,14] The two small broad doublets with a 2:1 ratio at 24.5 ppm ($^1J_{P\text{-}Rh} = 151.9$ Hz) and 21.7 ppm ($^1J_{P\text{-}Rh} = 146.4$ Hz) were assigned to the binuclear rhodium species $[Rh_2(CO)_5(TPPTS)_3]$ (**3**) by comparison with reported data for similar complexes of the general formula $[Rh_2(CO)_5(phosphine)_3]$.[12a,13] The percentage of each complex was estimated relative to the total amount of rhodium initially introduced in the medium by integration of the three signals. More precisely, the percentages calculation takes the number of phosphorus and rhodium atoms of each species into account. The percentages corresponding to **1**, **2** and **3** were found to be 65, 12 and 19%, respectively. As the sum was not equal to 100%, a low percentage (4%) of other rhodium species was suspected to be formed in such experimental conditions. The integration also indicated that 16% of free TPPTS ligand was formed. These results can be easily explained by considering the existence of an equilibrium between the three rhodium species as already observed with the analogous complex $[RhH(CO)(PR_3)_3]$ in organic or fluorous solvents.[13a,14] As shown in Scheme 2, the action of CO on an aqueous solution of **1** involved rapid conversion into **2** and free TPPTS. Once formed, **2** is in equilibrium with **3** *via* a reversible thermal elimination of H_2 and a phosphine displacement by CO.

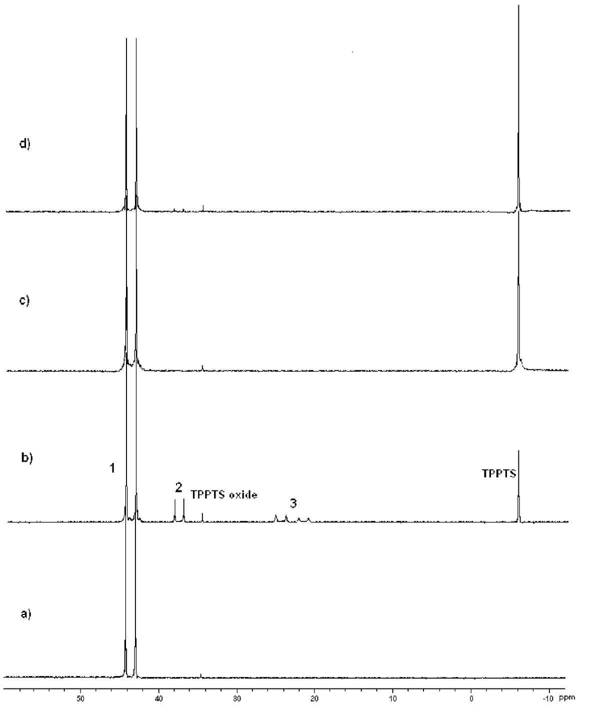


Figure 1. $^{31}P\{^1H\}$ NMR spectra at room temperature in D_2O of **a)** $[RhH(CO)(TPPTS)_3]$ (**1**) under N_2; **b) 1** under 50 atm (CO/H_2) after 1 h at 80 °C; **c) 1** + 2 equivs. of TPPTS under N_2; **d) 1** + 2 equivs. of TPPTS under 50 atm (CO/H_2) after 1 h at 80 °C.

As mentioned above, the stability of **1** was also studied in the presence of an excess of TPPTS. Interestingly, when two equivalents of TPPTS were added to **1**, the behavior of **1** changed since only a small amount of **2** (3%) was formed under the same conditions (Figure 1d),

$$\underset{\mathbf{1}}{2\ \mathrm{HRh(CO)(TPPTS)_3}} \xrightleftharpoons{-2\ \mathrm{TPPTS}\ +2\ \mathrm{CO}} \underset{\mathbf{2}}{2\ \mathrm{HRh(CO)_2(TPPTS)_2}} \xrightleftharpoons{+\mathrm{CO}\ -\mathrm{TPPTS}\ -\mathrm{H_2}} \underset{\mathbf{3}}{\mathrm{Rh_2(CO)_5(TPPTS)_3}}$$

Scheme 2.

indicating that the excess TPPTS inhibited the formation of the dimer **3**. These results are in good agreement with those reported in the literature.[14] Indeed, as already shown by Horváth and co-workers, an aqueous solution containing **1** and a three molar excess of TPPTS did not lead to the formation of new species up to 200 atm of CO/H$_2$. Actually, the fact that the five-coordinate complex **2** could not be detected demonstrates that an excess of TPPTS displaced the equilibrium between **1** and **2** towards **1** even under CO pressure. Obviously, this preliminary study clearly indicates that the equilibrium concentrations of the various species depend on the TPPTS concentration.

In the second part of this study, we evaluated the effect of RAME-β-CD on complex **1** under CO/H$_2$ pressure. As the rhodium nucleus in **1** is coordinated by three TPPTS ligands, three equivalents of RAME-β-CD were added to the water-soluble rhodium complex. After heating at 80 °C under 50 atm of 1:1 CO/H$_2$, the $^{31}P\{^1H\}$ NMR spectrum of the solution was recorded at room temperature under CO/H$_2$ pressure. A huge evolution of the signals both with regard to their number as well as for their chemical shifts and relative intensity had occurred (Figure 2).

So, when the spectrum of **1** under 50 atm of CO/H$_2$ is compared with the one without cyclodextrin, three major changes were observed:

(i) the doublets of Figure 2b showed a large decrease in intensity for **1** and a high increase for **2** and **3**. More precisely, an integration of the **1**, **2**, **3** and **4** signals gave 7, 11, 65 and 2% for the percentage of each complex, respectively. Surprisingly, these percentages did not change notably when the spectrum was recorded at 50 °C (8, 15, 55 and 3%, respectively at 50 °C), suggesting that the temperature does not considerably modify the proportions between the different species.

(ii) a new broad doublet appeared at 27 ppm ($^1J_{P\text{-}Rh}$ = 155.7 Hz). This new rhodium species **4** was identified by comparison of its chemical shift and rhodium-phosphorus coupling constant values with those of known rhodium complexes.[12a,13b] Actually, we found that the spectroscopic data of **4** are very similar to those of water-soluble binuclear rhodium complex in which each rhodium nucleus is coordinated by only one phosphine ligand. Therefore, the structure of **4** was established as [(TPPTS)(CO)$_2$Rh(μ-CO)$_2$Rh(CO)$_2$(TPPTS)]. The complex **4** is probably formed from complex **3** by phosphine displacement by CO as shown in Scheme 3.

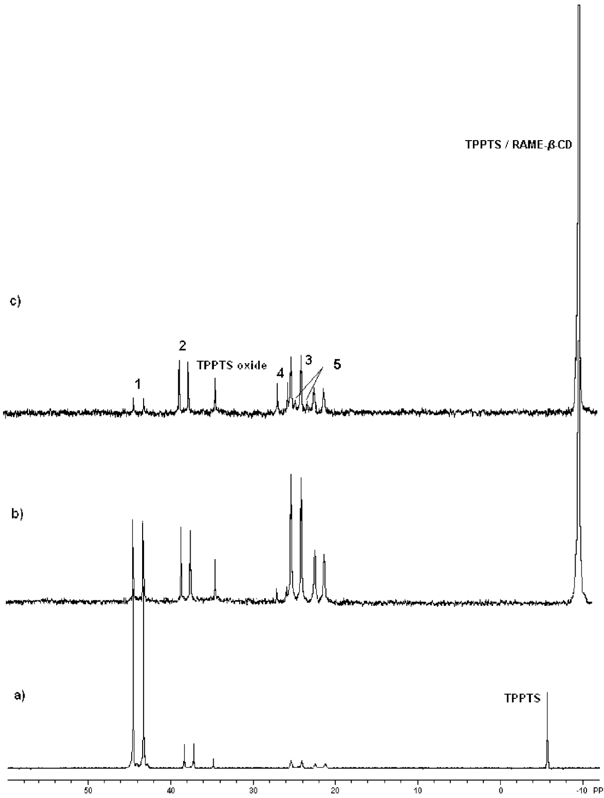


Figure 2. $^{31}P\{^1H\}$ NMR spectra at room temperature in D$_2$O of **a)** [RhH(CO)(TPPTS)$_3$] (**1**) under 50 atm (CO/H$_2$) after 1 h at 80 °C; **b)** **1** + 3 equivs. RAME-β-CD under 50 atm (CO/H$_2$) after 1 h at 80 °C; **c)** **1** + 9 equivs. RAME-β-CD under 50 atm (CO/H$_2$) after 1 h at 80 °C.

$$\underset{\mathbf{3}}{\mathrm{Rh_2(CO)_5(TPPTS)_3}} \xrightleftharpoons{+\mathrm{CO}\ -\mathrm{TPPTS}} \underset{\mathbf{4}}{\mathrm{Rh_2(CO)_6(TPPTS)_2}}$$

Scheme 3.

(iii) The signal of free TPPTS has disappeared and a new signal at – 9.6 ppm was observed. The latter signal is characteristic of the formation of an inclusion complex between TPPTS and RAME-β-CD.[8,9] In this case, the decoordinated TPPTS ligand represented 51% of the phosphorus. This clearly indicates that the free TPPTS which is formed in the equilibria between **1**, **2**, **3** and **4** has a natural tendency to associate to RAME-β-CD.

Both changes observed in the spectrum presented in Figure 2b strongly suggest that RAME-β-CD induced a shift of the equilibria between the various rhodium species towards the formation of phosphine low-coordinated rhodium species. In order to confirm the influence of RAME-β-CD on the equilibria, three times more RAME-β-CD (9 equivalents/**1**) were added in an aqueous solution of **1** and warmed at 80 °C for 1 hour under 50 atm of syngas (Figure 2c). The percentage of decoordinated TPPTS ligand was higher than that observed for a lower amount of RAME-β-CD (69% *vs.* 51%). It must be pointed out that the chemical shift of the TPPTS phosphine bound to the RAME-β-CD was similar to that observed at lower RAME-β-CD concentrations because the amount of TPPTS decoordinated by the excess RAME-β-CD is low (18%).[9] In the presence of the RAME-β-CD in excess, the percentages of **1**, **2** and **3** complexes were lower than those observed for a lower amount of RAME-β-CD (2, 9 and 38%, respectively *vs.* 7, 11 and 65%) and a new doublet close to the signals of **3** appeared. Although the very low intensity of this new doublet impeded an absolute assignment, this new species **5** could be a dimeric Rh(0) complex of formula $[(TPPTS)(CO)_2Rh(\mu\text{-}CO)_2Rh(CO)_3]$ and would be formed from complex **4** by loss of a TPPTS ligand according to Scheme 4.

Similar species $[Rh_2(CO)_7(PR_3)]$ have been reported to form from fragmentations of clusters $[Rh_4(CO)_{(12\text{-}x)}(PR_3)_x]$.[15] The appearance of this highly carbon monoxide-rich rhodium species and the low percentage of the whole of rhodium species containing TPPTS ligand (49%) strongly suggest that carbonyl-rhodium species are formed in this condition. This result demonstrates that the percentages of water-soluble rhodium species are directly dependent on the quantity of RAME-β-CD and confirms the displacement of the equilibria towards phosphine low-coordinated rhodium species in the presence of RAME-β-CD.

Although the spectra are not presented here, it is worth mentioning that the ^1H NMR spectra of the above solutions were also recorded at room temperature under CO/H_2 pressure after heating at 80 °C under 50 atm of 1:1 CO/H_2. Without RAME-β-CD, a quartet at $\delta = -9.7$ ppm ($^2J_{H\text{-}P} = 13.5$ Hz) was clearly observed in the hydride region. This quartet is consistent with trigonal bipyramidal geometry of complex **1** as previously noted[14] and confirms the presence of three TPPTS phosphines on the rhodium. When increasing amounts of RAME-β-CD were added to the medium (3 and 9 equivalents), the hydride signal disappeared. These ^1H NMR data prove undoubtedly that the hydride species are not stable in the presence of RAME-β-CD and are consistent with the formation of dinuclear rhodium species as evidenced by $^{31}P\{^1H\}$ NMR studies.

Once the influence of RAME-β-CD on the equilibrium concentrations of the rhodium complexes has been brought to the fore, we then turned our efforts to the study of **1** in conditions similar to the ones of the catalysis.[10] Indeed, we have to prove that the above observations are still valid for a system containing a 2-fold excess of TPPTS and a 12-fold excess of RAME-β-CD. Thus, an additional solution of **1** has been prepared with these proportions of TPPTS and cyclodextrin and the corresponding $^{31}P\{^1H\}$ NMR spectra were acquired (Figure 3).

$$Rh_2(CO)_6(TPPTS)_2 \xrightleftharpoons{+CO\ \ -TPPTS} Rh_2(CO)_7(TPPTS)$$

4 **5**

Scheme 4.

When compared to the spectrum of a solution of **1** containing a two molar excess of TPPTS (Figure 3a), the spectrum of Figure 3b tends to confirm the previous results. The percentage of **1** dramatically decreased whereas those of **2**, **3** and **4** increased. The **1**, **2**, **3** and **4** percentages were found to be 7, 16, 48 and 8%, respectively. Integration of the peak at −9.6 ppm showed that 72% of the phosphorus is decoordinated. As a consequence, even in the presence of an excess of TPPTS, the displacement of the equilibrium from **2** to **1** is not observed contrary to what was shown above (*vide infra* – Figure 1c and d). Actually, the molecular recognition ability of RAME-β-CD for TPPTS completely counterbalanced the effect of the excess of TPPTS ligand.

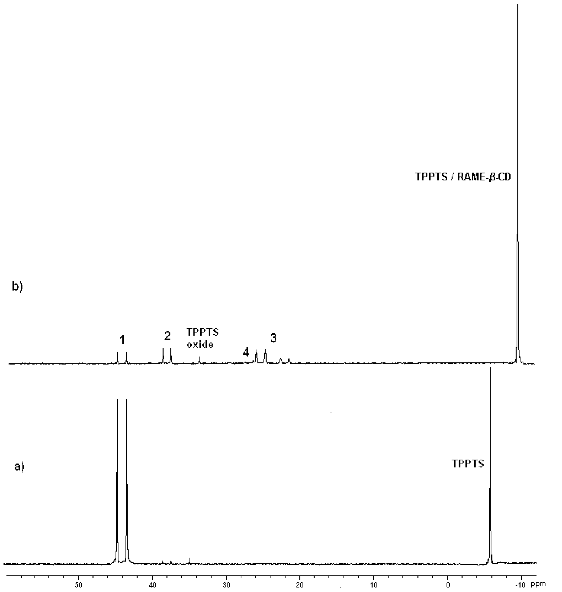


Figure 3. $^{31}P\{^1H\}$ NMR spectra at room temperature in D_2O of **a)** $[RhH(CO)(TPPTS)_3]$ (**1**) + 2 equivs. TPPTS under 50 atm (CO/H_2) after 1 h at 80 °C; **b)** **1** + 2 equivs. TPPTS + 12 equivs. RAME-β-CD under 50 atm (CO/H_2) after 1 h at 80 °C.

In the third part of this study, we have carried out two control experiments to confirm the effect of RAME-β-CD. First, we wanted to make sure that a modification of the physical and chemical characteristics of medium by oligosaccharide (ionic strength, polarity, viscosity...) was not responsible for the effect observed. With this aim in view, a control experiment was run in the same conditions than those described above, using RAME-α-CD which does not present any molecular recognition ability towards the TPPTS.[16] As explained above with RAME-β-CD, three equivalents of RAME-α-CD were added to the system. The mixture was shaken in an NMR tube for 1 h under 50 bar of CO/H_2 at 80 °C and the $^{31}P\{^1H\}$ NMR spectra acquired at room temperature (Figure 4).

As shown in Figure 4b, the spectrum is substantially similar to that obtained previously when no excess of TPPTS was added to the rhodium solution, the only relevant differences being a slight variation in the intensity of the signals. By integrating the three signals, the **1**, **2** and **3** percentages were found to be 57, 15 and 20%, respectively. These percentages are very close to those obtained with **1** under CO/H_2 pressure without excess of TPPTS (65, 12, 19%, respectively). Moreover, it can be noticed that the resonance of TPPTS was not shifted to higher field. So, these results suggest also that the formation of an inclusion complex between TPPTS and cyclodextrin is a key parameter to explain the effect of RAME-β-CD on complex **1**. Secondly, to confirm the importance of the inclusion complex formation in this equilibrated system, we wanted to compare RAME-β-CD with the RAME-γ-CD the trapping properties of which towards TPPTS are intermediate between those of RAME-α-CD and RAME-β-CD.[16] A last experiment was then carried out with **1** and a three molar excess of RAME-γ-CD under 50 atm for 1 h at 80 °C in an NMR tube. The spectrum which was recorded after cooling the solution at room temperature (Figure 5b) appeared to be quite similar to that corresponding to **1** in the same conditions without RAME-γ-CD (Figure 5a).

The percentages of **2** and **3** are slightly higher (21 and 23%, respectively) than those obtained when no cyclodextrin was added to the solution (see above). Consistently, a higher percentage of not coordinated TPPTS was observed (26% compared to 16% without cyclodextrin). Furthermore, complex **4** could not be detected by NMR in these conditions. Therefore, when using RAME-γ-CD as a host, the equilibria described in Scheme 2 are only slightly shifted to phosphine low-coordinated species. This result is totally in agreement with the weak ability of RAME-γ-CD to bind to TPPTS. Indeed, the association constants of RAME-γ-CD/TPPTS and RAME-β-CD inclusion complexes were found to be 50 and 1000 M^{-1} at 25 °C, respectively.[16] Finally, this last experiment unambiguously confirms our hypothesis concerning the role of RAME-β-CD.

To sum up, the whole of these results demonstrates that the RAME-β-CD can affect the equilibria between the various water-soluble rhodium species due to the formation of an inclusion complex between the methylated cyclodextrin and the TPPTS. From the point of view of the linear to branched aldehydes ratio, detailed mechanistic studies on the $[RhH(CO)(TPPTS)_3]$ hydroformylation catalyst systems have established that the two key catalytic species leading to linear and branched aldehydes are the coordinatively unsaturated complexes $[RhH(CO)(TPPTS)_2]$ (**6**) and $[RhH(CO)_2(TPPTS)]$ (**7**), respectively (Scheme 5).[2,14]

Without cyclodextrin, the reaction equilibria depicted in Scheme 5 lie in favor of **1** and **6** resulting in a high normal to branched aldehydes ratio. This behavior was attributed to the high stability of complex **1** due to the presence of highly ordered hydration sphere around the complex **1**.[14,17] In the presence of RAME-β-CD, the above equilibria lie undoubtedly in favor of phosphine low-coordinated rhodium species such as **2**, **3**, **4, 5** and likely **7** due to the formation of inclusion complexes between TPPTS and RAME-β-CD as evidenced by this HP NMR study. This shift of equilibria is very likely the

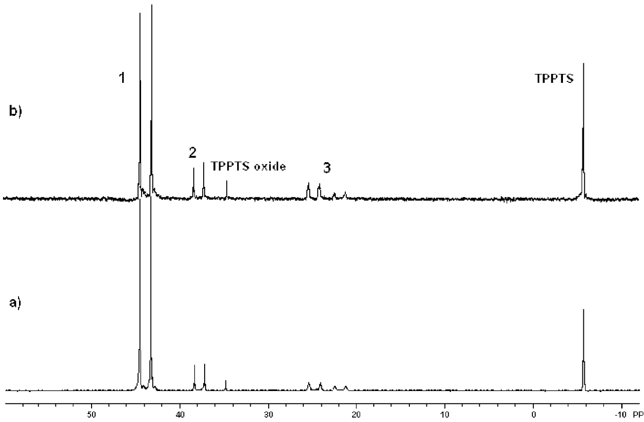


Figure 4. $^{31}P\{^1H\}$ NMR spectra at room temperature in D_2O of **a)** $[RhH(CO)(TPPTS)_3]$ (**1**) under 50 atm (CO/H_2) after 1 h at 80 °C; **b)** **1** + 3 equivs. RAME-α-CD under 50 atm (CO/H_2) after 1 h at 80 °C.

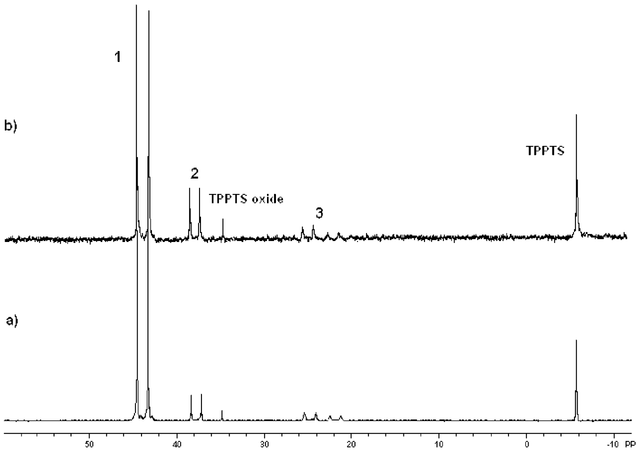
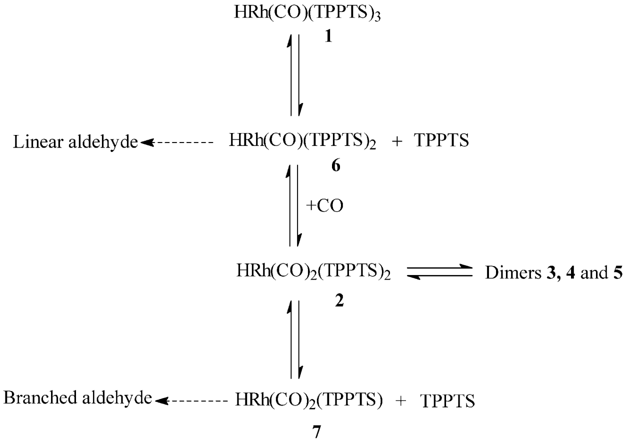


Figure 5. $^{31}P\{^1H\}$ NMR spectra at room temperature in D_2O of **a)** $[RhH(CO)(TPPTS)_3]$ (**1**) under 50 atm (CO/H_2) after 1 h at 80 °C; b) **1** + 3 equivs. RAME-γ-CD under 50 atm (CO/H_2) after 1 h at 80 °C.



Scheme 5.

reason for the decrease in the linear to branched aldehydes ratio observed in the cyclodextrin based hydroformylation processes.

Conclusion

The goal of this study has been widely achieved insofar as a better comprehension of the olefin hydroformylation catalyzed by rhodium complexes in the presence of methylated cyclodextrins has been possible thanks to the HP NMR technique. Thus, new water-soluble rhodium complexes have been evidenced and the presence of rhodium dimers in the solution brought us to clarify the role of RAME-β-CD. The formation of an inclusion complex between this cyclodextrin and the TPPTS was found to be the key to understanding the displacement of the equilibria between the rhodium species. Actually it has been proved that the TPPTS ligand which is initially added to the system or which results from a decoordination of a rhodium complex is trapped by the RAME-β-CD, inducing the formation of phosphine low-coordinated rhodium species responsible for the formation of the branched aldehyde. These conclusions lay the foundation for future investigations to improve the performances of rhodium-catalyzed hydroformylation reaction. Catalytic systems in which cyclodextrins and hydrosoluble ligands do not interact together are currently under investigation.

Experimental Section

General Remarks

Randomly methylated β-cyclodextrin (RAME-β-CD) was purchased from Aldrich. Randomly methylated α-cyclodextrin (RAME-α-CD) and randomly methylated γ-cyclodextrin (RAME-γ-CD) were prepared according to a procedure published by K. Takeo.[18] These cyclodextrins were partially methylated; statistically two OH groups per glucopyranose units were modified. Tris(3-sodium sulfonatophenyl)phosphine [TPPTS – P(m-$C_6H_4SO_3Na$)$_3$] was synthesized as reported by Gärtner et al.[19] The purity of the TPPTS was carefully controlled. In particular, ^{31}P solution NMR indicated that the product was a mixture of phosphine (*ca.* 98%) and its oxide (*ca.* 2%). The complex RhH(CO)(TPPTS)$_3$ (1) was prepared by a modification of the literature method.[20]

High pressure NMR experiments (HP-NMR) were carried out in a Varian 300 MHz instrument with a 10-mm diameter sapphire tube with a titanium cap[21] and referenced to external H_3PO_4.

HP-NMR Experiments

In a typical experiment, the rhodium complex [RhH(CO)(TPPTS)$_3$] (**1**) (0.04 mmol) and the required amount of TPPTS and methylated cyclodextrin were dissolved in 2 mL of degassed D_2O under nitrogen. The solution was placed into the sapphire NMR tube which was closed. After the mixture had been pressurized with a 1:1 mixture of CO/H_2 to 50 atm, the tube was shaken at 80 °C for 1 hour. The spectra were recorded at 25 °C.

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