Unexpected Effect of Cyclodextrins on Water-Soluble Rhodium Complexes[‡]

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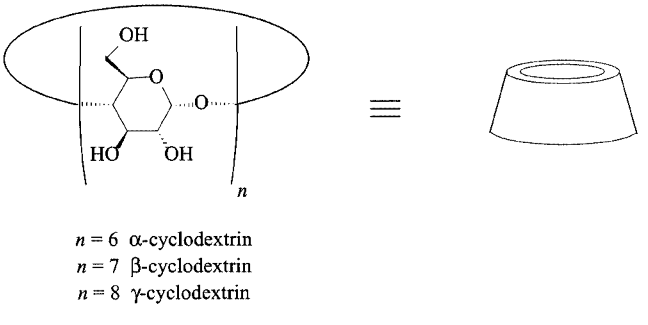
As shown by ^{31}P NMR spectroscopy, addition of β-cyclodextrin or randomly methylated β-cyclodextrin to an aqueous solution of [HRh(CO){P(m-$C_6H_4SO_3Na$)$_3$}$_3$] has no effect on the organometallic complex. In contrast, [HRh(CO){(p-tBuC_6H_4)P(m-$C_6H_4SO_3Na$)$_2$}$_3$] can be partially converted in the presence of the same β-cyclodextrin derivatives into the hydroxy complex [HORh(CO){(p-tBuC_6H_4)P(m-$C_6H_4SO_3$-Na)$_2$}$_2$], under nitrogen, or to the hydrido complex [HRh(CO)$_2${(p-tBuC_6H_4)P(m-$C_6H_4SO_3Na$)$_2$}$_2$] under carbon monoxide. This remarkable difference of behavior was attributed to the fact that the phosphane (p-tBuC_6H_4)P(m-$C_6H_4SO_3Na$)$_2$ forms more stable inclusion complexes with the β-cyclodextrin derivatives than the phosphane P(m-$C_6H_4SO_3Na$)$_3$.

Introduction

In the course of our work on the use of cyclodextrins as mass-transfer promoters in aqueous-phase organometallic catalysis, we found that cyclodextrins (Scheme 1) form inclusion compounds with the water-soluble ligands used to dissolve the catalyst in the aqueous phase.[1,2] We have reported that tris(3-sodiosulfonatophenyl)phosphane [TPPTS; P(m-$C_6H_4SO_3Na$)$_3$],[3,4] diphenyl(3-sodiosulfonatophenyl)phosphane [TPPMS; $(C_6H_5)_2$P(m-$C_6H_4SO_3$-Na)][5,6] and (4-*tert*-butylphenyl)bis(3-sodiosulfonatophenyl)phosphane [tBuTPPDS; (p-tBuC_6H_4)P(m-$C_6H_4SO_3$-Na)$_2$][7] are partially included in the hydrophobic cavity of the β-cyclodextrin derivatives. In the case of TPPMS and tBuTPPDS, it was also clearly demonstrated that the group included into the cavity is a non-sulfonated ring of the phosphane.



Scheme 1. Schematic representation of the shape of α-cyclodextrin (n = 6), β-cyclodextrin (n = 7) and γ-cyclodextrin (n = 8); the protons H-3 and H-5 are situated inside the host cavity, whereas protons H-1, H-2 and H-4 point outwards

Although we have assumed that these inclusion complexes can induce a decreased selectivity in the rhodium-catalyzed hydroformylation reaction by modifying the different equilibria between the catalytic species,[8] no spectroscopic evidence of an interaction of cyclodextrins with the catalysts has been obtained until now. In order to correct this, we have studied the influence of β-cyclodextrin (β-CD) or randomly methylated β-cyclodextrin (RAMEB) on two water-soluble, phosphane-modified rhodium hydroformylation catalysts by ^{31}P NMR spectroscopy. The water-soluble phosphanes used for this study were TPPTS and tBuTPPDS. These two phosphanes were chosen for their different affinity towards β-CD and RAMEB: the values of the association constants for the TPPTS/β-CD and tBuTPPDS/β-CD inclusion complexes were estimated to be 1,200 and 400,000 M^{-1} at 25 °C, respectively.[4,7] In the case of RAMEB, these values are lower and were estimated to be 1,000 and 250,000 M^{-1} at 25 °C for the TPPTS/RAMEB and tBuTPPDS/RAMEB inclusion complexes, respectively.[7,8]

Results and Discussion

Initial experiments were conducted with the complex [HRh(CO)(TPPTS)$_3$] (**1**). As shown in Figure 1, the ^{31}P NMR spectrum of **1** (3 mM) exhibits, besides the minor resonance of the phosphane oxide impurity at δ = 35.7 ppm, a characteristic sharp doublet at δ = 44.7 ppm ($J_{\mathrm{Rh,P}}$ = 156 Hz).[9,10]

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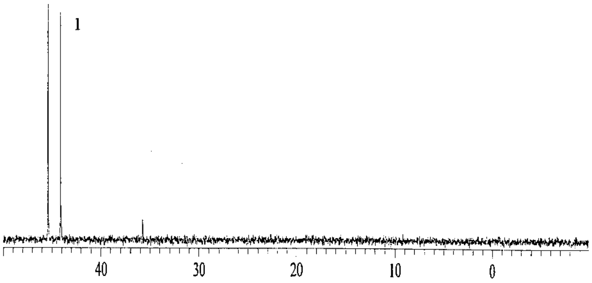


Figure 1. ^{31}P NMR spectrum of **1** (3 mM) at 27 °C in D_2O under nitrogen

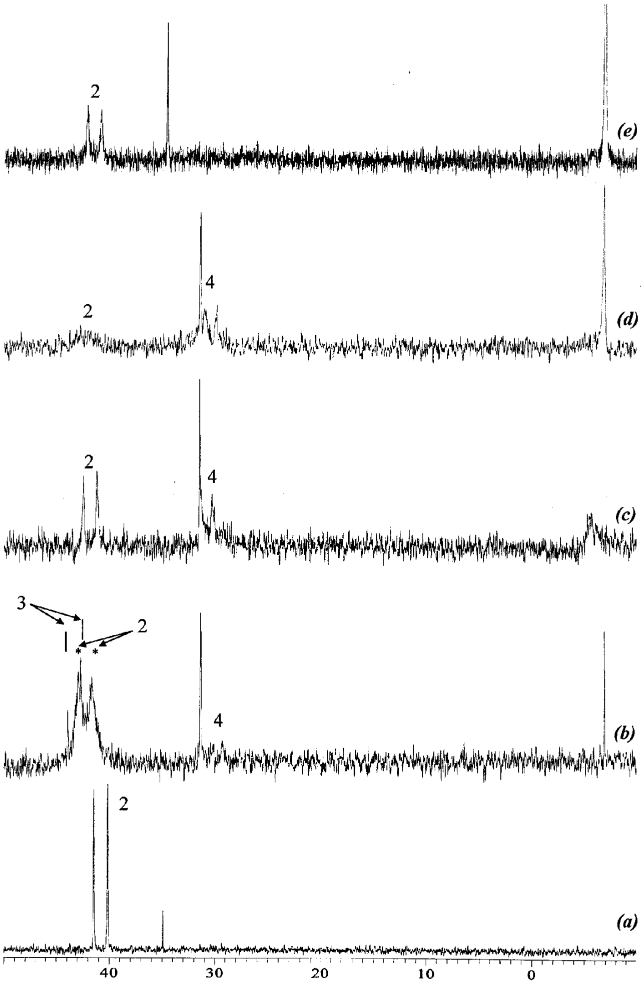


Figure 2. Effect of β-CD on complex **2**: (a) ^{31}P NMR spectrum of **2** (3 mM) in D_2O at 27 °C under nitrogen; (b) after addition of β-CD (9 mM) at 27 °C; (c) after 1 hour at 60 °C and recorded at 60 °C under nitrogen; (d) previous solution allowed to cool to 27 °C and recorded after 1 hour at 27 °C under nitrogen; (e) previous solution after addition of *t*BuTPPDS (9 mM) under 1 bar of hydrogen

When three equivalents of β-CD or RAMEB (9 mM) was added under nitrogen or carbon monoxide to an aqueous solution of **1**, no significant shift of any NMR signal was observed at different temperatures (20, 40 and 60 °C), suggesting that the cyclodextrin derivatives have no effect on the organometallic complex.

In the case of the complex [HRh(CO)(*t*BuTPPDS)$_3$] (**2**), addition of β-CD to the rhodium catalyst solution results in changes in the ^{31}P NMR spectrum. Indeed, the signal of **2** [$\delta = 40.8$ ppm (d, $J_{Rh,P} = 155$ Hz)] decreases significantly in intensity and three new signals are observed. The first signal at $\delta = -6.4$ ppm is due to the *t*BuTPPDS/β-CD inclusion complex.[7] The second signal at $\delta = 43.2$ ppm (d, $J_{Rh,P} = 155$ Hz) and the third signal at $\delta = 30.4$ ppm (d, $J_{Rh,P} = 131$ Hz) were attributed to two new rhodium species **3** and **4** containing less than three phosphanes, as noncoordinated phosphane was observed at $\delta = -6.4$ ppm (see Figure 2a and 2b).

Finally, it must be pointed out that the chemical shift difference for *t*BuTPPDS oxide ($\delta = 35$ ppm without β-CD vs. $\delta = 31.4$ ppm in the presence of β-CD) is due to the formation of an inclusion complex between β-CD and the phosphane oxide.[7]

Interestingly, when an aqueous solution of **2** was heated at 60 °C for one hour under nitrogen and the NMR spectra recorded at this temperature, the intensity of the signal of **4** increased significantly while the signal of **3** disappeared (Figure 2c). When the solution was allowed to cool to room temperature, only the signals of the *t*BuTPPDS/β-CD inclusion complex, **2** and **4** were observed (Figure 2d). The formation of **3** and **4** cannot be due to the temperature increase as no reaction occurred even at high temperature (80 °C) in the absence of cyclodextrins under the same experimental conditions.

As shown in Figure 3, addition of RAMEB to **2** under nitrogen also affects the ^{31}P NMR spectrum. However, only signals of **3** and the RAMEB-phosphane complex appear at room temperature; the formation of **4** requires heating of the complex solution to 60 °C (see Figure 3a−c).

As in the case of the β-CD, complex **3** disappears when the solution is warmed. It should be stressed that the chemical shift of *t*BuTPPDSO/RAMEB complex ($\delta = 30.1$ ppm is lower than that of *t*BuTPPDSO/β-CD complex ($\delta = 31.4$ ppm), probably owing to the affinity difference of phosphane oxide for each cyclodextrin. Interestingly, Figure 3c, 3d and 3e show that the proportion of different species does not change after heating or long reaction time (48 h), confirming that the transformation is complete, although not quantitative. Although the ^{31}P NMR spectra are not presented here, it is worth mentioning that it is possible to achieve the quantitative transformation of **2** into **4** by using a larger amount of RAMEB (20 mM) and high temperature (60 °C). Interestingly, when addition of RAMEB was carried out under carbon monoxide, the signal corresponding to the *t*BuTPPDS/RAMEB inclusion complex was always present but a sharp, new doublet was observed at $\delta = 37.1$ ppm ($J_{Rh,P} = 139$ Hz) (**5**; Figure 4).

Before discussing the nature of the new rhodium species observed in the presence of cyclodextrins under nitrogen or carbon monoxide, it must be pointed out that addition of methyl-α-D-glucopyranoside or an acyclic oligosaccharide composed of glucopyranose units such as maltose or maltoheptaose to **2** does not modify the NMR spectra of the rhodium complex and no new signal can be observed even

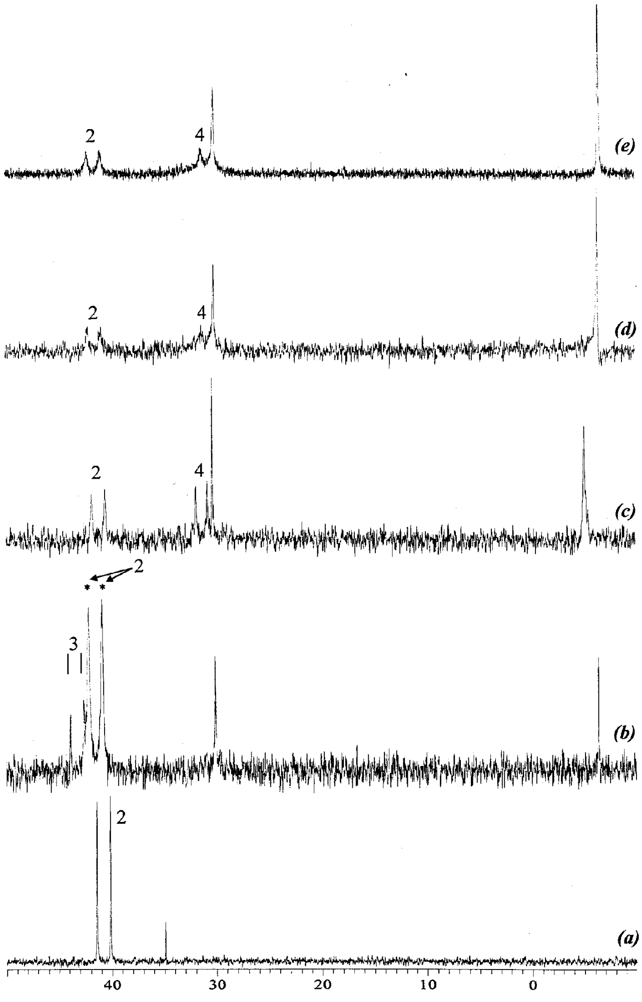
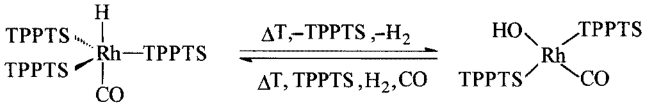


Figure 3. Effect of RAMEB on complex **2** under a nitrogen atmosphere: (a) ^{31}P NMR spectrum of **2** (3 mM) at 27 °C under nitrogen; (b) after addition of RAMEB (9 mM) at 27 °C; (c) after 1 hour at 60 °C and recorded at 60 °C under nitrogen; (d) previous solution allowed to cold to 27 °C and recorded after 1 hour at 27 °C under nitrogen; (e) previous solution recorded after 48 hours at 27 °C under nitrogen

at 40 °C or 60 °C. These experiments prove without a shadow of a doubt that the phenomenon observed with β-CD and RAMEB cannot be attributed to a solvent effect but must be due to the complexing properties of the β-cyclodextrin derivatives. Methyl α-D-glucopyranoside or acyclic oligosaccharides have the same subunits as the cyclodextrins but do not possess a lipophilic cavity that can host an organic group.

The new rhodium species **4** and **5** were identified by comparison of their chemical shift and rhodium-phosphorus coupling constant values with those of known rhodium complexes.[10−15] In particular, we found that the spectroscopic data of **4** ($\delta = 30.4$ ppm, $J_{\mathrm{Rh,P}} = 131$ Hz) are very similar to those of water-soluble hydroxy complexes {[HORh(CO)(TPPTS)$_2$]: $\delta = 31.8$ ppm, $J_{\mathrm{Rh,P}} = 129$ Hz; [HORh(CO){P(C$_6$H$_5$)$_2$[CH$_2$CH(CH$_3$)(CO$_2$Na)]}$_2$]: $\delta = 27$ ppm, $J_{\mathrm{Rh,P}} = 130$ Hz}.[13−5] As reported by Herrmann, the hydroxy complex [HORh(CO)(TPPTS)$_2$] can be obtained from [HRh(CO)(TPPTS)$_3$] by heating an aqueous solution of [HRh(CO)(TPPTS)$_3$] at reflux and can be quantitatively reconverted into [HRh(CO)(TPPTS)$_3$] under an H$_2$/CO atmosphere in the presence of an excess of TPPTS (Scheme 2).



Scheme 2. Equilibrium between [HRh(CO)(TPPTS)$_3$] and [HORh(CO)(TPPTS)$_2$] as reported by Herrmann and coworkers[13,14]

Our assignment was fully supported by experiments conducted under H$_2$ atmosphere and in the presence of an excess of *t*BuTPPDS. Under these experimental conditions complex **4** can be converted into **2** as shown in Figure 2e.

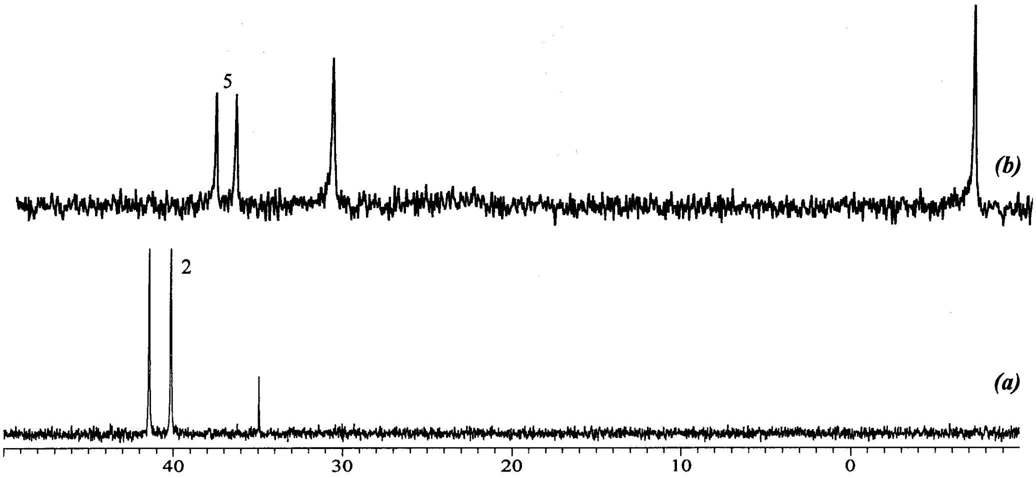
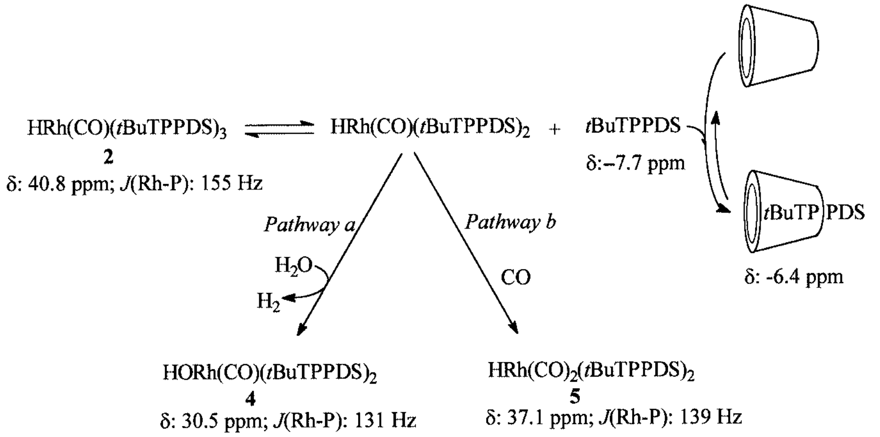


Figure 4. Effect of RAMEB on complex **2** under a carbon monoxide atmosphere: (a) spectrum of **2** (3 mM) in D$_2$O at 27 °C under carbon monoxide; (b) after addition of RAMEB (9 mM) at 27 °C under carbon monoxide



Scheme 3. Proposed mechanism for the formation of **4** and **5** from **2** in the presence of β-cyclodextrin derivatives

With respect to the rhodium species that forms under carbon monoxide, the spectroscopic data (δ = 37.1 ppm, $J_{\mathrm{Rh,P}}$ = 139 Hz) are very similar to those of the hydrido complex [HRh(CO)$_2$[P(C$_6$H$_5$)$_3$]$_2$] (δ = 39.9 ppm, $J_{\mathrm{Rh,P}}$ = 138 Hz), suggesting strongly that **5** is [HRh(CO)$_2$(*t*-BuTPPDS)$_2$].[16]

From a mechanistic point of view, the formation of an inclusion complex between the water-soluble phosphane and the cyclodextrin is probably the driving force of the reaction leading to the production of **4** (under nitrogen) or **5** (under carbon monoxide). Therefore the trapping of *t*BuTPPDS by the cyclodextrin can promote the dissociation of *t*BuTPPDS from **2** and, consequently, the formation of [HRh(CO)(*t*BuTPPDS)$_2$] as described in Scheme 3.

The complex [HRh(CO)(*t*BuTPPDS)$_2$] or its aqua form [HRh(H$_2$O)(CO)(*t*BuTPPDS)$_2$], either of which could be the unstable species **3**, would react with water (*pathway a* in Scheme 3) or a carbon monoxide molecule (*pathway b* in Scheme 3) to give rise to **4** and **5**, respectively. In the case of TPPTS, the affinity of cyclodextrin for the TPPTS is probably much too weak to observe an effect on the equilibrium described in Scheme 3, and therefore formation of the hydroxy or hydrido dicarbonyl complex is not promoted.

Conclusion

This work has clearly demonstrated that cyclodextrin can promote the formation of new species by trapping the ligand. This phenomenon is all the more important as the molecular recognition between the water-soluble ligand and the cyclodextrin is high. This finding is of interest for the development of transition metal chemistry in water because it could be used to generate easily coordinatively unsaturated organometallic complexes, which are catalytically active species in numerous reactions.

Experimental Section

General Remarks: The ^{31}P NMR spectra (121.49 MHz, referenced to external 85% H$_3$PO$_4$) were recorded on a Bruker DRX instrument. FTIR spectra were recorded on a Bruker IFS 55 spectrophotometer. D$_2$O (99.95% isotopic purity) was obtained from Merck. β-cyclodextrin (β-CD) and randomly methylated β-cyclodextrin (RAMEB) were purchased from Aldrich and dried carefully before use. The RAMEB used is a mixture of methylated-β-cyclodextrins, in which about fourteen of the twenty one hydroxy groups have been methylated. Tris(3-sodiosulfonatophenyl)phosphane [TPPTS; P(*m*-C$_6$H$_4$SO$_3$Na)$_3$] was synthesized as reported by Gärtner et al.[17] The purity of the TPPTS was carefully controlled. In particular, ^{31}P NMR spectroscopy indicated that the product was a mixture of the phosphane (ca. 98%) and its oxide (ca. 2%). The synthesis of (4-*tert*-butylphenyl)bis(3-sodiosulfonatophenyl)phosphane [*t*BuTPPDS; (*p*-*t*BuC$_6$H$_4$)P(*m*-C$_6$H$_4$SO$_3$Na)$_2$] was described in one of our previous publication.[18] The complex [HRh(CO)(TPPTS)$_3$] (**1**) was prepared by a modification of the literature method.[19]

[HRh(CO)(*t*BuTPPDS)$_3$] (2): [Rh(CO)$_2$(acac)] (100 mg) was introduced into a Schlenk tube and a *t*BuTPPDS solution (3.6 eq, 738 mg in 10 mL of degassed water) was added whilst stirring under CO/H$_2$ pressure (2 bar). After 6 hours, the crude reaction mixture was filtered and 20 mL of degassed dimethyl ethylene glycol ether was added to the solution. The pale green precipitate formed was collected by filtration, washed with dimethyl ethylene glycol ether and then dried under oil-pump vacuum: 535 mg, yield: 82%. ^{1}H NMR (300 MHz, D$_2$O, 25 °C): δ = −9.6 (q, $^{2}J_{\mathrm{H,P}}$ = 13.1 Hz, 1 H, H-Rh), 1.26 (s, 27 H, *t*Bu), 7.17 (m, 18 H), 7.48 (br. s, 6 H), 7.67 (m, 12 H) ppm. ^{31}P{^{1}H} NMR (121.49 MHz, D$_2$O, 25 °C): δ = 40.8 (d, $^{1}J_{\mathrm{P,Rh}}$ = 155 Hz, P) ppm. FTIR (KBr): $\tilde{\nu}$ = 2003 cm^{-1} (H-Rh), 1917 (CO).

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