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Cyclodextrin/Amphiphilic Phosphane Mixed Systems and their Applications in Aqueous Organometallic Catalysis

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Abstract: When mixed with a water-soluble phosphane capable of self-assembling into micelles, native or modified β-cyclodextrins (β-CDs) show very contrasting behavior depending on their neutral or ionic nature. In the post-micellar region, neutral β-CDs led to a micelle destructuring. Conversely, micelles remained stable over a well-defined range of ionic β-CD concentrations. In that case, the micelle destruction was only observed when using a large excess of ionic β-CDs. The catalytic performances of these micellar systems have been evaluated in a rhodium-catalyzed hydroformylation reaction of 1-decene. We showed that, using ionic β-CDs, the catalytic activity could be improved without a detrimental impact upon the regioselectivity. A linear/branched aldehyde ratio as high as 8.6 could be achieved. The best results were obtained with stoichiometric quantities of ionic randomly methylated β-CDs with respect to the phosphane with a beneficial effect on the decantation at the end of the reaction.

Keywords: cyclodextrins; hydroformylation; micelles; phosphanes; supramolecular chemistry

Introduction

Since the mid-1970s and the pioneering works of E. Kuntz,[1,2] the use of water in organometallic catalysis has been tackled but its application was limited to water-soluble substrates. For hydrophobic reactants, the problem has since partially been solved with the use of co-solvents,[3,4] surfactants,[5–14] amphiphilic phosphanes,[15–23] molecular receptors,[24–26] polymers[27] or dispersed particles,[28] all capable of improving the mass transfer between the substrate-containing organic phase and the catalyst. Among these strategies, the use of amphiphilic phosphanes appeared promising as the surface-active property and the coordination ability were incorporated into the same entity. Phosphane self-assembling led to micellar aggregates that are well-known to positively affect the catalytic performances of organometallic systems, increasing both activities and selectivities.[29–37] However, their interest was very relative as stable emulsions were often obtained at the end of the reaction,[29,30,33] thus rendering the catalyst recovery impossible. In this context, we envisaged the use of cyclodextrins (CDs) to avoid the emulsion problem. It has already been shown that, depending on the nature of both the CD and the surfactant, CDs could interact with amphiphilic compounds.[37–47] In fact, three different behaviors could be identified for CD/surfactant couples. In most cases, β-CDs were shown to have a deleterious effect on surfactant aggregates. Below the critical micellar concentration (cmc), a CD/surfactant supramolecular complex was formed, resulting in a delay in the micellization point. When used in excess in the post-micellar region, β-CDs led to a micelle destructuring. However, Milioto et al. clearly demonstrated that HP-α-CD or HP-γ-CD interacted with sodium alkanoates-based micelles.[41,42,43] In that case, CDs adsorbed on the micelle surface because of hydrogen bonding between the carboxylate groups of the micelle components and the CD hydroxyle functions. García-Río et al., for

their part, showed that above the cmc, native or sulfobutyl ether β-CD and sodium dodecyl sulfate co-existed in water without interacting.[46,47] Given the considerable haziness regarding the CD/surfactant interactions,[48] we were interested in evaluating the effects of neutral and ionic β-CDs in micellar organometallic catalysis.

Herein, we show that the appropriateness of a surface active sulfonated phosphane with well-defined ionic β-CDs could significantly improve the performances of the Rh-catalyzed hydroformylation of 1-decene in micellar conditions. Moreover, for some of the studied β-CDs, both the organic and aqueous phases could be separately recovered by simple decantation when the reaction was over, giving our system a gain over other catalytic micellar systems.

Results and Discussion

The recently described phosphane **1** (Figure 1)[21] has been used as both micelle-constitutive building block and water soluble rhodium-stabilizing ligand. In the studied catalytic system, phosphane **1** was always used in excess regarding the rhodium precursor (5 equiv.). Hence, non-coordinated **1** was always available to form micelles. All the studied neutral and ionic β-CDs are listed in Table 1. In the first part of the paper we focus our attention on the interactions existing between the neutral or ionic β-CDs and **1**. In the second part, the catalytic performances of a rhodium precursor in the presence of **1** and neutral or ionic CDs are discussed through the hydroformylation of 1-decene.

Isothermal Titration Calorimetry

The inclusion complex formation between neutral or ionic β-CDs and **1** was first studied using isothermal titration calorimetry (ITC). The stoichiometry and association constant (K_{ass}, Table 1) of each CD/**1** couple were determined at a low concentration (0.067 mM) to avoid heat variations resulting from the presence of micelles at higher concentration [cmc (**1**) = 0.6 mM]. Thus, at low concentration, the values only reflected the association constant relative to the CD/phosphane supramolecular complex. A 1/1 stoichiometry was found using ITC whatever the β-CD. Very different values were measured for K_{ass}, depending upon the CD shape, from 4,500 M^{-1} for DMEA-β-CD^+, Cl^- to 326,000 M^{-1} for RAME-β-CD. The lowest association constants measured for DMEA-β-CD^+, Cl^- and DMOA-β-CD^+, Cl^- probably resulted from a partial inclusion of the substituent hydrophobic part into the CD cavity which competed with the inclusion of **1**. SBE-β-CD^-, Na^+, for its part, displayed a low K_{ass} (8,070 M^{-1}) due to electrostatic repulsions between **1** and the CDs.

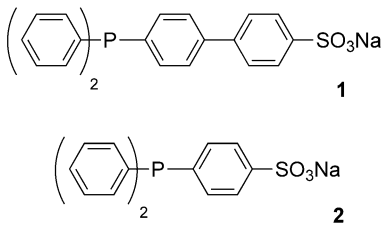


Figure 1. Water-soluble phosphanes **1** and **2**.

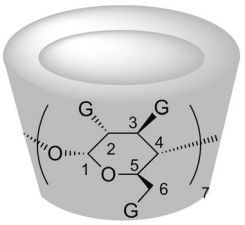
NMR Investigations

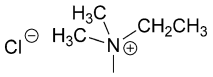
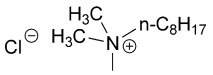
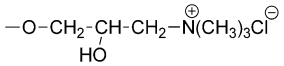
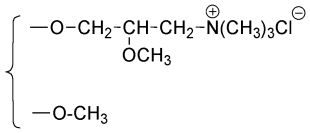
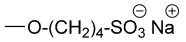
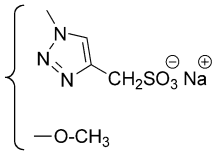
The existence of supramolecular complexes at high concentration (10 mM) of neutral or ionic CDs and **1** was revealed using NMR spectroscopy. The geometry of the CD/**1** complexes could be determined using a 2D NMR ROESY sequence which is sensitive to dipolar contacts between the CD host and the phosphane guest. The 2D ROESY NMR spectra of mixtures of **1** and neutral native β-CD or cationic HPTMA-β-CD^+, Cl^- are depicted in Figure 2 and Figure 3, respectively. The spectra clearly revealed dipolar contacts between components, indicative of inclusion of the sulfonated biphenyl and/or the phenyl moieties of **1** into the CD cavity. Both the phenyl and the biphenyl groups could not be included within the CD cavities at the same time, in line with the above 1/1 stoichiometry. Moreover, the recognition process depended upon the nature of the CD. While the native β-CD could interact with both the phenyl and the biphenyl groups (cross-peaks between H3 and H5 with all the aromatic protons, Figure 2), HPTMA-β-CD^+, Cl^- had a strong preference for phenyl groups (cross-peaks between H3 and H5 mainly with the phenyl protons, Figure 3). Cross-correlations were also detected in the 2D NMR ROESY spectrum of the SBE-β-CD^-, Na^+/**1** mixture with a marked preference for a CD/phenyl interaction (see the Supporting Information).

Tensiometry and CryoTEM Imaging

The intrinsic surface activity of neutral and ionic CDs has first been measured in pure water at 25 °C. While some of the CDs greatly impacted the surface tension γ (especially cationic CDs such as DMEA-β-CD^+, Cl^- and MPTMA-RAME-β-CD^+, Cl^-, see Figure 4), others had only a slight effect (for example, HPTMA-β-CD^+, Cl^-, native β-CD and SBE-β-CD^-, Na^+; Figure 4). No clear correlation could be established between the neutral or ionic CD character and the

Table 1. Structure of native and modified β-CDs and their association constant (K_{ass}) with phosphane **1**.



Cyclodextrin	Substituent (R)	Carbon bearing the R group	Number of R groups by CD	K_{ass} (CD/**1**) (M^{-1}) in water at 25 °C
Native β-CD	none	–	–	50,000
HP-β-CD	$-O-CH_2-CH(OH)-CH_3$	2, 3, 6	5.6	210,000
RAME-β-CD	$-O-CH_3$	2, 3, 6	12.6 (average number)	326,000
GUA-β-CD$^+$, Cl^-		6	1	161,500
DMEA-β-CD$^+$, Cl^-		6	1	4,500
DMOA-β-CD$^+$, Cl^-		6	1	5,280
HPTMA-β-CD$^+$, Cl^-		2	1	178,500
MPTMA-RAME-β-CD$^+$, Cl^-		2 2, 3, 6	1 14	53,500
SBE-β-CD$^-$, Na^+		2	1	8,070
SO_3CH_2Trz-RAME-β-CD$^-$, Na^+		6 2, 3, 6	1 12	48,900

CD′s intrinsic surface activity. On the other side, tensiometric measurements carried out into aqueous solutions containing **1** and various CD concentrations revealed a strong difference between neutral and ionic CDs (Figure 5).[49]

Addition of neutral CDs into aqueous solutions of **1** at the critical micellar concentration resulted in a significant increase in the surface tension indicative of an alteration of the micellar system. As neutral β-CDs had very little impact upon the surface tension when dissolved in pure water (Figure 4), the increase in γ observed in the presence of **1** was necessarily the consequence of the existence of neutral β-CD/**1** complexes and adequately corroborated previous results about the deleterious effect of neutral β-CDs on micelles.[50] As soon as the CD concentration increased, the micellar system was significantly altered.[51] The effect was particularly pronounced with excess native β-CD that rapidly led to a total destruction of micelles as the surface tension of pure water was recovered ($\gamma = 72\ mN \cdot m^{-1}$, Figure 5). In that case, the 3.0 mM/0.6 mM aqueous solution of β-CD/**1** only contained inclusion complexes having no affinity for the aqueous/organic interface (Figure 6).

Conversely, we showed that **1**-based micelles behaved very differently in the presence of ionic CDs. While an increase in the surface tension was observed upon addition of neutral β-CDs, addition of ionic β-CDs into aqueous solutions of **1** at the cmc induced a more or less marked decrease in the surface tension, indicative of new surface active entities (Figure 5). For example, γ dropped from $48\ mN \cdot m^{-1}$ without CD to $29\ mN \cdot m^{-1}$ with DMEA-β-CD$^+$, Cl^- at an approx. 0.8 mM concentration. Note that the drop in surface

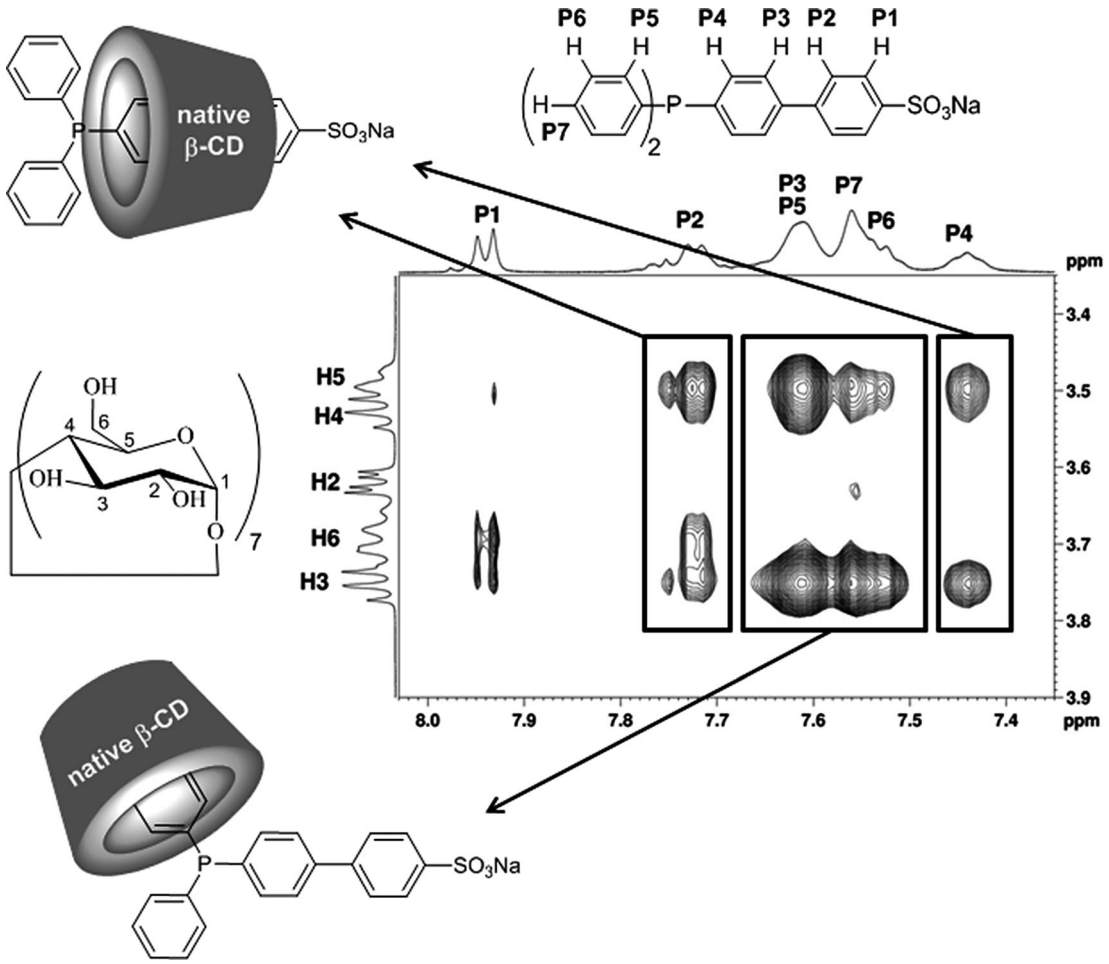


Figure 2. 2D ROESY spectrum of a stoichiometric mixture of native β-CD and **1** (10 mM/10 mM) at 25 °C in D_2O.

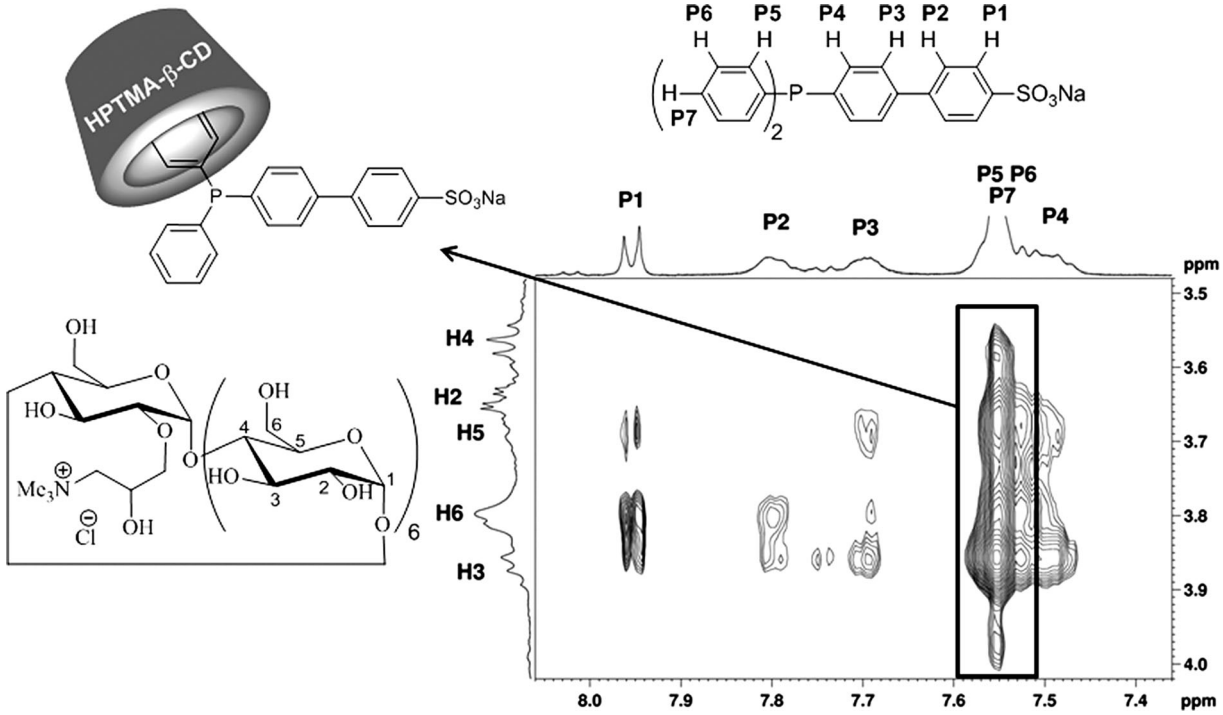


Figure 3. 2D ROESY spectrum of a stoichiometric mixture of HPTMA-β-CD^+, Cl^- and **1** (10 mM/10 mM) at 25 °C in D_2O.

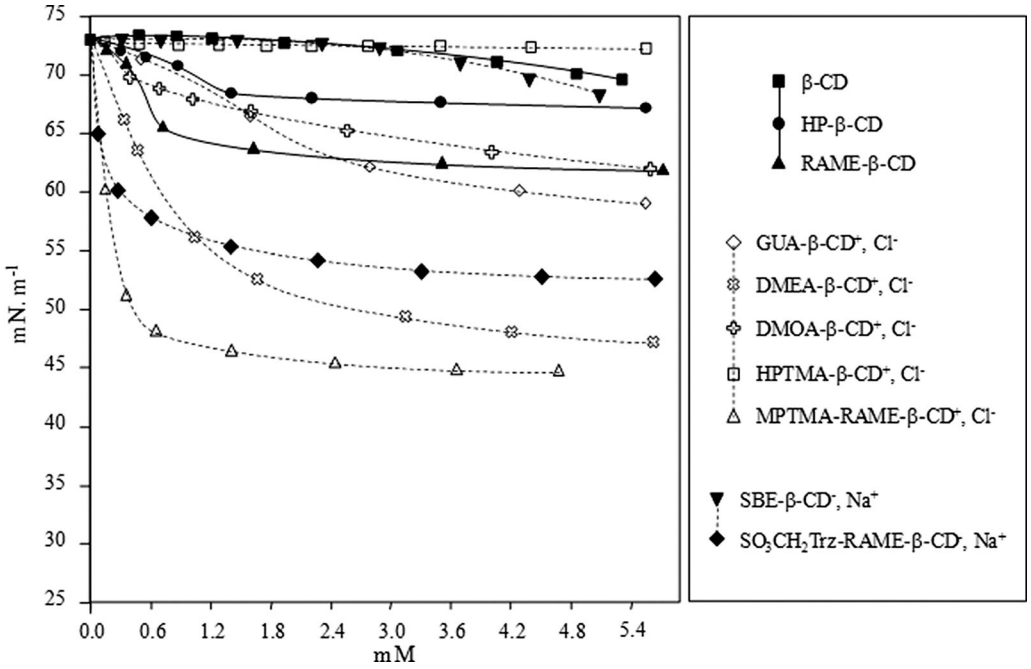


Figure 4. Effect of increasing concentrations of CDs on the surface tension of water (25 °C).

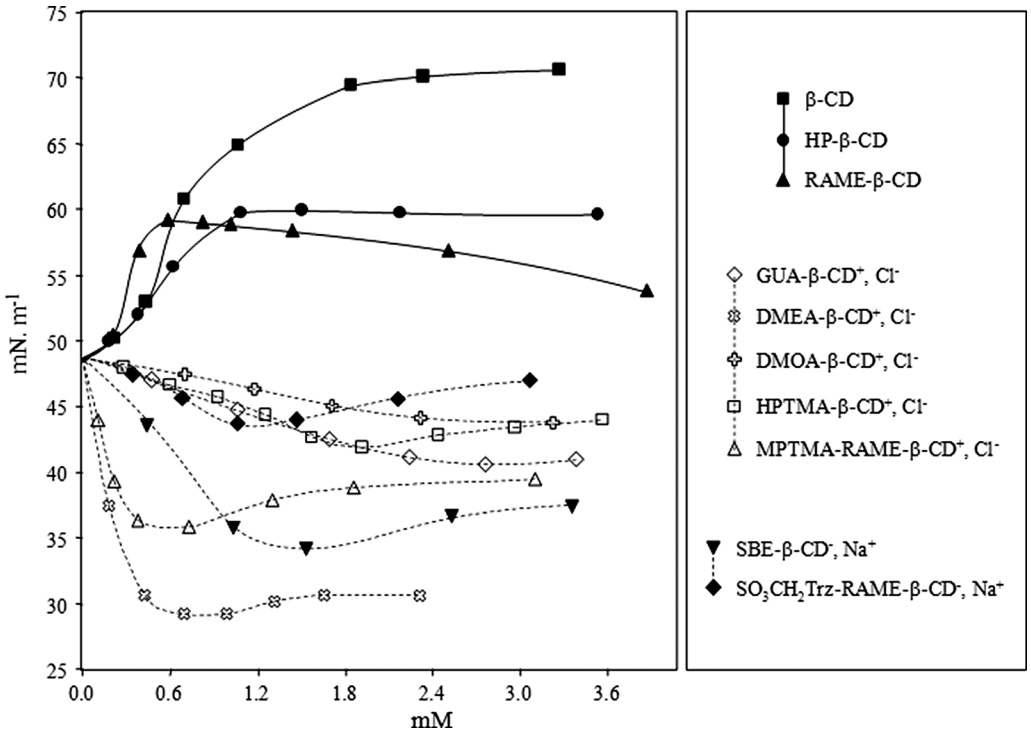


Figure 5. Effect of increasing concentrations of CDs on the surface tension of a 0.6 mM aqueous solution of **1** (25 °C).

tension did not exclusively result from the amphiphilic character of the ionic CDs. Indeed, although HPTMA-β-CD$^+$, Cl$^-$ had no effect on the surface tension when dissolved in pure water (72 mN·m^{-1} whatever the concentration, Figure 4), its impact upon the surface tension was not negligible when mixed with a micellar solution of **1** (γ dropped from 48 to 42 mN·m^{-1} when increasing the HPTMA-β-CD$^+$, Cl$^-$ concentration from 0 to 1.8 mM, Figure 5).

Cryo-TEM experiments confirmed the presence of micelles upon addition of ionic CDs into a solution of **1**. As examples, cryo-TEM images obtained for stoichiometric MPTMA-RAME-β-CD$^+$, Cl$^-$/**1** and SO_3CH_2Trz-RAME-β-CD$^-$, Na$^+$/**1** mixtures are dis-

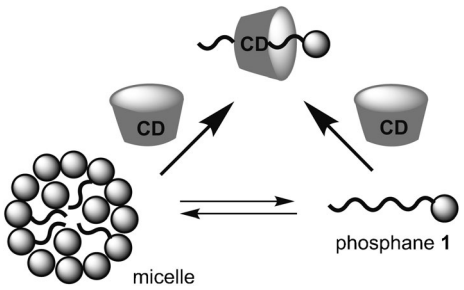


Figure 6. Micelle destruction in the presence of excess neutral β-CDs.

played in Figure 7 and Figure 8. The cryo-TEM images revealed spherical entities in a Gaussian distribution with an average diameter of 0.8 nm and a homogeneous dispersion. Of interest, the nature of the micellar aggregates significantly changed when using HPTMA-β-CD$^+$, Cl$^-$ as an additive. Vesicule-like aggregates were then observed (Figure 9). Thus, our micellar system supports the view that an interaction exists between the amphiphilic phosphane and ionic β-CDs. The decrease in γ suggests the formation of new amphiphilic supramolecular objects with more pronounced surface-active ability over a well-defined concentration range. However, it is not clear at this stage how these new entities were formed. Two hypotheses could be given (Figure 10). First, as previously described in the literature, ionic β-CDs could interact with the micelles outer sphere (electrostatic ammonium/sulfonate interaction, for example) and/or could partially penetrate into the micelle through a recognition process between the CD cavity and the sulfobiphenyl group of **1**. Second, "free" **1** molecules (in equilibrium with micelles) were captured by ionic CD cavities to furnish the amphiphilic CD/**1** supramolecular complexes responsible for the decrease in γ. Whatever the mechanism and contrary to what was observed with neutral β-CDs, the integrity of the mi-

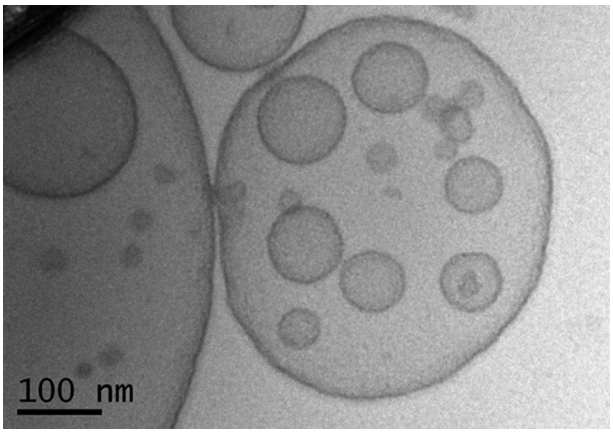


Figure 9. CryoTEM image of an HPTMA-β-CD$^+$, Cl$^-$/**1** mixture (4.5 mM/4.5 mM).

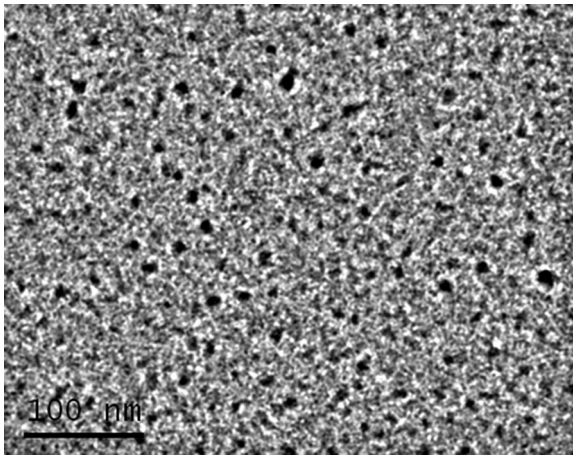


Figure 7. CryoTEM image of an MPTMA-RAME-β-CD$^+$, Cl$^-$/**1** mixture (4.5 mM/4.5 mM).

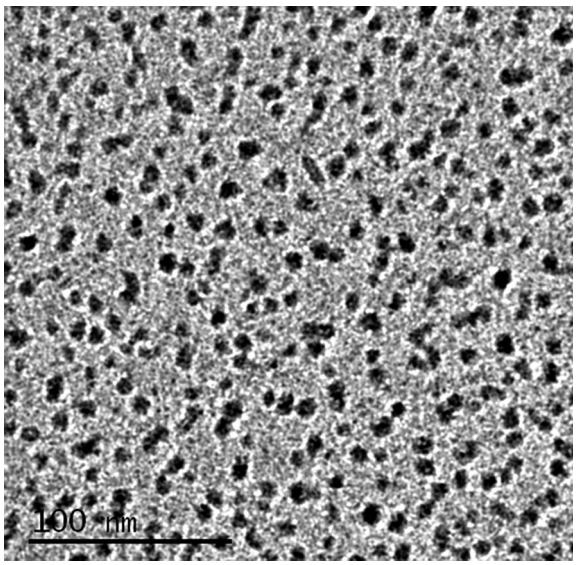


Figure 8. CryoTEM image of an SO_3CH_2Trz-RAME-β-CD$^-$, Na$^+$/**1** mixture (4.5 mM/4.5 mM).

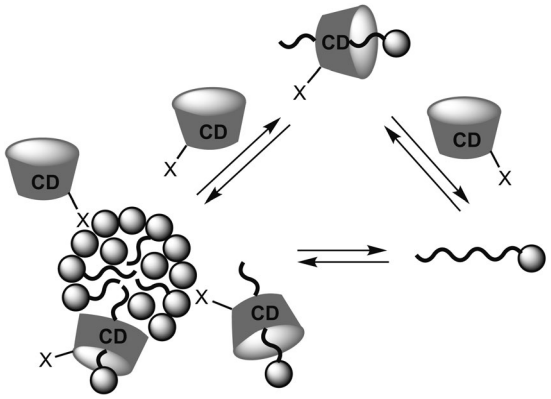


Figure 10. Possible interactions between ionic β-CDs and **1** (X = ionic substituent).

Table 2. Rhodium-catalyzed hydroformylation of 1-decene using neutral or ionic β-CDs as additives.[a]

Entry	Additive	Additive/**1**	Conversion [%][b]	Chemoselectivity[c]	l/b ratio[d]
1	–	0	15	96	9.1
2	β-CD	1	9	97	4.1
3	HP-β-CD	1	9	96	4.6
4	RAME-β-CD	1	15	93	3.6
5	RAME-β-CD	2	32	93	2.9
6	RAME-β-CD	4	67	93	2.6
7	α-D-methylglucopyranose	7	10	96	9.0
8	GUA-β-CD$^+$, Cl^-	1	65	95	7.5
9	DMEA-β-CD$^+$, Cl^-	1	41	95	7.1
10	DMOA-β-CD$^+$, Cl^-	1	59	96	8.3
11	HPTMA-β-CD$^+$, Cl^-	1	33	93	6.3
12	MPTMA-RAME-β-CD$^+$, Cl^-	1	41	95	8.6
13[e]	MPTMA-RAME-β-CD$^+$, Cl^-	1	40	96	8.6
14[f]	MPTMA-RAME-β-CD$^+$, Cl^-	1	42	93	8.4
15	MPTMA-RAME-β-CD$^+$, Cl^-	4	52	96	3.0
16	SBE-β-CD$^-$, Na^+	1	33	96	5.2
17	SO_3CH_2Trz-RAME-β-CD$^-$, Na^+	1	71	96	7.3

[a] *Experimental conditions:* Rh(acac)$(CO)_2$ (4.07×10^{-2} mmol), phosphane **1** (0.21 mmol), cyclodextrin (0.21 mmol) or α-D-methylglucopyranose (1.47 mmol), H_2O (11.5 mL), 1-decene (10.6 mmol), undecane (internal standard): 1 mmol (0.167 g), 1500 rpm, CO/H_2 (1/1): 20 bar, 80 °C, 6 h.
[b] Calculated with respect to the starting olefin.
[c] (mol of aldehydes)/(mol of converted olefins) × 100. The side products were mainly isomeric olefins.
[d] Ratio of linear to branched aldehyde product.
[e] Recycling of the aqueous phase of entry 12.
[f] Recycling of the aqueous phase of entry 13.

celles was not altered over a wide concentration range. Whereas the micelle destruction occurred at low neutral β-CDs concentration, large quantities of ionic β-CDs were necessary to totally destroy the micelles, the equilibrium being then totally displaced towards the formation of CD/**1** supramolecular complexes (Figure 10).

Catalysis

Once the behavior of neutral and ionic CDs in the presence of **1** had been clarified, the catalytic performances of each system was evaluated in the Rh-catalyzed hydroformylation of terminal alkenes. This model reaction has been chosen as it is of industrial importance, the resulting products being key intermediates in the synthesis of plasticizers, lubricants or surfactants.[52] Moreover, no less than three parameters (conversion, chemo- and regioselectivities) are indicative of the efficiency of the catalytic system. Table 2 collects the catalytic results obtained in the hydroformylation of 1-decene at 80 °C under 20 bar CO/H_2. Without CD or additive (entry 1), the catalytic activity was 5-fold that obtained with the well-known TPPTS (15% *vs.* 3%, respectively),[24] indicative of the surface active character of **1**. Concurrently, the linear to branched aldehydes ratio (l/b) was in the range of what was usually observed with micelles (l/b = 9.1).[53] This result was in agreement with the result obtained with **2** (Figure 1), a phosphane unable to self-assemble into micelles and for which a low l/b ratio of 2.8 was obtained.

Addition of stoichiometric amounts of neutral β-CDs into a micellar solution of **1** had a negative impact on the catalytic activity. The conversions were at most equivalent (15% conversion after 6 h with RAME-β-CD) or lower (9% conversion after 6 h with the native β-CD or HP-β-CD) than that measured without CD, in line with the rise in surface tension observed above (Figure 5). The decrease in regioselectivity (up to l/b = 3.6 with RAME-β-CD) also suggested a poor contribution of micelles in the catalytic process. Increasing the amount of RAME-β-CD led to a contrasting result. For example, with four equivalents of RAME-β-CD referred to **1**, the conversion underwent a 4.5-fold increase (entries 4 and 6) whereas the regioselectivity decreased from 3.6 to 2.6, a value closer to what was obtained with neutral CD-based systems in non-micellar conditions ($1.8 < l/b < 2.8$).[24]

The conversion increase resulted from the presence of "free" CDs (in excess with respect to the phosphane) that allowed for a better substrate transfer between the organic and aqueous phases. The l/b drop, for its part, was undoubtedly a consequence of both the masking of the surface activity of **1** and the resulting micelle destructuring. Indeed, as shown above,

neutral β-CDs strongly interacted with both the phenyl and biphenyl groups of **1**. Once **1** was included in the CD cavity, its amphiphilic character was masked resulting in micelle destruction and a subsequent decrease in the l/b ratio (Figure 6). The involvement of the neutral β-CD/**1** complexes in the micelle destabilization was also supported by a catalytic test carried out in the presence of the CD building block, namely α-D-methylglucopyranose, in which **1** could not be included. In that case, the catalytic results were comparable to those obtained without CD (compare entries 1 and 7) which indirectly confirmed the implication of the CD cavity in the micelle destructuring process. Thus, the conversion and the regioselectivity could not be improved at the same time in the presence of neutral β-CDs.

In sharp contrast to neutral β-CDs, the use of a stoichiometric amount of cationic β-CDs regarding **1** greatly improved the conversion of 1-decene without any significant loss in either chemoselectivity or regioselectivity. For example, the conversion measured using GUA-β-CD$^+$, Cl$^-$ as an additive reached 65% after 6 h reaction time with a 95% aldehyde chemoselectivity and a 7.5 l/b ratio (Table 2, entry 8). Even HPTMA-β-CD$^+$, Cl$^-$ (that did not adsorb at the aqueous/air interface) gave a better conversion than that obtained without CD. The high l/b ratios confirmed the presence of micelles in the catalytic solution and corroborated cryo-TEM experiments. Lower l/b values have been obtained for micelle-free systems. For example, a catalytic test carried out under the same catalytic conditions with RAME-β-CD as additive and TPPTS as ligand led to a 100% conversion within 6 h, a 95% aldehyde selectivity but a low l/b ratio (1.8),[54] thus highlighting the necessity of a well-designed phosphane to reach a high regioselectivity.

Of interest, note that a partial methylation of the β-CDs had a beneficial impact upon the decantation of the micellar system once the reaction was complete. Indeed, the phase separation occurred within a few minutes with the partially methylated RAME-β-CD when several hours were necessary with non-methylated CDs. Once the aqueous phase had been recovered, the reusability of the catalytic system was clearly established using MPTMA-RAME-β-CD$^+$, Cl$^-$ as additive (Table 2, entries 13 and 14). No trace of rhodium could be detected in the organic phase by ICP-AES, i.e., below the detection limit (0.2 ppm). To unambiguously prove the absence of rhodium in the organic phase, that of entry 14 was recovered after reaction and submitted to another catalytic experiment as follows: 1-decene (10.6 mmol) was added to the organic phase and the resulting solution was mixed with an MPTMA-RAME-β-CD$^+$, Cl$^-$-containing solution that did not contain any Rh(acac)(CO)$_2$. At 80 °C under 50 bar CO/H$_2$, no conversion could be detected even after 24 h reaction time.

Concerning anionic β-CDs (SBE-β-CD$^-$, Na$^+$ and SO$_3$CH$_2$Trz-RAME-β-CD$^-$, Na$^+$), the conversion increase suggested that anionic CDs also favored the exchange between the hydrophobic substrate-containing micelle core and the catalyst-containing aqueous solution (Table 2, entries 16 and 17). The l/b values were indicative of micelles in the medium (as revealed by cryo-TEM experiments), even if the regioselectivity measured with SBE-β-CD$^-$, Na$^+$ reflected a lower contribution of the micelle in the catalytic system (Table 2, entry 16). SO$_3$CH$_2$Trz-RAME-β-CD$^-$, Na$^+$, for its part, was the most efficient ionic CD in terms of activity (Table 2, entry 17). Moreover, as underlined above for raandomly methylated CDs, a rapid decantation was observed once the reaction was complete when using these CDs. Note that better conversions and regioselectivities were measured with ionic β-CDs (when compared to neutral β-CDs) whatever the association constant between the CD and **1**. Increasing the ionic β-CDs amounts led to an increase in the conversion and a concomitant decrease in the l/b ratio resulting from a total disorganization of the micelle building blocks. For example, with four equivalents of MPTMA-RAME-β-CD$^+$, Cl$^-$ with respect to **1**, the conversion slightly increased from 41 to 52% whereas the l/b ratio significantly decreased from 8.6 to 3.0 (entries 12 and 15). Thus, as observed above for neutral CDs, excess ionic CDs led to a total destruction of **1**-based micelles. The difference between neutral and ionic β-CDs lies in the fact that the destruction process was delayed for ionic β-CDs due to the existence of stable amphiphilic entities over a well-defined concentration range.

Conclusions

To sum up, we have found that the addition of ionic β-CDs in stoichiometric proportions into an amphiphilic phosphane **1**-containing micellar solution unexpectedly improved the performances of the Rh-catalyzed hydroformylation of 1-decene in which complementary properties of the ligand and the surfactant were expressed in a single material. An average 4-fold increase in the catalytic activity was obtained without any detrimental effect on the regioselectivity. Additionally, the main advantage of the present system was the easy recovery of both the aqueous and organic phases at the end of the reaction when randomly methylated β-CDs were used as additives. The results of this structure-activity investigation have provided compelling evidence that the CD/phosphane association could be of great interest in the hydroformylation of terminal alkenes. However, we believe that this work is not restricted to the hydroformylation reaction and could be extended to other catalytic systems in aqueous media.

Experimental Section

Materials

All chemicals were purchased from Acros and Aldrich Chemicals in their highest purity. All solvents were used as supplied without further purification. Distilled water was used in all experiments. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ^{1}H nuclei, 121 MHz for ^{31}P nuclei and 75 MHz for ^{13}C nuclei. NMR ROESY experiments were performed on a Bruker Avance spectrometer operating at 500 MHz for ^{1}H with a TXI probe at 295 K with a mixing time of 500 ms. $CDCl_3$ (99.50% isotopic purity) and D_2O (99.92% isotopic purity) were purchased from Euriso-Top. The correct assignments of the chemical shifts were confirmed when necessary by two-dimensional correlation measurements attained by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC experiments. Mass spectra were recorded on a MALDI-TOF/TOF Bruker Daltonics Ultraflex II in the positive reflectron mode with 2,5-DHB as matrix. The absence of rhodium traces in the organic phase has been checked using an ICP-AES Activa Horiba Jobin Yvon spectrometer.

Surface Tension

Interfacial tension measurements were performed using a KSV Instruments digital tensiometer (Sigma 70) with a platinum plate. The precision of the force transducer of the surface tension apparatus was 0.1 $mN \cdot m^{-1}$. The experiments were performed at 293 ± 0.5 K controlled with a thermostatted bath Lauda (RC6 CS).

Isothermal Titration Calorimetry

An isothermal calorimeter (ITC200, MicroCal Inc., USA) was used for determining the formation constant of the studied complexes. The following titration protocol was used: a degassed aqueous solution of phosphane **1** (204. 5 μL; phosphate buffer: pH 6.5) was titrated at 298 K with a solution of cyclodextrin (same buffer) in a 40 μL syringe. The concentrations of phosphane **1** and cyclodextrins in stock solutions were 0.067 and 2.5 mM, respectively. After addition of an initial aliquot of 0.4 μL, 7 aliquots of 5.4 μL of the cyclodextrin solution were delivered over 10.8 s. The corresponding heat flow was recorded as a function of time. The time interval between two consecutive injections was 100 s and agitation speed was 1000 rpm for all experiments. In addition, the heat effects due to dilution of cyclodextrin were corrected for by performing blank titrations. The areas under the peak following each injection (obtained by integration of the raw signal) were then expressed as the heat effect per mole of added cyclodextrins. Binding constants were finally determined by non-linear regression analysis of the binding isotherms using built-in binding models within MicroCal Origin 7.0 software package (MicroCal, Northampton, MA). Each titration experiment was performed three times to ensure reproducibility of the results. Note that at pH 6.5, no phosphonium species existed in the buffer solution as confirmed by ^{31}P NMR measurements. Thus, ITC measurements were only related to CDs/**1** supramolecular complexes.

Cryo-TEM

Specimens for cryo-TEM observation were prepared using a cryoplunge cryo-fixation device (Gatan, USA) in which a drop of the aqueous suspension was deposited on to glow-discharged holey-type carbon-coated grids (Ted Pella Inc., USA). The TEM grid was then prepared by blotting the drop containing the specimen to a thin liquid layer that remained across the holes in the support carbon film. The liquid film was vitrified by rapidly plunging the grid into liquid ethane cooled by liquid nitrogen. The vitrified specimens were mounted in a Gatan 910 specimen holder (Gatan, USA) that was inserted in the microscope using a CT-3500-cryotransfer system (Gatan, USA) and cooled with liquid nitrogen. TEM images were then obtained from specimens preserved in vitreous ice and suspended across a hole in the supporting carbon substrate.

Microscopy

The samples were observed under low dose conditions ($< 10\ e^{-}/A^{2}$), at $-178\,^{\circ}C$, using a JEM 1230 'Cryo' microscope (Jeol, Japan) operated at 80 kV and equipped with an LaB_6 filament. All the micrographs were recorded on a Gatan 1.35 K × 1.04 K × 12 bit ES500W CCD camera.

Catalytic Experiments

All catalytic reactions were performed under nitrogen using standard Schlenk techniques. In a typical experiment, $Rh(acac)(CO)_2$ ($4.07 \cdot 10^{-2}$ mmol), phosphane **1** (0.21 mmol), and the additive (0.21 mmol) were dissolved in 11.5 mL of water. The resulting aqueous phase and the olefin (10.6 mmol) were charged under nitrogen into a 50-mL reactor heated at the desired temperature. The mixture was mechanically stirred using a multipaddle unit (1500 rpm) and the autoclave was pressurized under 20 atm CO/H_2 (1:1) using a gas reservoir connected to the reactor through a high-pressure regulator valve allowing us to keep the pressure constant in the reactor during the reaction. Once the reaction was complete, the organic phase was analyzed by gas chromatography on a Shimadzu GC-17 A gas chromatograph equipped with a methylsilicone capillary column (30 m × 0.32 mm) and a flame ionization detector (GC:FID).

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