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Heptakis(2,3-di-*O*-methyl-6-*O*-sulfopropyl)-β-cyclodextrin: A Genuine Supramolecular Carrier for Aqueous Organometallic Catalysis

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Abstract: The behavior of heptakis(2,3-di-*O*-methyl-6-*O*-sulfopropyl)-β-cyclodextrin as inverse phase transfer catalyst in biphasic Tsuji–Trost and hydroformylation reactions has been investigated. In terms of activity, this methylated sulfopropyl ether β-cyclodextrin is much more efficient than the randomly methylated β-cyclodextrin, which was the most active cyclodextrin known to date. From a selectivity point of view, the intrinsic properties of the catalytic system are fully preserved in the presence of this cyclodextrin as the chemo- or regioselectivity was found to be identical to that observed without a mass transfer promoter in the hydroformylation reaction. The efficiency of this cyclodextrin was attributed to its high surface activity and to the absence of interactions with the catalytically active species and the water-soluble phosphane used to dissolve the organometallic catalyst in the aqueous phase.

Keywords: aqueous organometallic catalysis; cyclodextrins; hydroformylation; molecular recognition; phase-transfer catalysis; Tsuji–Trost reaction

Introduction

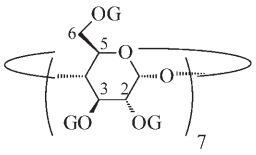
During the past decade, ecological requirements have pressed chemists to develop clean processes and technologies. In this context, organometallic catalysis in an aqueous-organic two-phase system appeared as an environmental friendly technique for producing organic compounds.[1] Indeed, the organometallic catalyst which is solubilized by hydrophilic ligands in the aqueous phase can be easily separated from the reaction products by simple phase decantation at the end of the reaction. However, faced with the insolubility of most organic compounds in water, addition of mass transfer promoters is required to obtain commercially viable reaction rates.[2]

Numerous studies have clearly demonstrated the efficiency of cyclodextrins (CDs) as a mass transfer promoter in aqueous phase organometallic catalysis.[3] Indeed, by forming water-soluble inclusion complexes with highly hydrophobic substrates, β-CD derivatives greatly increase the solubility of these compounds in water, and consequently, avoid mass transfer limitations. Among the different CDs used in such work, the randomly methylated-β-CD (RAME-β-CD – Figure 1) appeared to be the most efficient.[4]

The RAME-β-CD was a native β-CD partially *O*-methylated with statistically 1.8 OH groups modified per glucopyranose unit. The OH groups in the C-6 position were fully methylated whereas those in C-2 and C-3 positions were partially methylated. The outstanding effect of RAME-β-CD on reaction rates was attributed to its slight surface activity and to the presence of a deep hydrophobic host cavity that accommodates properly the substrate. Nevertheless, RAME-β-CD did not constitute an optimal solution. Indeed, RAME-β-CD can form inclusion complexes with the hydrosoluble phosphane ligands used to dissolve the transition metal in the aqueous phase.[5] These inclusion complexes were responsible for the decrease in the linear to branched aldehydes ratio during the rhodium-catalyzed hydroformylation reaction[6] and a drop in cyclodextrin activity in some experimental conditions.[7] Consequently, there is a real interest to find cyclodextrins that do not interact with the ligands or the organometallic catalyst.

In this context, one of us has reported recently the synthesis of a new methylated derivative of sulfopropyl-β-cyclodextrin: heptakis(2,3-di-*O*-methyl-6-*O*-sulfopropyl)-β-CD (KSPDM-β-CD – Figure 1).[8] This CD contains 7 sulfopropyl groups on the primary face and 14

Structure of the chemically modified β-cyclodextrin



G: **H** or **R**

Abbreviations	R *(number of R group by CD)*	Carbon bearing the OR group(s)
RAME-β–CD	$-CH_3$ *(12.6)*	2, 3, 6
TRIME-β-CD	$-CH_3$ *(21)*	2, 3, 6
KSPDM-β-CD	$-(CH_2)_3SO_3K$ *(7)* and $-CH_3$ *(14)*	6 2 and 3
SBE_7-β-CD	$-(CH_2)_4SO_3Na$ *(7)*	2, 3, 6

Figure 1. Structures of β-cyclodextrin derivatives used in this work.

methyl groups on the secondary face and was able to form an inclusion complex with organic compounds such as 2-naphthoic acid. As KSPDM-β-CD possesses an extended hydrophobic cavity and a structure similar to that of a surfactant due to the presence of well-identified hydrophobic and hydrophilic parts, it was of great interest to compare the behavior of this CD with that of RAME-β-CD in aqueous-phase organometallic catalysis.

In this paper, the surface activity of KSPDM-β-CD and its ability to bind to common water-soluble phosphanes have been investigated by surface-tension measurements and by NMR spectroscopy, respectively. The efficiency of KSPDM-β-CD as a mass transfer promoter in Tsuji–Trost and hydroformylation reactions is also reported.

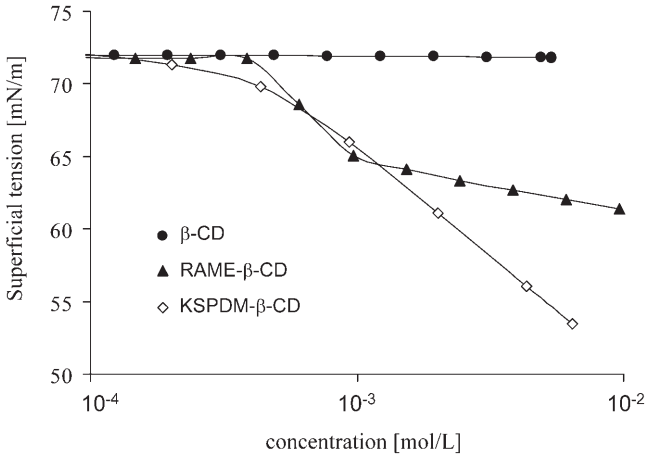


Figure 2. Surface tensions of aqueous solutions containing CDs at 25 °C.

Results and Discussion

First of all, to evaluate the mass transfer potential of KSPDM-β-CD, its surface activity has been compared to that of other CDs. In Figure 2 are depicted the surface activities of β-CD, RAME-β-CD and KSPDM-β-CD as a function of their concentration.

As already reported in the literature,[9] the native β-CD exhibited no surface active property as no variation of the surface tension was observed with this CD whatever the concentration. On the contrary, the curve obtained for the RAME-β-CD is characteristic of an adsorption phenomenon at the air-water interface as the surface tension decreased when the RAME-β-CD concentration increased. In fact, the nature of the RAME-β-CD, having both hydrophobic and hydrophilic moieties, is responsible for its tendency to concentrate at the air-water interface. Interestingly, a break of the slope was clearly observed at 10^{-3} M^{-1}concentration with this methylated CD. This break may be associated to the formation of aggregates in the bulk solution as observed for classical surfactants or hydrotropic agents. However, contrary to what is observed with surfactant, it must be pointed out that the surface tension did not remain constant above the 10^{-3} M^{-1} concentration and continued to decrease suggesting that adsorption of RAME-β-CD at the interface occurs always above this

concentration. When increasing the concentration of KSPDM-β-CD in water, a regular decrease in the superficial tension was measured with no aggregation phenomenon in the concentration range 10^{-4}–10^{-2} M^{-1}. More importantly, at high concentrations ($>10^{-3}$ M^{-1}), its surface activity is higher than that of RAME-β-CD. The KSPDM-β-CD shape and the high flexibility of the sulfopropyl arms make KSPDM-β-CD unable to self-organize in water to generate detectable aggregate structures in the concentration range 10^{-4}–10^{-2} M^{-1}. As a matter of fact, Shinkai et al. previously showed with sulfopropylcalixarenes that the existence of a critical micelle concentration, i.e., a concentration at which the monomeric molecules aggregate to form micelles in the bulk solution, required a cone-shape structure whereas cylindrical molecules did not form such aggregates for concentrations up to 10^{-2} M^{-1}.[10]

Second, as it has been demonstrated that inclusions between RAME-β-CD and phosphanes greatly affected the performance of catalytic systems,[6,7] an NMR study has been performed to provide information about the ability of KSPDM-β-CD to interact with hydrosoluble phosphane ligands. Two phosphanes widely used in aqueous organometallic catalysis have been chosen for this study: the sodium salt of the *meta*-substituted trisulfonated triphenylphosphine (TPPTS) and the sodium salt of the *meta*-substituted monosulfonated triphenylphosphine (TPPMS). The $^{31}P\{^1H\}$ NMR spectrum of TPPTS in the presence of KSPDM-β-CD is displayed in Figure 3.

For comparison, the $^{31}P\{^1H\}$ NMR spectrum of TPPTS recorded in the presence of RAME-β-CD was also indicated (Figure 3b). The spectrum obtained with RAME-β-CD showed induced chemical shifts of the ^{31}P NMR signal of the phosphane which denoted the formation of an inclusion complex in solution.[11] By contrast, the $^{31}P\{^1H\}$ NMR spectrum of TPPTS in the presence of KSPDM-β-CD (Figure 3c) was superimposable to that without CD (Figure 3a). Similarly, the ^1H NMR spectra of the same mixtures also revealed strong chemical shifts of the aromatic protons of TPPTS in the presence of RAME-β-CD (Figure 4b) and no change in the presence of KSPDM-β-CD (Figure 4c).

To confirm the 1D NMR results, 2D NMR experiments have been performed to detect spatial interactions between the sulfonated ligands and the modified β-CDs. In particular, T-ROESY experiments were very helpful for that purpose.[12] Although the T-ROESY spectrum of a 1:1 mixture of RAME-β-CD and TPPTS revealed intense cross-peaks,[11] the observation of the T-ROESY spectrum of a 1:1 mixture of KSPDM-β-CD and TPPTS showed a complete lack of cross-peaks for the aromatic protons of the phosphane with any proton of KSPDM-β-CD. Consequently, KSPDM-β-CD proved unable to interact with TPPTS to form an inclusion complex.

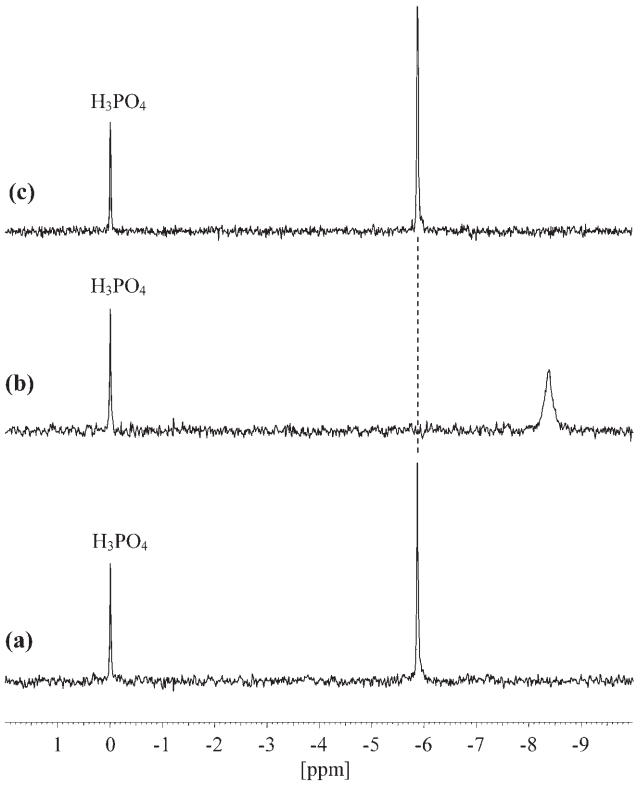


Figure 3. Effect of CDs on the $^{31}P\{^1H\}$ NMR spectrum of TPPTS (3 mM) in D_2O with H_3PO_4 as external reference: **(a)** without CD; **(b)** with RAME-β-CD (3 mM); **(c)** with KSPDM-β-CD (3 mM).

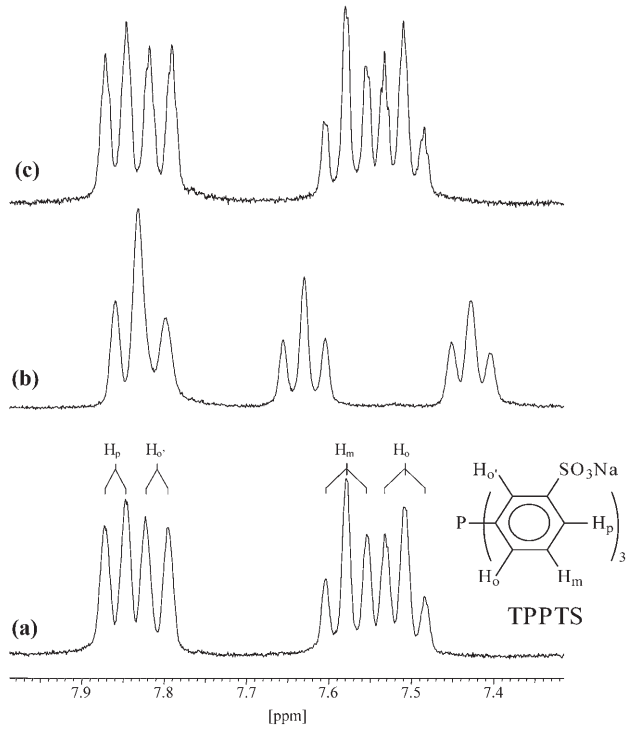


Figure 4. Effect of CDs on the ^1H NMR spectrum of TPPTS (3 mM) in D_2O: **(a)** without CD; **(b)** with RAME-β-CD (3 mM); **(c)** with KSPDM-β-CD (3 mM).

The behavior of the KSPDM-β-CD towards the TPPMS ligand was found to be notably different. Thus, the chemical shifts observed in the $^{31}P\{^1H\}$ and ^1H NMR spectra of a KSPDM-β-CD/TPPMS mixture revealed the formation of an adduct between those two compounds. The stoichiometry for this adduct was determined by a continuous variation technique (Job's method). The Job's plot derived from the $^{31}P\{^1H\}$ NMR data showed a maximum at $r = 0.5$ and a symmetrical shape, indicative of a 1:1 stoichiometry. In order to determine whether this 1:1 adduct is a true inclusion complex or adduct resulting from external interaction phenomena, a T-ROESY experiment has also been performed. The T-ROESY spectrum of a KSPDM-β-CD/TPPMS mixture (1:1) proved undoubtedly the formation of true inclusion complexes between KSPDM-β-CD and TPPMS (Figure 5).

Indeed, cross-peaks between the non-sulfonated aromatic ring of TPPMS (7.40–7.20 ppm) and two different groups of CD protons (the methyl groups of the CD and internal protons of the CD cavity) were clearly observed (Figure 5). These contacts showed that one of the non-sulfonated aromatic rings was included in the cavity whereas the other remained at the periphery of the secondary face. Logically according to the TPPMS structure, weak interactions between some protons of the sulfonated ring of TPPMS and the methyl groups protons of the CD were observed. Finally, no contact was observed between the methylene groups of the alkyl arms and the phosphane, confirming the penetration of TPPMS by the secondary face of the CD. The stability constant for this 1:1 inclusion complex was determined by computer fitting of the phosphorus chemical shift titration curves and was found to be very low ($K_a < 50\ M^{-1}$ at 25 °C) compared to that calculated for the RAME-β-CD/TPPMS inclusion complex ($K_a = 8000\ M^{-1}$ at 25 °C).[13]

The absence of interaction between TPPTS and KSPDM-β-CD or the poor affinity of KSPDM-β-CD for TPPMS was rationalized by performing supplementary experiments with the permethylated β-CD (TRIME-β-CD – Figure 1). The $^{31}P\{^1H\}$ and ^1H NMR spectra of a TRIME-β-CD/TPPTS mixture showed that TPPTS did not interact with TRIME-β-CD, demonstrating that the absence of interaction between TPPTS and KSPDM-β-CD was due to the permethylation of the CD secondary face and not to the sulfopropyl groups grafted on the primary face. Concurrently, it has also been found that the affinity of TRIME-β-CD for TPPMS was notably lower ($K_a = 400\ M^{-1}$ at 25 °C) than that of RAME-β-CD for TPPMS ($K_a = 8000\ M^{-1}$ at 25 °C), confirming that the molecular recognition process is greatly affected by the degree of methylation of the CD secondary face.

Although the TRIME-β-CD cannot interact strongly with the phosphane ligands, it is worth mentioning that TRIME-β-CD cannot be exploited as a mass transfer promoter in aqueous organometallic catalysis because of its too low solubility in water at high temperature and its high solubility in organic solvent.[9] By contrast, thanks to the presence of seven sulfonate groups, KSPDM-β-CD was highly soluble in water ($> 10^{-2}$ mol/L) and insoluble in organic solvents such as heptane or toluene. In addition, the KSPDM-β-CD exhibited interesting surface-tension properties.

As the KSPDM-β-CD fulfils all requirements for an application in aqueous organometallic catalysis, this

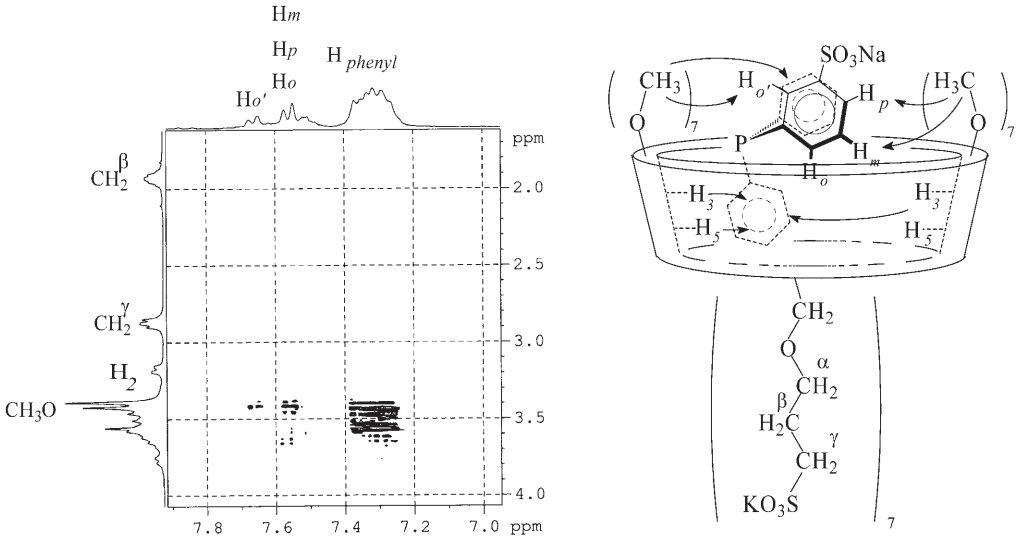


Figure 5. Partial contour plot of the T-ROESY spectrum of a solution containing KSPDM-β-CD (3 mM) and TPPMS (3 mM) in D_2O at 25 °C with a 300 ms mixing time. The interactions between the different protons and the deduced orientation of TPPMS in the CD cavity are also shown.

CD has been used as mass transfer promoter in two organometallic reactions.

First, catalytic experiments have been carried out to evaluate the benefit that might be obtained with KSPDM-β-CD in a Tsuji–Trost reaction. The reaction consisted in the cleavage of allyl undecyl carbonate that was chosen as a model substrate since it has previously been demonstrated that its insolubility in water allows us to detect more easily the effect of a mass transfer promoter in the catalytic solution (Figure 6).[14]

Reactions were carried out using $Pd(OAc)_2$ as catalyst precursor and TPPTS as a ligand. Results were compared to those obtained in the same conditions with RAME-β-CD and a random sulfobutyl ether β-CD containing about seven sulfobutyl groups (SBE_7-β-CD – Figure 1). It must be noticed that the SBE_7-β-CD exhibits no surface activity and is unable to interact strongly with TPPTS due to electronic repulsions between the anionic group of the CD and the sulfonate groups of the TPPTS ($K_a = 21\ M^{-1}$ for the SBE_7-β-CD/TPPTS couple at 25 °C).[15] As can be seen in Figure 6, the initial activity obtained with KSPDM-β-CD in the cleavage of allyl undecyl carbonate was 2.5 times higher than that measured with RAME-β-CD, which was our best mass transfer promoter to date. Moreover, the reaction mixture is strictly biphasic, separates readily and can be recycled three times without loss of catalytic activity. Although KSPDM-β-CD and SBE_7-β-CD have structural similarities, the former was 13 times more efficient than the latter in terms of initial activity.

The catalytic study has been extended to the hydroformylation of linear terminal alkenes which constitutes a more informative reaction in terms of chemo- and regioselectivity than the cleavage of allyl undecyl carbonate. In particular, the aldehydes selectivity and the linear to branched ratio (l/b ratio) of aldehyde products are indicative of the nature of the catalytic species and of interactions between the CD and the phosphane, respectively.[6] Indeed, we have demonstrated that the l/b ratio decrease observed in the presence of RAME-β-CD (1.8 *vs.* 2.8 without CD) was due to trapping of the phosphane ligand by CD and it is suspected that the high aldehydes selectivity (97% *vs.* 59% without CD) is due to an interaction between the CD and the catalytic rhodium species during coordination of the olefin on the metal center.

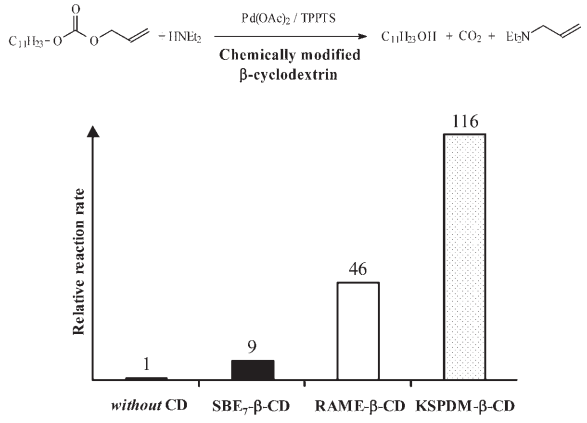


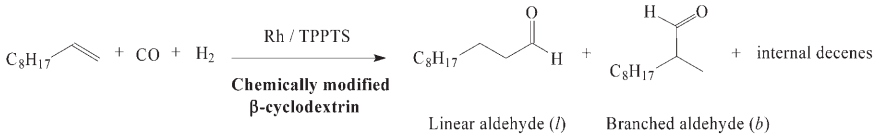
Figure 6. Effect of various CDs on the relative reaction rate. The relative reaction rate was defined as the ratio between the initial catalytic activity in the presence of CD and the initial catalytic activity without CD. The initial catalytic activity without CD is 1.4 μmol/h. Experimental conditions: $Pd(OAc)_2$ (0.044 mmol), TPPTS (0.401 mmol), CD (0.176 mmol), water (2 g), allyl undecyl carbonate (1.12 mmol), diethylamine (2.24 mmol), heptane (2 g) and dodecane (0.56 mmol – internal standard); *T*: 20 °C.

The hydroformylation experiments were conducted using 1-decene as a model substrate in an autoclave heated at 80 °C and pressurized with 40 atm of CO/H_2. Expected reaction products were undecanal, 2-methyldecanal and internal decenes which result from an undesired alkene isomerization. The hydrosoluble rhodium catalyst was formed *in situ* by addition of $[Rh(acac)(CO)_2]$ and TPPTS in water. For comparison, the results obtained with SBE_7-β-CD and RAME-β-CD were also indicated.

Using RAME-β-CD, a 61% conversion was obtained with a low 1.8 linear/branched aldehydes ratio and a high 97% chemoselectivity in aldehydes (entry 2 in Table 1). By contrast, the conversion obtained with KSPDM-β-CD was higher (82%), a 60% aldehyde selectivity was obtained and a 2.6 l/b aldehydes ratio was measured. Actually, the aldehyde selectivity and the l/b aldehydes ratio were close to those obtained in the hydroformylation of 1-decene without CD (compare entries 1 and 4 in Table 1). As expected, decreasing the amount of KSPDM-β-CD led to lower activities since the transfer of the substrate from one phase to the other constitutes the rate-determining step of this biphasic reaction. The l/b aldehyde ratios and the chemoselectivities were unaffected by the amount of KSPDM-β-CD and remained identical to those observed without CD derivative (entries 4, 5 and 6). In all experiments performed with the KSPDM-β-CD, it should be pointed out that the phase separation was fast and that no emulsion was observed at the end of the reaction. As observed in the Tsuji–Trost reaction, the effect of the SBE_7-β-CD on the conversion was much less important than that of KSPDM-β-CD or RAME-β-CD (compare entry 3 with entries 2 and 4). Surprisingly, the l/b aldehydes ratio decrease observed with the SBE_7-β-CD indicates that this CD modified the equilibria between the different catalytic species despite its very low capacity to bind to TPPTS ligand.

The results obtained in the Tsuji–Trost and hydroformylation reactions demonstrate that the KSPDM-β-CD is a much more efficient mass transfer promoter than RAME-β-CD and SBE_7-β-CD. Indeed, the conversions were always higher than those obtained with RAME-β-CD and SBE_7-β-CD. Furthermore, KSPDM-β-CD acted as a *real* mass transfer promoter. Contrary to what

Table 1. Hydroformylation of 1-decene by Rh(acac)$(CO)_2$/TPPTS system.[a]



Entry	Cyclodextrin	CD/Rh	Conversion[b] [%]	Aldehydes selectivity[c] [%]	l/b aldehyde ratio[d]
1	(–)	0	2	59	2.8
2	RAME-β-CD	12	61	97	1.8
3	SBE_7-β-CD	12	21	57	2.1
4	KSPDM-β-CD	12	82	60	2.6
5	KSPDM-β-CD	6	61	55	2.6
6	KSPDM-β-CD	3	18	57	2.7

[a] *Experimental conditions:* Rh(acac)$(CO)_2$: 1.1 μmol; TPPTS: 5.5 μmol; water: 0.32 mL; 1-decene: 0.55 mmol; *n*-undecane (internal standard): 0.05 mmol; P(CO/H_2: 1/1) = 40 bar; $T = 80\,^{\circ}C$; Reaction time: 2 hours.
[b] Calculated with respect to the starting olefin.
[c] (Mol. of aldehydes)/(mol. of converted olefins) × 100.
[d] Ratio of linear to branched aldehyde product.

was observed with RAME-β-CD and SBE_7-β-CD, KSPDM-β-CD interacted neither with the catalytic rhodium center nor with TPPTS since no variation of the aldehydes selectivity and the l/b aldehydes ratio was observed with this CD relative to the experiments conducted without CD.

The explanation of these results lies in well-designed structure of KSPDM-β-CD. Indeed, the permethylation on the secondary face of KSPDM-β-CD avoided TPPTS trapping in contrast to what was observed with the partially substituted RAME-β-CD. Moreover, the lipophilic character of the 14 methyl groups on the secondary face is counterbalanced by the hydrophilic sulfopropyl arms. The resulting structure is therefore more surface active than the water-soluble RAME-β-CD or SBE_7-β-CD in the 10^{-4}–$10^{-2}\,M^{-1}$ concentration range, allowing a better mass transfer between the aqueous and organic phases.

Conclusion

The results of this structure-activity investigation have provided compelling evidence that the structure of the mass transfer promoter is a key aspect of aqueous organometallic catalysis mediated by cyclodextrin derivatives. KSPDM-β-CD appears as a genuine supramolecular carrier since it does not interact with the hydrosoluble ligand or catalytic species and its surface active properties allow an efficient mass transfer without the formation of emulsion. Work is currently underway to exploit these outstanding properties in other biphasic transition-metal catalyzed reactions.

Experimental Section

General Methods

The ^1H and ^{31}P NMR spectra were recorded at 300.13 and 121.49 MHz on Bruker Avance DRX, respectively. ^1H and $^{31}P\{^1H\}$ chemical shifts are given in ppm relative to external references: sodium 3-(trimethylsilyl)propionate-d_4 (98% atom D) in D_2O for ^1H NMR and H_3PO_4 in H_2O for $^{31}P\{^1H\}$ NMR. The 2D T-ROESY experiments were run using the software supplied by Bruker. Mixing times for T-ROESY experiments were set at 300 ms. The data matrix for the T-ROESY was made of 512 free induction decays, 1 K points each, resulting from the co-addition of 32 scans. The real resolution was 1.5–6.0 Hz/point in F2 and F1 dimensions, respectively. They were transformed in the non phase-sensitive mode after QSINE window processing. Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (25 m × 0.25 mm) and a flame ionization detector (GC:FID). The 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/m. The experiments were performed at $25\,^{\circ}C \pm 0.5\,^{\circ}C$ controlled by a thermostatted bath Lauda (RC6 CS). The samples were freshly prepared by dissolving the desired amount of cyclodextrin derivative in ultrapure water (Fresenius Kabi, France).

Materials

D_2O (99.95% isotopic purity) was obtained from Merck. The sodium salt of the *meta*-substituted trisulfonated triphenylphosphine [TPPTS – P(*m*-$C_6H_4SO_3Na)_3$] was synthesized as reported by Gärtner et al.[16] The sodium salt of the *meta*-substituted monosulfonated triphenylphosphine [TPPMS – $(C_6H_5)_2$P(*m*-$C_6H_4SO_3Na$)] was prepared by a literature method.[17] Randomly methylated β-CD (RAME-β-CD) and per-

methylated β-CD (TRIME-β-CD) were purchased from Aldrich. Random sulfobutyl ether β-CD (SBE_7-β-CD) was prepared according to the general procedure of Stella and Rajewski.[18] The synthesis of heptakis(2,3-di-*O*-methyl-6-*O*-sulfopropyl)-β-cyclodextrin (KSPDM-β-CD) was described in one of our previous publications.[8]

General Procedure for the Catalytic Experiments:

Tsuji–Trost reaction: $Pd(OAc)_2$ (0.044 mmol, 10 mg), TPPTS (0.401 mmol, 228 mg), cyclodextrin derivatives (0.176 mmol) and water (2 g) were introduced under nitrogen atmosphere into a Schlenk tube. After stirring with a magnetic bar for 1 h, the yellow solution was transferred into a mixture of allyl undecyl carbonate (1.12 mmol), diethylamine (2.24 mmol), heptane (2 g) and dodecane (0.56 mmol – internal standard). The medium was stirred at 1000 rpm at room temperature and the reaction was monitored by quantitative gas chromatographic analysis of the organic layer.

Hydroformylation reaction: A stainless 150-mL autoclave, equipped with a carousel containing 8 vessels with Teflon stirring bar, was used. In a typical experiment, each vessel was charged with $Rh(acac)(CO)_2$ (1.1 μmol), TPPTS (5.5 μmol) and cyclodextrin derivatives dissolved in 0.32 mL of water and the organic phase composed of 1-decene (550 μmol) and undecane (50 μmol – GC internal standard). The autoclave was heated at 80 °C and pressurized with 40 atm of CO/H_2 (1/1). The time corresponding to the addition of CO/H_2 was considered as the beginning of the reaction. The mixture was stirred for 2 h at 80 °C. The reaction medium was sampled after the reaction for GC analyses of the organic phase after decantation.

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