Hydroformylation of 1-decene in aqueous medium catalysed by rhodium–alkyl sulfonated diphosphines system in the presence of methylated cyclodextrins. How the flexibility of the diphosphine backbone influences the regioselectivity

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Interaction between α-cyclodextrin or β-cyclodextrin and the alkyl sulfonated diphosphines DPPETS (tetrasulfonated 1,2-bis(diphenylphosphino)ethane), DPPPTS (tetrasulfonated 1,3-bis(diphenylphosphino)propane) and DPPBTS (tetrasulfonated 1,4-bis(diphenylphosphino)butane) was investigated by NMR and UV-Visible spectroscopy. Contrary to α-cyclodextrin, β-cyclodextrin forms inclusion complexes with each sulfonated diphosphine. Continuous variation plots and titration experiments obtained from ^{1}H and ^{31}P NMR data indicated the formation of 1 : 1 inclusion complexes and allowed the calculation of the association constants for each complex. Information on the structures of these complexes were obtained by T-ROESY NMR experiments. The potential of these ligands associated with methylated α- or β-cyclodextrin during the reaction of hydroformylation of 1-decene was studied. In all cases, the presence of cyclodextrins increased the conversion and the chemoselectivity whereas the linear to branched ratio of the aldehyde product decreased. This decrease in regioselectivity was attributed to the formation of low-coordinated phosphine species. In fact, in order to reduce steric hindrance around the metal center, a mono-dissociation of the bidentate ligand seemed to occur when the inclusion complex between the cyclodextrin and 1-decene approached the metal center. In the case of methylated-β-cyclodextrin, the phenomenon is accentuated since one of the two diphenylphosphino groups of the bidentate could be trapped by this cyclodextrin leading to the formation of a second-sphere coordination adduct.

Introduction

Organometallic aqueous biphasic processes present a smart solution to recovering and recycling aqueous organometallic catalysts.[1] The catalyst is retained in the water phase by using water-soluble phosphines. The most widespread ligand is the sodium salt of trisulfonated triphenylphosphine (TPPTS), which is industrially applied in the hydroformylation of propene and butene.[2] For lower olefins (less than four carbons), the solubility in water is sufficient to obtain a good activity.[3] In the case of the hydroformylation of higher olefins, the activity is very low due to their poor solubility in water.[4] In order to increase the mass transfer between the two layers, different solutions have been proposed such as the addition of a cosolvent,[5] a surfactant,[5f,6] amphiphilic ligands[7] or an inverse phase transfer agent such as a cyclodextrin (CD).[8] Indeed, the CD, by forming an inclusion complex with the substrate, is able to increase the activity of the reaction. For example, during the hydroformylation of 1-decene, the presence of randomly methylated-β-cyclodextrin (Rame-β-CD) gave a conversion of 100% and a selectivity to aldehyde of 95%.[9] Unfortunately, the β-CDs form inclusion complexes with the hydrosoluble phosphine (TPPTS) used to maintain the transition metal in water.[10] In fact, due to the association with the TPPTS ligand, the Rame-β-CD is able to dissociate TPPTS from the rhodium species. This phenomenon induces the formation of low coordinated phosphine species[11] responsible for the decrease in linear to branched ratio (1.8 *vs* 2.8 without Rame-β-CD). Interestingly, we have recently demonstrated that the combination of randomly methylated-α-cyclodextrin (Rame-α-CD) or Rame-β-CD and sulfonated xantphos as the ligand allowed not only an increase in activity but also an increase in linear to branched ratio.[12] This result is explained firstly by the interactions between the sulfonated xantphos and the methylated CD, which are too weak to induce dissociation of the ligand from the organometallic complex. Secondly, concurrently to the constraint generated by the bulky sulfonated xantphos ligand, the additional steric hindrance of the CD cavity on the substrate compelled the latter to react preferentially by its terminal carbon, leading to very high regioselectivity towards linear aldehyde.

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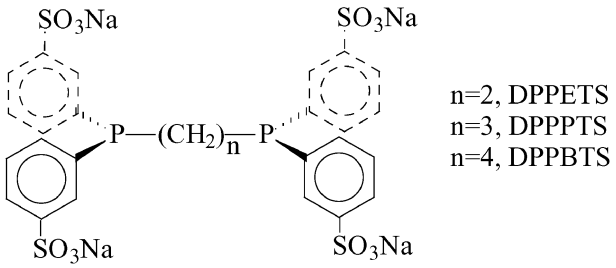


Scheme 1 Alkyl sulfonated diarylphosphines.

In this context, we were interested to learn if a similar behavior would be observable with other bidentate phosphines, such as alkyl sulfonated diarylphosphines (Scheme 1). The DPPETS (tetrasulfonated 1,2-bis(diphenylphosphino)ethane), DPPPTS (tetrasulfonated 1,3-bis(diphenylphosphino)propane) and DPPBTS (tetrasulfonated 1,4-bis (diphenylphosphino)butane) have been chosen since these diphosphines have already been used for hydroformylation of various olefins (1-octene, 1-decene, styrene derivatives, methyl acrylate).[5d–f,13]

In this article, first we report the supramolecular interaction between DPPETS, DPPPTS or DPPBTS and α-cyclodextrin (α-CD) or β-cyclodextrin (β-CD) (Table 1). Secondly, the effect of the combination between these diphosphines and Rame-α-CD or Rame-β-CD on the activity and selectivity during the hydroformylation of 1-decene was investigated.

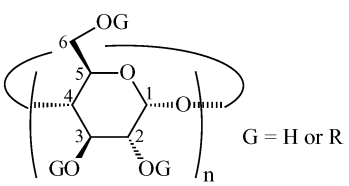
Results and discussion

The interactions between the sulfonated diphosphines and α-CD or β-CD were studied by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. The ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of each sulfonated diphosphine are superimposable on those observed in the presence of α-CD. These results clearly prove the absence of inclusion complexes between the sulfonated diphosphines and α-CD. On the contrary, concerning the mixture of sulfonated diphosphines and β-CD, the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra exhibited chemical shift variations for the phosphorus and the protons of the phosphine and for most of the protons of the β-CD. The most important variations for the chemical shift were observed for the protons situated inside the hydrophobic cavity of the β-CD (H-3 and H-5), illustrating the formation of inclusion complexes with the sulfonated diphosphines.

The stoichiometry of these inclusion complexes with β-CD was provided by the NMR-titrations using the continuous variation technique (Job's method).[14] For each phosphine, a series of samples containing variable ratios of β-CD and diphosphine was prepared keeping the total concentration of species constant (1 mM in the present cases). The differences of chemical shift in ^{1}H NMR spectra were measured as a function of the molar ratio. The three Job's plots derived from the corresponding ^{1}H NMR spectra (by following the H-3 proton of the β-CD) show a maximum at $r = 0.5$ and highly symmetrical shapes, indicating that the stoichiometry of inclusion complexes in solution is 1 : 1. As an example, the Job plot for β-CD/DPPBTS is depicted in Fig. 1.

The structures of these inclusion complexes were determined from two-dimensional T-ROESY NMR experiments. For the three sulfonated diphosphines, the same cross-peaks were observed between the protons of the β-CD and those of the three diphosphines, suggesting the same geometry for the three complexes. The spectra for the complex β-CD/DPPBTS are presented in Fig. 2 as an illustration of this inclusion phenomenon. The strongest interactions are observed between the H-3 and H-5 protons (internal protons of the β-CD) and the aromatic protons H-*p*, H-*m* and H-*o* of DPPBTS. A weaker interaction is present between the proton H-5 of the β-CD and H-*o*′. The two H-6 protons of the β-CD are in interaction with the protons H-*o*, H-*m* and H-*o*′ of DPPBTS. In addition, the two types of methylene groups of the DPPBTS, $(CH_2)\alpha$ and $(CH_2)\beta$, are correlated with H-3 whereas only $(CH_2)\alpha$ is weakly in interaction with H-5. These cross-peaks suggest an inclusion of one aromatic ring by the secondary face of the β-CD as schematically represented in Scheme 2 (Complex A). However, such a penetration can neither explain the interaction with the H-6 protons of the β-CD and H-*o* or H-*o*′ nor the interaction between H-5 and H-*o*′. Indeed, another type of 1 : 1 complex is present in solution implicating a penetration of the phosphine by the primary face of the β-CD (Scheme 2, Complex B). In this last complex, we notice the absence of an interaction between the protons of the β-CD and the alkyl chain since for the two 1 : 1 complexes the orientation of the sulfonate group in the cavity is different.

Table 1 Structure of CDs used in this work



Abbreviation	*n*	Substituent (R)	Carbon bearing the OR group	Number of R group by CD
α-CD	6	(—)	(—)	0
Rame-α-CD	6	$-CH_3$	2, 3 and 6	10.8
β-CD	7	(—)	(—)	0
Rame-β-CD	7	$-CH_3$	2, 3 and 6	12.6

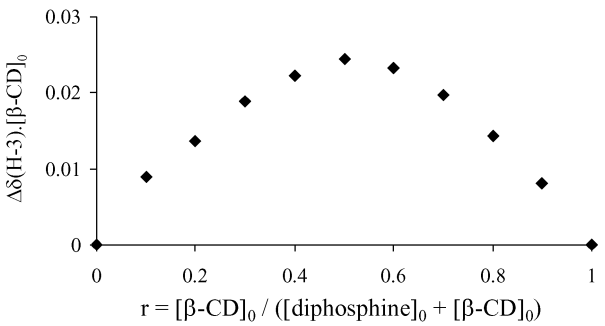


Fig. 1 Continuous variation plots (Job's plot) derived from the ^{1}H NMR data for β-CD and DPPBTS system.

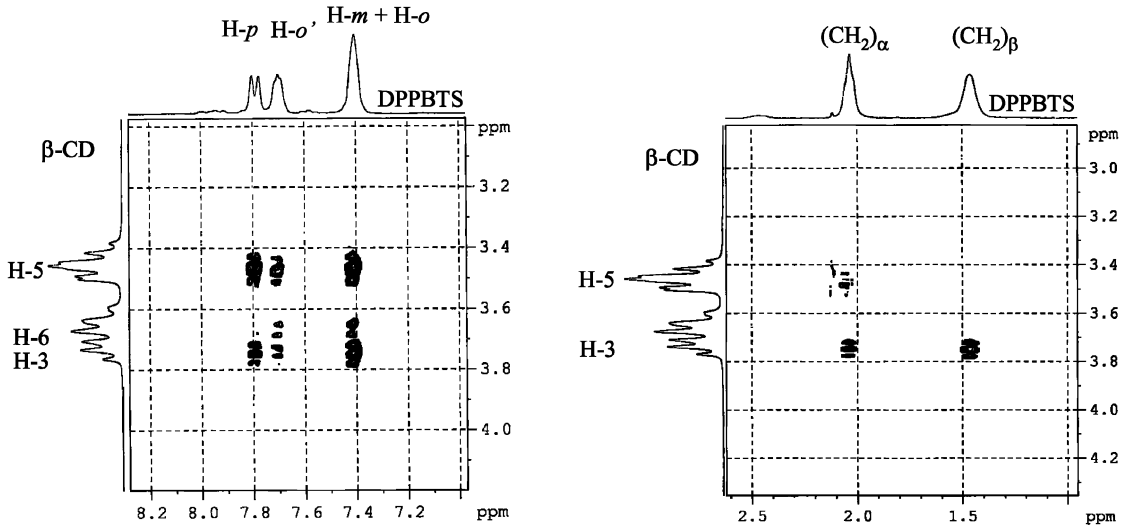


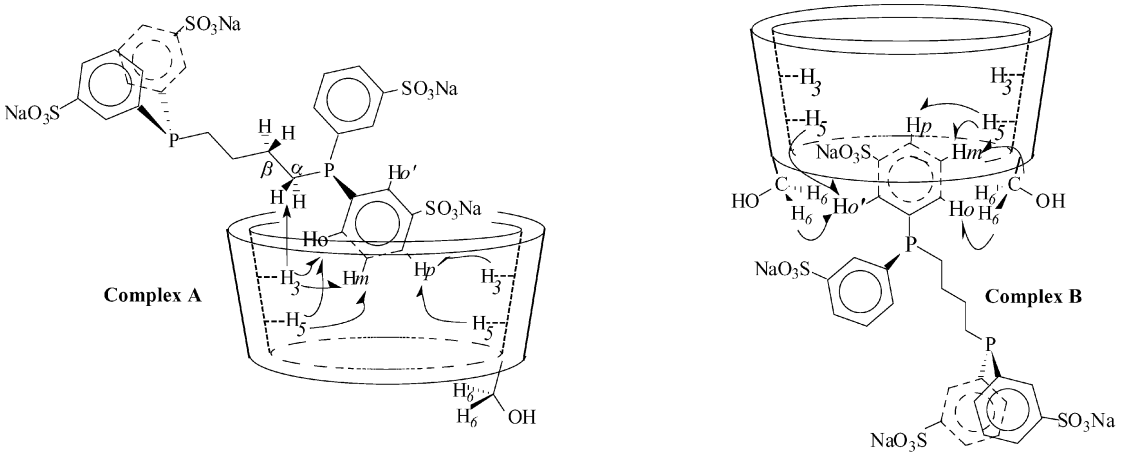
Fig. 2 Partial contour plot of the T-ROESY spectra of a solution containing DPPBTS (5 mM) and β-CD (5 mM) in D_2O at 298 K with a 300 ms mixing time.

The association constants of each inclusion complex were evaluated at 298 K from ^{31}P NMR spectroscopic data (classical titration method) and UV-Vis spectroscopic data (spectral displacement methods). The association constant calculated by assuming a 1 : 1 inclusion mechanism are summarized in Table 2. For each experimental technique, the data are in the same order of magnitude. In all cases, the values obtained are higher in the case of NMR measurements compared to UV-Vis. This discrepancy observed between the two techniques could be due to the presence of different types of 1 : 1 complexes. The length of the alkyl chain seems not to have an effect on the value of the association constant. We notice that the association constant between β-CD and sulfoxantphos was twenty times lower (80 M^{-1}).[12] This difference may be due to the flexibility of the alkyl chain compared to the rigid xanthene skeleton, enabling a better fit between the host and the guest. As shown in Scheme 2, when the β-CD includes one aromatic ring of the DPPBTS, the alkyl chain bearing the other diphenylphosphino group moves away in order to reduce steric interactions. In the case of sulfoxantphos, the formation of an inclusion complex with β-CD is more difficult due to the proximity of the two diphenylphosphino groups.[12] In fact, the absence of a flexible bridge between the two phosphine moieties eliminates the possibility that the steric hindrance can be reduced by rotating away. Indeed, this ligand is unable to reduce steric hindrance by simple rotation of one of the two diphenylphosphino groups because of the rigid backbone.

Table 2 Association constant (K/ M^{-1}) of the DPPETS, DPPPTS and DPPBTS with the β-CD in water at 298 K

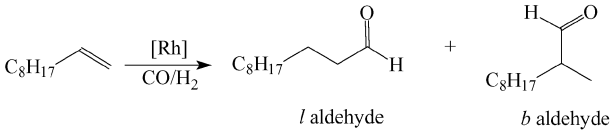
Phosphine	K^a	K^b
DPPETS	1530 ± 150	813 ± 80
DPPPTS	1898 ± 190	927 ± 90
DPPBTS	1590 ± 160	851 ± 85

[a] Determined by ^{31}P NMR shift titration. [b] Determined from UV-Vis spectroscopic data with a spectral displacement method.



Scheme 2 Structures proposed for β-CD/DPPBTS inclusion complexes. The main interactions observed in T-ROESY spectra are also indicated.

Table 3 Hydroformylation of 1-decene by Rh–sulfonated diphosphine system[a]



Entry	Phosphine	CD	Conversion[b] (%)	Selectivity[c] (%)	l/b[d]
1	DPPETS	None	25	27	2.8
2	DPPETS	Rame-α-CD	73	75	2.1
3	DPPETS	Rame-βCD	75	60	1.6
4	DPPPTS	None	16	55	2.6
5	DPPPTS	Rame-α-CD	51	65	2.3
6	DPPPTS	Rame-β-CD	66	65	1.9
7	DPPBTS	None	1	25	3
8	DPPBTS	Rame-α-CD	15	90	1.6
9	DPPBTS	Rame-β-CD	35	94	1.2

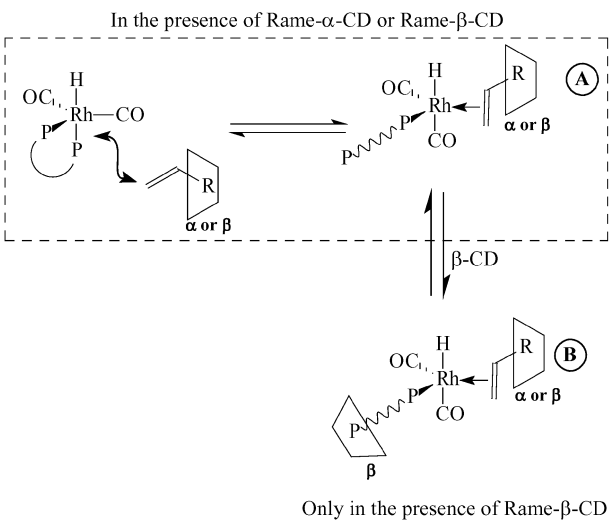
[a] Experimental conditions: $Rh(acac)(CO)_2$: 1.1 μmol; sulfonated diphosphine: 2.2 μmol; CD: 13 μmol; water: 0.32 mL; 1-decene: 550 μmol; *n*-undecane (internal standard): 50 μmol; $P(CO/H_2: 1/1) = 20$ bar; $T = 80$ °C; time: 24 h. [b] Olefin conversion. [c] Aldehydes selectivity. [d] Linear to branched aldehydes ratio.

The behavior of the association CD–sulfonated diphosphine was studied in the hydroformylation of 1-decene in aqueous system by using a $Rh(acac)(CO)_2$–DPPETS, DPPPTS or DPPBTS combination with Rame-α-CD or Rame-β-CD. The results are summarized in Table 3.

For comparison, the results in the absence of CD are also given. The conversions were equal to 25%, 16% and 1% for the DPPETS, DPPPTS and DPPBTS, respectively (entries 1, 4, 7). These conversions are increased by a factor 3, 3 and 15 in the presence of Rame-α-CD (entries 2, 5, 8) and by a factor 3, 4 and 35 (entries 3, 6, 9) in the presence of Rame-β-CD for the DPPETS, DPPPTS and DPPBTS, respectively. The higher reaction rate observed in the presence of these methylated CDs is due to the complexation of 1-decene inside the hydrophobic cavity and the surface active properties of these CDs. In fact, the CD forms a host/guest complex with the water-insoluble olefin at the liquid/liquid interface that facilitates the reaction of the olefin with the water-soluble rhodium catalyst.

The selectivity in aldehydes was low in the absence of CD (27%, 55% and 25% for the DPPETS, DPPPTS and DPPBTS, respectively), the major part of 1-decene was isomerized into internal olefins. This chemoselectivity was higher in the presence of Rame-α-CD (multiplied by a factor 3, 1.2 and 4 for the DPPETS, DPPPTS and DPPBTS, respectively) or Rame-β-CD (multiplied by a factor 2, 1.2 and 4 for the DPPETS, DPPPTS and DPPBTS, respectively). So for these two methylated CDs, a protective effect of the cavity can be observed. It is worth noting that an interaction of these CDs with the rhodium species, during the coordination of the olefin, is not to be excluded to explain the chemoselectivity increase.

These methylated CDs have an influence on the regioselectivity of the hydroformylation reaction. In the presence of CD, the linear to branched aldehydes ratio (l/b) is decreased for each phosphine and this decrease is more important in the case of Rame-β-CD (2.8, 2.6 and 3 without CD *vs* 1.6, 1.9 and 1.2 for the DPPETS, DPPPTS and DPPBTS, respectively) compared to Rame-α-CD (2.8, 2.6 and 3 without CD *vs* 2.1, 2.3 and 1.6 for the DPPETS, DPPPTS and DPPBTS, respectively). As described in the literature, this behavior can be attributed to the formation of low-coordinated rhodium species which induces a poor selectivity in linear aldehyde.[4,15] Carbonyl rhodium species, such as $HRh(CO)_4$ coming from the dissociation of diphosphine from the metal, could also explain a lower regioselectivity, but the formation of such a species does not take place since an important part of these catalytic species would be soluble in the organic layer preventing recycling of the aqueous layer. Indeed, recycling experiments gave the same activity (see experimental section) and the organic layer was colorless at the end of the reaction. Consequently, the catalytic rhodium species is coordinated to a water-soluble phosphine that keeps it in the aqueous layer. As the active catalytic species is $HRh(CO)_2$ (sulfonated diphosphine),[5e] the only possibility to have a low-coordinated phosphine species is that the bidentate behaves as a monodentate in the presence of CD. The formation of such species could take place when the inclusion complex between the CD and 1-decene was approaching to the metal center as shown in Scheme 3A. In fact, the mono-dissociation of the bidentate ligand occurs to reduce the steric hindrance generated around the metal centre by the coordination of 1-decene included in the CD cavity. Although this phenomenon is observed with both methylated CDs, it is more accentuated with the Rame-β-CD than with the Rame-α-CD. Indeed, the l/b ratio are smaller with this CD than those observed with the Rame-α-CD. The formation of an inclusion complex between Rame-β-CD and the sulfonated diphosphine is probably at the origin of this decrease. In fact, the mono-dissociation of the bidentate ligand during the coordination of the 1-decene could be promoted by the trapping of the non-coordinated diphenylphosphino moiety of diphosphine into the Rame-β-CD cavity as schematically represented in Scheme 3B. This species has



Scheme 3 Proposed mechanism for the decrease in l/b ratio during the hydroformylation of 1-decene.

the particularity to possess a CD acting as a second-sphere coordination ligand. This result must be underlined since there are only a few examples of a second-sphere coordination adduct between a CD and an organometallic complex bearing a phosphine.[8c,16]

Conclusion

We have demonstrated that the presence of Rame-α or Rame-β-CD during the hydroformylation of 1-decene using alkyl sulfonated diphosphine based rhodium catalysts, results in an increase in the activity and chemoselectivity, but a decrease in linear to branched ratio of the formed aldehydes.

This decrease in regioselectivity is due to a CD inducing mono-dissociation of the ligand during coordination of the olefin. Thus, contrary to the sulfonated xantphos ligand, where an increase in l/b ratio was observed in the presence of these CDs, the use of the alkyl sulfonated diphosphines does not lead to preferential formation of linear aldehydes. This result is attributed to the great flexibility of the alkyl chain compared to the xanthene skeleton.

In view of the contrasting results obtained with the current ligands and the more rigid sulfonated xantphos ligand it is interesting to study also ligands that have properties in between these extremes, such as water-soluble equivalent of BISBI[17] (2,2′-bis(diphenylphophinomethyl)-1,1′-biphenyl) or BINAP[18] (2,2′-bis{di[*p*-(3-phenylpropyl)phenyl]phosphino}-1,1′-bisnaphthalene). In the latter scenario it would also be very exciting to investigate the effect of ligand encapsulation[19] on the enantioselective outcome during aqueous organometallic catalysis processes mediated by β-CD derivatives.

Experimental

General methods

The ^{1}H and ^{31}P NMR spectra were recorded at 300.13 and 121.49 MHz on a Bruker Avance DRX spectrometer, respectively. ^{1}H and $^{31}P\{^{1}H\}$ chemical shifts are given in ppm relative to external references: sodium [D_4]3-(trimethylsilyl)-propionate (98% atom D) in D_2O for ^{1}H NMR and H_3PO_4 in H_2O for $^{31}P^{1}\{H\}$ NMR. The 2D T-ROESY experiments were run using the software supplied by Bruker. T-ROESY experiments were preferred to classical ROESY experiments as this sequence provides reliable dipolar cross-peaks with a minimal contribution of scalar transfer. 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 per point in F2 and F1 dimension, respectively. They were transformed in the non phase-sensitive mode after QSINE window processing. UV-Vis spectroscopy was performed on a Perkin Elmer Lamba 19 spectrometer. The cell used was placed in a cuvette holder and the temperature was kept constant at 298 ± 0.1 K by means of a thermostated bath. Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (30 m × 0.32 mm) and a flame ionization detector (GC : FID).

Materials

D_2O (99.95% isotopic purity) was obtained from Merck. Dicarbonylacetylacetonato rhodium(I) and organic compounds (undecane, 1-decene) were purchased from Aldrich Chemicals in their highest purity and used without further purification. RAME-α-CD was prepared by adapting a procedure reported by Y. Kenechi *et al.*[20] RAME-β-CD was purchased from Aldrich Chemicals. These two CDs were partially methylated. Methylation occurred at positions 2, 3, or 6 and 1.8 OH groups per glucopyranose unit were statistically modified. DPPETS,[13a,21] DPPPTS[21] or DPPBTS[21] was prepared as reported in the literature.[22] The purity of these diphosphines was carefully controlled. In particular, ^{1}H and $^{31}P\{^{1}H\}$ NMR analysis indicated that each diphosphine was only sulfonated in the *meta* position and less than 1% of its oxide was present. In addition, molecular formulas determined by elemental analysis are in good agreement with the theoretical formula. Carbon monoxide–hydrogen mixture (1 : 1) were used directly from cylinders (>99.9% pure; Air Liquide). Distilled deionized water was used in all experiments. All solvents and liquid reagents were degassed by bubbling argon for 15 min before each use or by two freeze-pump-thaw cycles before use.

Continuous variation plots (Job's plot)

The NMR measurements for the Job's plot were taken on 11 samples. The series of samples containing variable ratio (from 0 to 1) of β-CD and sulfonated diphosphine was prepared keeping the total concentration of species constant (1 mM in this present case). The differences of chemical shift in ^{1}H were measured as a function of the molar ratio.

Calculation of association constants by NMR spectroscopy

The phosphorus atom was chosen for evaluating the association constant. Assuming a 1 : 1 inclusion mechanism, the observed chemical shift of the phosphorus atom (δ_{OBS}) and the complex concentration [COMP] are described as follows:

$$\delta_{OBS} = (\delta_{Phos.}\,[Phos.] + \delta_{COMP}\,[COMP])/[Phos.]_T \qquad (1)$$

$$[COMP] = -1/2\,[(1/K + [CD]_T + [Phos.]_T)^2 - 4\,[CD]_T\,[Phos.]_T]^{1/2} + 1/2\,(1/K + [CD]_T + [Phos.]_T)$$

where K and $[\ ]_T$ stand for association constant and total, respectively. For a given value of K, [COMP] is known and δ_{COMP} may be calculated from (1) for each $[CD]_T$. Standard deviation over δ_{COMP} is minimized relative to K to obtain the 1 : 1 association constant.[23]

Calculation of association constants by UV-Vis spectroscopy

The determination of the association constant is based on a spectral displacement method with methyl orange (MO) in its basic form.[23] Indeed, the addition of sulfonated diphosphine to a solution containing β-CD and MO leads to the formation of the β-CD–sulfonated diphosphine complex, thus decreasing the concentration of the β-CD/MO complex initially present. The resulting absorbance variation is directly linked to the added concentration of sulfonated diphosphine, but also to

the association constant of β-CD–sulfonated diphosphine inclusion compound. In practice, spectra were recorded between 520–530 nm. The concentrations for MO, β-CD and sulfonated diphosphine were fixed at 0.1 mM, 0.1 mM and 0.3 mM, respectively. The first derivatives of these spectra were used for quantitative analysis by an algorithmic treatment described elsewhere.[23]

Catalytic experiments

All catalytic reactions were performed under argon using standard Schlenk techniques. 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), sulfonated diphosphine (2.2 μmol) and CD (13 μmol) 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 pressurized with 20 atm of CO/H_2 (1/1). The mixture was stirred for 24 h at 80 °C. The reaction medium was sampled after the reaction for GC analyses of the organic phase after decantation.

Recycling experiments have been realised in the case of Rh/DPPBTS/Rame-α-CD or Rame-β-CD system. For these recycling experiments, a stainless 25 mL autoclave, equipped with a stirring bar, was used. For the first batch, the autoclave was charged with $Rh(acac)(CO)_2$ (0.033 mmol), DPPBTS (0.066 mmol) and CD (0.40 mmol) dissolved in 9.5 mL of water and the organic phase composed of 1-decene (16.5 mmol) and undecane (1.5 mmol GC internal standard). The autoclave was pressurized with 20 atm of CO/H_2 (1/1). The mixture was stirred for 24 h at 80 °C. After reaction, the autoclave was cooled to room temperature and the CO/H_2 was evacuated. After 30 minutes of decantation, the solution was removed from autoclave under an argon atmosphere. The biphasic system is easily separated by simple decantation under an argon atmosphere. The catalytic aqueous layer and a new organic phase (composed of 1-decene (16.5 mmol) and undecane (1.5 mmol)) were introduced in the autoclave. The second batch was carried out using the same procedure as described above. For each methylated CD, this system is recyclable at least two times keeping the same conversion and selectivity.

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