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Water-Soluble Triphenylphosphane-3,3′,3″-tricarboxylate (*m*-TPPTC) Ligand and Methylated Cyclodextrins: A New Combination for Biphasic Rhodium-Catalyzed Hydroformylation of Higher Olefins

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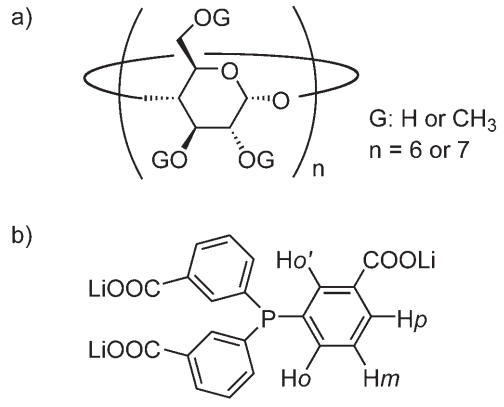
Abstract: The methylated cyclodextrins/*m*-TPPTC [tris(*m*-carboxyphenyl)phosphane trilithium salt] couples proved to be more efficient than the well-known methylated cyclodextrins/TPPTS [tris(*m*-sulfonatophenyl)phosphane trisodium salt] systems in terms of activities and selectivities to perform the Rh-catalyzed hydroformylation of higher olefins in an aqueous-organic system. The interactions cyclodextrins/*m*-TPPTC have been fully studied by NMR spectroscopy.

Keywords: cyclodextrin; hydroformylation; phosphane; rhodium; water-soluble ligand

Rhodium-catalyzed hydroformylation in an aqueous-organic two-phase system appears to be an economical and safe approach.[1] Indeed, an aqueous biphasic system allows quantitative recycling of the catalyst and decreases harmful emissions and costs associated with solvent recycling. Unfortunately, the industrial viability of the biphasic hydroformylation process has only been demonstrated in the case of lower olefins such as propene and butene with a Rh/TPPTS [TPPTS = tris(*m*-sulfonatophenyl)phosphane trisodium salt] catalytic system.[2] In the case of higher olefins (five or more carbon atoms), the olefin solubility is too low for industrially important rates to be achieved and the presence of a mass transfer promoter is required.[3] Among the different approaches proposed to increase the solubility of higher olefins, the use of chemically modified β-cyclodextrins such as methylated cyclodextrins preserves some economical viability.[4] Indeed, the methylated cyclodextrins that are cheap, non-toxic and bulk commercially available compound allowed us to achieve the hydroformylation of higher olefins with high reaction rate and chemoselectivity, while avoiding the formation of an emulsion and the partition of the rhodium catalyst between the organic and aqueous phases.[5] However, it was found that the regioselectivity, i.e., the linear to branched aldehydes ratio can be decreased due to interaction between the TPPTS ligand and the cyclodextrin.[6] In this context, it was of great interest to evaluate in a cyclodextrin-based hydrofomylation process the behavior of rhodium complexes associated to the highly water-soluble ligand *m*-TPPTC [tris(*m*-carboxyphenyl) phosphane trilithium salt] (Scheme 1), a carboxylated analogue of the sulfonated TPPTS ligand.[7] Actually, while *m*-TPPTC has been widely used in organometallic reactions,[8] its performances have never been described in the hydroformylation of olefins and the behavior of this phosphane ligand towards CDs has never been investigated. We describe herein our preliminary results concerning the *m*-TPPTC/CDs couple and the catalytic activity of the rhodium/*m*-TPPTC system in the hydroformylation of 1-octene, 1-decene and 1-dodecene.

The interaction between *m*-TPPTC and native or randomly methylated α-cyclodextrin or β-cyclodextrin (Scheme 1) has been studied by NMR spectroscopy. First, as no chemical shift was detected on the



a) Native cyclodextrin: α-CD (n = 6, G = H), β-CD (n = 7, G = H); Randomly methylated cyclodextrins: Rame-α-CD (n = 6, G = H or CH_3, DS: 1.8), Rame-β-CD (n = 7, G = H or CH_3, DS: 1.8).
b) *m*-TPPTC.

Scheme 1.

^{1}H NMR spectra of α-CD/*m*-TPPTC or Rame-α-CD/*m*-TPPTC mixtures at various concentrations, it was concluded that α-CDs did not interact with the phosphane. By contrast, native β-CD and *m*-TPPTC strongly interacted together as evidenced by NMR spectroscopy. In order to determine the stoichiometry of the complex in solution, we plotted the Job's diagrams based on the induced chemical shifts of selected protons in *m*-TPPTC and β-CD (Figure 1) as well as the induced chemical shift of the *m*-TPPTC phosphorus atom.

At 5 and 25 °C, the Job's diagrams showed a maximum at host/(host+guest) ratio of 0.40 consistent with a mixture of 1:1 and 1:2 β-CD/*m*-TPPTC complexes. By contrast, at 80 °C, the Job's plot were much more symmetrical and indicative of a 1:1 β-CD/*m*-TPPTC complex. This was consistent with a decrease in the association constant between the CD and the phosphane which was generally observed when increasing the temperature. The apparent association constants of these adducts were evaluated by a competition method with methyl orange (MO) from UV-VIS spectroscopic data.

The association constant values were found to be $1923\,M^{-1}$ for the 1:1 β-CD/*m*-TPPTC complex, and $256\,M^{-1}$ for the 1:2 β-CD/*m*-TPPTC complex. The behavior of the β-CD/*m*-TPPTC supramolecular complex then appeared to be very different from that observed for the β-CD/TPPTS couple for which a 1:1 stoichiometry was measured and an association constant of $1200\,M^{-1}$ was calculated.[9] The natural tendency of carboxylates to form dimeric species in solution might be an explanation for the presence of 1:2 complexes in the case of the *m*-TPPTC ligand.

Accordingly, T-ROESY spectra were recorded to determine whether the 1:1 and 1:2 β-CD/*m*-TPPTC adducts were true inclusion complexes or adducts resulting from external interaction phenomena. The T-ROESY spectrum of a β-CD/*m*-TPPTC mixture for which concentrations have been chosen to maximize the 1:1 complex, evidenced the presence of correlation peaks between the aromatic protons and inner protons of β-CD, indicating that guests parts were included in its cavities. An important part of the contour plot obtained by this sequence is displayed in Figure 2.

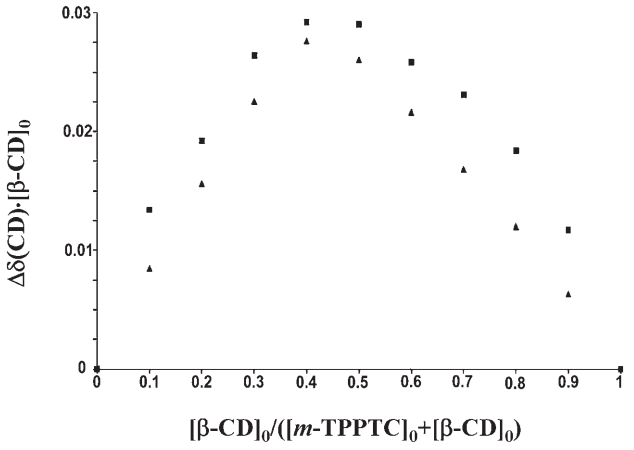


Figure 1. Continuous variation plots (Job's plot) derived from the ^{1}H NMR data for the β-CD/*m*-TPPTC system: ■ = H-1, ▲ = H-3 (25 °C).

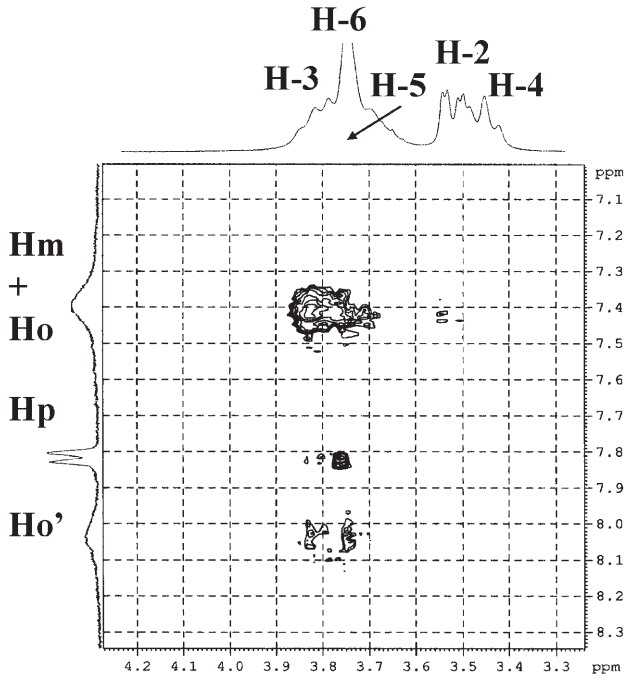
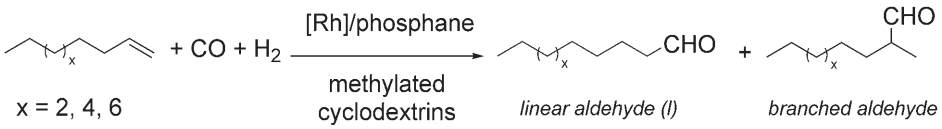


Figure 2. 2D T-ROESY NMR spectrum of a 1:1 β-CD/*m*-TPPTC complex in D_2O (25 °C).

Table 1. Biphasic rhodium-catalyzed hydroformylation of higher olefins with TPPTS or *m*-TPPTC as hydrosoluble ligand and RAME-β-CD or RAME-β-CD as mass transfer promoter[a]



Entry	Olefin	Ligand	Cyclodextrin	Conversion [%][b]	Selectivity [%][c]	*l*/*b* ratio[d]
1	1-octene	*m*-TPPTC	-	94	87	2.3
2	1-octene	TPPTS	-	2	45	2.8
3	1-octene	*m*-TPPTC	RAME-α-CD	100	92	2.0
4	1-octene	TPPTS	RAME-α-CD	32	93	3.0
5	1-octene	*m*-TPPTC	RAME-β-CD	100	95	1.5
6	1-octene	TPPTS	RAME-β-CD	91	97	1.7
7	1-decene	*m*-TPPTC	-	43	86	2.4
8	1-decene	TPPTS	-	2	59	2.8
9	1-decene	*m*-TPPTC	RAME-α-CD	80	95	2.0
10	1-decene	TPPTS	RAME-α-CD	21	91	2.8
11	1-decene	*m*-TPPTC	RAME-β-CD	100	96	1.5
12	1-decene	TPPTS	RAME-β-CD	90	98	1.8
13	1-dodecene	*m*-TPPTC	-	16	83	2.3
14	1-dodecene	TPPTS	-	1	72	2.8
15	1-dodecene	*m*-TPPTC	RAME-α-CD	68	83	2.1
16	1-dodecene	TPPTS	RAME-α-CD	5	85	2.8
17	1-dodecene	*m*-TPPTC	RAME-β-CD	88	85	1.6
18	1-dodecene	TPPTS	RAME-β-CD	31	83	1.7

[a] *Experimental conditions:* $Rh(acac)(CO)_2$: 1.1 μmol; ligand: 5.5 μmol; CD: 13 μmol; water: 0.32 mL; olefin: 550 μmol; *n*-undecane (internal standard): 50 μmol; $P(CO/H_2: 1/1) = 40$ bar; $T = 80\,^{\circ}C$; time: 3 h.
[b] Olefin conversion.
[c] Aldehyde selectivity.
[d] Linear to branched aldehydes ratio.

Intense correlations peaks between the H*o* and H*m* protons of the phosphane with the inner protons H-3 and H-5 of the CD were indicative of an inclusion of one of the aromatic rings of the phosphane in the CD cavity. As the correlation peak was much more intense with H-3, the inclusion process seemed to occur by the secondary face of the CD. A correlation peak between Hp and H-5 also revealed the closeness between them. The proton H*o'* correlated with H-3 and H-5 in a less intense way than the other phosphane protons. Starting from these observations, the geometry of the inclusion complex could be deduced as a bent phosphane in the CD cavity. Interestingly, a similar orientation has been described in the case of TPPTS-β-CD inclusion complex.[10]

The behavior of *m*-TPPTC was then studied in the hydroformylation of 1-octene, 1-decene and 1-dodecene in a biphasic system using $Rh(acac)(CO)_2$ as catalyst precursor and methylated CDs (Rame-α-CD or Rame-β-CD) as mass transfer promoters. For comparison, the same experiments have been performed with TPPTS as a ligand. The results are summarized in Table 1. Without CD and with TPPTS as a ligand, the conversions were very low whatever the olefin due to the low mass transfer between the two layers (entries 2, 8, 14). By contrast, the conversions obtained with *m*-TPPTC were notably higher (multiplied by a factor of 47, 21 and 16 for 1-octene, 1-decene and 1-dodecene, respectively). The surface activity of *m*-TPPTC might be responsible for its higher efficiency in the hydroformylation reaction. As anticipated (Figure 3), interfacial tension measurements performed with *m*-TPPTC and TPPTS clearly revealed two different behaviors: TPPTS is a hydrotropic compound whereas *m*-TPPTC behaves as a surface active compound. At the ligand concentration used in the catalytic experiments (17 mM), the surface tensions (ST) were 42 mNm^{-1} and 62 mNm^{-1} for *m*-TPPTC and TPPTS, respectively.

It should be pointed out that the selectivities in aldehydes in the absence of CDs were also higher with *m*-TPPTC ligand than with TPPTS ligand, whereas the regioselectivities were slightly lower (entries 1 and 2, 7 and 8, 13 and 14). The higher acidity of TPPTS compared to *m*-TPPTC might be advocated to explain such behaviors.[8e] Indeed, Fell et al. have shown that in the presence of a ligand possessing a stronger π-acidity, a higher selectivity to linear aldehyde was observed.[11] A recent determination of the basicity of the carboxylated phosphane *m*-TPPTC showed that this ligand seems to be more electron-rich, e.g., less acid than its sulfonated analogue.[8e] This feature had

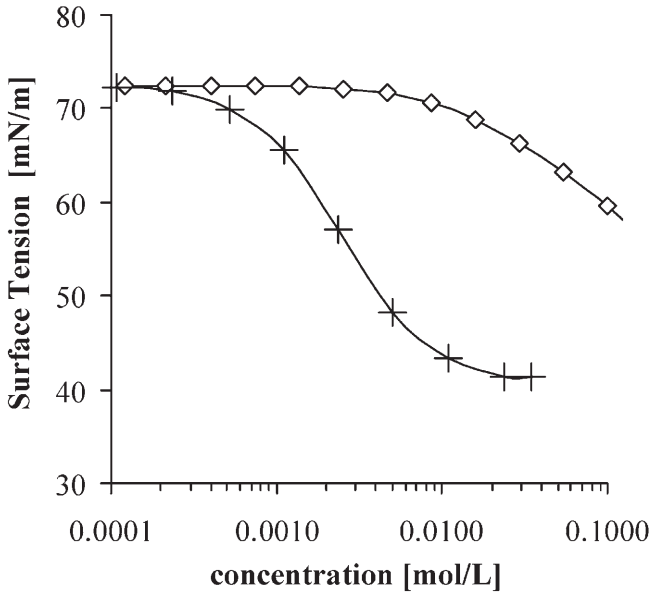


Figure 3. Surface tension of TPPTS (◇) and *m*-TPPTC (+) curves in water at 20 °C.

already some consequences on the Rh-catalyzed C–C bond formation, where the ligand *m*-TPPTC showed a very high efficiency and selectivity compared to TPPTS.[8a,c–e]

When methylated CDs were used as mass transfer promoters, the conversions were increased whatever the ligand or the olefin (compare entries 9 and 11 with 7, for example). Actually, the inclusion of olefins in the hydrophobic cavity of the CDs led to the formation of host/guest complexes at the liquid/liquid interface that greatly enhanced the reaction rate. Using methylated CDs also improved the chemoselectivity due to the protective effect of the CD cavity, which compelled the substrate to react in a more controlled way (compare entries 3 and 5 with 1, for example). It is worth noting that, once the olefin was coordinated to the rhodium, an interaction of these CDs with the catalytic species could not be excluded to explain the chemoselectivity increase. Contrary to activities and chemoselectivities, the regioselectivities of the hydroformylation reaction strongly depended on the nature of the ligand and the CDs. With TPPTS as ligand, the linear to branched aldehydes ratios (*l/b*) measured in the presence of Rame-α-CD were rather close or identical to those observed without CD whereas a decrease in the *l/b* ratios was observed for Rame-β-CD. By contrast, with *m*-TPPTC as ligand, the *l/b* ratio was decreased in the presence of both methylated CDs though only Rame-β-CD was able to trap *m*-TPPTC. As the *l/b* ratio decrease observed with the CD derivatives has been attributed in previous works to the formation of inclusion complexes between the ligand and the cyclodextrin, this phenomenon with the Rame-α-CD and *m*-TPPTC is clearly unexpected. One way to explain this result could be a CD-induced decoordination process during the coordination of the olefin/Rame-α-CD inclusion complex on the rhodium center to reduce steric hindrance around the metal. A similar hypothesis was recently invoked to explain the *l/b* ratio decrease in the hydroformylation of 1-decene with a Rame-α-CD/alkyl-sulfonated diphosphane combination for which no inclusion complex was detected.[12]

The cyclodextrins/*m*-TPPTC interactions have thus been studied and were found to be very peculiar. The methylated CDs/*m*-TPPTC couples therefore showed interesting features for Rh-catalyzed hydroformylation reactions. The methylated CDs/*m*-TPPTC systems proved to be more efficient than the well-known methylated CDs/TPPTS ones in terms of activities and selectivities in the hydroformylation of higher olefins. Experiments are currently under way to refine our understanding of the catalytic process to explain the loss of regioselectivity observed with the Rame-α-CD.

Experimental Section

General Remarks

The ^{1}H NMR spectra were recorded on a Bruker Avance DRX spectrometer. 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/point in F2 and F1 dimensions, respectively. They were transformed in the non-phase-sensitive mode after QSINE window processing. UV-VIS spectroscopy was performed on a Perkin–Elmer Lamba 25 spectrometer. The cell used was placed in a cuvette holder and the temperature was kept constant at 298 K ±0.1 by means of a thermostated bath. 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.$^{-1}$ The experiments were performed at 293 K ±0.5 controlled by a thermostated bath Lauda (RC6 CS). Gas chromatographic analyses were carried out 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). D_2O (99.95% isotopic purity) was obtained from Merck. Dicarbonylacetylacetonatorhodium(I) was purchased from Aldrich Chemicals in its highest purity and used without further purification. Organic compounds (undecane, 1-octene, 1-decene and 1-dodecene) were purchased from Aldrich Chemicals in their highest purity and used without further purification. Rame-α-CD was prepared by adapting a proce-

dure reported by Y. Kenichi et al.[13] Rame-β-CD was purchased from Aldrich Chemicals. TPPTS and *m*-TPPTC were prepared as reported in the literature.[14] Carbon monoxide/hydrogen mixtures (1:1) were used directly from cylinders (>99.9% pure; Air Liquide). Distilled deionized water was used in all experiments. All liquid reagents were degassed by bubbling nitrogen 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 a variable ratio (from 0 to 1) of β-CD and *m*-TPPTC was prepared keeping the total concentration of species constant (10 mM in this present case). The differences of chemical shift in ^{1}H NMR spectra were measured as a function of the molar ratio.

Calculation of Association Constant

The characterization of the β-CD-*m*-TPTTC complexes by the competitive method is realized in two steps. First of all, the inclusion compound between β-CD and MO (methyl orange) is characterized by the well-known titration method, leading to a formation constant K equal to 2500 M^{-1}. In a second time, various amounts of *m*-TPPTC are added to solutions containing a fixed composition of β-CD and MO, leading to various values of absorbance. In the following, β-CD-MO represents the molecular complex between β-CD and MO, while β-CD/MO stands for a solution of β-CD and MO; by analogy, β-CD/MO/*m*-TPPTC stands for the solutions containing β-CD, MO and *m*-TPPTC. The absorbance of an aqueous MO solution is described by the Beer–Lambert law: $A_{MO} = \varepsilon_{MO} \times [MO]_T$.

When cyclodextrin is added, there is a modification of the absorbance: $A_{\beta\text{-CD/MO}} = \varepsilon_{MO} \times [MO] + \varepsilon_{\beta\text{-CD-MO}} \times [\beta\text{-CD-MO}]$. The absorbance of the pure β-CD-MO complex is thus described by $A_{\beta\text{-CD-MO}} = \varepsilon_{\beta\text{-CD-MO}} \times [MO]_T$.

When *m*-TPPTC, which does not absorb in the studied region, is added, the previous relations are still valid, but the [β-CD-MO] concentration is weaker, consecutively to the formation of complexes between β-CD and *m*-TPPTC: $A_{\beta\text{-CD/MO/}m\text{-TPPTC}} = \varepsilon_{MO} \times [MO] + \varepsilon_{\beta\text{-CD-MO}} \times [\beta\text{-CD-MO}]$.

$$[\beta\text{-CD}] = \frac{A_{\beta\text{-CD/MO/}m\text{-TPPTC}} - A_{MO}}{K \times (A_{\beta\text{-CD-MO}} - A_{\beta\text{-CD/MO/}m\text{-TPPTC}})}$$

This concentration is then used to calculate a theoretical value of the total concentration of *m*-TPPTC ($[m\text{-TPPTC}]_T$), by postulating values for the various expected formations constants. Three kinds of inclusion compounds have been investigated (K_{11}, K_{21} and K_{12} being, respectively, the formation constantsof the 1:1, 2:1 and 1:2 complexes between β-CD and *m*-TPPTC):

i) 1:1 complex:

$$[m\text{-TPPTC}]_T = \left([\beta\text{-CD}]_T - [\beta\text{-CD}] - \frac{K \times [MO]_T \times [\beta\text{-CD}]}{1 + K \times [\beta\text{-CD}]}\right) \times \left(\frac{1 + K_{11} \times [\beta\text{-CD}]}{K_{11} \times [\beta\text{-CD}]}\right)$$

ii) mixture of 1:1 and 2:1 complexes:

$$[m\text{-TPPTC}]_T = \left([\beta\text{-CD}]_T - [\beta\text{-CD}] - \frac{K \times [MO]_T \times [\beta\text{-CD}]}{1 + K \times [\beta\text{-CD}]}\right) \times \frac{1 + K_{11} \times [\beta\text{-CD}] + K_{21} \times K_{11} \times [\beta\text{-CD}]^2}{K_{11} \times [\beta\text{-CD}] + 2 \times K_{21} \times K_{11} \times [\beta\text{-CD}]^2}$$

iii) mixture of 1:1 and 1:2 complexes:

$$[m\text{-TPPTC}]_T = [m\text{-TPPTC}] + K_{11} \times [\beta\text{-CD}] \times [m\text{-TPPTC}] + 2 \times K_{12} \times K_{11} \times [\beta\text{-CD}] \times [m\text{-TPPTC}]^2$$

with

$$[\text{m-TPPTC}] = \sqrt{\frac{[\beta\text{-CD}]_T - [\beta\text{-CD}] - \frac{K \times [MO]_T \times [\beta\text{-CD}]}{1 + K \times [\beta\text{-CD}]}}{K_{11} \times K_{12} \times [\beta\text{-CD}]} + \left(\frac{K_{11} \times [\beta\text{-CD}]}{2 \times K_{11} \times K_{12} \times [\beta\text{-CD}]}\right)^2} - \frac{K_{11} \times [\beta\text{-CD}]}{2 \times K_{11} \times K_{12} \times [\beta\text{-CD}]}$$

The amount of dissociated β-CD-MO depends not only on the concentration of added substrate, but also on the stabilities and stoichiometries of the complexes thus formed. Such perturbation of the equilibrium in the presence of *m*-TPPTC may be described by the concentration of free β-CD, which is calculated from the recorded absorbance by the following relation:

For each case, the difference between the theoretical and experimental values of $[m\text{-TPPTC}]_T$ is then minimized by a home-made algorithmic procedure. The stoichiometry inducing the weaker difference between theory and experiment is then supposed to be the correct one and the corresponding formation constants are thus known.

T-ROESY Experiment

The T-ROESY spectrum was conducted with [*m*-TPPTC] = 2.5 mM and [β-CD] = 7.5 mM in order to favor the 1:1 complex, even if the exclusive formation of this compound is unachievable. For such concentrations and using the formation constants calculated by the UV-VIS competition method, 28% of β-CD and 83% of *m*-TPPTC are complexed within the 1:1 stoichiometry, while the 1:2 inclusion concerns only 1% of β-CD and 9% of *m*-TPPTC.

Catalytic Experiments

All catalytic reactions were performed under nitrogen using standard Schlenk techniques. A stainless steel, 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), ligand (TPPTS or *m*-TPPTC) (5.5 μmol) and CD (13 μmol) dissolved in 0.32 mL of water and the organic phase composed of olefin (550 μmol) and undecane (50 μmol – GC internal standard). The autoclave was pressurized with 40 atm of CO/H_2 (1/1). The mixture was stirred for 3 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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