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Cyclodextrins as first and second sphere ligands for Rh(I) complexes of lower-rim PTA derivatives for use as catalysts in aqueous phase hydrogenation

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ABSTRACT

The rhodium complex [Rh(cod)Cl(*N*-tBuBzPTA)]PF_6 (**2**) was obtained by reacting the appropriate Rh(I) precursor with the lower-rim PTA derivative [*N*-tBuBzPTA]PF_6 (tBuBz = 4-*tert*-butylbenzyl; PTA = 1,3,5-triaza-7-phosphaadamantane). The solubility and stability in water of **2** were increased in the presence of native-β-cyclodextrin (β-CD). The interaction of **2** with mono-amino β-cyclodextrin (β-$CDNH_2$, 2 equiv.) led to a supramolecular Rh assembly (**3**), identified by ^{31}P, ^{1}H and 2D T-ROESY NMR experiments. The catalytic activity of **3** was evaluated in the water-phase hydrogenation of unsaturated and allylic alcohols and preliminary results are presented here.

1. Introduction

Self-assembly has recently emerged as a very effective tool to access new organometallic catalysts by means of host–guest interactions. Reek et al. [1] exploited the coordination ability of a nitrogen donor group on Zn(II) porphyrins to build a library of supramolecular phosphorus-containing bidentate ligands. Breit and Seiche [2] focused on self-assembly of complementary species by hydrogen bonding in aprotic solvents. Both strategies led to very efficient catalysts whose performances have been demonstrated in numerous reactions [3–9]. Other supramolecular strategies have also been exploited, usually in organic phase, via metal-directed self-assembly [10–12], acid–base interactions [13,14], or via a pseudorotaxane molecule [15]. We recently demonstrated that supramolecular ligands are also accessible in aqueous media via the hydrophobic interaction between the cavity of nitrogen-containing β-cyclodextrins (CDs) and an appropriate water soluble phosphine [16–18]. Inclusion of the phosphine within the CD cavity by the NH_2-containing face resulted in the formation of a rigid chelating bidentate ligand (for example to Pt and Rh precursors) with the nitrogen and the phosphorus atoms on the same side of the supramolecular edifice.

We extended the scope of the supramolecular approach in aqueous media following on our interest on the application of water soluble ligands derived from tailored *N*-quaternizations of the cage-like aminophosphine PTA (PTA = 1,3,5-triaza-7-phosphaadamantane) and their interactions with CDs [19,20]. Hereby we report on the stabilization effects of mono-amino β-CD (β-$CDNH_2$, Fig. 1) on a Rh complex of [1-(4-*tert*-butyl)-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl] hexafluorophosphate (**1**). The corresponding supramolecular P,N,N heterotridentate-stabilized complex was tested in the proof-of-concept hydrogenation of unsaturated and allylic alcohols in water and the preliminary results are here presented.

2. Experimental section

2.1. General methods

All synthetic manipulations were carried out under a purified atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. [*N*-*t*BuBzPTA]Br [20] and $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) [21] were prepared as described in the literature. The details of characterizations are reported in the Supporting information section.

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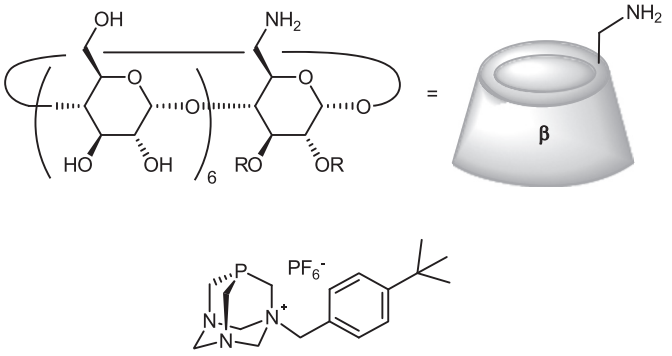


Fig. 1. β-$CDNH_2$ and the lower rim PTA derivative [*N*-tBuBzPTA]PF_6 (**1**).

2.2. Synthesis of 1-(4-tert-butyl)-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl hexafluorophosphate (*1*)

For the synthesis of ligand **1**, 1-(4-*tert*-butyl)-benzyl-1-azonia-3,5-diaza-7-phosphaadamantyl bromide (0.50 g, 1.3 mmol) was placed in a Schlenk tube and dissolved in dried and degassed dichloromethane (20 mL). In another Schlenk tube, ammonium hexafluorophosphate (0.23 g, 1.43 mmol) was dissolved in dried THF (6 mL) and the solution obtained was added dropwise to the solution of the ligand, causing the precipitation of a white solid. The reaction mixture was left stirring at room temperature for 1 h. The precipitate was then separated by filtration and the clear colourless solution dried under vacuum to obtain a white powder ((yield: 0.40 g, 68%), $C_{17}H_{27}N_3P_2F_6$ (449.35 g mol^{-1}).

2.3. Synthesis of complex [Rh(cod)Cl(N-tBuBzPTA)]PF_6 (*2*)

A Schlenk tube was charged with $[RhCl(cod)]_2$ (0.27 g, 0.55 mmol) and **1** (0.49 g, 1.09 mmol). Dried and degassed dichloromethane (45 mL) was added and the reaction was left stirring for 1 h 30 min at room temperature. The mixture was then filtered and the resulting yellow solution concentrated to about 10 mL volume. Cold dried pentane (25 mL) was added and the resulting yellow precipitate was collected on a G3 sintered-glass filter, washed with cold pentane (2 × 4 mL) and dried under vacuum ((yield: 0.46 g, 61%), $C_{25}H_{39}N_3ClP_2F_6Rh$ (695.89 g mol^{-1}).

2.4. Formation of supramolecular complexes [Rh(cod)Cl(N-tBuBzPTA)] PF_6·(β-$CDNH_2$)$_2$ (*3*)

A Schlenk tube was charged with **2** (5.0 mg, 7.0×10^{-3} mmol) and β-$CDNH_2$ (16 mg, 1.4×10^{-2} mmol). Degassed deuterium oxide (2 mL) was added and the reaction was left stirring for 1 h at room temperature. A clear yellow solution was obtained.

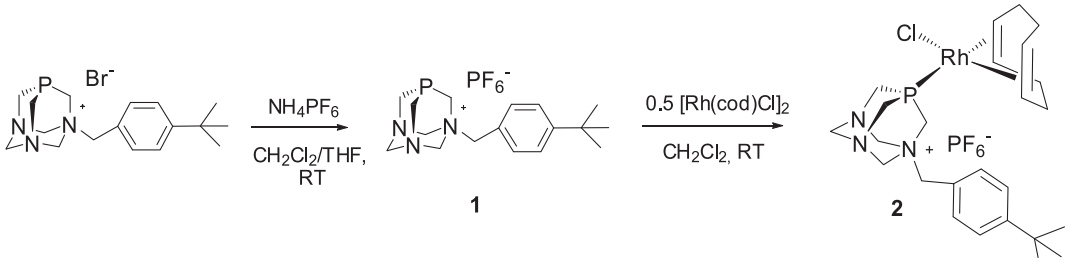
2.5. Catalytic hydrogenation tests

Typically, the unsaturated alcohol (5.5 mmol) and 1-butanol (1.4 mmol, GC internal standard) were added in a steel autoclave to an aqueous solution (10 mL) containing the rhodium complex **2** (5.5 μmol) and CD (11.0 μmol). The reactor was then pressurized with H_2, and heated to 30 °C. The catalytic run was monitored during time by withdrawing aliquots of the reaction mixture which were analysed by GC. For 2-methyl-3-buten-2-ol, recycling tests were carried out by recovering the phase containing the catalyst and repeating the hydrogenation tests in the presence of fresh substrate.

3. Results and discussion

3.1. Synthesis of rhodium complexes

Rh–PTA complexes have received attention due to their catalytic activity both in hydrogenation and hydroformylation reactions [22,23].



Scheme 1. Syntheses of ligand **1** and complex **2**.

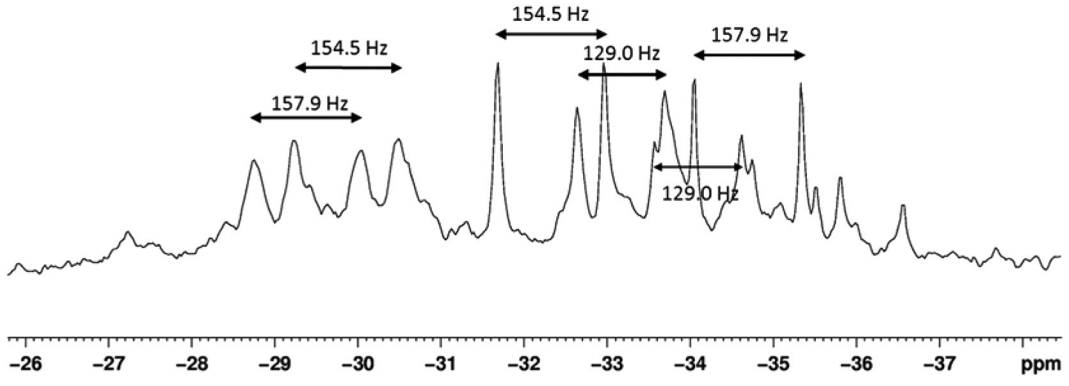


Fig. 2. Diagnostic regions of $^{31}P\{^1H\}$ NMR spectrum of a 2:1 mixture of β-$CDNH_2$ and **2** in D_2O at 25 °C after 1 h.

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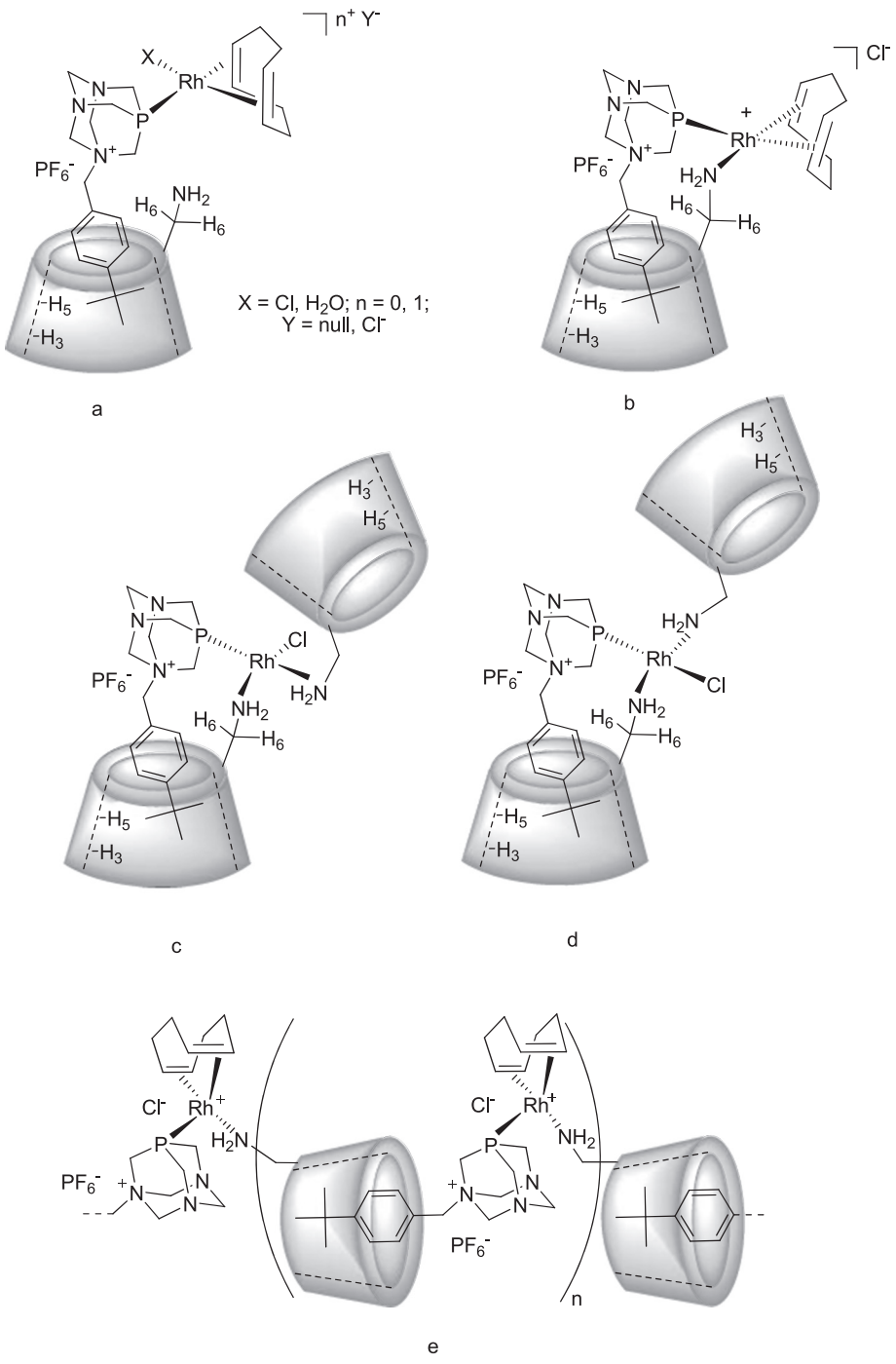

Scheme 2. Proposed supramolecular species formed between Rh-complex **2** and β-CDNH$_2$.

The novel PTA derivative [*N*-tBuBzPTA]PF$_6$ (**1**) and its corresponding Rh(I) complex, namely [Rh(cod)Cl(*N*-tBuBzPTA)]PF$_6$ (**2**) (Scheme 1) were synthesized and characterized in solution by NMR and ESI–MS techniques (see SI). Anion exchange from known [*N*-tBuBzPTA]Br [20] was easily accomplished by reaction with NH_4PF_6 in a CH_2Cl_2/THF mixture at room temperature, in order to avoid the presence of bromide that is a competing ligand to Rh.

Complex **2** was obtained as shown in Scheme 1 and characterized by elemental analysis, ESI–MS and NMR in solution. The $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ showed a doublet at −33.1 ppm ($^1J_{RhP}$ = 160 Hz) and a heptet centred at −143.8 ppm ($^1J_{PF}$ = 716 Hz) due to PF_6 anion. The ESI–MS spectrum of **2** exhibited the peaks at 304.25 m/z corresponding to [*N*-tBuBzPTA]$^+$ and at 552.08 due to [Rh(cod)Cl(*N*-tBuBzPTA)]$^+$ + 2.

Complex **2** showed low solubility in water at room temperature (<5 mg/mL). By heating to 80 °C for 30 min, it was possible to dissolve completely a 5 mg sample of **2** in 5 mL of D_2O. However, extensive decomposition to phosphine oxide was evidenced by $^{31}P\{^1H\}$ NMR [24]. A different approach was needed to obtain stable aqueous solutions of **2** at 25 °C. Thus, we studied the effect of added CDs and

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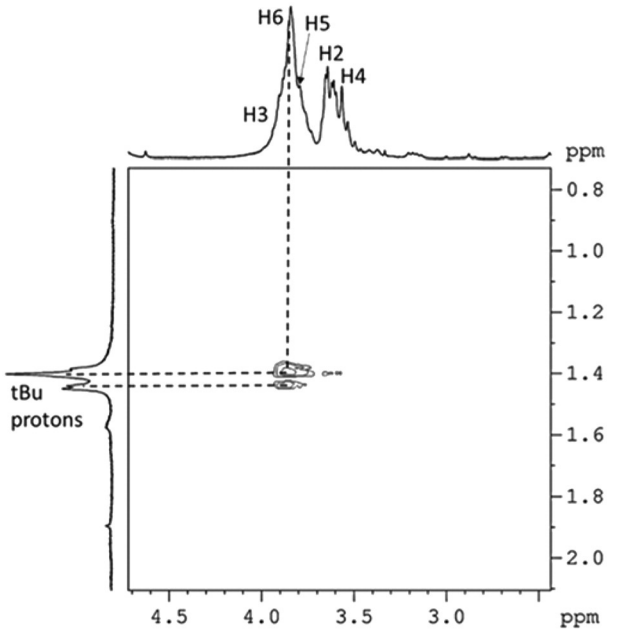


Fig. 3. Partial 2D T-ROESY NMR spectrum (*t*Bu protons) of a 2:1 mixture of β-$CDNH_2$ and **2** at room temperature in D_2O.

as expected, both the solubility and the stability in water of the complex were increased by the addition of either native β-CD or β-$CDNH_2$.

3.2. In-situ formation of supramolecular complexes

In order to enhance water solubility, inclusion of **2** in cyclodextrins can be expected upon recognition of the *t*Bu-benzyl group, which is known to be well recognized by the β-CD cavity [25,26]. At first, addition of 1 equiv. of native β-CD (8.0 mg, 7.0×10^{-3} mmol) to a suspension of **2** (5 mg, 7.0×10^{-3} mmol) in D_2O (2 mL) was tested, showing however that this ratio was clearly insufficient to solubilise **2** completely at 25 °C. Conversely, when 2 equiv. of native β-CD (16 mg, 1.4×10^{-2} mmol) were used under the same conditions, a clear yellow solution was obtained. We reasoned that under these conditions both the hydrophobic character of cod ligand and *t*Bu-benzyl group might be masked into the hydrophobic CD cavity. Interestingly, also the stability in water of complex **2** was increased. $^{31}P\{^1H\}$ NMR spectra showed that a significant amount

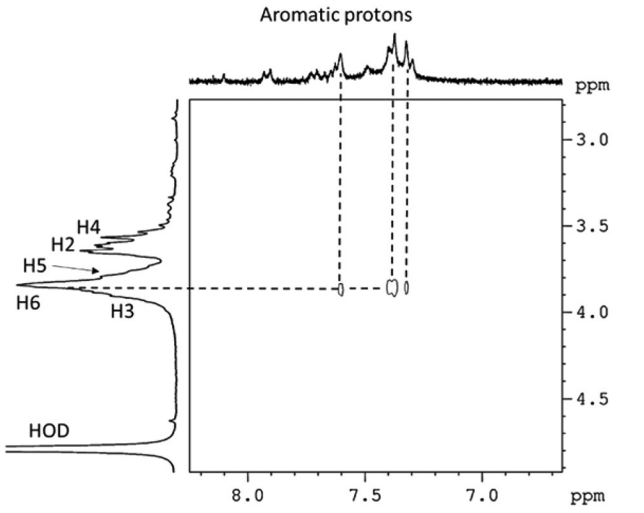
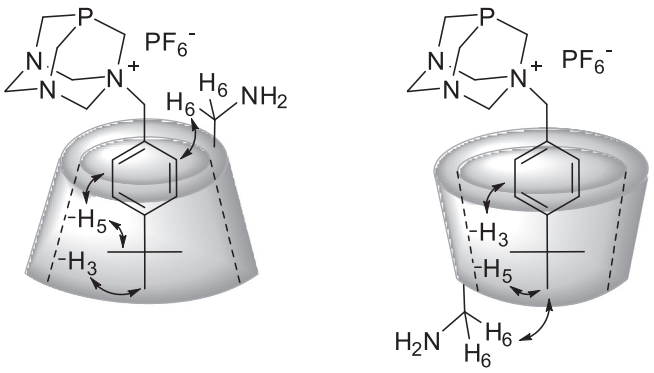


Fig. 4. Partial 2D T-ROESY NMR spectrum (aromatic protons) of a 2:1 mixture of β-$CDNH_2$ and **2** at room temperature in D_2O.



Scheme 3. Possible dipolar interactions resulting from inclusion of **1** within the β-$CDNH_2$ cavity from the primary (left) or the secondary (right) face.

of **2** was found unchanged in solution either after 24 h at room temperature (ca. 60%) or after 5 h heating to 80 °C (ca. 42%), respectively.

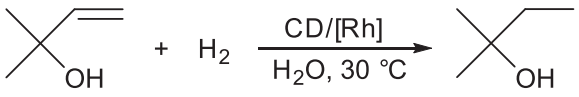
A different behaviour was observed upon addition of β-$CDNH_2$ (2 equiv.) to a solution of **2**, as witnessed by the corresponding $^{31}P\{^1H\}$ NMR spectrum. The initial doublet centred at δ −33.1 ppm ($^1J_{RhP}$ = 160 Hz) corresponding to **2** was replaced by 6 doublets falling in the range between −28 and −37 ppm, with $^1J_{RhP}$ in the range 129–158 Hz (Fig. 2). Attempts to separate the different components of the mixture or grow crystals suitable for X-ray diffraction data collection failed to date.

Different Rh-phosphine species can be hypothesized to form in solution, including chloride complexes (higher $^1J_{RhP}$) and aquo complexes (lower $^1J_{RhP}$), keeping a coordinated Rh(η^4-cod) moiety, with mixed first and second sphere coordination giving P,N and P,N,N complexes, derived from various substitution degrees on the metal centre, as shown in Scheme 2.

To confirm that the *t*Bu-phenyl group was to a large extent included into the β-$CDNH_2$ cavity, 2D T-ROESY NMR experiments have been carried out. This particular NMR sequence, commonly used to identify the recognition process between the CD "host" and the phosphine ligand "guest", evidenced the existence of dipolar contacts between the protons of the *t*Bu-phenyl group of **2** and the β-$CDNH_2$ inner protons H-3 and H-5, hence the expected inclusion within the β-CD cavity (Figs. 3 and 4). Moreover, weak correlations were also observed between the aromatic protons and the H-6 and H-5 CD protons (Fig. 4), indicative of a weak penetration of the ligand into the CD cavity. Accordingly, inclusion of **2** took place through the β-$CDNH_2$ primary face confirming that the nitrogen and the phosphorus atoms were located on the same side of the CD. As no cross-peaks were observed between the aromatic protons and H-3, inclusion through the CD secondary face can be excluded (Scheme 3).

3.3. Catalytic unsaturated and allylic alcohol hydrogenation tests

The possible use of the supramolecular β-CD/rhodium complex assemblies as homogeneous aqueous-phase catalysts was at first evaluated in the proof-of-concept hydrogenation of a water soluble substrate, namely 2-methyl-3-buten-2-ol (Scheme 4). The choice of this model substrate was motivated not only by its high solubility in water, but also because no C═C isomerization can take place, thus limiting the number of products to analyse. The effect of the CD nature on the activity and stability of the catalytic system was assessed, comparing the combination of **2**/native β-CD and **2**/β-$CDNH_2$ under 10 and 20 bar H_2



Scheme 4. Rh-catalysed hydrogenation of 2-methyl-3-buten-2-ol.

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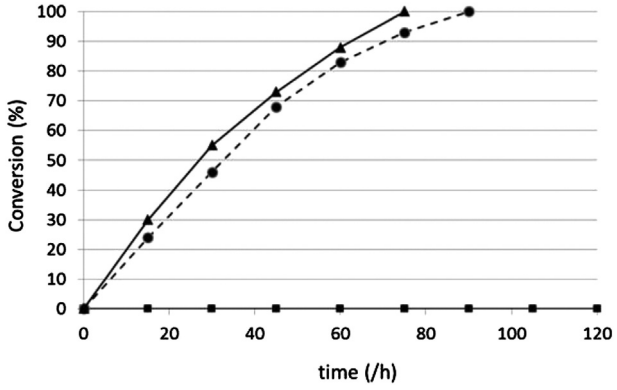

Fig. 5. Hydrogenation of 2-methyl-3-buten-2-ol in the presence of i) native β-CD/**2** (2:1), pH_2, 10 bar (–■–), ii) β-$CDNH_2$/**2** (2:1), pH_2, 10 bar (–●–) and iii) β-$CDNH_2$/**2** (2:1), pH_2, 20 bar (–▲–), respectively. Reaction conditions: **2**, 5.5 × 10-3 mmol; CDs, 11.0 × 10-3 mmol; substrate, 5.5 mmol; H_2O, 10 mL; 30 °C.

pressure. Homogeneous solutions were invariably observed without any metal particle deposition, and could be recovered at the end of each test. However, the formation of catalytically active Rh nanoparticles stabilized by β-$CDNH_2$ could not be ruled out.

In the presence of native β-CD and **2** (1:1 or 2:1 ratios) under 10 bar H_2, no reduction of allylic alcohol could be observed (Fig. 5). The situation was very different when the catalytic tests were carried out in the presence of **2**/β-$CDNH_2$. Under 10 bar H_2, the reaction was completed within 90 min. Increasing the H_2 pressure from 10 to 20 bar allowed decreasing the reaction time to 80 min. The catalytic system could be efficiently recycled without any loss either in catalytic activity or selectivity (Table 1, runs 1–3). Other unsaturated alcohols were also hydrogenated in very good yields within 80 min (Table 1, runs 4–6). Note that, whatever the substrate, no isomerization of the C═C double bond took place during the course of the reaction.

In order to prove further that the presence of the amino group on the CD was of crucial importance to stabilize the catalyst in water, a mixture of native β-CD and decylamine, which is also recognized and included in the CD cavity, was also tested as a blank run. Rhodium aggregation took place suggesting that the inclusion of **2** in the CD cavity alone is not enough to guarantee adequate catalyst stability under these conditions. Thus, the formation of a supramolecular complex by the inclusion of lower-rim modified PTA into the amino-modified CD, endowed with two donor atoms (P from the phosphine and N from the CD) capable of efficiently binding to Rh(I) seems to offer an adequate approach and provide a more stable and efficient catalytic system for water phase C═C bond hydrogenation under mild conditions. Work is in progress to extend the scope of the catalytic systems to more challenging substrates.

4. Conclusions

In this work, we reported the synthesis of supramolecular rhodium complexes bearing a lower rim PTA derivative as phosphine ligand and β-$CDNH_2$ as first and second sphere ligands. These Rh-complexes showed stability in water phase, allowing their use as precursors in the catalytic hydrogenation of a small library of unsaturated alcohols under mild conditions of temperature and H_2 pressure in neat water.

Acknowledgements

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Table 1
Rh-catalysed hydrogenation of unsaturated alcohols in the presence of a 2:1 mixture of β-$CDNH_2$ and **2**.

Run	Substrate	Product	Conversion (%)	Selectivity (%)
1	2-Methyl-3-buten-2-ol	2-Methylbutan-2-ol	100	100
2[a]	2-Methyl-3-buten-2-ol	2-Methylbutan-2-ol	99	100
3[b]	2-Methyl-3-buten-2-ol	2-Methylbutan-2-ol	99	100
4	Propargylic alcohol	Propan-1-ol	100	100
5	3-Methyl-2-buten-1-ol	3-Methylbutan-1-ol	93	100
6	2-Methyl-2-propen-1-ol	2-Methylpropan-1-ol	100	100

Conditions: **2**, 5.5 × 10^{-3} mmol; β-$CDNH_2$, 11.0 × 10^{-3} mmol; substrate, 5.5 mmol; H_2O, 10 mL; pH_2, 20 bar; 30 °C; 80 min.
[a] Performed with the recovered aqueous phase of run 1.
[b] Performed with the recovered aqueous phase of run 2.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.11.030.

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