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Conference paper

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New water-soluble Schiff base ligands based on β -cyclodextrin for aqueous biphasic hydroformylation reaction

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Abstract: The synthesis of water-soluble rhodium(I) salicylaldiminato and salicylhydrazonic complexes has been achieved employing two preparative routes. Schiff base condensation between 6^A-deoxy-6^A-amino- β -CD or 6^A-deoxy-6^A-hydrazino- β -CD and 5-sodiosulfonato-2-hydroxybenzaldehyde (sulfonated salicylaldehyde) (**1**) or 5-sodiosulfonato-3-*tert*-butyl-2-hydroxybenzaldehyde (sulfonated ^tBu-salicylaldehyde) (**2**) led to the formation of the corresponding imine or hydrazone ligands (**3**, **4**, **5** and **6**). Reaction of $[\text{Rh}(\text{COD})_2^+\text{BF}_4^-]$ with these new ligands in an alkaline solution formed the corresponding rhodium complexes quantitatively. These rhodium(I) complexes could also be prepared in one-pot by mixing, in stoichiometric proportions, the modified β -CDs with the sulfonated salicylaldehyde and with the rhodium precursor in an alkaline solution at room temperature. These rhodium complexes were applied as catalysts in the aqueous biphasic hydroformylation of 1-decene as a model reaction.

Keywords: aqueous biphasic catalysis; cyclodextrin; hydroformylation; MAM-17; salicylaldimine; salicylhydrazone; Schiff base.

Introduction

Salicylate ligands are chelating ligands used in a wide range of organometallic applications and particularly for catalytic applications. In order to decrease the environmental impact of metal-catalyzed reactions, the use of water as solvent has been explored with these ligands by many authors. In this respect, two strategies can be used: the first uses hydrophobic ligands dispersing the catalyst in the aqueous phase (e.g. in ethylene polymerisation [1–3], or Suzuki-Miyaura couplings [4, 5]) and the second uses hydrosoluble salicylate ligands permitting to solubilize the catalyst in the aqueous phase (e.g. in ring-closing metathesis [6], ethylene polymerization [7], hydrogenation [8] or Sonogashira couplings (salen) [9, 10]). More recently, sulfonated

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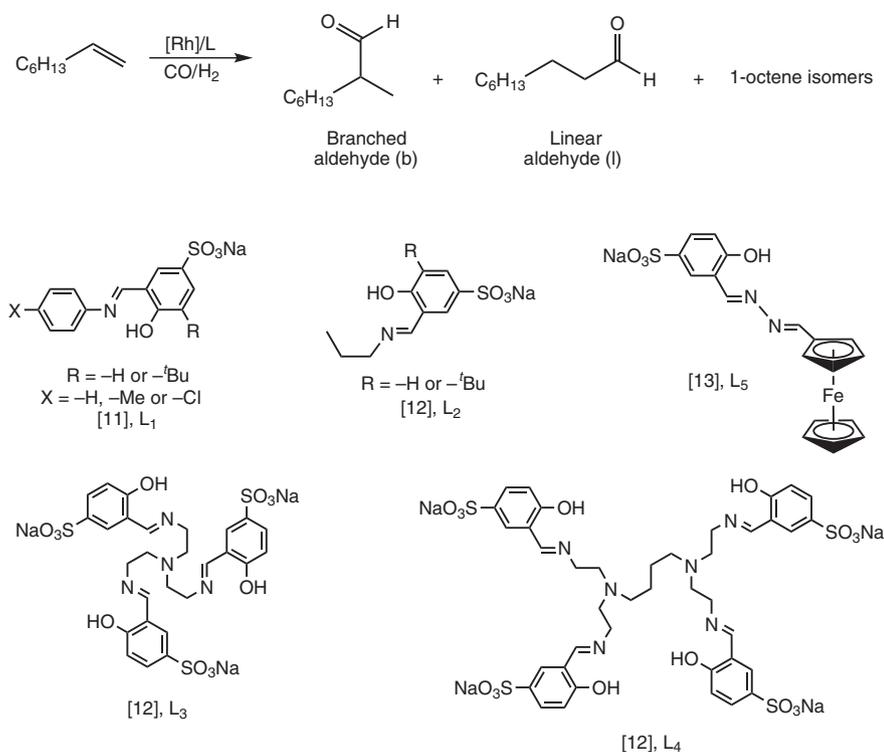


Fig. 1: Hydroformylation of 1-octene.

salicylidimine and salicylhydrazone ligands have been successfully applied in the rhodium-catalyzed aqueous biphasic hydroformylation of 1-octene (Fig. 1) [11–13].

In the reported work, TOFs between 200 h⁻¹ and 350 h⁻¹ could be attained with the water-soluble catalysts formed by combining the previous deprotonated ligands (L₁–L₅, Fig. 1) with the dimeric precursor [RhCl(COD)]₂. These *N,O*-bidentate ligands led to regioselectivities lower than 1.5 except for catalysts containing L₁ (where R = -^tBu and X = -H) which led to a l/b aldehyde ratio of 2.4 at 50 bar of syngas and 95 °C. This behavior is thought to originate from the bulkiness generated close to the metal center favoring the linear aldehyde formation. Linear-to-branched ratios close to this value of 2.4 (2.6 and 2.8, respectively) can be reached using catalyst precursors containing L₃ and L₂ (where R = -^tBu) at lower syngas pressure and temperature (30 bar and 75 °C) but the chemoselectivity dropped from 99 % to 52 % and 56 %, respectively.

The sustainability of these processes comes from the fact that the catalyst could be recovered at the end of the reaction after decantation and could subsequently be reused. However, depending on the ligand used, pronounced leaching of the catalyst in the organic phase was observed after several runs.

Parallel to this, cyclodextrins (CDs) have proven to be of particular interest in organometallic chemistry. Indeed, when specifically modified, these macrocycles are able to coordinate a metal precursor to form supramolecular catalysts with exceptional activities and selectivities [14–21]. In this context, and with the objective of synthesizing salicylic ligands based on cyclodextrin, we decided to study the condensation of salicylaldehydes with 6^A-deoxy-6^A-amino- β -CD and 6^A-deoxy-6^A-hydrazino- β -CD in order to form hydrosoluble Schiff base ligands. The combination of the salicylidimine skeleton with CDs has already been done with the hope of mimicking enzymes. In these previous cases, the ligands were synthesized starting from hydrophobic salicylaldehydes and were combined with copper(II) [22] or manganese(III) [23–25] in order to study their electrochemical behavior for catalytic oxidation reactions. We focused our attention on sulfonated salicylaldehydes in order to obtain highly hydrophilic ligands able to immobilize rhodium catalyst in the aqueous phase to perform hydroformylation reaction of long chain olefins.

Results and discussion

Synthesis of sulfonatosalicylaldimines and sulfonatosalicylhydrazones

6^A-Deoxy-6^A-amino- β -cyclodextrin (β -CDNH₂) [26], 6^A-deoxy-6^A-hydrazino- β -cyclodextrin (β -CDNHNH₂) [27] and the sulfonated salicylaldehyde **1** and **2** (Scheme 1) were prepared according to previously described procedures [12].

Briefly, the modified β -CDNH₂ was readily obtained via a three-step procedure. Native cyclodextrin (β -CD) was first selectively monotosylated (β -OTs) using *p*-toluenesulfonyl chloride in alkaline solution. Then, the 6^A-deoxy-6^A-azido- β -cyclodextrin (β -CDN₃) was isolated after nucleophilic substitution of β -OTs by sodium azide in DMF solution. Finally, the β -CDN₃ was reduced by the Staudinger reaction in the presence of triphenylphosphine to obtain β -CDNH₂. In the second step, if hydrazine monohydrate is used as nucleophile, β -CDNHNH₂ is obtained.

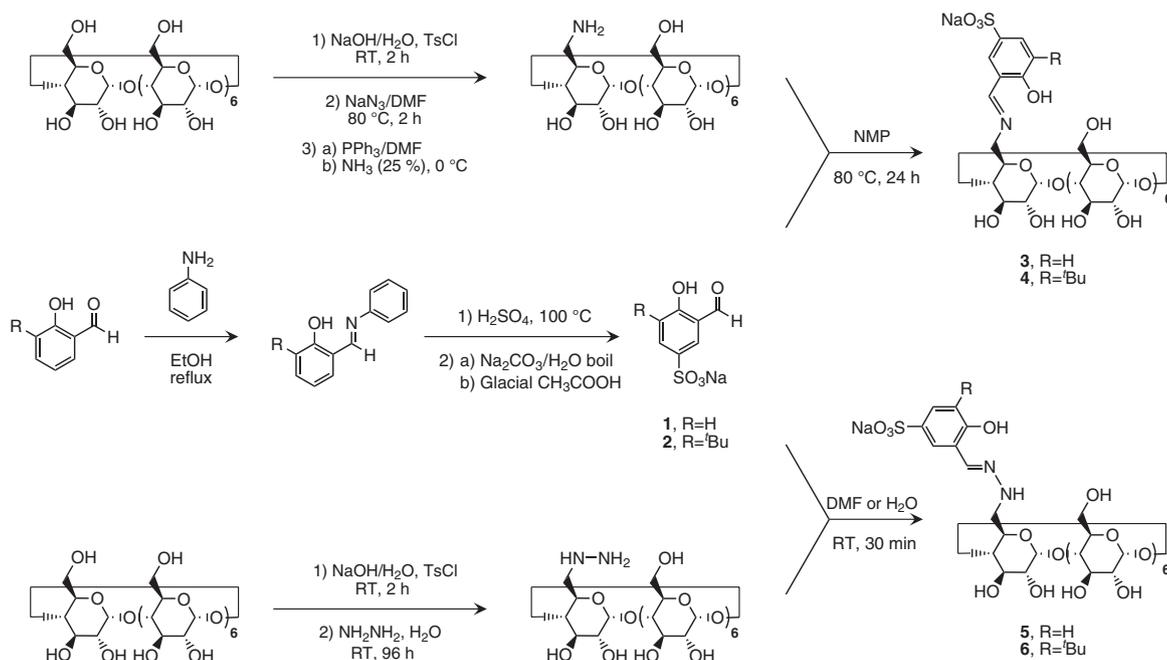
The sulfonated salicylaldehydes **1** and **2** were prepared by sulfonation of the anilin salicylalimine in sulfuric acid. Then, the sulfonated imines were hydrolysed to give the monosodium salt of the sulfonatosalicylaldehydes (yield = 57 % for **1** and 67 % for **2**).

Ligands **3** and **4** were synthesized by a Schiff base condensation in anhydrous *N*-methylpyrrolidone (NMP) at 80 °C for 24 h, followed by a precipitation with acetone (yield **3** = 80 %, yield **4** = 73 %). Ligands **5** and **6** were, for their part, synthesized by Schiff base condensation in DMF at room temperature for 30 min followed by a precipitation with THF (yield **5** = 67 %, yield **6** = 55 %) (Scheme 1).

Characterization of the water-soluble ligands

Sulfonatosalicylaldimines

Both ligands **3** and **4** were characterized by NMR, MALDI-TOF and FT-IR techniques. ¹³C NMR spectra of the ligands carried out in DMSO-*d*₆ showed a downfield shift of the aldehyde carbon from 191.7 ppm and 198.8 ppm (respectively for **1** and **2**) to 167.9 ppm and 168.8 ppm (for **3** and **4**), highlighting the formation of



Scheme 1: Synthesis route for ligand **3**, **4**, **5** and **6**.

the imine functional group. Similarly, in the ^1H NMR spectra, signals of the aldehyde protons (10.26 ppm for **1** and 9.78 ppm for **2**) disappeared and were replaced by imine protons signals at 8.61 ppm and 8.60 ppm, respectively for **3** and **4**. MALDI-TOF spectra obtained in the negative mode validate the previous observations by revealing signals at $m/z=1316$ and 1372 , respectively for **3** and **4**, corresponding to the species $[\text{M}-\text{Na}]^-$. Similar conclusions were obtained from the FT-IR spectra as the imine formation was confirmed by typical $\text{C}=\text{N}$ absorption bands at 1653 cm^{-1} and 1651 cm^{-1} , respectively for **3** and **4**.

It should be underlined that when the NMR characterizations of ligands **3** and **4** were done in D_2O , a remaining signal of the aldehyde was present at 8.44 ppm and 8.47 ppm, respectively. However, in anhydrous $\text{DMSO}-d_6$, no aldehyde was observed reflecting a partial stability of the synthesized salicylaldimines in water.

Sulfonatosalicylhydrazones

The synthesis of these derivatives is easier than the previous salicylaldimines. Indeed, the coupling between the salicylaldehyde and $\beta\text{-CDNH}_2$ could be achieved in water. However, after synthesis optimization,

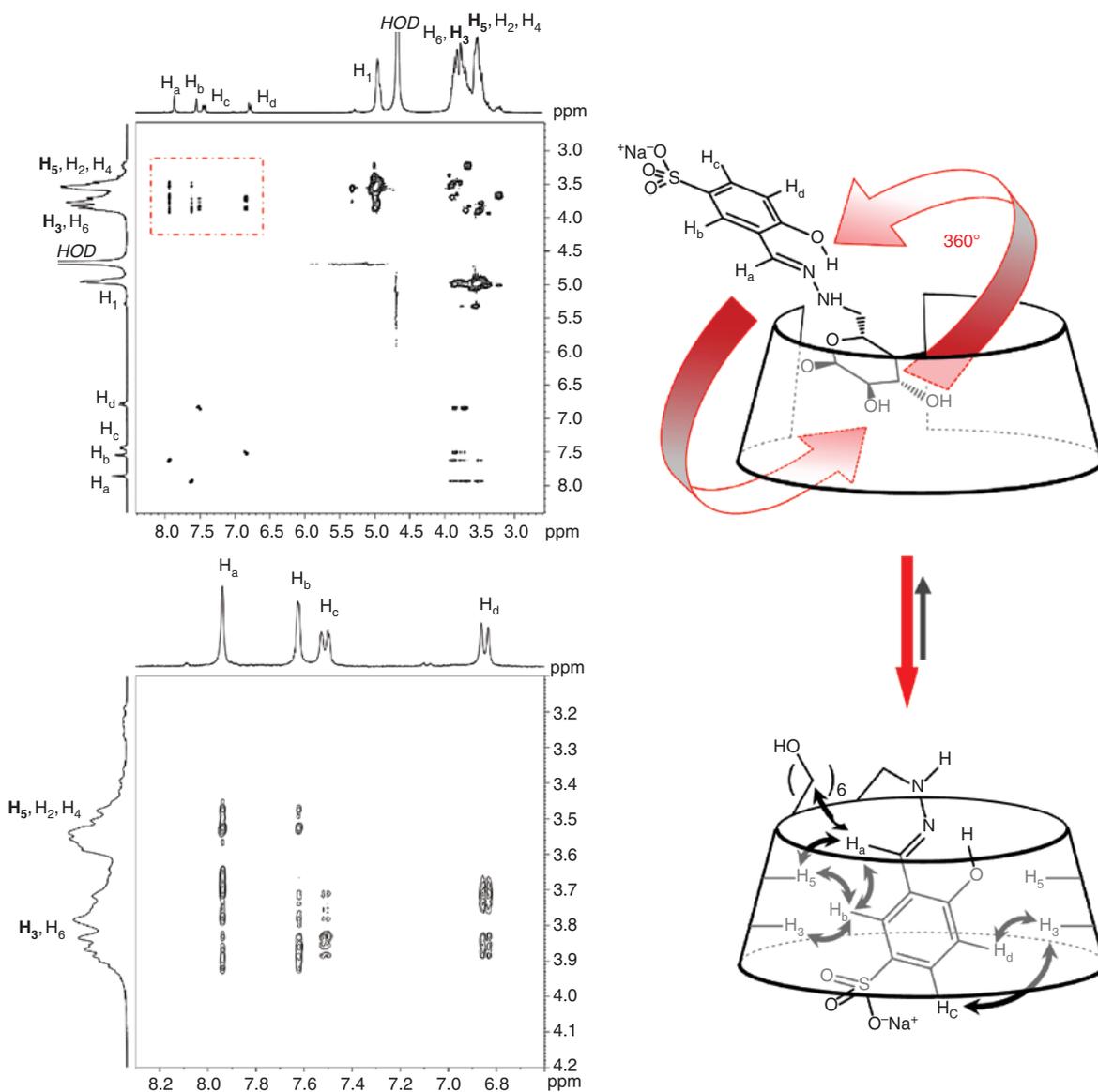


Fig. 2: ROESY NMR spectrum of **5** in D_2O (10 mM, 298 K).

the Schiff base condensation was realized in anhydrous DMF to obtain a higher isolated yield. Again, the synthesized salicylhydrazones were fully characterized (see ESI). Contrary to ligands **3** and **4**, NMR characterisation of these new salicylhydrazones could be done in D_2O without any significant hydrolysis of the ligand.

In order to check the conformation of the CD in ligands **5** and **6**, ROESY experiments were conducted. These experiments could not be carried out with ligands **3** and **4** since these ligands have limited stability in water.

Strong correlations between the aromatic protons of **5** and the CD moiety were highlighted (Fig. 2). Given that these involve the internal protons of the CD (i.e. H_3 and H_5), it can be deduced that inclusion of the salicylic moiety into the CD cavity took place. The salicylate H_a and H_b protons interact preferentially with the internal H_5 and H_3 protons of the CD, respectively. In addition, absence of correlations between salicylate H_c and H_d protons with internal H_5 protons of the CD suggests an inclusion via the primary face of the CD. Moreover, the substitution of the CD with the salicylate moiety has been done on the primary face of the CD, generating steric hindrance on this side. So, all these observations led us to assume a 360° rotation of the glucopyranose unit bearing the salicylate group leading to a self-inclusion of this moiety (Fig. 2). Such behavior is common for these macrocycles [28, 29].

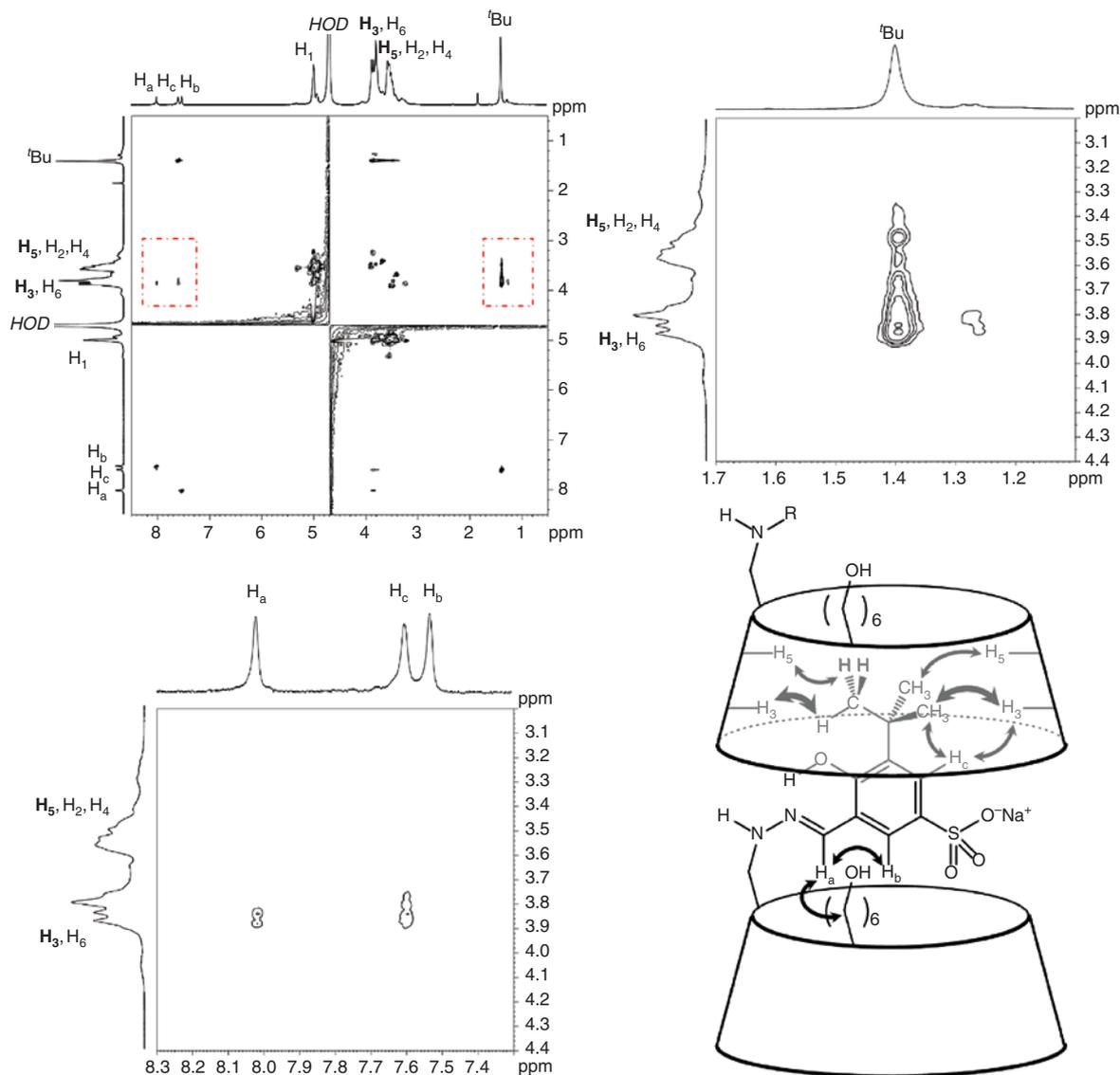


Fig. 3: ROESY NMR spectrum of **6** in D_2O (10 mM, 298 K).

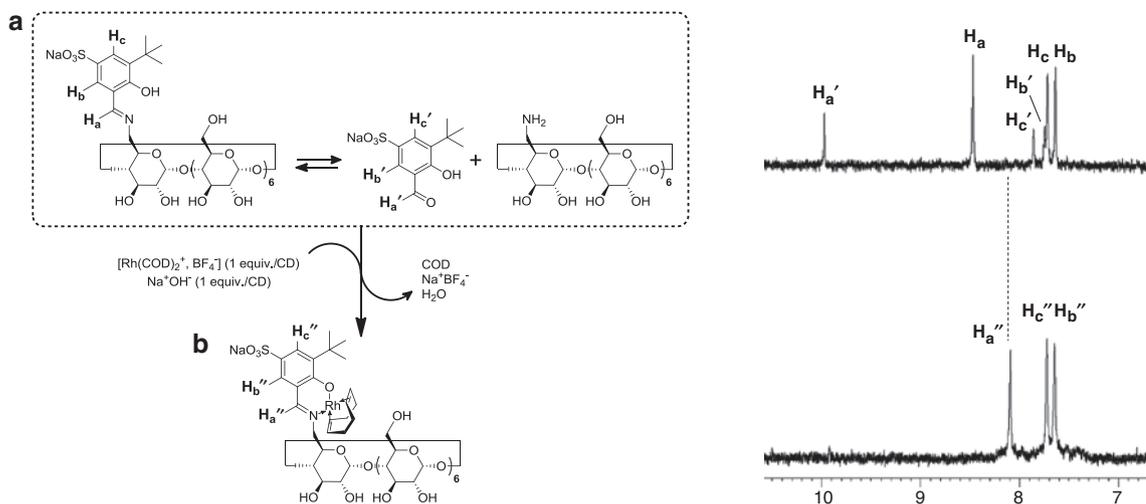


Fig. 4: ^1H NMR in D_2O (10 mM, under N_2 and at 20°C) of (a) ligand **4** and (b) complex Rh-**4**.

However, the complexation phenomenon with ligand **6** seems to be different. Strong correlation between the *tert*-Butyl group of the salicylate moiety and the internal CD protons combined with weak interactions between the aromatic protons of the salicylic moiety and the internal CD protons suggests an inter-inclusion with CD cavity occupied by the *tert*-Butyl group (Fig. 3). Indeed, in the case of a self-inclusion, strong correlations would also appear with the aromatic protons. The strongest correlation was observed between the internal H_3 proton of the CD and the *tert*-Butyl group which suggests an inclusion through the secondary face of the CD (Fig. 3).

Synthesis and characterisation of water-soluble sulfonated Rh(I) complexes

The synthesis of the organometallic rhodium complexes of **3**, **4**, **5** and **6** was achieved via two different routes: starting from the Schiff base ligands or starting from sulfonated salicylaldehydes (**1** and **2**) and β -CDNH₂ or β -CDNHNH₂. In both cases, addition of one equivalent of the Rh precursor $[\text{Rh}(\text{COD})_2^+\text{BF}_4^-]$ to an equimolar aqueous solution of salicylaldehydes (**1** or **2**) and β -CD (β -CDNH₂ or β -CDNHNH₂), or Schiff base ligands (**3**, **4**, **5** or **6**) leads to the formation of the rhodium complexes. Infrared spectroscopy of these complexes indicates coordination of the Rh center as the $\nu(\text{C}=\text{N})$ band shifted for example from 1651 cm^{-1} in ligand **4** to 1600 cm^{-1} in the rhodium complex **4** (Rh-**4**). Moreover, the D_2O ^1H NMR spectra of Rh-**4** exhibit an upfield shift of the imine proton from 8.47 ppm to 8.09 ppm (Fig. 4).

Contrary to the metal-free salicylaldimine ligands (**3** and **4**), the corresponding rhodium complexes (Rh-**3** and Rh-**4**) showed a better water-stability. Indeed, no imine hydrolysis was observed in these cases (Fig. 4 for Rh-**4**).

Catalysis

The Schiff base rhodium complexes were then evaluated in the aqueous biphasic hydroformylation of 1-decene as a model reaction (Table 1).

The catalyst was firstly formed by mixing the rhodium precursor $[\text{Rh}(\text{COD})_2^+\text{BF}_4^-]$ in water with both one equivalent of ligand **3** and NaOH. Under 50 bar of CO/H_2 pressure and at 80°C , an olefin conversion of 81%, a selectivity in aldehydes of 72% and a low linear-to-branched aldehyde ratio of 1.4 was obtained after 6 h (entry 1). Unfortunately, the recovered organic layer was completely black at the end of the reaction

complexes were proved to be stable. The salicylhydrazones are, for their part, more stable given that they did not instantly undergo hydrolysis in water. Interest of these new ligands in the aqueous biphasic hydroformylation reaction is rather limited due to a thermal decomposition of the catalysts under CO/H_2 atmosphere leading to a pronounced leaching in the organic layer during the catalytic act. Nevertheless, the use of these ligands in other reactions are currently under investigation in our laboratory.

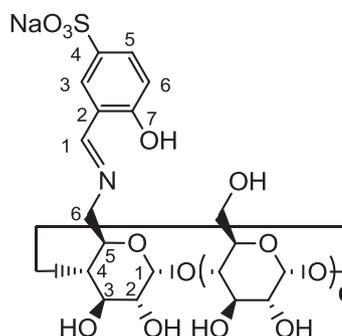
Experimental part

General details

All reagents and solvents were purchased from Fisher Scientific and Aldrich Chemicals in their highest purity. All chemicals were used as supplied without further purification. Sulfonated salicylaldehydes **1** and **2** were prepared according to literature procedure [12]. β -CD was provided by Roquette Frères. 6^A-Deoxy-6^A-amino- β -CD and 6^A-deoxy-6^A-hydrazino- β -CD were synthesized according to slightly modified published procedures [26, 27]. Carbon monoxide/hydrogen mixture (1:1) was used directly from cylinders (>99.9 % pure; air liquide). Distilled water was used in all experiments. NMR spectra were recorded on a Bruker DRX300 spectrometer operating at 300 MHz for ¹H nuclei and 75 MHz for JMOD experiments. DMSO-*d*₆ (99.80 % isotopic purity) and D₂O (99.92 % isotopic purity) were purchased from Euriso-Top. Chemical shifts are given in ppm relative to external reference: sodium [D₄]-3-(trimethylsilyl)propionate (98 % D) in D₂O for ¹H NMR spectra. Gas chromatography analysis were done on a Shimadzu GC-17A gas chromatograph equipped with a poly-dimethylsiloxane capillary column (30 m × 0.32 mm) and a flame ionization detector. Mass spectra were recorded on a MALDI-TOF-TOF Bruker Daltonics Ultraflex II with 2,5-dihydroxybenzoic acid as the matrix.

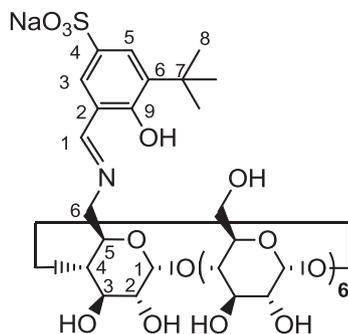
Synthesis of ligands **3**, **4**, **5** and **6**

Ligands **3** and **4** were synthesized following the same procedure: 0.5 g of 6^A-deoxy-6^A-amino- β -CD (4.41×10^{-1} mmol) was dissolved under inert atmosphere in anhydrous NMP (10 mL). One equivalent of the sulfonated salicylaldehyde **1** or **2** was added and the mixture was stirred at 75 °C during 24 h. Then the mixture was cooled at room temperature and precipitation with acetone was realized. After filtration and vacuum drying, the Schiff base ligand was obtained as a light yellow solid (yield = 79 % for **3** and 70 % for **4**).



Ligand **3**

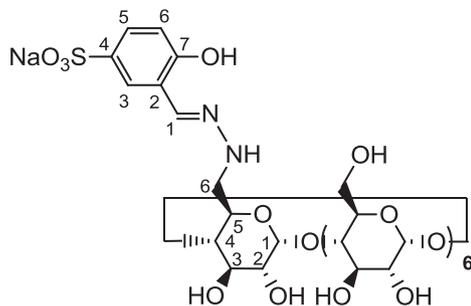
¹H NMR (DMSO, 298 K): δ 3.35 (overlap with HDO, m, 14H, H-2_{CD}, H-4_{CD}); 3.36–4.10 (m, 28H, H-3_{CD}, H-5_{CD}, H-6_{CD}); 4.48–4.65 (bs, 6H, OH-6_{CD}); 4.83 (m, 7H, H-1_{CD}); 5.72 (m, 14H, OH-2_{CD}, OH-3_{CD}); 6.78 (d, ³J₆₋₅ = 8.57 Hz, 1H, H₆); 7.53 (d, ³J₅₋₆ = 8.60 Hz, 1H, H₅); 7.67 (s, 1H, H₃); 8.62 (s, 1H, H₁); 13.85 (bs, 1H, OH₇). JMOD NMR (DMSO, 298 K): δ 49.1 (C-6^A_{CD}); 57.7–60.8 (C-6_{CD}); 70.2 (C-3^A_{CD}); 72.5 (C-5_{CD}); 72.9 (C-2_{CD}); 73.5 (C-3_{CD}); 81.5–82.6 (C-4_{CD}); 84.1 (C-4^A_{CD}); 102.0–103.0 (C-1_{CD}); 116.6 (C₆); 117.3 (C₂); 129.5 (C₃); 130.7 (C₅); 139.0 (C₄); 162.8 (C₇); 167.9 (C₁).



Ligand 4

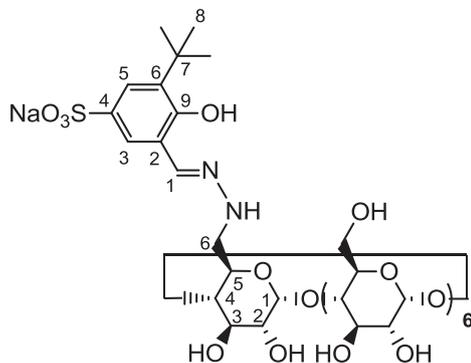
^1H NMR (DMSO, 298 K): δ 1.37 (s, 9H, H_8); 3.35 (overlap with HDO, m, 14H, H-2_{CD} , H-4_{CD}); 3.48–3.98 (m, 28H, H-3_{CD} , H-5_{CD} , H-6_{CD}); 4.48 (bs, H, OH-6_{CD}); 4.87 (bs, 1H, H-1_{CD}); 5.78 (bs, 14H, OH-2_{CD} , OH-3_{CD}); 7.51 (d, $^4J_{3-5} = 1.53$ Hz, 1H, H_3); 7.53 (d, $^4J_{3-5} = 1.53$ Hz, 1H, H_5); 8.59 (s, 1H, H_1); 14.59 (bs, 1H, OH_9). JMOD NMR (DMSO, 298 K): δ 29.5 (C_8); 34.9 (C_7); 58.1 ($\text{C-6}_{\text{CD}}^{\text{A}}$); 60.5 (C-6_{CD}); 70.4 ($\text{C-3}_{\text{CD}}^{\text{A}}$); 72.5 (C-5_{CD}); 72.9 (C-2_{CD}); 73.5 (C-3_{CD}); 82.0 (C-4_{CD}); 84.5 ($\text{C-4}_{\text{CD}}^{\text{A}}$); 102.4 (C-1_{CD}); 117.1 (C_6); 127.4 (C_5); 127.9 (C_3); 136.3 (C_2); 138.0 (C_4); 162.3 (C_9); 168.9 (C_1).

Ligands 5 and 6 were synthesized following the same procedure: 0.1 g of 6^A-deoxy-6^A-hydrazino- β -CD (87 μmol) was dissolved under inert atmosphere in anhydrous DMF (3 mL). One equivalent of the sulfonated salicylaldehyde 1 or 2 was added and the mixture was stirred at room temperature during 1 h. Then, precipitation with THF was realized. After filtration and vacuum drying, the Schiff base ligand was obtained as a light yellow solid (yield = 82 % for 3 and 79 % for 4).



Ligand 5

^1H NMR (D_2O , 298 K): δ 3.15–3.91 (m, 42H, H-2_{CD} , H-3_{CD} , H-4_{CD} , H-5_{CD} , H-6_{CD}); 4.94–5.03 (m, 7H, H-1_{CD}); 6.75 (d, $^3J_{6-5} = 8.67$ Hz, 1H, H_6); 7.47 (dd, $^3J_{5-6} = 8.67$ Hz, $^4J_{5-3} = 2.02$ Hz, 1H, H_5); 7.67 (d, $^4J_{3-5} = 2.02$ Hz, 1H, H_3); 8.03 (s, 1H, H_1). JMOD NMR (D_2O , 298 K): δ 58.7 ($\text{C-6}_{\text{CD}}^{\text{A}}$); 59.4–60.1 (C-6_{CD}); 69.3 ($\text{C-3}_{\text{CD}}^{\text{A}}$); 71.4–72.1 (C-5_{CD} , C-2_{CD}); 72.9–73.3 (C-3_{CD}); 80.4–81.1 (C-4_{CD}); 83.9 ($\text{C-4}_{\text{CD}}^{\text{A}}$); 101.9–102.2 (C-1_{CD}); 115.6 (C_6); 118.8 (C_2); 126.6 (C_3); 127.1 (C_5); 134.8 (C_4); 144.0 (C_1); 158.6 (C_7).



Ligand 6

¹H NMR (D₂O, 298 K): δ 1.40 (s, 9H, H₈); 3.20–3.88 (m, 42H, H-2_{CD}, H-3_{CD}, H-4_{CD}, H-5_{CD}, H-6_{CD}); 5.00 (m, 7H, H₁); 7.53 (s, 1H, H₃); 7.58 (s, 1H, H₅); 8.04 (s, 1H, H₁). **JMOD NMR (D₂O, 298 K):** δ 29.2 (C₈); 34.6 (C₇); 59.8 (C-6^A_{CD}); 60.2 (C-6_{CD}); 69.2 (C-3^A_{CD}); 71.9–72.0 (C-5_{CD}, C-2_{CD}); 73.1 (C-3_{CD}); 79.9–81.1 (C-4_{CD}); 83.4 (C-4^A_{CD}); 101.9–102.5 (C-1_{CD}); 118.4 (C₆); 124.2 (C₅); 125.6 (C₃); 133.3 (C₂); 136.7 (C₄); 145.1 (C₁); 158.1 (C₉).

Catalytic experiments

All the high-pressure hydroformylation experiments were carried out in a 25 mL stainless steel autoclave supplied by Parr. All catalytic reactions were performed under nitrogen using standard Schlenk techniques. [Rh(COD)₂⁺BF₄⁻] (41 μ mol) and ligand **3**, **4**, **5** or **6** (1 equiv.) were dissolved in 11.5 mL of degassed water under an inert atmosphere and mixed together overnight. The resulting aqueous phase and an organic phase composed of 1-decene (2.85 g; 500 equiv.) were charged under an inert atmosphere into the 25 mL reactor, which was heated at 60 °C or 80 °C. Mechanical stirring equipped with a multi-paddle unit was then started (1500 rpm) and the autoclave was pressurized with 20 bar or 50 bar of CO/H₂ (1:1) from a gas reservoir connected to the reactor through a high pressure regulator valve keeping the pressure in the reactor constant throughout the whole reaction. The reaction medium was sampled after 6 h of reaction for NMR analyses of the organic phase after decantation.

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References

- [1] S. Mecking, A. Held, F. M. Bauers. *Angew. Chem. Int. Ed.* **41**, 544 (2002).
- [2] F. M. Bauers, S. Mecking. *Macromolecules* **34**, 1165 (2001).
- [3] M. A. Zuideveld, P. Wehrmann, C. Röhr, S. Mecking. *Angew. Chem. Int. Ed.* **43**, 869 (2004).
- [4] E. G. Bowes, G. M. Lee, C. M. Vogels, A. Decken, S. A. Westcott. *Inorg. Chim. Acta* **377**, 84 (2011).
- [5] B. J. Tardiff, J. C. Smith, S. J. Duffy, C. M. Vogels, A. Decken, S. A. Westcott. *Can. J. Chem.* **85**, 392 (2007).
- [6] J. B. Binder, I. A. Guzei, R. T. Raines. *Adv. Synth. Catal.* **349**, 395 (2007).
- [7] B. Korthals, I. Göttker-Schnetmann, S. Mecking. *Organometallics* **26**, 1311 (2007).
- [8] H. Brunner, C. Keck. *Zeitschrift Anorg. und Allg. Chemie* **631**, 2555 (2005).
- [9] M. Bakherad, A. Keivanloo, B. Bahramian, M. Hashemi. *Tetrahedron Lett.* **50**, 1557 (2009).
- [10] L. Yu, X. Jiang, L. Wang, Z. Li, D. Wu, X. Zhou. *Eur. J. Org. Chem.* **2010**, 5560 (2010).
- [11] L. C. Matsinha, S. F. Mapolie, G. S. Smith. *Dalton Trans.* **44**, 1240 (2014).
- [12] E. B. Hager, B. C. E. Makhubela, G. S. Smith. *Dalton Trans.* **41**, 13927 (2012).
- [13] S. Siangwata, N. Baartzes, B. C. E. Makhubela, G. S. Smith. *J. Organomet. Chem.* **796**, 26 (2015).
- [14] F. Hapiot, H. Bricout, S. Tilloy, E. Monflier. *Eur. J. Inorg. Chem.* **2012**, 1571 (2012).
- [15] R. Gramage-Doria, D. Armspach, D. Matt, L. Toupet. *Dalton Trans.* **41**, 8786 (2012).
- [16] F. Hapiot, S. Tilloy, E. Monflier. *Chem. Rev.* **106**, 767 (2006).
- [17] F.-X. Legrand, M. Ménand, M. Sollogoub, S. Tilloy, E. Monflier. *New J. Chem.* **35**, 2061 (2011).
- [18] M. Guitet, F. Marcelo, S. A. de Beaumais, Y. Zhang, J. Jiménez-Barbero, S. Tilloy, E. Monflier, M. Ménand, M. Sollogoub. *Eur. J. Org. Chem.* **2013**, 3691 (2013).
- [19] D. N. Tran, F.-X. Legrand, S. Menuel, H. Bricout, S. Tilloy, E. Monflier. *Chem. Commun.* **48**, 753 (2012).
- [20] J. Leblond, J. Potier, S. Menuel, H. Bricout, C. Machut-Binkowski, D. Landy, S. Tilloy, E. Monflier, F. Hapiot. *Catal. Sci. Technol.* **7**, 3823 (2017).
- [21] F.-X. Legrand, N. Six, C. Slomianny, H. Bricout, S. Tilloy, E. Monflier. *Adv. Synth. Catal.* **353**, 1325 (2011).
- [22] E. Deunf, E. Zaborova, S. Guieu, Y. Blériot, J. N. Verpeaux, O. Buriez, M. Sollogoub, C. Amatore. *Eur. J. Inorg. Chem.* **2010**, 4720 (2010).
- [23] A. Puglisi, G. Tabbi, G. Vecchio. *J. Inorg. Biochem.* **98**, 969 (2004).
- [24] V. Lanza, G. Vecchio. *J. Inorg. Biochem.* **103**, 381 (2009).

- [25] R. Breslow, X. Zhang, R. Xu, M. Maletic, R. Merger. *J. Am. Chem. Soc.* **118**, 11678 (1996).
- [26] W. Tang, S.-C. Ng. *Nat. Protoc.* **3**, 691 (2008).
- [27] K. A. Martin, M. A. Mortellaro, R. W. Sweger, L. E. Fikes, D. T. Winn, S. Clary, M. P. Johnson, A. W. Czarnik. *J. Am. Chem. Soc.* **117**, 10443 (1995).
- [28] J. Potier, S. Menuel, N. Azaroual, E. Monflier, F. Hapiot. *Eur. J. Org. Chem.* **2014**, 1547 (2014).
- [29] S. Menuel, N. Azaroual, D. Landy, N. Six, F. Hapiot, E. Monflier. *Chem. Eur. J.* **17**, 3949 (2011).

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