

# Hydroformylation of 1-Octene in Supercritical Carbon Dioxide with Alkyl P-Donor Ligands on Rhodium Using a Peracetylated $\beta$ -Cyclodextrin as a Solubiliser

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**Keywords:** Hydroformylation / Supercritical carbon dioxide / Rhodium / Cyclodextrins / P ligands

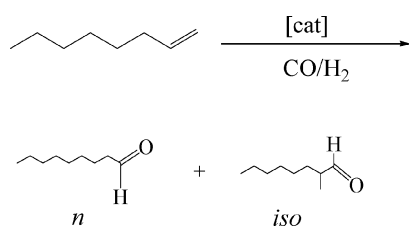
The presence of peracetylated  $\beta$ -cyclodextrin in the reaction medium allowed for an increase in the solubility of rhodium species modified by alkyl P-donor ligands in the catalytic hydroformylation of 1-octene in supercritical carbon dioxide. These results were explained by considering an interaction

between the peracetylated  $\beta$ -cyclodextrin and the P-donor ligands.

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## Introduction

Hydroformylation involves the addition of carbon monoxide and hydrogen to a carbon–carbon double bond to form the corresponding linear and branched aldehydes. The reaction (Scheme 1) is mostly accomplished with a rhodium- or cobalt-based catalyst.<sup>[1]</sup> The main products are used for the production of alcohols, carboxylic acids, aldol products, diols, acetals, ethers, acroleins and esters.<sup>[2]</sup> Specifically, the hydroformylation of 1-octene is performed in the production of plasticizer alcohols and biodegradable detergents.<sup>[1]</sup>



Scheme 1. Hydroformylation of 1-octene.

The application of supercritical carbon dioxide (scCO<sub>2</sub>) as a reaction medium in homogeneous catalysis has been investigated by a number of research groups in recent years since it is inert, nontoxic, nonflammable, cheap, readily available and environmentally acceptable.<sup>[3]</sup> In addition, gases are completely miscible with scCO<sub>2</sub>; therefore, gas-

phase reactant concentrations would be higher in it than in organic solvents.<sup>[4]</sup>

Unfortunately, ionic and polar reagents are generally not very soluble in scCO<sub>2</sub>, which restricts its application in catalytic processes.<sup>[4]</sup> To overcome this limitation, ligands modified by the incorporation of perfluorinated chains,<sup>[5]</sup> polysilanes<sup>[6]</sup> and carbonyl groups<sup>[7]</sup> have been employed. Other possibilities include the use of soluble surfactants or mass transfer agents, which induce the formation of micelles with a high-density fluid phase<sup>[8,9]</sup> and thus increase the solubility of the catalyst in the scCO<sub>2</sub>.

It has recently been reported that peracetylated cyclodextrin exhibits a high degree of miscibility with dense CO<sub>2</sub> over a broad range of concentrations.<sup>[10]</sup> Interestingly, Monflier et al. have recently demonstrated that peracetylated  $\beta$ -cyclodextrin has a great ability to form inclusion complexes with various arylphosphanes in a scCO<sub>2</sub> medium.<sup>[11]</sup> A similar phenomenon had also been observed with sulfonated arylphosphanes in water by using hydro-soluble cyclodextrins.<sup>[12]</sup>

In a previous work we reported the use of P-donor ligands (**1–3**, Figure 1) containing a branched alkylic chain in the hydroformylation of 1-octene in supercritical carbon

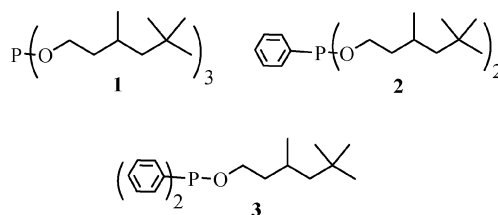


Figure 1. P-donor ligands containing a branched alkylic chain used in the hydroformylation of 1-octene in scCO<sub>2</sub>: phosphite ligand (**1**), phosphonite ligand (**2**) and phosphinite ligand (**3**).

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dioxide. These ligands formed rhodium catalytic systems that were not soluble in  $\text{scCO}_2$ . Despite this fact, conversions up to 82% and selectivities up to 94% were achieved using these systems.<sup>[13]</sup> Therefore, we considered the possibility of increasing the solubility of these catalytic systems in  $\text{scCO}_2$  by forming inclusion complexes between the peracetylated cyclodextrin and the ligands.

Here we present the hydroformylation of 1-octene with the  $[\text{Rh}(\text{acac})(\text{CO})_2]$  catalytic system associated with branched alkyl phosphite, phosphonite and phosphinite ligands (**1–3**, Figure 1) in supercritical carbon dioxide with a peracetylated cyclodextrin as a mass transfer promoter (Figure 2).

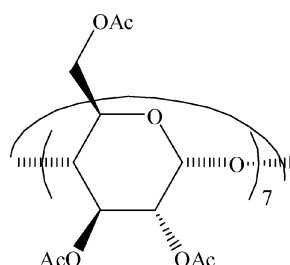


Figure 2. Peracetylated cyclodextrin (Per-Ac- $\beta$ -CD).

## Results and Discussion

Ligands **1–3** were synthesised as reported by Giménez et al. by the reaction of the commercially available 3,5,5-trimethylhexanol with phosphorus trichloride or the corresponding chlorophenylphosphane in diethyl ether in the presence of pyridine.<sup>[13]</sup> Peracetylated  $\beta$ -cyclodextrin was purchased from Aldrich Chemicals and used without further purification. This CD is a cyclic oligosaccharide composed of seven D-glucopyranose residues linked by  $\alpha$ -(1,4) bonds. Each glucopyranose unit was fully acetylated.

### Inclusion Studies

As the formation of inclusion complexes is difficult to prove experimentally in supercritical conditions, some attempts to observe the interaction between ligand **1** and Per-Ac- $\beta$ -CD were performed by using toluene as a solvent instead of supercritical  $\text{CO}_2$ . Unfortunately, the formation of inclusion species in toluene was rejected by analysing the reactivity of the  $[\text{Rh}(\text{acac})(\text{CO})_2]/\mathbf{1}$  system in the presence of Per-Ac- $\beta$ -CD with CO and  $\text{H}_2$  with high-pressure NMR spectroscopy. Indeed, the species detected in these conditions were comparable to the ones reported by us without the cyclodextrin:<sup>[13]</sup> the major species observed in the  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra were  $[\text{RhH}(\text{CO})(\mathbf{1})_3]$  and  $[\text{RhH}(\text{CO})_2(\mathbf{1})_2]$ . It must be noted that this result is not surprising as the formation of inclusion complexes in organic media is seldom observed with cyclodextrin derivatives because of the lack of hydrophobic forces. Nevertheless, inclusion complexes may be formed in  $\text{scCO}_2$ .

In this context, the ability of Per-Ac- $\beta$ -CD to form inclusion complexes with ligands **1–3** was investigated by performing quantum chemical calculations on the Per-Ac- $\beta$ -CD/ligand systems.

For the Per-Ac- $\beta$ -CD/**1** system, the inclusion complex was constructed using geometries separately optimised for Per-Ac- $\beta$ -CD and for **1**. The glycosidic oxygen atoms of Per-Ac- $\beta$ -CD were placed onto the  $XY$  plane and their centre was defined as the centre of the coordination system. The complexation of **1** was then investigated by moving one of its alkylic chains along the  $Z$  axis at fixed increments of 0.2 Å. All energy minimizations were performed without any geometry constraints. Two different inclusion orientations were considered: the orientation in which **1** points toward the narrower native  $\beta$ -CD ring (containing 7 acetyl groups), indicated here as the primary rim, and the other in which **1** points toward the wider native  $\beta$ -CD rim (containing 14 acetyl groups), indicated here as the secondary rim. Figure 3 depicts the stabilisation energy variation of the inclusion processes of **1** with Per-Ac- $\beta$ -CD at different distances and orientations.

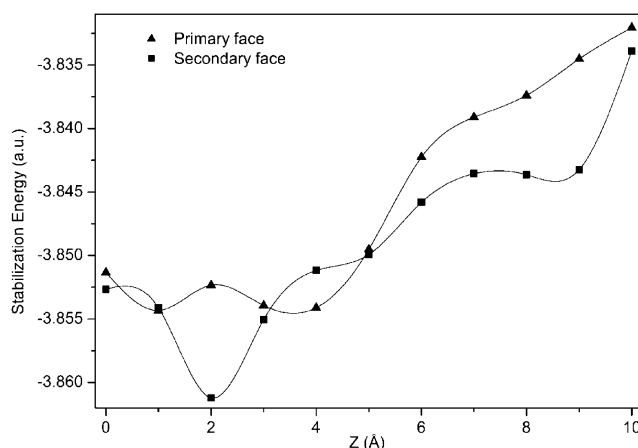


Figure 3. Graphic diagram for the inclusion process of the phosphite **1** with Per-Ac- $\beta$ -CD through the primary ( $\blacktriangle$ ) and secondary ( $\blacksquare$ ) faces.

In both cases, favourable interactions take place between the two species. The energy of the complex decreases as the alkylic chain enters into the Per-Ac- $\beta$ -CD cavity, and again increases because of crowding (i.e. steric hindrance) between the alkylic chains remaining outside the cavity and the acetyl groups of the Per-Ac- $\beta$ -CD rims. However, we notice that the more favourable minimum energy structure of the Per-Ac- $\beta$ -CD/**1** complex occurs through the secondary rim. Figure 4 (a) displays the computer-generated structure of this complex.

The energy variation involved in the inclusion emulsion indicates that the complexes prefer to adopt an inclusion geometry with the alkyl chain inside the host cavity in order to increase the van der Waals attraction between the host and guest. This is supported by the van der Waals surfaces of the Per-Ac- $\beta$ -CD/**1** complex [see Figure 4 (b and c)], where one can clearly see that the alkylic chain of the phos-

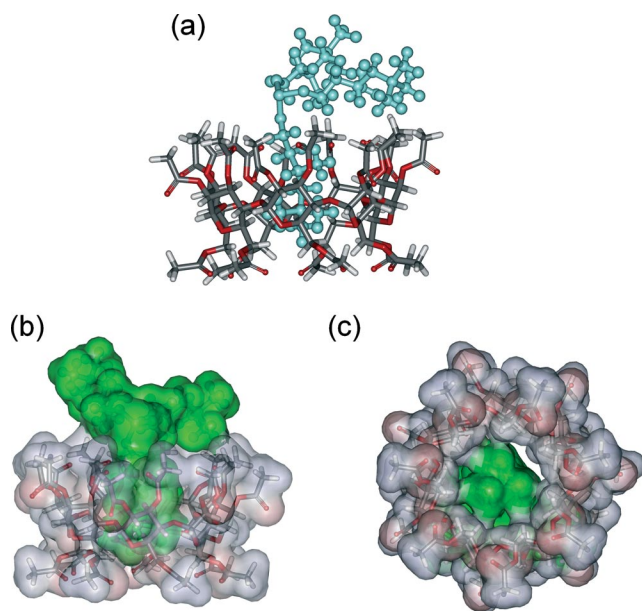


Figure 4. (a) Side view of the computer-generated structure of the Per-Ac- $\beta$ -CD/1 inclusion complex. (b) Side view and (c) bottom view of the van der Waals surfaces of the Per-Ac- $\beta$ -CD/1 inclusion complex.

phite **1** fits tightly in the Per-Ac- $\beta$ -CD cavity, which leads to the formation of stable inclusion complexes.

For ligands **2** and **3**, calculations also confirm that Per-Ac- $\beta$ -CD can host an alkylic chain of the ligand in its cavity. Figure 5 shows the most stable computer-generated structure of the Per-Ac- $\beta$ -CD/2 and Per-Ac- $\beta$ -CD/3 inclusion complexes.

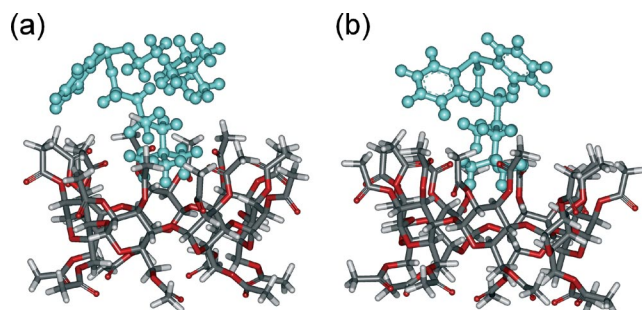


Figure 5. Side view of the computer-generated structure of the (a) Per-Ac- $\beta$ -CD/2 and (b) Per-Ac- $\beta$ -CD/3 inclusion complexes.

The possibility of including one of the ligand's aromatic rings into the Per-Ac- $\beta$ -CD cavity was also investigated and calculations indicated that this could hardly occur.

By comparing Figures 4 and 5, it is clear that ligand **1** is positioned more deeply in the Per-Ac- $\beta$ -CD cavity than ligands **2** and **3**, which strongly suggests that the Per-Ac- $\beta$ -CD/1 inclusion complex is more stable than the two others. The shallower penetration of ligands **2** and **3** into the CD cavity is likely a consequence of the steric hindrance between the external aromatic ring and the  $\beta$ -CD border.

## Solubility Studies

As ligand **1** has the greater ability of interaction with the Per-Ac- $\beta$ -CD, solubility studies were performed with it. The solubility of the new  $[\text{Rh}(\text{acac})(\text{CO})_2]/1/\text{Per-Ac-}\beta\text{-CD}$  catalytic system was studied in an autoclave equipped with view windows. In a previous work, we observed by visual inspection through the windows of the autoclave that the  $[\text{Rh}(\text{acac})(\text{CO})_2]/1\text{--}3$  catalytic systems had no apparent solubility in  $\text{scCO}_2$  up to 240 atm and 80 °C.<sup>[13]</sup> When similar solubility studies were performed with  $[\text{Rh}(\text{acac})(\text{CO})_2]$  ( $6 \times 10^{-3}$  M), ligand **1** (P/Rh = 6) and Per-Ac- $\beta$ -CD (Per-Ac- $\beta$ -CD/Rh = 6) in the autoclave with  $\text{CO}/\text{H}_2$  at 20 atm and 80 °C, we observed at 140 atm the formation of an initial suspension, which at 250 atm turned into an orange-coloured solution (Figure 6) (solubility of at least  $6 \times 10^{-3}$  M). The presence of the Per-Ac- $\beta$ -CD favoured the solubility of the species formed under hydroformylation conditions in  $\text{scCO}_2$ .

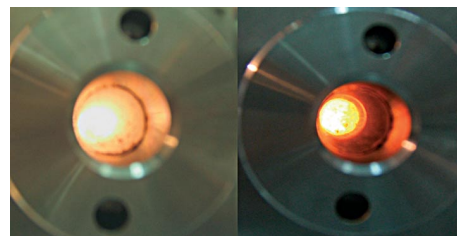


Figure 6. View of the autoclave window for the  $[\text{Rh}(\text{acac})(\text{CO})_2]/1/\text{Per-Ac-}\beta\text{-CD}$  system at 80 °C and at (a) 200 atm and (b) 250 atm (solubilised).

## Hydroformylation of 1-Octene

We performed the catalytic hydroformylation of 1-octene using the in situ formed catalyst precursor  $[\text{Rh}(\text{acac})(\text{CO})_2]/1\text{--}3$  with the addition of peracetylated  $\beta$ -cyclodextrin. The results are summarised in Table 1.

The addition of Per-Ac- $\beta$ -CD has a positive effect on the total conversion when the reaction is performed at conditions of partial solubility (167 atm) (from 49% in entry 1 to 96% in entry 2, Table 1), although the chemoselectivity in aldehydes decreases to 77%. An increase in the amount of internal aldehydes associated with olefin isomerisation was also observed (entry 2, Table 1). The reaction rate increase was attributed to a higher solubility of rhodium species in the reaction medium because of the formation of inclusion complexes between ligand **1** and Per-Ac- $\beta$ -CD. However, the selectivity decrease suggests strongly that the catalytically active species in the presence of Per-Ac- $\beta$ -CD are different from those observed without cyclodextrin.

When the reaction is performed under homogeneous conditions (250 atm), the effect of the addition of Per-Ac- $\beta$ -CD depends on the temperature and CD/Rh ratio. At 100 °C the conversion and the selectivity decrease (entries 3 and 4, Table 1). The decrease in conversion could be due

Table 1. Hydroformylation of 1-octene using [Rh(acac)(CO)<sub>2</sub>]/L(1–3)/Per-Ac-β-CD in scCO<sub>2</sub>.<sup>[a]</sup>

| Entry             | L | CD/Rh | T [°C] | P <sub>CO</sub> [atm] | P <sub>H<sub>2</sub></sub> [atm] | P <sub>TOT</sub> <sup>[b]</sup> [atm] | % Conv. <sup>[c]</sup> | % S <sub>a</sub> <sup>[d]</sup> | <i>n</i> /iso/ <i>int</i> <sup>[e]</sup> | % S <sub>i</sub> <sup>[f]</sup> |
|-------------------|---|-------|--------|-----------------------|----------------------------------|---------------------------------------|------------------------|---------------------------------|------------------------------------------|---------------------------------|
| 1 <sup>[g]</sup>  | 1 | 0     | 100    | 10                    | 10                               | 167                                   | 49                     | 90                              | 80:20:–                                  | 10                              |
| 2                 | 1 | 6     | 100    | 10                    | 10                               | 167                                   | 96                     | 77                              | 45:33:22                                 | 22                              |
| 3 <sup>[g]</sup>  | 1 | 0     | 100    | 10                    | 10                               | 250                                   | 82                     | 89                              | 78:22:–                                  | 11                              |
| 4                 | 1 | 6     | 100    | 10                    | 10                               | 250                                   | 71                     | 71                              | 80:17:3                                  | 29                              |
| 5                 | – | –     | 80     | 10                    | 10                               | 250                                   | 99                     | 20                              | 28:42:30                                 | 80                              |
| 6                 | 1 | 0     | 80     | 10                    | 10                               | 250                                   | 98                     | 76                              | 77:22:1                                  | 24                              |
| 7                 | 1 | 6     | 80     | 10                    | 10                               | 250                                   | 87                     | 84                              | 75:24:1                                  | 16                              |
| 8                 | 1 | 12    | 80     | 10                    | 10                               | 250                                   | 39                     | 20                              | 67:33:–                                  | 80                              |
| 9                 | 1 | 6     | 80     | 2.5                   | 2.5                              | 250                                   | 25                     | 64                              | 70:12:18                                 | 36                              |
| 10 <sup>[h]</sup> | 1 | 6     | 80     | 10                    | 10                               | 250                                   | 23                     | 80                              | 26:48:26                                 | 20                              |
| 11                | 2 | 6     | 80     | 10                    | 10                               | 250                                   | 65                     | 75                              | 44:40:16                                 | 25                              |
| 12                | 3 | 6     | 80     | 10                    | 10                               | 250                                   | 98                     | 54                              | 48:37:15                                 | 46                              |

[a] Reaction conditions: scCO<sub>2</sub>; [Rh(acac)(CO)<sub>2</sub>] = 0.06 mmol; Rh/L = 6, L = 0.36 mmol; 1-octene = 12 mmol; 1-octene/Rh = 200; V = 25 mL; t = 3 h. [b] Total pressure. [c] Total conversion by GC. [d] Selectivity for aldehydes. [e] *int* = 3-ethylheptanal and 4-propylhexanal. [f] Selectivity for internal octenes. [g] Ref.<sup>[13]</sup> [h] substrate = *trans*-2-octene.

to a dilution effect. Upon decreasing the temperature to 80 °C, the addition of Per-Ac-β-CD has an opposite effect: the selectivity improves but the total conversion is ca. 10% lower than without the cyclodextrin (entries 6 and 7, Table 1). It should be noticed that the regioselectivity (*n*/*iso* = 3.5) was of the order expected for this kind of P-donor ligand,<sup>[1b]</sup> which suggests that Per-Ac-β-CD did not greatly modify the nature of the catalytically active species under these conditions. However, when the reaction was performed at a higher CD/Rh ratio, the conversion and selectivity decreased to 39 and 20% respectively (entry 8, Table 1), which suggests that species without coordinated ligands could be formed at high CD/Rh ratios. This hypothesis was supported by an experiment performed without any ligand. Indeed, the aldehyde selectivity was close to those obtained with CD/Rh = 12 (entry 8 vs. 5, Table 1).

As observed in conditions of partial solubility, the experiments conducted in homogeneous conditions indicate that the addition of Per-Ac-β-CD modifies the nature of the catalytically active species. In fact, the interaction of the Per-Ac-β-CD with **1** likely induced a shift of the equilibrium between the various rhodium species towards the formation of low coordination phosphane rhodium species which are responsible for the formation of the isomerised olefins. It should be noticed that a similar but less marked phenomenon was also observed in the aqueous/organic biphasic hydroformylation reaction promoted by methylated β-cyclodextrins.<sup>[14]</sup>

Since we observed a significant amount of isomerisation, we used the [Rh(acac)(CO)<sub>2</sub>]/**1**/Per-Ac-β-CD system under the same conditions in the hydroformylation of *trans*-2-octene. In this experiment the distribution of aldehydes (entry 10, Table 1) indicates that the isomerisation rate is slower than the hydroformylation rate for this system.

When the [Rh(acac)(CO)<sub>2</sub>]/**2** or **3**/Per-Ac-β-CD systems were used, the conversion obtained was better in the case of **2** and was of the same order for the catalytic system with ligand **3** compared with the analogous systems without the cyclodextrin. Unfortunately, the selectivity in aldehydes was not improved (entries 11 and 12, Table 1).<sup>[13]</sup>

## Conclusions

Peracetylated β-cyclodextrin greatly affects the catalytic behaviour of rhodium complexes modified by branched allylic phosphite ligands in scCO<sub>2</sub>. The addition of peracetylated β-cyclodextrin has a positive effect on the solubility of the catalytic systems through an interaction with the ligand. Nevertheless, this interaction could lead to the formation of low coordination phosphane rhodium species. This phenomenon was explained by a displacement of the equilibria between the various rhodium species.

## Experimental Section

**General:** Reagents were purchased from Aldrich and Fluorochem and used without further purification. 1-octene was filtered through alumina before use. Carbon dioxide (SCF Grade, 99.999%) was supplied by Air Products, carbon monoxide (99.99%) was supplied by Air Liquid and hydrogen C-50 was supplied by Carburios Metalicos.

**Safety Warning:** Experiments involving pressurised gases can be hazardous and must be conducted with suitable equipment and under the appropriate safety conditions only.

High-pressure NMR experiments (HPNMR) were carried out in a 10-mm-diameter sapphire tube with a titanium cap equipped with Teflon/polycarbonate protection.<sup>[15]</sup>

Gas chromatography analyses were performed with a Hewlett–Packard 5890A apparatus in an HP-5 (5% diphenylsilicone/95% dimethylsilicone) column (25 m × 0.2 mm) for the separation of the products and undecane was added as an internal standard after the reaction.

**Calculations:** Calculations were performed at the PM3 level of theory using the GAUSSIAN 03 program.<sup>[16]</sup> The initial geometries were constructed with the help of the Molden program,<sup>[17]</sup> as previously reported.<sup>[18]</sup>

**Catalysis:** Hydroformylation experiments were carried out in a Parr autoclave (25 mL) with magnetic stirring. The autoclave was equipped with a liquid inlet, a gas inlet, a CO<sub>2</sub> inlet and a thermocouple. An electric heating mantle kept the temperature constant.

**Standard Hydroformylation Experiment in scCO<sub>2</sub>:** The [Rh(acac)(CO)<sub>2</sub>] complex (0.06 mmol) and the peracetylated cyclodextrin

(Per-Ac- $\beta$ -CD) (0.36 mmol) were introduced into the evacuated autoclave. Then the autoclave was purged with nitrogen/vacuum cycles. After that, 1-octene (12 mmol) and the ligand (0.36 mmol) were added. The system was pressurised with 20 atm of  $\text{CO}/\text{H}_2$  (1:1), and liquid  $\text{CO}_2$  was introduced until a total pressure of 60 bar was reached. The autoclave was heated to the desired temperature. When thermal equilibrium was reached, the total pressure was adjusted with a Thar syringe pump. After the reaction time, the autoclave was cooled down to 0 °C and depressurised. Undecane was added to the final mixture and this was analysed by GC. The products were identified by GC/MS.

**Solubility Studies:** The solubility studies were carried out in a Thar reactor (100 mL) equipped with sapphire windows and magnetic stirring. The autoclave was charged with the ligand (0.33 mmol), the  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.055 mmol) and the Per-Ac- $\beta$ -CD. The autoclave was purged with nitrogen/vacuum cycles. Then, the reactor was pressurised with  $\text{CO}$ ,  $\text{H}_2$  and  $\text{CO}_2$ . The system was heated to 80 °C, and the total pressure was increased gradually up to 250 atm. The solubility was monitored by visual inspection through the sapphire windows with a mirror due to safety requirements.

**HPNMR:** In a typical experiment, the NMR tube was filled under  $\text{N}_2$  with a solution of  $[\text{Rh}(\text{acac})(\text{CO})_2]$  (0.04 mmol), the ligand **1** (0.24 mmol), the Per-Ac- $\beta$ -CD (0.24 mmol) and  $[\text{D}_8]$ toluene (2 mL). The tube was pressurised to 20 atm of  $\text{CO}/\text{H}_2$  (1:1) and left at 70 °C for 1 h. The NMR spectra were then recorded.

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- [1] a) C. D. Frohning, C. W. Kohlpaintner, in *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**, ch. 2.1, pp. 29; b) P. W. N. M. van Leeuwen, C. Claver (Eds.), *Rhodium Catalyzed Hydroformylation*, Kluwer Academia Publishers, Dordrecht, **2000**.
- [2] A. M. Trzeciak, J. J. Ziolkowski, *Coord. Chem. Rev.* **1999**, 190–192, 883–900.
- [3] P. G. Jessop, W. Leitner (Eds.), *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, Weinheim, New York, **1999**.
- [4] a) P. G. Jessop, T. Ikariya, R. Noyori, *Chem. Rev.* **1999**, 99, 475–493; b) W. Leitner, *Acc. Chem. Res.* **2002**, 35, 746–756; c) D. J. Cole-Hamilton, *Science* **2003**, 299, 1702–1706; d) P. G. Jessop, *J. Supercrit. Fluids* **2006**, 38, 211–231.
- [5] Some examples are found in: a) S. Kainz, D. Koch, W. Baumann, W. Leitner, *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 1628–1630; b) A. M. Banet Osuna, W. Chen, E. G. Hope, R. D. W. Kemmitt, D. R. Paige, A. M. Stuart, J. Xiao, L. Xu, *J. Chem. Soc., Dalton Trans.* **2000**, 4052–4055; c) D. R. Palo, C. Erkey, *Organometallics* **2000**, 19, 81–86.
- [6] a) M. F. Sellin, I. Bach, J. M. Webster, F. Montilla, V. Rosa, T. Avilés, M. Poliakoff, D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* **2002**, 4569–4576; b) F. Montilla, V. Rosa, C. Prevete, T. Avilés, M. Nunes da Ponte, D. Masi, C. Mealli, *Dalton Trans.* **2003**, 2170–2176; c) F. Montilla, A. Galindo, R. Andrés, M. Córdoba, E. de Jesús, C. Bo, *Organometallics* **2006**, 25, 4138–4143.
- [7] a) Y. Hu, W. Chen, L. Xu, J. Xiao, *Organometallics* **2001**, 20, 3206–3208; b) C. D. Ablan, D. Sheppard, E. J. Beckman, M. M. Olmstead, P. G. Jessop, *Green Chem.* **2005**, 7, 590–594.
- [8] J. Eastoe, A. Dupont, D. C. Steytler, *Curr. Opin. Colloid Interface Sci.* **2003**, 8, 267–273.
- [9] G. B. Jacobson, C. T. Lee, K. P. Johnston, *J. Org. Chem.* **1999**, 64, 1201–1206.
- [10] a) V. K. Potluri, J. Xu, R. Enick, E. Beckman, A. D. Hamilton, *Org. Lett.* **2002**, 4, 2333–2335; b) V. K. Potluri, A. D. Hamilton, C. F. Karanikas, S. E. Bane, J. Xu, E. J. Beckman, R. M. Enick, *Fluid Phase Equilib.* **2003**, 211, 211–217.
- [11] a) G. Filardo, M. Di Blasi, A. Galia, A. Ponchel, H. Bricout, A. D. Sayede, E. Monflier, *J. Supercrit. Fluids* **2006**, 36, 173; b) A. Galia, E. C. Navarre, O. Scialdone, M. Ferreira, G. Filardo, S. Tilloy, E. Monflier, *J. Phys. Chem. B* **2007**, 111, 2573.
- [12] a) M. Canipelle, L. Caron, C. Christine, S. Tilloy, E. Monflier, *Carbohydr. Res.* **2002**, 337, 281–286; b) L. Caron, C. Christine, S. Tilloy, E. Monflier, D. Landy, S. Fourmentin, G. Surpateanou, *Supramol. Chem.* **2002**, 14, 11–20; c) E. Monflier, S. Tilloy, C. Méliet, A. Mortreux, D. Landy, S. Fourmentin, G. Surpateanou, *New J. Chem.* **1999**, 23, 469–472.
- [13] M. Gimenez-Pedros, A. Aghmiz, N. Ruiz, A. M. Masdeu-Bultó, *Eur. J. Inorg. Chem.* **2006**, 1067–1075.
- [14] E. Monflier, H. Bricout, F. Hapiot, S. Tilloy, A. Aghmiz, A. M. Masdeu-Bultó, *Adv. Synth. Catal.* **2004**, 346, 425–431.
- [15] A. Cusanelli, U. Frey, D. T. Richens, A. Merbach, *J. Am. Chem. Soc.* **1996**, 118, 5265–5271.
- [16] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. M. Junior, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *GAUSSIAN 03 program*, Gaussian, Inc., Pittsburgh PA, **2003**.
- [17] G. Schaftenaar, J. H. Noordik, *J. Comput. Aid. Mol. Des.* **2000**, 14, 123–134.
- [18] A. D. Sayede, A. Ponchel, G. Filardo, A. Galia, E. Monflier, *J. Mol. Struct.* **2006**, 777, 99–106.

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