

## Micellar effect in rhodium catalysed hydroformylation of high olefin in water

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*High linear alkenes (1-octene and 1-decene) have been hydroformylated using water-soluble rhodium complexes associated with sulfonated diphosphines in the presence of ionic surfactants, a dendrimer or methanol. In all cases, the hydroformylation activities were higher than in experiments without additives. The selectivity in aldehydes was higher when we used cetyltrimethylammoniumhydrogensulfate (CTAHSO<sub>4</sub>) as the surfactant or methanol as the co-solvent.*

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# 3

*This chapter was published in a slightly modified form: Marta Giménez-Pedrós, Ali Aghmiz Carmen Claver, Anna M. Masdeu-Bultó and Denis Sinou, *J. Mol. Catal A: Chemical*. 2003, 200, 157-163*

### 3.1. Introduction

The catalytic hydroformylation of long chain alkenes is an interesting reaction for transforming alkenes into aldehydes using carbon monoxide and hydrogen [1, 2]. The hydroformylation of linear olefins is a well-known industrial process and a key step in the manufacture of oxo alcohols.

Hydroformylation can be carried out in biphasic aqueous systems using a rhodium catalyst associated with the water-soluble ligand sodium trisulfonated triphenylphosphine (TPPTS =  $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$ ) [3]. Since this system was first used in 1984 by Rhône-Poulenc/Ruhr-Chemie in the industrial hydroformylation of propene [4, 5, 6], research into biphasic catalysis has become very active [7]. However, this process is limited to short-chain alkenes (propene and 1-butene) because a certain solubility of the alkene in water is required [8]. This process is therefore not economically viable for long-chain alkenes, which are not very soluble in water. One way to increase the solubility of the substrates in water is to add surfactants to the system [7]. The amphiphilic nature of these substances drastically lowers the surface tension of water because aggregates such as micelles or vesicles form above the critical micelle concentration (c.m.c) [9]. These aggregates increase the solubility of hydrophobic substances thus improving the mass transfer [10, 11]. This strategy has been used in the hydroformylation of alkenes with Rh-TPPTS systems [12, 13, 14]. In the hydroformylation of 1-dodecene, the activity increases in the presence of cationic surfactants such as cetyltrimethylammonium bromide (CTAB). In hydroformylation of  $\omega$ -alkene carboxylic acids methyl esters up to  $\omega$ -decene, cationic tensids were the best systems. The hydroformylation of alkenes between  $C_6$ - $C_{16}$  in reverse micellar systems has been studied by Vyve and Renken using sodium dodecylsulfate (SDS) in association with butanol as a co-solvent [15]. Reaction rates were

high in the hydroformylation of 1-dodecene with Rh-TPPTS in a microemulsion using nonionic surfactants of alkylpolyglycoether [16].

Dendrimers are perfect monodisperse macromolecules with a regular and highly branched three-dimensional architecture [17]. Dendritic macromolecules contain a large number of symmetrically arranged branches that result in a three-dimensional globular shape. At high molecular weights these structures may approximate spheres. Functionalising dendrimers with hydrophilic groups on the periphery, they adopt structures that resemble micelles. These micelles are a new class of dendritic macromolecules where an interior hydrophobic is surrounded by a hydrophilic surface. Dendrimers with carboxylate chain ends act as micelles in water since their hydrophobic interior dissolves organic molecules that are insoluble in water. Therefore, these macromolecules may act as surfactants. Fréchet et al [18] reported the synthesis of a “*unimolecular micelle*” based on a polyether structure that contained carboxylate groups on the surface and they tested its solubilization properties in water using pyrene as model. They found that polyether dendrimers were powerful solubilizers, and showed that the dendrimer can solubilize pyrene in water at concentrations ( $5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ) lower than the ones needed for sodium dodecylsulfate (SDS) ( $8.1 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ ).

Another way to increase the solubility of alkenes in water is to add a co-solvent to the system. This was widely studied in catalytic systems using water-soluble rhodium complexes and TPPTS as a ligand. For example, the hydroformylation of 1-octene was studied in the presence of co-solvents such as ethanol, methanol, acetonitrile and acetone [19]. The co-solvents increase the concentration of alkene in water. The best result was obtained when

ethanol was used as the co-solvent. Adding alcohols as co-solvents was also studied by Bahrmann and Bogdanovic [20], who found that the reaction rate was enhanced when MeOH was added.

Diphosphines generally provide higher selectivities in hydroformylation in organic media [21, 22], but the sulfonated diphosphines have hardly been investigated. This is probably because it is difficult to prepare pure sulfonated ligands.

The sulfonated biphenyl derivative BISBIS [8, 23, 24] and BINAS [25] associated with the  $[\text{Rh}(\text{acac})(\text{CO})_2]$  complex (acac = acetylacetonate) has higher activities and selectivities than the rhodium-TPPTS system in the hydroformylation of propene under the same reaction conditions. The BISBIS-Na system is also active in the hydroformylation of higher olefins such as 1-hexene.

Alkyl sulfonated diarylphosphines have hardly been studied in hydroformylation. The system Rh-dppets (dppets:  $(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})\text{P}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_2$ ) [26] gave a low conversion in the hydroformylation of 1-octene. The  $[\text{Rh}(\text{acac})(\text{CO})_2]/\text{dppbts}$  system (dppbts:  $(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})\text{P}(\text{CH}_2)_4\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_2$ ) has also been studied in the hydroformylation of methyl acrylate but this provided very poor chemo- and regioselectivity [27].

We recently studied the use of chiral sulfonated diphosphines as ligands in the rhodium asymmetric hydroformylation of styrene in a biphasic aqueous system. The conversions in water were low but the enantiomeric excesses were quite similar to those reported for organic solvents [28, 29].

In this paper, we describe how adding anionic and cationic surfactants, sodium dodecylsulfate (SDS) and cetyl trimethylammonium hydrogensulfate (CTAHSO<sub>4</sub>), and a polyether dendritic molecule (dendrimer **12**) respectively,

affects the hydroformylation of long-chain alkenes (1-octene and 1-decene) in the presence of the rhodium complexes  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$  (cod = 1,5-cyclooctadiene) associated with sulfonated diphosphines.

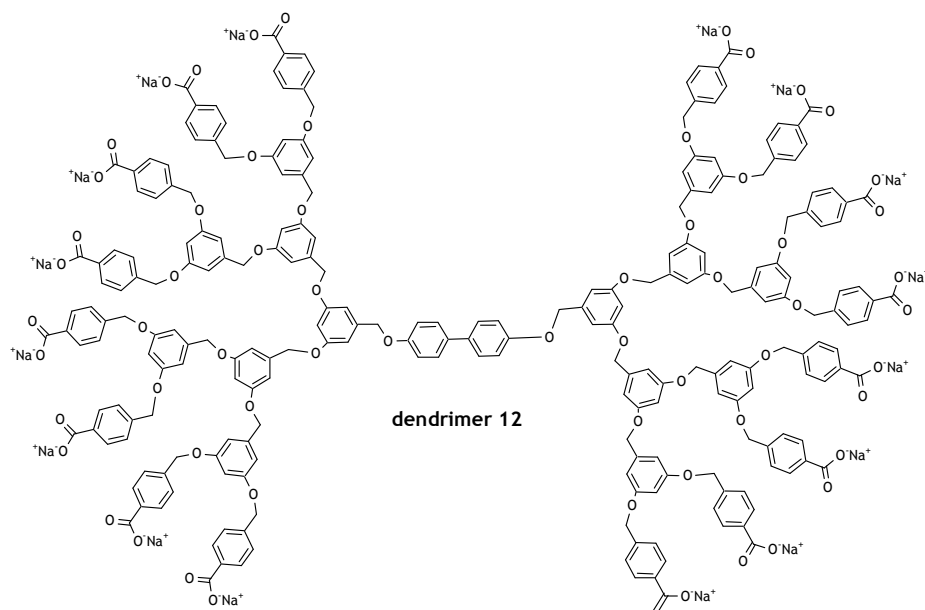


Figure 1.

### 3.2. Experimental

#### *General methods*

The rhodium catalyst precursors were synthesised using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. All other reagents were used as supplied. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and NMR spectra were recorded on a Varian Gemini spectrometer operating at <sup>1</sup>H (300 or 400 MHz), <sup>13</sup>C (75.43 or 100.57 MHz), Chemical shifts were reported relative to tetramethylsilane for <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} as internal

reference. Mass spectrometry was performed in an Voyager- DP RP spectrometer (EI-HR). The complex  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2$  [30] and the diphosphines dpppts and dppbts were prepared as previously reported [31, 32]. Dendrimer 12 was prepared by a modified previously reported procedure [18]. Gas chromatography analyses were performed using a Hewlett-Packard 5890A chromatograph in an Ultra-2 (5 % diphenylsilicone/95% dimethylsilicone) column (25 m x 0.2 mm  $\varnothing$ ) to separate the products. The pH's were measured with a pH-meter Crison micro pH 2001.

#### *Synthesis of dendrimer 12 (Schemes 1 and 2)*

##### *Procedure I: synthesis of dendritic benzyl alcohols. (3, 5, 7)*

A mixture of the dendritic benzyl bromide (2.05 equiv), 3,5-dihydroxybenzylalcohol **2** (1.00 equiv.), potassium carbonate (2.50 equiv) and 18-crown-6 (0.2 equiv) in acetone was heated at reflux and stirred under nitrogen for 24 h. After this reaction time, the mixture was evaporated under reduced pressure, and the residue was washed with water and dichloromethane. The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 50 ml). The combined extracts were dried with  $\text{MgSO}_4$ , evaporated under reduced pressure and purified by flash chromatography.

##### *Procedure II: synthesis of dendritic benzyl bromides (4, 6, 8)*

Triphenylphosphine (1.25 equiv.) and carbon tetrabromide (1.25 equiv) were added to a solution of dendritic benzyl alcohol (1.00 equiv.) dissolved in the minimum amount of tetrahydrofuran and stirred at room temperature under nitrogen. The reaction was monitored by TLC and additional aliquots of  $\text{CBr}_4$  and  $\text{PPh}_3$  were added at *ca.* 15 min. intervals, if it was necessary to force

completion of reaction. The reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 ml). The combined extracts were dried with MgSO<sub>4</sub>, evaporated under reduced pressure and purified by flash chromatography.

*Synthesis of (MeO<sub>2</sub>C)<sub>2</sub>-[G-1]-OH (3)*

Procedure I was used to prepare this compound from methyl- 4-bromomethylbenzoate **1** (6 g, 0.026 mol), 3,5-dihydroxybenzyl alcohol **2** (1.78 g, 0.037 mol), potassium carbonate (1.65 g, 0.037 mmol) and 18-crown-6 (0.25 g, 0.25 mmol). The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 1:9 ether:CH<sub>2</sub>Cl<sub>2</sub>) to give **3** as a white crystalline solid. 4.46 g (81%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm): 3.55 (t, 1H, OH), 3.92 (s, 6H, OCH<sub>3</sub>), 4.58 (d, 2H, *J* = 5.2 Hz, CH<sub>2</sub>OH), 5.08 (s, 4H, OCH<sub>2</sub>), 6.42 (t, 1H, *J* = 2.8 Hz, ArH), 6.55 (d, 2H, *J* = 1.6 Hz, ArH), 7.42 and 8.03 (AB<sub>q</sub>, 8H, *J* = 8.4 Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm): 52.39, 65.26, 69.55, 101.43, 106.01, 127.17, 129.89, 130.096, 142.23, 144.01, 160.03, 167.06.

*Synthesis of (MeO<sub>2</sub>C)<sub>2</sub>-[G-1]-Br (4)*

Procedure II was used to prepare this compound from (MeO<sub>2</sub>C)<sub>2</sub>-[G-1]-OH **3** (4.46 g, 0.011 mol), triphenylphosphine (3.35 g, 0.013 mol) and carbon tetrabromide (4.23 g, 0.013 mol). The product was purified by flash chromatography eluting with hexane: CH<sub>2</sub>Cl<sub>2</sub> (1:1) and then with gradually increasing proportions of CH<sub>2</sub>Cl<sub>2</sub> (up to pure CH<sub>2</sub>Cl<sub>2</sub>) to give **4** as a crystalline white solid. 4.10 g (80%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm): 3.91 (s, 6H, OCH<sub>3</sub>), 4.39 (d, 2H, CH<sub>2</sub>Br), 5.08 (s, 4H, OCH<sub>2</sub>), 6.51 (t, 1H, *J* = 2.4 Hz, ArH), 6.63 (d, 2H, *J* = 2.4 Hz, ArH), 7.48 and 8.05 (AB<sub>q</sub>, 8H, *J* = 8.0 Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)

$\delta$ (ppm): 33.58, 52.42, 69.68, 102.39, 108.53, 127.23, 130.02, 130.15, 141.93, 159.99, 167.50.

*Synthesis of (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-OH (5)*

Procedure I was used to prepare this compound from (MeO<sub>2</sub>C)<sub>2</sub>-[G-1]-Br **4** (4.10 g, 8.21 mmol), 3,5-dihydroxybenzyl alcohol **2** (0.56 g, 4.1 mmol), potassium carbonate (1.41 g, 0.010 mol) and 18-crown-6 (0.21 g, 0.82 mmol). The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 1:9 ether:CH<sub>2</sub>Cl<sub>2</sub>) to give **5** as a white crystalline solid. 2.90 g (74%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 2.20 (1t, 1H, *J* = 1.4 Hz, OH), 3.92 (s, 12H, OCH<sub>3</sub>), 4.61 (d, 2H, *J* = 5.4 Hz, CH<sub>2</sub>OH), 4.97 and 5.10 (each s, 12H, OCH<sub>2</sub>), 6.45 and 6.53 (each t, 3H, *J* = 2.0 Hz, ArH), 6.55 and 6.64 (each d, 6H, *J* = 2.0 Hz, ArH), 7.42 and 8.03 (AB<sub>q</sub>, 16H, *J* = 8.0 Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 52.17, 65.17, 69.39, 60.72, 101.36, 101.60, 105.64, 106.34, 126.97, 129.68, 129.87, 141.88, 143.52, 159.82, 159.89, 166.84.

*Synthesis of (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-Br (6)*

Procedure II was used to prepare this compound from (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-OH **5** (2.90 g, 2.96 mmol), triphenylphosphine (0.97 g, 3.71 mmol) and carbon tetrabromide (1.23 g, 3.71 mmol). Aliquots were added up to 3 equiv. of PPh<sub>3</sub>/CBr<sub>4</sub> to force the completion of the reaction. The product was purified by flash chromatography eluting with hexane: CH<sub>2</sub>Cl<sub>2</sub> (1:2) and then with gradually increasing proportions of CH<sub>2</sub>Cl<sub>2</sub> (up to pure CH<sub>2</sub>Cl<sub>2</sub>) to give **6** as a crystalline white solid. 2.20 g (71%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 3.92 (s, 12H, OCH<sub>3</sub>), 4.39 (s, 2H, CH<sub>2</sub>Br), 4.95 and 5.09 (each s, 12H, OCH<sub>2</sub>), 6.47 and 6.53 (each t, 3H, *J* = 2.2 Hz, ArH), 6.59 and 6.65 (each d, 6H, *J* = 2.2 Hz, ArH),



7.46 and 8.03 (AB<sub>q</sub>, 16H, *J* = 8.7 Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm): 31.16, 52.33, 69.53, 101.18, 101.73, 105.79, 106.54, 108.56, 127.13, 128.75, 128.91, 129.81, 130.83, 142.07, 159.97, 166.98.

*Synthesis of (MeO<sub>2</sub>C)<sub>8</sub>-[G-3]-OH (7)*

Procedure I was used to prepare this compound from (MeO<sub>2</sub>C)<sub>4</sub>-[G-2]-Br **6** (2.20 g, 2.11 mmol), 3,5-dihydroxybenzyl alcohol **2** (0.14 g, 1.03 mmol), potassium carbonate (0.39 g, 2.80 mmol) and 18-crown-6 (0.05 g, 0.20 mmol). The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 1:9 ether:CH<sub>2</sub>Cl<sub>2</sub>) to give **7** as a white crystalline solid. 2.00 g (94%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>): 2.17 (s, 1H, OH), 3.89 (s, 24H, OCH<sub>3</sub>), 4.59 (d, 2H, *J* = 6.0 Hz, CH<sub>2</sub>OH), 4.93 and 5.05 (each s, 28H, OCH<sub>2</sub>), 6.45-6.62 (m, 21H, ArH), 7.42 and 8.03 (AB<sub>q</sub>, 16H, *J* = 8.0 Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(ppm): 52.41, 64.90, 69.60, 69.94, 101.24, 101.80, 105.83, 106.55, 127.20, 129.88, 130.10, 130.72, 142.09, 160.02, 160.10, 167.05.

*Synthesis of (MeO<sub>2</sub>C)<sub>8</sub>-[G-3]-Br (8)*

Procedure II was used to prepare this compound from (MeO<sub>2</sub>C)<sub>8</sub>-[G-3]-OH **7** (2.00 g, 1.03 mmol), triphenylphosphine (0.32 g, 1.21 mmol) and carbon tetrabromide (0.40 g, 1.21 mmol). Aliquots were added up to 6 equiv. of PPh<sub>3</sub>/CBr<sub>4</sub> to force the completion of the reaction. The product was purified by flash chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub> and then with gradually increasing proportions of ether (up to 3% ether-CH<sub>2</sub>Cl<sub>2</sub>) to give **8** as a white solid. 0.88g (43%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) δ(ppm): 3.92 (s, 24H, OCH<sub>3</sub>), 4.36 (d, 2H, CH<sub>2</sub>Br), 4.94 and 5.05 (each s, 28H, OCH<sub>2</sub>), 6.50-6.51 and 6.60-6.63 (each m, 21H, ArH) and 7.43-8.00 (AB<sub>q</sub>, 32H, *J* = 8.0Hz, PhH). <sup>13</sup>C NMR (CDCl<sub>3</sub>)

$\delta$ (ppm): 33.70, 52.31, 69.54, 69.86, 69.99, 101.73, 102.26, 106.52, 108.32, 127.13, 130.03, 130.48, 139.41, 142.01, 160.00, 166.97.

*Synthesis of  $\{(MeO_2C)_8-[G-3]\}_2-[C]$  (10)*

A mixture of  $(MeO_2C)_8-[G-3]-Br$  **8** (0.88 g, 0.41 mmol), 4-4'-dihydroxybiphenyl **9** (0.035 g, 0.19 mmol), potassium carbonate (0.32 g, 2.32 mmol) and 18-crown-6 (8.00 mg, 0.03 mmol) dissolved in 100 ml of dry tetrahydrofuran was heated at reflux and stirred under nitrogen for 48 h. After the reaction had completed, an excess of **9** (0.35 g, 10 equiv) was added. The mixture was then evaporated under reduced pressure and dissolved into 100 ml of dichloromethane and 100 ml of water. The aqueous layer was extracted with  $CH_2Cl_2$  (3 x 50 ml). The combined extracts were dried with  $MgSO_4$  and evaporated under reduced pressure. The product was purified by flash chromatography eluting with 10% ether- $CH_2Cl_2$  and then with gradually increasing proportions of ether (up to 15% ether- $CH_2Cl_2$ ). The product was obtained as a white solid 0.51 g (89%).  $^1H$  NMR (300MHz,  $CDCl_3$ )  $\delta$ (ppm): 3.88 (s, 48H,  $OCH_3$ ), 4.94 and 5.06 (s, 60H,  $OCH_2$ ), 6.51-6.65 (m, 42H, ArH), 6.90 (A,  $AB_q$ , 4H,  $J = 8.1$  Hz, core), 7.36 (B,  $AB_q$ , 4H,  $J = 8.1$  Hz, core) 7.45 and 7.99 ( $AB_q$ , 64 H,  $J = 8.0$  Hz, PhH).  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$ (ppm): 52.34, 69.54, 69.99, 101.73, 106.61, 127.15, 129.87, 130.05, 139.58, 142.02, 160.01, 166.96.

*Synthesis of  $\{(HO_2C)_8-[G-3]\}_2-[C]$  (11)*

To a solution of  $\{(MeO_2C)_8-[G-3]\}_2-[C]$  **10** (0.51 g, 0.12 mmol) in 14 ml of tetrahydrofuran was added potassium hydroxide (2.00 g, 36 mmol) dissolved in 3 ml of water. Methanol (6 ml) was added to this two-phase system to give a homogeneous solution. The solution was heated at reflux for 6 h during which time a precipitate formed. The reaction mixture was evaporated to

dryness and the residue was redissolved in water and the mixture was heated at reflux for 12 h. After cooling to room temperature, the reaction mixture was added dropwise to stirred mixture of water (300 ml) and glacial acetic acid (10 ml). The precipitate was filtered off and dried to give **11** as a brown solid. 0.44 g (90%).

$^1\text{H}$  NMR (400MHz, DMSO- $d_6$ )  $\delta$ (ppm): 4.99 and 5.14 (s, 60H, OCH<sub>2</sub>), 6.51-6.70 (m, 42H, ArH), 6.80 (A, AB<sub>q</sub>, 4H,  $J = 8.4$  Hz, core), 7.38 (B, AB<sub>q</sub>, 4H,  $J = 8.4$  Hz, core) 7.51 and 7.94 (AB<sub>q</sub>, 64 H,  $J = 8.0$  Hz, PhH).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>)  $\delta$ (ppm): 68.77, 69.16, 101.20, 106.70, 115.18, 115.70, 127.41, 129.55, 130.59, 139.58, 141.78, 159.454, 167.29.

MS FAB:  $m/z$ : 4038.56 [M-H]<sup>+</sup>, 2112.39 [M-H-C<sub>113</sub>H<sub>91</sub>O<sub>30</sub>]<sup>+</sup>, 1944.47 [M-H-C<sub>125</sub>H<sub>99</sub>O<sub>31</sub>].

### Catalysis

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was kept in a Teflon vessel. The inside of the cap of the autoclave was also Teflon-covered to prevent the solution from coming into direct contact with the stainless steel. An electric heating mantle kept the temperature constant.

*Standard hydroformylation experiment.* The complex [Rh( $\mu$ -OMe)(cod)]<sub>2</sub> (0.05 mmol) and the ligand (0.12 mmol) in water (6 ml) or water/methanol (3ml/3ml) were stirred for 1h at room temperature. NaOH (0,25 M) was then added to adjust the pH to the desired value. The surfactant in the corresponding concentration and the substrate (15 mmol) were added, and the resulting solution was introduced into the evacuated autoclave. The system was pressurised and heated. When thermal equilibrium was reached, more gas



We adjusted the initial pH of the aqueous phase to 11 because in the literature, activity was reported to be higher in basic medium than in neutral medium in the hydroformylation of 1-octene catalysed by  $[\text{Rh}(\mu\text{-Cl})(\text{cod})_2]/\text{TPPTS}$  [33]. At the end of the reaction generally the pH decreased. In this study we chose an anionic surfactant, sodium dodecyl sulfate (SDS), and a cationic surfactant, cetyltrimethylammonium hydrogensulfate ( $\text{CTAHSO}_4$ ). The c.m.c values for these surfactants in water at 25°C are  $8 \cdot 10^{-3}$  M (SDS) and  $9.2 \cdot 10^{-4}$  M ( $\text{CTAHSO}_4$ ), respectively. To test how the concentration of the surfactants affect the conversion, we used three concentrations of surfactants ( $C_1 = 6.3 \cdot 10^{-3}$  M,  $C_2 = 1.8 \cdot 10^{-2}$  M, and  $C_3 = 3.0 \cdot 10^{-2}$  M). We also test the effect of a dendritic molecule as a surfactant, the polyether dendrimer **11** (scheme 2) ( $C_4 = 8 \cdot 10^{-4}$  M) insoluble in water was added to the catalytic solution and the pH was adjusted to 11 with a NaOH (0.25 M) solution in order to form the dendritic salt **12** (Figure 1).

#### *Synthesis of dendrimer 12*

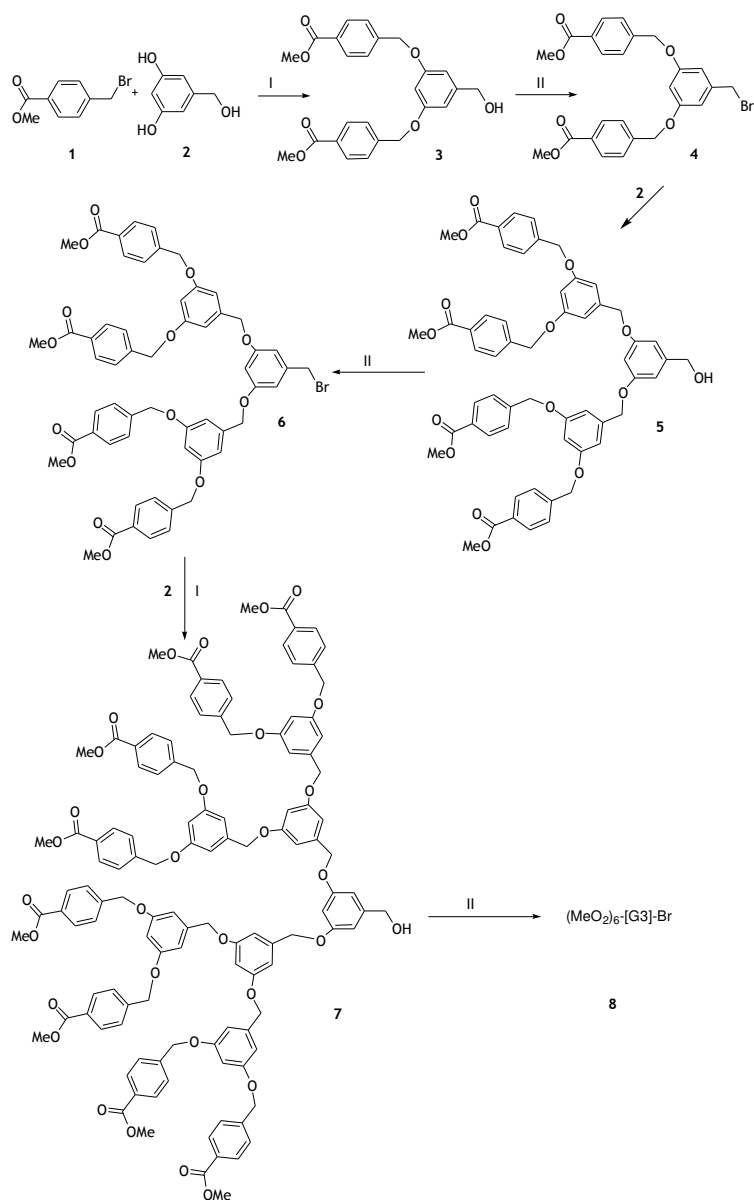
The procedure described by Fréchet et al. (Schemes 1 and 2) [18] was used to prepare dendrimer **12**. To obtain a “*unimolecular micelle*” using a convergent growth synthesis, the starting material, which will become the chain ends, must contain potentially hydrophilic functional groups. The monomer used was the 3,5-dihydroxybenzyl alcohol (**2**). The growth process basically consists of two steps: activation by bromination and coupling by alkylation (Scheme 1 and 2).

The chain ends of the final macromolecule had to be carboxylate groups. However, they could not be present in the starting material because they are unstable in the intermediate alkylation and bromination steps. Therefore, the

carboxylate group had to be protected with methyl esters. The starting material chosen for the synthesis was methyl *p*-bromomethylbenzoate (**1**). Two molecules of **1**, which will become the chain ends, coupled readily with the monomer 3,5-dihydroxybenzyl alcohol (**2**) in the presence of potassium carbonate and 18-crown-6 in acetone at reflux. These gave the first generation alcohol (MeO<sub>2</sub>C)<sub>2</sub>-[G1]-Br (**3**) in 81% yield. The activation of **3** with carbontetrabromide/triphenylphosphine proceeded smoothly to give (MeO<sub>2</sub>C)<sub>2</sub>-[G1]-Br (**4**) in 80% yield. The reaction of 2.05 equiv. of **4** with **2**, in the same conditions as those described above, gave the next generation alcohol (MeO<sub>2</sub>C)<sub>4</sub>-[G2]-OH (**5**) in 74% yield. The bromination of **5** with CBr<sub>4</sub>/PPh<sub>3</sub> gave (MeO<sub>2</sub>C)<sub>4</sub>-[G2]-Br (**6**) in 71% yield. The third generation alcohol (MeO<sub>2</sub>C)<sub>8</sub>-[G3]-OH (**7**) was accomplished in 94% yield. The activation of **7** with CBr<sub>4</sub>/PPh<sub>3</sub> gave (MeO<sub>2</sub>C)<sub>8</sub>-[G3]-Br (**8**) in 43% yield. The yield observed in this step is low because the reactivity of the alcohol decreases increasing the generation number. Finally, the coupling of **8** with the bifunctional core 4,4'-dihydroxyphenyl (**9**) (Scheme 2) in the same conditions as the alkylation steps gave the polyether (MeO<sub>2</sub>C)<sub>16</sub>-[G3]<sub>2</sub>-C (**10**) in 89% yield. The methylester groups were deprotected by alkaline hydrolysis. To overcome the problems of the solubility of **10** in water and potassium hydroxide in organic solvents the reaction was carried out in a mixture of tetrahydrofuran/water/methanol. The acidification of this reaction mixture gave (HO<sub>2</sub>C)<sub>8</sub>-[G3]<sub>2</sub>-OH (**11**) in 90% yield and the complete desprotection of the methylester groups was confirmed by <sup>1</sup>H NMR. The polyacid **11** is insoluble in water and, when it was titrated with sodium hydroxide, it gave the sodium salt **12**.

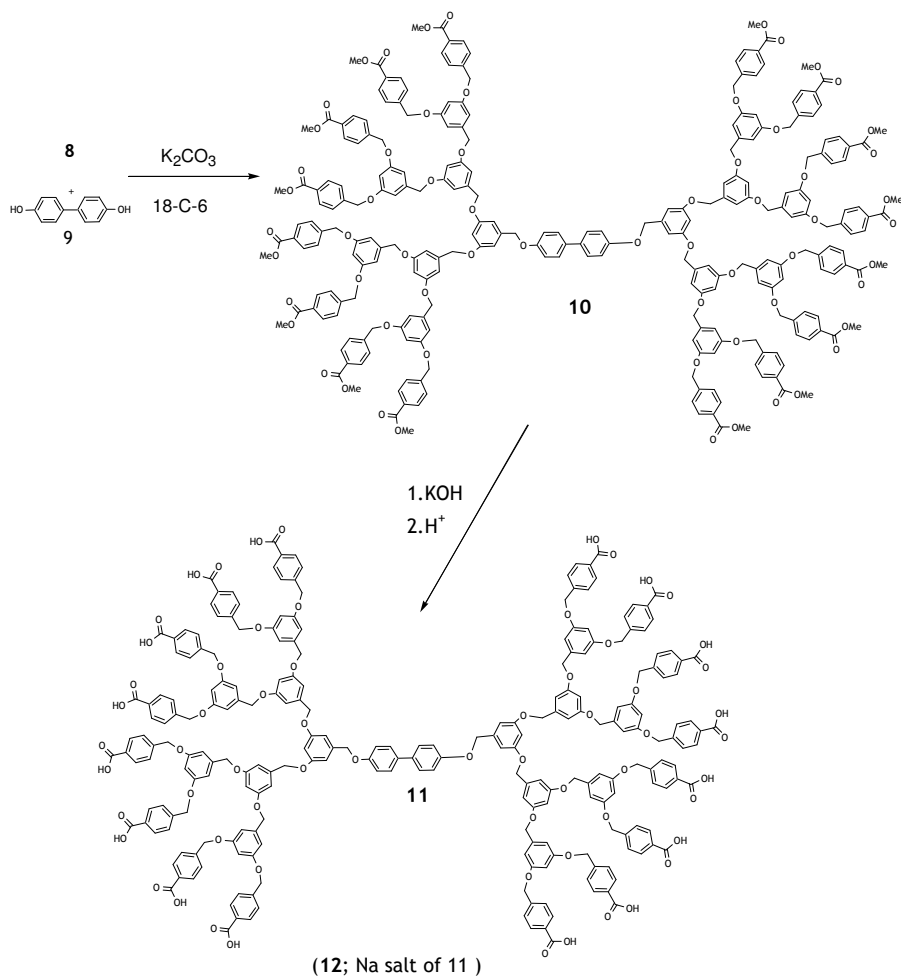
The dendritic species were characterised with <sup>1</sup>H and <sup>13</sup>C NMR. The characteristic resonances, which made it possible to identify the dendritic species, are the ones due to terminal phenyl ring, which is *p*-substituted with

methylesters, that gave an AB quartet between 7.40 and 8.00 ppm, and the resonance of the methylesters groups that appears around 3.80 ppm. The resonance corresponding to the aromatic intern protons appears between 6.70 - 6.63 ppm while all benzylic protons resonate between 4.91- 5.01 ppm, except the protons corresponding to the group CH<sub>2</sub>OH or CH<sub>2</sub>Br, depending on the dendritic specie, which appear as a singlet between 4.3 - 4.6 ppm. By integrating and comparing the signals, the generation number and the structure were confirmed.



Scheme 1. Reagents I: K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, II: CBr<sub>4</sub>, PPh<sub>3</sub>. Reaction scheme for preparation of dendritic fragments





Scheme 2. Reaction scheme for preparation of carboxy-terminated dendritic macromolecule  $\{(HO_2C)_8-[G-3]\}_2-[C]$

#### Hydroformylation of 1-octene in aqueous systems

Table 1 shows the results of 1-octene hydroformylation in water using  $[Rh(\mu-OMe)(cod)]_2/dppbts$  as the precursor (entries 1-7). For comparison purposes, the results without surfactant are also given. In the conditions we studied, the

products formed were the isomeric aldehydes *n*-nonanal and *iso*-nonanal, and the isomerization products 2-*trans*-octene, 2-*cis*-octene, and 3-*trans*-octene. No hydrogenation product was observed. Table 1 also shows, therefore, the selectivity in isomerization products.

Table 1. Hydroformylation of 1-octene (**13a**) in aqueous systems using [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/L (L = dppbts (**16**) and dpppts (**17**)) as the catalyst precursors <sup>a</sup>

Entry	Ligand	[Surfactant] <sup>b</sup>	P (bar) H <sub>2</sub> /CO	T (°C)	Conv(%) <sup>c</sup>	S <sub>ald</sub> (%) <sup>d</sup>	n/i	S <sub>isom</sub> (%) <sup>e</sup>
1	16	-	7/7	80	5	40	72/28	55
2	16	SDS (C <sub>2</sub> )	7/7	80	8	38	72/28	50
3	16	SDS (C <sub>3</sub> )	7/7	80	98	31	65/35	62
4	16	SDS (C <sub>3</sub> )	7/7	65	5	55	72/28	45
5	16	CTAHSO <sub>4</sub> (C <sub>1</sub> )	7/7	80	24	96	79/21	1
6	16	CTAHSO <sub>4</sub> (C <sub>3</sub> )	7/7	80	95	79	75/25	12
7	16	<b>12</b> (C <sub>4</sub> )	7/7	80	4	24	66/34	67
8	17	-	7/7	80	5	80	75/25	< 1
9	17	SDS (C <sub>2</sub> )	7/7	80	33	25	73/27	73
10	17	SDS (C <sub>3</sub> )	7/7	80	66	12	75/25	79
11	17	SDS (C <sub>2</sub> )	25/25	80	30	60	69/31	30
12	17	SDS (C <sub>2</sub> )	17/33	80	13	62	71/29	31
13	17	CTAHSO <sub>4</sub> (C <sub>1</sub> )	7/7	80	17	82	58/42	12

<sup>a</sup> Reaction conditions: substrate = 15 mmol, [Rh( $\mu$ -OMe)(cod)]<sub>2</sub> = 5 × 10<sup>-3</sup> M, substrate/precursor = 500, solvent = H<sub>2</sub>O (6ml), P/Rh ratio = 4 (L/[Rh( $\mu$ -OMe)(cod)]<sub>2</sub> molar ratio = 4), time = 24 h, pH 11.

<sup>b</sup> Concentration: C<sub>1</sub> = 6.3 × 10<sup>-3</sup> M, C<sub>2</sub> = 1.8 × 10<sup>-2</sup> M, C<sub>3</sub> = 3.0 × 10<sup>-2</sup> M, C<sub>4</sub> = 8.0 × 10<sup>-4</sup> M.

<sup>c</sup> Aldehyde conversion measured by gas chromatography.

<sup>d</sup> Selectivity in aldehydes defined as percent aldehyde conversion/percent total conversion.

<sup>e</sup> Selectivity in isomerised products defined as percent isomerization products/percent total conversion.

<sup>f</sup> Loss of catalyst in the organic layer

The aldehyde conversion and selectivity in aldehydes of the catalyst  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{dppbts}$  were very low both without any additive (Table 1, entry 1) and with the addition of SDS at low concentration (Table 1, entry 2). Adding anionic surfactant SDS at a higher concentration (Table 1, entry 3) increased the activity (complete conversion was observed at the same reaction time). However, the selectivity was low and similar to the one obtained without additive. Regioselectivity was the same in water as at a low concentration of SDS (Table 1, entry 2), but a higher concentration of surfactant increased the amount of *iso*-nonanal.

To prevent the formation of isomerization products by  $\beta$ -elimination, we performed one experiment at 65 °C. Decreasing the temperature of the reaction effectively enhanced the selectivity in aldehydes; unfortunately the conversion was very low (Table 1, entry 4).

Using dendrimer 12 (Table, entry 7) as a surfactant low conversion was observed, similar to the one obtained with the system without additive (Table 1, entry 7 vs. entry 1). Unfortunately a decrease in aldehydes selectivity and in the regioselectivity was observed obtaining mainly isomers as reaction products.

Adding cationic surfactant  $\text{CTAHSO}_4$  increased the conversion and selectivity in aldehydes (Table 1, entries 5 and 6). This could be due to two factors: the substrate is efficiently dissolved in the micellar system, or the cationic micelle has a positive charged surface that attracts the catalytic rhodium species to the micelle surface through the sulfonated groups, which are negatively charged [12]. This promotes the contact between the substrate and catalyst. However, high concentrations of surfactant can lead to a loss of

catalyst in the organic phase. This can be easily observed because the organic phase became coloured.

In fact, when we used the highest concentration of cationic surfactant, which was above c.m.c. (Table 1, entry 6), there was a loss of catalyst in the organic phase. At concentrations above c.m.c., there is an equilibrium between the free surfactant and the micellar species. Electrostatic interaction between anionic species of the rhodium complex and cationic-surfactant-free species may have been responsible for the loss of catalyst in the organic phase. At a lower concentration of surfactant (Table 1, entry 5), which is closer to c.m.c, this phenomenon did not occur and there was a slight increase in conversion and a higher selectivity. The regioselectivity was better than that of the system without additive: with cationic surfactant, regioselectivity in nonanal was around 80 %.

Table 1 shows the results when the precursor  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{dpppts}$  was used (entries 8-13). If we compare the different systems, we can see that the Rh/dpppts system was more selective in aldehydes than the Rh/dppbts system when no additive was added (Table 1, entry 8 vs. entry 1).

Adding SDS to the Rh/dpppts system had the same effect as in the Rh/dppbts system. Conversion increased but selectivity decreased when we raised the concentration of the surfactant. To improve the selectivity, we increased the pressure to 50 bar (Table 1, entries 11 and 12). When the hydrogen:carbon monoxide ratio was 1:1, selectivity improved but conversion remained the same (Table 1, entry 11 vs. entry 9). On the other hand, when the  $\text{H}_2:\text{CO}$  ratio was changed to 1:2, there was a drop in conversion (Table 1, entry 12). The regioselectivities obtained in the presence of SDS were similar to those obtained without additive.

Adding CTAHSO<sub>4</sub> had the same effect as the system that used dppbts as the ligand (Table 1, entry 13) i.e. both the activity and the selectivity increased. Note that regioselectivity in nonanal was lower than that of the system that used dppbts as the ligand (Table 1, entry 13 vs. entry 5).

If we compare the two systems [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts and [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dpppts, we can conclude that the system with dpppts is more selective in aldehydes with no additive. Adding SDS enhanced the total conversion, but not the selectivity in aldehydes. On the other hand, adding CTAHSO<sub>4</sub> enhanced both total conversion and selectivity but conversion was still low. Finally, regioselectivities in nonanal were higher when dppbts was used as the ligand and CTAHSO<sub>4</sub> was used as the surfactant.

#### *Hydroformylation of 1-decene in aqueous systems*

Table 2 shows the results of the hydroformylation of 1-decene. Interestingly, when [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts was used as the precursor (Table 2, entries 14-19), the conversion observed in the hydroformylation of 1-decene was higher than that of 1-octene in water (Table 1, entry 1). However, the selectivity in aldehydes was low, and the main products obtained were isomerization products.

Adding SDS to the system [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts (Table 2, entries 15 and 16, vs. Table 1, entries 2 and 3) has the same effect than in the case of 1-octene. The conversion increased with increasing amount of surfactant, but the selectivity in aldehydes and the regioselectivity in nonanal decreased.

Table 2

Hydroformylation of 1-decene (**13b**) in aqueous systems using  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{L}$  (L = dppbts (**16**) and dpppts (**17**)) as the catalyst precursors<sup>a</sup>

Entry	Run	Ligand	[Surfactant] <sup>b</sup>	Conv(%) <sup>c</sup>	$S_{\text{ald}}$ (%) <sup>d</sup>	n/i	$S_{\text{isom}}$ (%) <sup>e</sup>
14	1	16	-	15	20	73/27	80
15	1	16	SDS ( $C_2$ )	48	31	75/25	69
16	1	16	SDS ( $C_3$ )	88	25	65/35	75
17	1	16	CTAHSO <sub>4</sub> ( $C_1$ )	63	97	78/22	3
18	2	16	CTAHSO <sub>4</sub> ( $C_1$ )	72	96	69/31	4
19	1	16	-	-	-	-	-
20	1	17	SDS ( $C_2$ )	-	-	-	-
21	1	17	SDS ( $C_3$ )	68	21	74/26	76
22	1	17	CTAHSO <sub>4</sub> ( $C_1$ )	3	86	55/45	13

<sup>a</sup> Reaction conditions: substrate = 15 mmol,  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2 = 5 \times 10^{-3}$  M, substrate/precursor = 500, solvent = H<sub>2</sub>O (6ml), P/Rh ratio = 4, P = 14 atm, H<sub>2</sub>/CO = 7/7, T = 80 ° C, time = 24 h, pH 11.

<sup>b</sup> Concentration:  $C_1 = 6.3 \times 10^{-3}$  M,  $C_2 = 1.8 \times 10^{-2}$  M,  $C_3 = 3.0 \times 10^{-2}$  M.

<sup>c</sup> Aldehyde conversion measured by gas chromatography.

<sup>d</sup> Selectivity in aldehydes.

<sup>e</sup> Selectivity in isomerised products.

Adding CTAHSO<sub>4</sub> (Table 2, entry 17) improves both the conversion and the selectivity; it is to be noted that they are even higher than those obtained in the case of 1-octene. A conversion of 63 % with selectivity in aldehydes of up to 97 % was achieved. Additionally, we were able to recycle the system, the conversion and selectivity in aldehydes being maintained (Table 2, entry 18).

When the system Rh-dpppts was used no conversion was detected. Adding SDS resulted in a high increase of the conversion in the highest concentration

studied. However the selectivity was low and the main products were isomerized products (Table 2, entry 21).

Adding CTAHSO<sub>4</sub> improved the activity only very slightly (Table 2, entry 22). If we compare this result with those from the same system in the hydroformylation of 1-octene (Table 1, entry 13, vs. Table 2, entry 22) we can see that the regioselectivity in nonanal was very low when dpppts was used as the ligand.

#### *Hydroformylation in aqueous-methanolic systems*

To compare the strategies for improving the mass transfer between the two phases, we also studied the effect of a co-solvent such as methanol. When methanol was used as the co-solvent, [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dppbts or [Rh( $\mu$ -OMe)(cod)]<sub>2</sub>/dpppts as the catalyst precursor, and 1-octene as the substrate (Table 3, entries 22 and 23), activities were higher than those obtained in water (Table 1, entries 1 and 7), while the regioselectivities in nonanal were lower. When Rh-dppbts was used as the ligand (Table 3, entry 22), selectivity in aldehydes was 90 %. When 1-octene was used as the substrate, the results for both total conversion and selectivity in aldehydes were highest when methanol was used as the co-solvent. However, regioselectivity in nonanal was low with this system.

Table 3

Hydroformylation of 1-octene (**13a**) and 1-decene (**13b**) in aqueous-methanolic systems using  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2/\text{L}$  (L = dppbts (**16**) and dpppts (**17**) as catalyst precursors.<sup>a</sup>

Entry	Ligands	Substrate	Conversion (%) <sup>b</sup>	$S_{\text{ald}}$ (%) <sup>c</sup>	n/iso	$S_{\text{isom}}$ <sup>d</sup>
23	16	13a	60	90	58/42	3
24	17	13a	67	57	68/32	42
25	16	13b	14	79	74/26	11
26	17	13b	60	23	71/29	60

<sup>a</sup> Reaction conditions: substrate = 15 mmol,  $[\text{Rh}(\mu\text{-OMe})(\text{cod})]_2 = 5 \cdot 10^{-3}$  M, substrate/precursor = 500, solvent = H<sub>2</sub>O/MeOH (3/3 mL), P/Rh ratio = 4, time = 24 h, pH = 11, T = 80 °C, pressure = 14 atm (CO/H<sub>2</sub> = 1/1)

<sup>b</sup> Aldehyde conversion measured by gas chromatography.

<sup>c</sup> Selectivity in aldehydes.

In the hydroformylation of 1-decene, adding methanol considerably increased conversion when the Rh-dpppts system was used (Table 3, entry 26). When dppbts was used as the ligand (Table 3, entry 25), activity did not improve and only selectivity in aldehydes improved. Regioselectivities with both ligands dppbts and dpppts were similar to those obtained when water was the only solvent.



### **3.4. Conclusions**

In the Rh-sulphonated diphosphine hydroformylation of 1-octene and 1-decene, selectivities and total conversions are modified when surfactants are added or a co-solvent is used.

In the hydroformylation of 1-octene, the results for conversion and selectivity in aldehydes were best when methanol was the co-solvent and dppbts was the ligand, but regioselectivities in nonanal were lower. Adding surfactants increased the conversion with the systems Rh-dpppts and Rh-dppbts. However, selectivity in aldehydes did not improve when SDS was added. The addition of dendrimer **12** did not improve the results, obtaining low conversion and low aldehydes selectivity. Adding CTAHSO<sub>4</sub> increased both the total conversion and the selectivity, and there was a slight improvement in regioselectivity in nonanal. However, a high concentration of surfactant led to a loss of the catalyst in the organic phase.

For 1-decene hydroformylation, the results were best when CTAHSO<sub>4</sub> was used as the surfactant and dppbts was used as the ligand: conversion was 63 % and selectivity in aldehydes was 97 %. Moreover, we could recycle the system maintaining the same activity and selectivity in aldehydes. Adding SDS increased activity, but unfortunately selectivity in aldehydes did not improve. When methanol was used as the co-solvent with the system Rh-dppbts, selectivity increased but the activity was similar to the activity in water.

### **Acknowledgements**

We thank the *Ministerio de Educación, Cultura y Deporte* (PB97-04070CO5-01), the *Generalitat de Catalunya* (ACI-96) and the Commission for the European Communities (COSTD10 Action01) for their financial support.

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