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Micellar Effects in Olefin Hydroformylation Catalysed by Neutral, Calix[4]arene-Diphosphite Rhodium Complexes

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Abstract: The combination of calixarene-derived surfactants and *neutral* rhodium complexes containing a hemispherical "1,3-calix-diphosphite" ligand led to efficient catalysts for the hydroformylation of octene and other olefins in water. While the surfactants allowed the formation of micelles that dissolve both the catalyst and the alkene, thereby resulting in high olefin:rhodium ratios, the diphosphite provided a tight envelope about the catalytic centre able to drive the reaction towards the linear aldehydes. Best results in the hydroformylation of 1-octene were obtained when using [tetra(*p*-sulfonato)]-(tetra-*n*-butoxy)-calix[4]arene as surfactant. With this additive remarkable linear to branched aldehyde ratios of up to 62 were obtained, the corresponding activities being higher than those observed when operating in an organic solvent [turnover frequencies (TOFs) up to 630 mol(converted 1-octene)·mol(Rh)$^{-1}$·h^{-1}].

Keywords: catalysis in water; hemispherical diphosphites; hydroformylation; large bite angles; micelles; surfactants

Introduction

Hydroformylation is a major industrial process that produces aldehydes from olefins, carbon monoxide and hydrogen. It is classically carried out in the presence of a cobalt or a rhodium catalyst.[1,2] The most important applications of the industrially produced aldehydes are plasticizers and detergent alcohols. Hydroformylation can be achieved in biphasic aqueous systems using water-soluble phosphines. For example, Ruhrchemie and Rhône–Poulenc developed the industrial propene hydroformylation using the tris-sulfonated triphenylphosphine (TPPTS).[3,4] Nevertheless, due to low solubility of long-chain olefins in water, this catalytic system can only be applied to short-chain olefins. A possible way to overcome this issue is to add surfactants[5] to the reaction mixture.[6–8]

Results and Discussion

Recently, we reported on the remarkable olefin hydroformylation properties of 1,3-calix[4]-diphosphites having both phosphorus atoms substituted by the bulky 1,1′-binaphthalene-2,2′-dioxy ("bino") moiety (Figure 1).[9,10] The high regioselectivity observed with these ligands toward the production of linear aldehydes was attributed to the ability of the diphosphites to form upon chelation a tight molecular pocket able to control the shape of the outcoming product. The

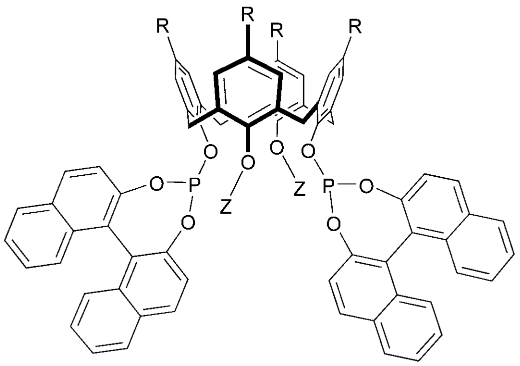
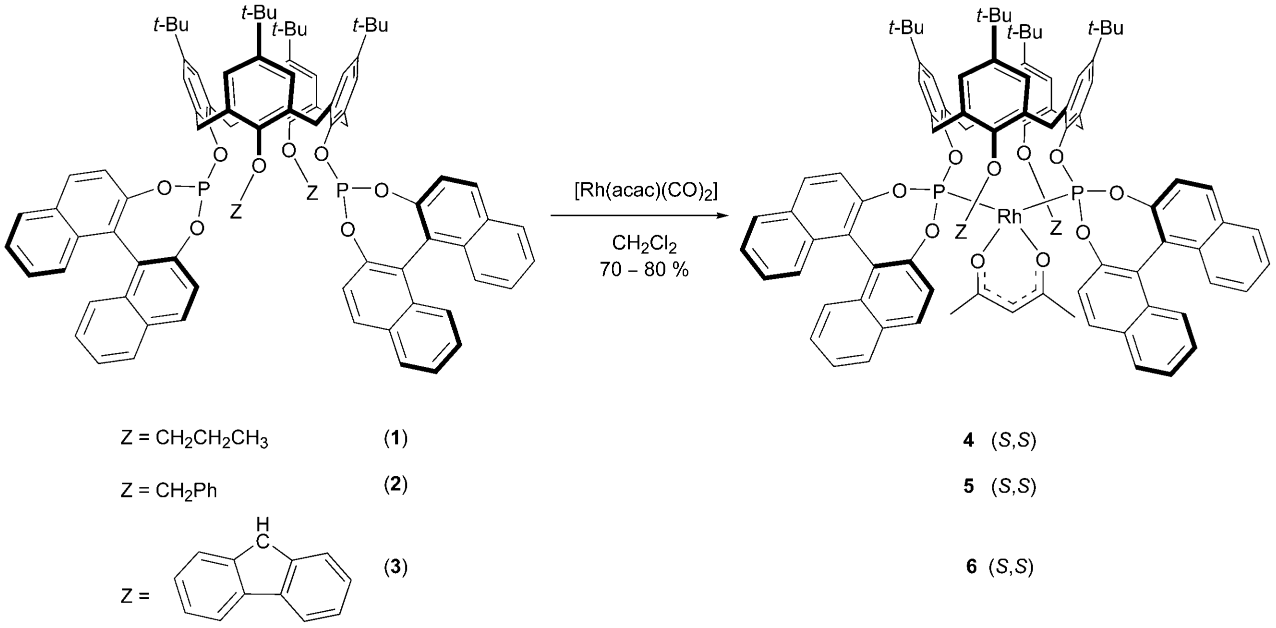


Figure 1. General formula of hemispherical "1,3-calix[4]arene diphosphites".



Scheme 1. Synthesis of complexes **4**–**6**.

pocket is formed by the presence of the bino substituents and two alkoxy groups connected to the calixarene's lower rim. Thus, these diphosphites, the natural bite angles of which are close to 103°, provide a "tridimensional" metal embrace and therefore were referred to as "hemispherical" ligands. Their ability to envelope the catalytic centre is much more pronounced than with other diphosphanes having a large bite angle.[11–20] Pursuing our efforts to develop environmentally friendly reactions, we now describe the use of neutral [Rh(acac)(1,3-calix-diphosphite)] complexes in *aqueous* hydroformylation. These experiments were carried out with particular surfactants, namely sulfonated-calix[4]arenes, a type of surfactant which to date was not used in catalytic reactions. In this study we also report the first X-ray structure of a rhodium chelate complex containing a hemispherical diphosphite.

Reaction of the *cone*-calixarenes **1**–**3** with [Rh(acac)(CO)$_2$] in CH_2Cl_2 gave the chelate complexes **4**–**6**, respectively, in yields of between 70 and 80% after work-up (Scheme 1). Each mass spectrum shows a strong peak corresponding to the [M$^+$] ion. All NMR spectra are consistent with a C_2-symmetrical molecule. For example, the ^{31}P NMR spectrum of **4** shows a doublet centred at 126.6 ppm ($J_{\mathrm{Rh,P}}$= 328 Hz), while the corresponding ^{1}H NMR spectrum displays two AB systems for the ArCH_2Ar methylenic protons.

The solid state structure of **4** was determined by a single X-ray diffraction study, which confirmed the chelating behaviour of the disphosphite. The observed large P–Rh–P angle, 101.5°, reflects the relatively large separation between the two phosphorus atoms, which is imposed by the calixarene backbone and which prevents formation of a chelate ring with an ideal bite angle of 90°. Note that the value of the P–M–P angle is close to the one found in the recently reported structure of [Pd(C_3H_5)·**1**]PF_6.[9] The coordination environment deviates from the planar geometry generally adopted by [Rh(acac)(diphosphane)] complexes.[21] This is best seen by considering the non-zero dihedral angle between the PRhP and ORhO planes (16.3°). This distortion obviously minimises the steric interactions between the binaphthyl units and the flat acetylacetonate ligand. In fact, the rhodium-acac moiety sits deep in a molecular pocket generated by two symmetrically located naphthyl moieties. It is further noteworthy that, owing to the presence of a typically flattened cone conformation, the O-propyl groups are pushed towards the rhodium centre, thereby increasing the confinement of the metal centre (Figure 2).

We began the catalytic study by assessing two of these [Rh(acac)L] complexes (**4** and **5**) in the hydroformylation of 1-octene at 50 °C in toluene under 20 bar using 2:1, 1:1 and 1:2 CO/H_2 mixtures (Scheme 2 and Table 1). The tests were carried out without addition of free ligand. Increasing the partial pressure of hydrogen induced significants rate enhancement. For example, with **5**, after 2.5 h of reaction time the conversion increased from 6.8 to 38.8% when the V(CO)/V(H_2) ratio passed from 1:1 to 1:2 (Table 1, entries 2 and 3). This increase cannot be explained by standard kinetics, which predict that a 30% increase of the partial H_2 pressure would at most double the rate.[22] A possible explanation for this phenomenon is the existence of equilibria involving

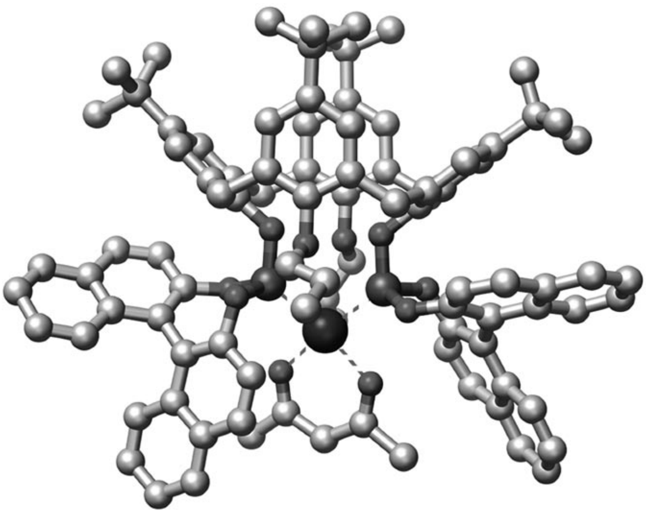
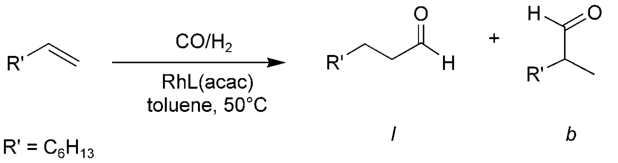


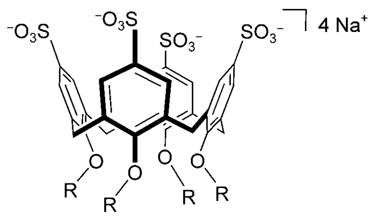
Figure 2. Molecular structure of **4** (*S,S*). P–Rh–P angle 101.5°. Dihedral angles between facing phenoxy rings of the calixarene: 4.6° (O3/O4), 82.9° (O5/O8). Dihedral angle between P–Rh–P and acac: 16.3°. The molecule crystallises with 2/3 molecule of $CHCl_3$ lying out of the cavity (not shown).



Scheme 2. Hydroformylation of 1-octene in toluene (using **4** and **5**).

an inactive $[RhL(CO)_2]_2$ dimer,[23] which owing to the particular confinement created in this dimer by the two hemispherical ligands would render difficult the formation of active hydrido-carbonyl species at lower partial hydrogen pressures. We noted that the rate increase was not accompanied by a significant modification of the regioselectivity. As previously observed in reactions performed at higher temperatures,[9,10] the regioselectivities were lower with **4** than **5** (Table 1, entries 3 and 4).

For the catalytic study carried out in water, only the precatalyst giving the best results in toluene, namely complex **5** (with benzyl substituents) was used. The experiments were done in the presence of various upper rim-sulfonated calixarenes (**7**–**10**). The calixarenes **8**–**10**, bearing linear alkyl chains at the lower rim, were prepared according to a general method reported by Shinkai starting from the tetrasulfonated calix[4]arene **7**.[24–26] Typically, **7** was alkylated by the appropriate alkyl halide in the presence of NaOH in a mixture of water and dimethyl sulfoxide. The ^1H NMR data of these sulfonated compounds are all consistent with the formation of calixarenes in the cone conformation.



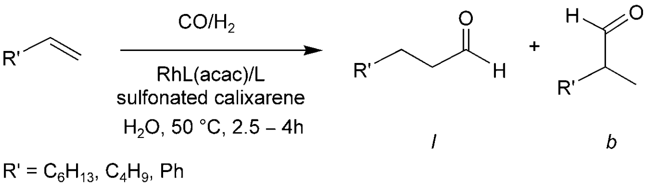
7 R = H
8 R = n-C_4H_9
9 R = n-C_6H_{13}
10 R = n-C_8H_{17}

Three olefins were used, namely 1-octene, 1-hexene and styrene. The tests were carried out in 8 mL of water, at 50 °C and under 20 bar of CO/H_2 with a $V(CO)/V(H_2)$ ratio of 1:2 (Scheme 3). The rhodium complex was first dissolved in the olefin, before being introduced into the autoclave. At the end of each run performed in the presence of any surfactant, an emulsion was recovered, which remained stable after standing for several days. In the absence of surfactant, two phases could be observed. In this case, the catalyst was contained in the organic phase.

Table 1. Rhodium-catalyzed hydroformylation of 1-octene using complexes **4** and **5** in toluene.[a]

Entry	[Rh]	P(CO/H$_2$) V(CO)	 V(H$_2$)	Conv.[b] [%]	TOF[c]	Product distribution Isomer. olefins [%]	 Aldehydes [%]	*l*:*b*[d]
1	**5**	2	1	1	10	1.0	traces	
2	**5**	1	1	6.8	70	1.2	98.8	16.8
3	**5**	1	2	38.8	390	4.6	95.4	14.5
4	**4**	1	2	42.3	420	1.1	98.9	6.1

[a] 1-Octene (5 mmol), [Rh] (2 μmol), 1-octene/Rh = 2500, $P(CO/H_2)_{total}$ = 20 bar, T = 50 °C, 2.5 h, toluene/n-decane (15 mL/0.5 mL). Stainless steel autoclave, 100 mL.
[b] Determined by GC using decane as standard.
[c] Mol(converted 1-octene)·mol(Rh)$^{-1}$·h^{-1}.
[d] The *l:b* aldehyde ratio takes into account the branched aldehydes (which consist mainly of 2-methyloctanal).



Scheme 3. Hydroformylation experiments performed with complex **4** and sulfonated calixarenes **7–10** in water.

1-Octene Hydroformylation

The outcome of the catalytic runs strongly depended on the presence of surfactant. When the catalysis was performed without surfactant (Table 1, entry 1), the hydroformylation process occurred in the octene layer, in which the catalyst was found to be soluble. These conditions led to an activity of the catalyst of 360 mol(octene)·mol(Rh)$^{-1}$·h^{-1}, which nearly corresponds to the activity observed when operating in toluene. The addition of surfactant modified the reaction mixture and led to the formation of micelles. We observed that high linear to branched aldehyde ratios (*l:b* > 20) were only observed when the catalytic reaction was carried out in the presence of diphosphite in excess. With ligand **2**, for example, the *l:b* ratio increased from 3.2 to 61.8 on going from an L:Rh ratio of 1 to an L:Rh ratio of 10 (Table 2, entries 3 and 6). As observed by other authors, excess ligand is necessary to prevent the formation of "naked" rhodium, which behaves as an unselective catalyst.[27] As a general trend, excepted with **10**, the use of 100 mg instead of 50 mg of sulfonated calixarene led to a higher activity without a significant loss of selectivity. For example, the TOF increased from 420 to 550 mol(octene)·mol(Rh)$^{-1}$·h^{-1} when, respectively, 50 and 100 mg of surfactant **7** were used (Table 1, entries 4 and 5). Further, changing the alkyl substituents of the surfactant induced considerable variations of the catalytic results. The *n*-butyl substituted calixarene **8** gave the highest TOF [TOF = 1160 mol(octene)·mol(Rh)$^{-1}$·h^{-1} at a conversion of 44.7% after 1 hour] and the highest regioselectivity (*l:b* > 100) (see Supporting Information, Table S2, entry 6). We finally found that the activity as well as the selectivity drastically droped when using [Rh(acac)(CO)$_2$] alone (that is in the absence of diphosphite) (Table 2, entries 11 and 12). Overall, operating in a water/surfactant medium led to higher activities than in an organic medium, both media giving high linear selectivities.

1-Hexene Hydroformylation

These experiments were carried out with complex **5**. As above, a CO:H$_2$ ratio of 1:2 and ligand:[Rh] ratio of 10 were used. The highest activity, 750 mol(hexene)·mol(Rh)$^{-1}$·h^{-1}, was observed in the presence of the butyl-substituted surfactant **8**. In this case, the corresponding *l:b* ratio was 15.7 (Table 3, entry 2). For comparison, when repeating these experiments in toluene, the activity was 4 times lower than when operating in the water/**8** system (same selectivity). As with 1-octene, the other surfactants (**7**, **9**, and **10**) led to

Table 2. Rhodium-catalyzed hydroformylation of 1-octene.[a]

Entry	Sulfonated-calixarene	Conv.[b] [%]	TOF[c]	Product distribution Isomer. olefins (%)	Product distribution Aldehydes (%)	*l:b*[d]
1[f]	/	36.1	360	1.5	34.6	24.1
2[e]	**8** (50 mg) (R = n-C_4H_9)	54.2	540	0.5	53.7	2.1
3[e]	**8** (100 mg) (R = n-C_4H_9)	65.0	650	1.4	63.6	3.2
4[f]	**7** (50 mg) (R = H)	42.4	420	2.4	40.0	25.7
5[f]	**7** (100 mg) (R = H)	55.2	550	3.0	52.2	14.2
6[f]	**8** (100 mg) (R = n-C_4H_9)	63.1	630	1.8	61.3	61.8
7[f]	**9** (50 mg) (R = n-C_6H_{13})	56.5	570	2.6	53.9	27.6
8[f]	**9** (100 mg) (R = n-C_6H_{13})	60.2	600	1.3	58.9	21.2
9[f]	**10** (50 mg) (R = n-C_8H_{17})	48.2	480	1.9	46.3	6.4
10[f]	**10** (100 mg) (R = n-C_8H_{17})	42.1	420	7.7	34.4	5.8
11[g]	**/**	13.3	60	7.9	5.4	2.0
12[g]	**8** (100 mg) (R = n-C_4H_9)	14.9	70	4.9	10.0	1.9

[a] 1-Octene (2.5 mmol), **5** (1 μmol), 1-octene/Rh = 2500, V(H$_2$)/V(CO) = 2/1, P(CO/H$_2$)$_{\text{total}}$ = 20 bar, T = 50 °C, 2.5 h, H$_2$O/*n*-decane (8 mL/0.1 mL). Stainless steel autoclave, 100 mL.
[b] Determined by GC using decane as standard.
[c] Mol(converted 1-octene)·mol(Rh)$^{-1}$·h^{-1}.
[d] The *l:b* aldehyde ratio takes into account the branched aldehydes (which consist mainly of 2-methyloctanal).
[e] No excess of **2**.
[f] Addition of an excess of 10 equiv./**5** of **2**.
[g] Catalyst used with no additional ligand: [Rh(acac)(CO)$_2$] (2 μmol).

Table 3. Hydroformylation of 1-hexene and styrene using complex **5**.[a]

Entry	Sulfonated-calixarene (R)	Conv.[b] [%]	TOF[c]	Product distribution Isomer. olefins [%]	Aldehydes *l* (%)	 *b* (%)	*l:b*[d]
1-hexene							
1	**7** (R=H) (100 mg)	21.4	270	37.4	58.4	4.2	13.9
2	**8** (R=n-C_4H_9) (100 mg)	59.6	750	3.2	91.0	5.8	15.7
3	**9** (R=n-C_6H_{13}) (100 mg)	37.4	470	traces	91.6	8.4	10.9
4	**10** (R=n-C_8H_{17}) (50 mg)	28.0	350	traces	88.5	11.5	7.7
5	/	39.4	490	3.0	88.3	8.7	10.1
styrene							
6	**7** (R=H) (100 mg)	12.5	80	/	54.4	45.6	1.2
7	**8** (R=n-C_4H_9) (100 mg)	22.7	140	/	46.7	53.3	0.9
8	**9** (R=n-C_6H_{13}) (100 mg)	27.0	170	/	63.5	36.5	1.7
9	**10** (R=n-C_8H_{17}) (50 mg)	37.7	230	/	66.7	33.3	2.0
10	/	8.9	60	/	78.7	21.3	3.7

[a] Olefin (2.5 mmol), **5** (1 μmol), olefin/Rh=2500, excess of 10 equiv./**5** of **2**, $V(H_2)/V(CO)=2/1$, $P(CO/H_2)_{total}=20$ bar, $T=50\,°C$, 4 h, H_2O/n-decane (8 mL/0.1 mL). Stainless steel autoclave, 100 mL.

[b] Determined by GC using decane as standard.

[c] Mol(converted olefin)·mol(Rh)$^{-1}$·h^{-1}.

[d] The *l:b* aldehyde ratio takes into account the branched aldehydes.

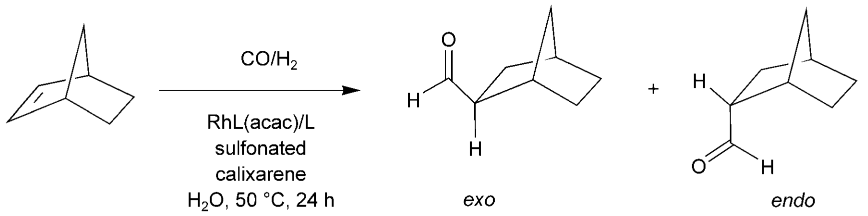
lower activities and selectivities (Table 3, entries 1–4). We noted that when **5** was used without any surfactant (that is, operating in a two phase water/olefin system; see Table 3, entry 5), the activity and the selectivity were comparable to those obtained with **9**, while being superior to those found with **7** and **10**. Overall, these findings clearly demonstrate the usefulness of surfactant **8** for carrying out the hydroformylation of 1-hexene in an aqueous medium.

Styrene Hydroformylation

It is well-known that with conventional rhodium-phosphine catalysts, styrene leads mainly to the corresponding branched aldehyde, namely 2-phenylpropanal. When operating in water and without using a surfactant, complex **5**, in the presence of 10 equiv. of free ligand, produced the linear aldehyde with 78.7% selectivity [TOF=60 mol(styrene)·mol(Rh)$^{-1}$·h^{-1}; Table 3, entry 10]. For comparison, operating in toluene with the same complex, but without adding free ligand, led to a TOF of 70 mol(styrene)·mol(Rh)$^{-1}$·h^{-1} and 58.4% of linear aldehyde. Operating in a water/surfactant medium significantly improved the activity of the catalyst [TOFs up to 230 mol(styrene)·mol(Rh)$^{-1}$·h^{-1}]. We noted that both the activity and the selectivity increased when the alkyl substituants of the sulfonated calixarenes became longer (Table 3, entries 6–9). With the more efficient additive **10** (octyl substituents) an activity of 230 mol(styrene)·mol(Rh)$^{-1}$·h^{-1} and a regioselectivity toward the linear product of 66.7% were obtained (Table 3, entry 9). It is worth mentioning here that in these reactions, which were all carried with optically pure (*S,S*)-**5**, the branched aldehyde was produced in modest optical yields (*ee*s ranging from 21 to 27%).

Asymmetric Hydroformylation of Norbornene

Complex **6**, which was obtained from the optically pure calixarene **3** (having appended fluorenyl groups) was assessed in the aqueous asymmetric hydroformylation of norbornene (Scheme 4). This reaction led mainly to the *endo*-aldehyde, thus contrasting with



Scheme 4. Asymmetric hydroformylation of norbornene. These experiments were carried out with complex **6** and sulfonated-calixarenes **7**–**10** in water.

Table 4. Rhodium-catalyzed hydroformylation of norbornene.[a]

Entry	Sulfonated-calixarene (R)	Conv.[b] [%]	Product distribution[b] *endo* (%)	*ee* (*endo*)[c] (%)	*exo* (%)
1	**7** ($R=H$) (100 mg)	93.0	100	3 (*R*)	traces
2	**8** ($R=n\text{-}C_4H_9$) (100 mg)	66.2	100	39 (*R*)	traces
3	**9** ($R=n\text{-}C_6H_{13}$) (100 mg)	38.0	100	33 (*R*)	traces
4	**10** ($R=n\text{-}C_8H_{17}$) (50 mg)	37.7	84.0	36 (*R*)	16.0
5	/	64.7	88.3	35 (*R*)	11.7

[a] Norbornene (0.4 mmol), **6** (2 μmol), norbornene/Rh = 200, excess of 10 equiv./**6** of **3**, $V(H_2)/V(CO)=2/1$, $P(CO/H_2)_{total}=$ 20 bar, $T=50\,°C$, 24 h, H_2O/*n*-decane (8 mL/0.1 mL). Stainless steel autoclave, 100 mL.

[b] Determined by GC using decane as standard.

[c] Determined by GC using a chiral column (Chirasil-DEX CB, 25 m × 0.25 mm) after reduction into the alcohols and using decane as standard.

our previous experiments performed in toluene.[10] We have no rationale for this change in behaviour. Note that in the presence of sulfonated calixarenes bearing H, n-C_4H_9, or n-C_6H_{13} substituents at the lower rim, the *endo* selectivity was close to 100% (Table 4, entries 1–3). The *n*-butyl-substituted surfactant **8** gave the highest optical induction, *ee* = 39%, the absolute conformation being *R* (Table 4, entry 3). Although the observed *ee*s were moderate, the enantioselectivity observed with complex **6** is one of the highest reported yet for norbornene hydroformylation experiments that lead to *endo* aldehydes.[10,28–30]

Remarks about the Regioslectivity of the Catalyst and the Role of the Surfactant

The results presented above unambiguously show that when operating in an olefin-water-surfactant medium, the linear aldehyde selectivities obtained with "1,3-calix diphosphite" **5** are almost as high as those observed in toluene. This suggests that in both media, water or toluene, the selectivity of the system is mainly controlled by the intrinsic properties of the ligand, notably its shape. As confirmed for the first time by an X-ray diffraction study, the rhodium atom (see above) of the catalytic precursor is deeply embedded in a molecular pocket formed by two almost parallel naphthyl planes and the two propyloxy groups. The net result is a restricted reaction domain, with the outcoming aldehyde adopting the shape (namely as elongated as possible) which best fits with that of the catalytic pocket.

In most examples outlined above, the reactivity in the water/surfactant medium was higher than when operating in organic solvents. One may wonder what the role of the surfactant is in these systems. As established by Shinkai et al., the aggregation properties of calixarene sulfonates in water are strongly dependent upon the length of the appended alkyl groups.[26] In the case of $(RO)_6$-calix[6]arene hexasulfonates, three types of compounds were identified, non-micellar calixarenes (e.g., for R = methyl), micelle-forming calixarenes (e.g., for R = butyl), and unimolecular micellar calixarenes (e.g., for R = dodecyl). Light-scattering measurements made on these calix[6]arenes (concentration in water: 1.0×10^{-3} M) gave an estimation of the aggregation number at 30 °C. The study showed that the C_6-substituted calix[6]arene formed small micelles constituted of 6 calixarenes, while the C_{12}-substituted calix[6]arene gave smaller aggregates (dimer or trimer).[24] In the Shinkai's classification, the sulfonated calix[4]arene **8** (*n*-butyl substituents), which gave the best results in octene and hexene hydroformylations, belongs to the micelle-forming calixarenes group. It appears therefore likely that in the hydroformylation reactions presented above the catalytic species operates inside the micelle, with the lipophilic C_4-chains acting as an efficient solvent for the catalyst/olefin mixture. This creates locally high Rh:alkene ratios, which incidentally lead to high activities. If the length of the surfactant substituents is changed, the catalyst environment also changes and, logically, its performance may be drastically modified.

Conclusions

In conclusion, in *water* and in the presence of *sulfonated calix[4]arenes* the *neutral* calix-diphosphite rhodium complex **5** efficiently drives olefin hydroformylation reactions towards the formation of linear aldehydes. The presence of the surfactant had a direct impact on both catalyst activity and regioselectivity of the reaction. The performance of the catalytic system was shown to be strongly dependent on the nature of the lipophilic tails, the best results being obtained with the *n*-butyl-substituted calixarene in the case of 1-octene. Obviously, micelles were formed in this case, which allow the formation of microenvironments characterised by a high metal:olefin ratio. Overall, this study shows, for the first time, that highly regioselective hydroformylation can be carried out in water without water-soluble phosphines.

Experimental Section

General Methods

All syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and were distilled immediately prior to use. Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded by using a Bruker AVANCE 300 spectrometer. ^1H NMR spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuterated solvents (77.16 ppm for $CDCl_3$) and the ^{31}P NMR data are given relative to external H_3PO_4. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Université de Strasbourg. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm; used for the aldehyde detection) or with a Chirasil-DEX CB column (25 m × 0.25 mm; used for the *ee* determination after reduction of the aldehydes into alcohols). The calixarene-diphosphites **1–3**,[10] the sulfonated-calixarenes **7–10**[24] and the complexes **5**[10] and **6**[10] were prepared according to literature procedures.

(*S*,*S*)-Acetylacetato-{5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene}rhodium(I) (4)

A solution of $Rh(acac)(CO)_2$ (0.094 g, 0.36 mmol) in CH_2Cl_2 (5 mL) was added to a solution of (*S*,*S*)-5,11,17,23-tetra-*tert*-butyl-25,27-dipropyloxy-26,28-bis(1,1′-binaphthyl-2,2′-dioxyphosphanyloxy)calix[4]arene (**1**) (0.500 g, 0.36 mmol) in CH_2Cl_2 (250 mL). The solution turned from green to yellow within a few minutes. After 16 h, the solvent was evaporated to dryness. The yellow solid was washed with cold hexane (−78 °C), then dried under vacuum; yield: 0.458 g (80%). IR (KBr): $\nu = 1514$, 1579 (acac) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.07$ (d, $^3J_{H,H} = 8.7$ Hz, 2H, $C\mathit{H}$ arom), 7.75 (d, $^3J_{H,H} = 8.8$ Hz, 4H, CH arom), 7.70 (d, $^3J_{H,H} = 8.2$ Hz, 2H, $C\mathit{H}$ arom), 7.48 (d, $^3J_{H,H} = 7.6$ Hz, 2H, CH arom), 7.30–7.21 (m, 8H, CH arom), 7.11–6.99 (m, 6H, CH arom), 6.93 (d, $^4J_{H,H} = 2.3$ Hz, 2H, *m*-ArH), 6.53 (d, $^4J_{H,H} = 2.2$ Hz, 2H, *m*-ArH), 6.40 (d, $^4J_{H,H} = 2.2$ Hz, 2H, *m*-ArH), 6.25 (d, $^4J_{H,H} = 2.2$ Hz, 2H, *m*-ArH), 5.42 and 3.42 (AB system, $^2J_{H,H} = 12.6$ Hz, 4H, $ArC\mathit{H}_2Ar$), 5.27 and 2.86 (AB system, $^2J_{H,H} = 13.0$ Hz, 4H, $ArC\mathit{H}_2Ar$), 4.55 (s, 1H, $C\mathit{H}$-acac), 4.43–4.28 (m, 4H, $OC\mathit{H}_2$), 2.30–2.22 (m, 4H, $C\mathit{H}_2CH_3$), 1.08 [s, 18H, $C(CH_3)_3$], 1.00 (t, $^3J_{H,H} = 7.4$ Hz, 6H, $CH_2C\mathit{H}_3$), 0.78 [s, 18H, $C(C\mathit{H}_3)_3$], 0.28 (s, 6H, CH_3 of acac); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 183.45$ (s, *C*O-acac), 152.31–118.99 (arom C’s), 98.15 (s, CH of acac), 77.32 (s, $O\mathit{C}H_2$), 33.86 (s, $Ar\mathit{C}H_2Ar$), 33.77 (s, $Ar\mathit{C}H_2Ar$), 33.62 [s, $\mathit{C}(CH_3)_3$], 33.53 [s, $\mathit{C}(CH_3)_3$], 31.24 [s, $C(\mathit{C}H_3)_3$], 31.05 [s, $C(\mathit{C}H_3)_3$], 25.26 (s, CH_3 of acac), 23.10 (s, $\mathit{C}H_2CH_3$), 10.33 (s, $CH_2\mathit{C}H_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 126.6$ (d, $J_{P,Rh} = 328$ Hz); MS (ESI TOF): $m/z = 1586.55$ $[M+Na]^+$, 1563.56 $[M]^+$, 1463.52 $[M-C_5H_7O_2\ (acac)]^+$ expected isotopic profiles; anal. calcd. for $C_{95}H_{97}O_{10}P_2Rh$: C 72.97, H 6.25; found: C 72.91, H 6.31.

Crystals of **4** (yellow) suitable for X-ray diffraction were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **4**.

Crystal Structure of 4·2/3 $CHCl_3$

$Mr = 1643.32$, monoclinic, $P2_1$, $a = 12.726(2)$, $b = 20.115(3)$, $c = 17.111(3)$ Å, $\beta = 102.440(10)$, $V = 4277.3(13)$ Å^3, $Z = 2$, $D_x = 1.276\ mg\,m^{-3}$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 1.32\ cm^{-1}$, $F(000) = 1722$, $T = 90(2)$ K. Data were collected on a Oxford Diffraction Xcalibur Saphir 3 diffractometer (graphite $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structure was solved with SIR-97,[31] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELX-97[32] and full-matrix least-square techniques (use of F^2; x, y, z, β_{ij} for P, C and O atoms, x, y, z in riding mode for H atoms; 1009 variables and 10539 observations with $I > 2.0\,\sigma(I)$; calcd. $w = 1/[\sigma^2(F_0^{\,2}) + (0.0943P)^2]$ where $P = (F_o^{\,2} + 2F_c^{\,2})/3$. $R1 = 0.0681$, $wR2 = 0.1570$, $S_w = 0.925$, $\Delta\rho < 0.56$ eÅ^{-3}, Flack parameter $= -0.04(3)$. CCDC 705626 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. The “Alerts Level A” in the checkcif are mainly due to the *tert*-butyl groups, which display a large thermal motion (near disorder or free rotation for the C48 and C52 quaternary $\mathit{C}Me_3$ atoms).

General Procedure for the Hydroformylation Experiments

The hydroformylation experiments were carried out in a glass-lined, 100-mL stainless steel autoclave containing a magnetic stirring bar. In a typical run, the autoclave was charged successively under nitrogen with [Rh(acac)L] (L = **1–3**) dissolved in the olefin, ligand, solvent (toluene or a water-surfactant mixture), and 0.1 mL of decane. Once closed, the autoclave was flushed twice with syngas (CO/H_2 1:1 v/v), then pressurised with a CO/H_2 mixture and heated at 50 °C. During the experiments, several samples were taken and analysed by GC. At the end of the runs performed with a surfactant an emulsion was recovered, which remained stable for long periods (whatever the sulfonated calixarene used). In the absence of surfactant, two phases could be observed. In this case, the catalyst was contained in the organic phase. All reactions were performed at a pressure of 20 bar. This value corresponds to a pressure frequently used in the literature.[1]

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