DOI: 10.1002/ejoc.201000245

# Solvent-Free Olefin Hydroformylation Using Hemispherical Diphosphites

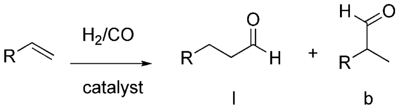
Laure Monnereau,[a] David Sémeril,*[a] and Dominique Matt*[a]

**Keywords:** Calixarenes / Rhodium / Solvent-free hydroformylation / Diphosphite / Olefins

With rhodium complexes containing hemispherical diphosphite ligands derived from a calixarene skeleton, olefins can be hydroformylated efficiently under *solvent-free* conditions. For example, in the hydroformylation of 1-octene ($T = 80$ °C, $P = 20$ bar, olefin:Rh = 200000:1) one of the catalysts investigated resulted in a TOF of 17290 mol(converted 1-octene)·mol(Rh)$^{-1}$·h$^{-1}$, the regioselectivity towards the linear aldehyde reaching then 97.9 %.

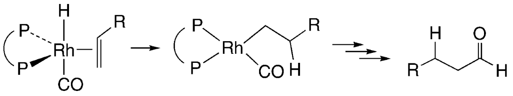
## Introduction

The hydroformylation of olefins (or oxo process) is an important catalytic process, which was discovered by Roehlen in 1938. In this reaction, aldehydes are produced from olefins, carbon monoxide and hydrogen in the presence of a transition metal catalyst (Scheme 1). The development of hydroformylation is considered one of the premier achievements of 20th century industrial chemistry. The annual production of oxo-aldehydes reached about $9 \times 10^6$ tons in 2008. One of the most performing metal used for this reaction is rhodium.[1]



Scheme 1. Transition metal-catalyzed hydroformylation of α-olefins.

Rhodium complexes catalyse hydroformylation of olefins under very mild conditions. Despite their high activity, the simple rhodium salts that were initially employed are not attractive because they give high amounts of branched aldehydes, such as, e.g., isobutyraldehyde when starting from propylene. Addition of phosphorus ligands, typically triarylphosphanes or triarylphosphites, usually results in active catalysts displaying good selectivity, at least with linear α-olefins which lead to high proportions of linear aldehydes.[2] This modified rhodium technology, which originally led to 85% *n*-butanal selectivity in the hydroformylation of propene,[3] was put into commercial production by Union Carbide in 1976.[4–8] Since this date, many efforts have been made to improve the linear selectivity of these catalysts. A very efficient approach towards this goal was initiated in 1992 by Casey, who found that chelating disphosphanes with a large natural bite angle increase the regioselectivity.[9] This concept has been thoroughly studied and extended to other catalytic reactions by van Leeuwen.[10–12] The most important feature of this class of ligands[13–18] concerns their ability to favour the formation of trigonal-bipyramidal hydrido carbonyl species in which the two phosphorus atoms occupy equatorial sites (Scheme 2). Mainly for steric reasons, these intermediates orientate the olefin insertion step towards the formation of a linear alkyl–rhodium complex, which ultimately will then result in formation of a linear aldehyde.[19–21]



Scheme 2. Equatorial-equatorial configuration of the two phosphorus atoms leading to the formation of the linear aldehyde.

Recently, we reported on the synthesis and catalytic properties of calix[4]arene-based diphosphites having both phosphorus atoms substituted by the bulky 1,1′-binaphthalene-2,2′-dioxy moiety.[22,23] In these ligands, which adopt an hemispherical shape, the phosphorus atoms are attached to the oxygen atoms of two distal phenolic rings (rings 1 and 3) and therefore have been referred to as "1,3-calixdiphosphites". They readily form chelate complexes in which the ligand bite angle is significantly larger than 90°. Combination of such diphosphites with $[Rh(acac)(CO)_2]$ led to highly regioselective hydroformylation catalysts. The high linear aldehyde selectivities obtained with these ligands were attributed to the ability of the hemispherical ligand not only to behave as a chelator with a large bite angle, but also as a ligand confining the metal in a tight molecular pocket, thereby increasing the steric pressure on the catalytic centre. Both features act cooperatively so as to orientate the reaction towards the formation of linear Rh-alkyl intermediates. It is noteworthy that the selectivities towards linear aldehydes were considerably superior to those ob-

---

[a] Laboratoire de Chimie Inorganique Moléculaire et Catalyse,
Université de Strasbourg, Institut de Chimie,
UMR 7177 CNRS,
1 rue Blaise-Pascal, 67008 Strasbourg cedex, France
E-mail: dsemeril@chimie.u-strasbg.fr
dmatt@chimie.u-strasbg.fr

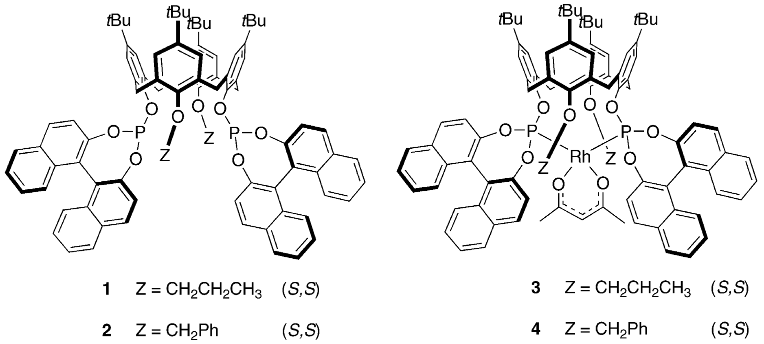


Figure 1. Hemispherical “1,3-calix[4]arene-diphosphites” (left) and complexes (right) used in this study.

tained with related diphosphites having smaller P-substituents.[24,25] Recently, we showed that these neutral complexes may also be used in *aqueous* medium, provided a sulfonated calix[4]arene acting as surfactant is added to the reaction mixture.[26] No significant loss of regioselectivity was observed. Under these conditions, micelles formed, the catalytic process taking place in concentrated microenvironments characterised by a high metal-to-olefin ratio, which incidentally increases the rate of the reaction. Continuing our efforts to develop eco-friendly catalytic systems, we decided to investigate the efficiency in *solvent-free* hydroformylation of two catalysts derived from 1,3-calix-diphosphites, namely the rhodium complexes **1** and **2** (Figure 1). *Solvent-free* synthesis has recently become increasingly attractive, but it has rarely been applied to hydroformylation.[27–29]

## Results and Discussion

Preliminary runs were carried out in order to determine the influence on the catalytic outcome of additional free ligand as well as that of a particular $CO/H_2$ ratio. We first assessed complex **3** in the *solvent-free* hydroformylation of 1-octene and styrene. The tests were performed at 80 °C in 4-hour runs with an α-olefin-to-Rh ratio of 5000. A pressure of 20 bar $CO/H_2$ (1:1) was applied to the experiments with 1-octene and of 10 bar $CO/H_2$ (1:1) for those with styrene. These conditions resulted in conversions of 84.7% (1-octene) and 68.6% (styrene), respectively. The corresponding linear aldehyde selectivities were 70.2% (1-octene) and 36.9% (styrene) (Table 1, entries 1 and 5). To improve the performance of this catalyst, we added an excess of ligand with the hope of preventing formation of “naked” rhodium,[30] which behaves as an unselective catalyst. In the case of 1-octene, addition of 4 equiv. of **1** increased the l:b ratio to 69.9. With 9 equiv. of **1**, the l:b ratio reached 85.0 (Table 1, entries 2 and 3). For styrene hydroformylation, the maximum of regioselectivity towards linear aldehyde (76.6%) was observed when adding only 4 equiv. of diphosphite **1** (Table 1, entries 5–7).

As frequently observed with phosphane–rhodium catalysts, the activities increased when increasing the partial hydrogen pressure.[26] Thus, with a carbon $CO/H_2$ ratio of 1:2 instead of 1:1 the conversion rose from 75.4–88.7 for 1-octene and from 64.1–91.9% for styrene, without altering significantly the regioselectivities (Table 1, entries 3, 4, 6 and 8).

Taking into account the above results, the hydroformylation tests presented hereafter were all performed using a $CO:H_2$ ratio of 1:2. For the hydroformylation of 1-octene,

Table 1. Varying the amount of free ligand **1** and the partial $H_2$ pressure in the hydroformylation of 1-octene and styrene using **3**.[a]

| Entry | Free L[b] | $P(CO/H_2)$ $V(CO)/V(H_2)$ | Conversion (%) | TOF[c] | Product distribution |  |
|---|---|---|---|---|---|---|
|  |  |  |  |  | Isomerisation (%) | Aldehydes (%) [l (%)/b (%) = l:b] |
| 1-Octene $P(CO/H_2)$ = 20 bar |  |  |  |  |  |  |
| 1 | 0 | 1:1 | 84.7 | 1060 | 6.4 | 78.3 [70.2:29.8 = 2.3] |
| 2 | 4 | 1:1 | 78.2 | 980 | 6.7 | 68.7 [98.6:1.4 = 69.9] |
| 3 | 9 | 1:1 | 75.4 | 940 | 7.3 | 70.9 [98.8:1.2 = 85.0] |
| 4 | 9 | 1:2 | 88.7 | 1110 | 7.1 | 81.6 [98.8:1.2 = 84.5] |
| Styrene $P(CO/H_2)$ = 10 bar |  |  |  |  |  |  |
| 5 | 0 | 1:1 | 68.6 | 860 | / | 68.6 [36.9:63.1 = 0.6] |
| 6 | 4 | 1:1 | 64.1 | 800 | / | 64.1 [76.6:23.4 = 3.3] |
| 7 | 9 | 1:1 | 63.8 | 800 | / | 63.8 [76.1:23.9 = 3.2] |
| 8 | 4 | 1:2 | 91.9 | 1150 | / | 91.9 [81.1:18.9 = 4.3] |

[a] α-Olefin (10 mmol), **3** (2 µmol, α-olefin:Rh = 5000), 80 °C, 4 h. The conversions were determined by GC using decane (0.5 mL) as internal standard. [b] Additional free ligand (equiv./Rh). [c] $mol(conv.\ olefin)\cdot mol(Rh)^{-1}\cdot h^{-1}$.

1-hexene, allyl benzyl ether, and 2-vinylnaphthalene 9 equiv. of free phosphite were added to the catalyst precursor. For styrene, only 4 equiv. of additional diphosphite were used.

### Hydroformylation of 1-Octene

These experiments were carried out with **3** and **4** at 50 and 80 °C under 20 bar $CO/H_2$ (Table 2, entries 1–10). As previously observed when toluene or water was used as solvent, replacement of the propyloxy substituents of the calix[4]arene moiety by two bulky benzyloxy groups led to lower reaction rates and higher linear aldehyde selectivity (i.e. higher l:b ratio).[23,26] For example, at 80 °C, conversions of 88.7% (l:b = 84.5) and 80.7% (l:b = 122.6) were observed with catalysts **3** and **4**, respectively (Table 2, entries 5 and 6). Seeking for the highest catalytic activity, we decided to increase the 1-octene-to-Rh ratio. Thus, applying an olefin:Rh ratio of 20000:1 resulted in TOFs of 4470 and 4050 mol(converted octene)·mol(Rh)$^{-1}$·h$^{-1}$, for complexes **3** and **4**, respectively. With an olefin:Rh ratio of 200000, the TOFs rose to 17209 (**3**) and 15640 (**4**) mol(converted octene)·mol(Rh)$^{-1}$·h$^{-1}$ (Table 2, entries 7–10). We observed that a decrease of the rhodium concentration induced a slight decrease of the percentage of linear aldehyde. Note that similar high activities were previously reported for Xantphites, but these ligands gave lower regioselectivities.[31]

### Hydroformylation of 1-Hexene

Good selectivities were also obtained in the hydroformylation of 1-hexene. Thus, using precatalyst **3** at 50 °C under 20 bar $CO/H_2$ led to a l:b ratio of 34.5. Applying the same conditions to **4** led to a l:b ratio of 38.8 (Table 3, entries 1 and 2). Repeating these experiments at 80 °C resulted in slightly lower selectivities with both complexes, but the reaction rates increased by ca. 50%. As previously observed for experiments carried out in toluene,[23] the propyl-substituted catalyst **3** showed higher activities than **4**. Thus, at 80 °C, TOFs of 830 and 680 mol(conv. hexene)·mol(Rh)$^{-1}$·h$^{-1}$ were obtained with **3** and **4**, respectively (Table 3, entries 3 and 4).

### Hydroformylation of Allyl Benzyl Ether

Reduction of the linear aldehyde obtained by hydroformylation of allyl benzyl ether, followed by cleavage of the benzyl group, is a potential method for synthesising 1,4-butanediol. The latter constitutes an important chemical product that is used industrially as solvent as well as for the manufacturing of plastics and fibers.[32] Operating at 120 °C, the *solvent-free* hydroformylation of allyl benzyl ether led to mixtures containing ca. 50% of aldehydes and 50% of benzyl propyl ether (Table 4, entries 1 and 2). The large amount of hydrogenated olefin produced under these conditions, which makes this method industrially non viable, simply reflects the relative difficulty to hydroformylate

Table 2. *Solvent-free*, rhodium-catalysed hydroformylation of 1-octene using complexes **3** and **4**.[a]

| Entry | [Rh] | $T$ (°C) | Time (h) | Conversion (%) | TOF[b] | Product distribution | |
|---|---|---|---|---|---|---|---|
| | | | | | | By-product Isomerisation (%) | Aldehydes (%) [l (%)/ b (%) = l:b] |
| 1 | **3** | 50 | 1 | 44.8 | 2240 | 2.2 | 42.6 [100:0 >100[c]] |
| 2 | **3** | 50 | 4 | 85.3 | 1070 | 3.0 | 82.3 [98.9:1.1 = 89.7] |
| 3 | **4** | 50 | 1 | 36.8 | 1840 | 1.8 | 35.0 [100:0 >100[c]] |
| 4 | **4** | 50 | 4 | 85.8 | 1070 | 2.7 | 83.1 [99.1:0.9 = 113.8] |
| 5 | **3** | 80 | 4 | 88.7 | 1110 | 7.1 | 81.6 [98.8:1.2 = 84.5] |
| 6 | **4** | 80 | 4 | 80.7 | 1010 | 12.8 | 67.9 [99.2:0.8 = 122.6] |
| 7[d] | **3** | 80 | 4 | 89.2 | 4470 | 10.6 | 78.6 [98.9:1.1 = 94.2] |
| 8[d] | **4** | 80 | 4 | 81.1 | 4050 | 9.3 | 71.8 [99.0:1.0 = 97.6] |
| 9[e] | **3** | 80 | 4 | 34.6 | 17290 | 1.6 | 33.0 [97.9:2.1 = 46.6] |
| 10[e] | **4** | 80 | 4 | 31.3 | 15640 | 2.3 | 29.0 [98.3:1.7 = 58.6] |

[a] α-Olefin (10 mmol), [Rh] (2 µmol, α-olefin:Rh = 5000), (additional free L):[Rh] = 9, $P(CO/H_2)$ = 20 bar, $V(CO):V(H_2)$ = 1:2. The conversions were determined by GC using decane (0.5 mL) as standard. [b] mol(conv. olefin)·mol(Rh)$^{-1}$·h$^{-1}$. [c] Exact value not determined because of a very low amount of branched aldehydes. [d] 1-Octene (40 mmol), [Rh] (2 µmol, 1-octene:Rh = 20000). [e] 1-Octene (40 mmol), [Rh] (0.2 µmol, 1-octene:Rh = 200000).

Table 3. *Solvent-free*, rhodium-catalysed hydroformylation of 1-hexene using complexes **3** and **4**.[a]

| Entry | [Rh] | $T$ (°C) | Time (h) | Conversion (%) | TOF[b] | Product distribution | |
|---|---|---|---|---|---|---|---|
| | | | | | | By-product Isomerisation (%) | Aldehydes (%) [l (%)/b (%) = l:b] |
| 1 | **3** | 50 | 4 | 41.6 | 520 | 1.2 | 40.4 [97.2:2.8 = 34.5] |
| 2 | **4** | 50 | 4 | 36.9 | 450 | 2.3 | 34.6 [97.5:2.5 = 38.8] |
| 3 | **3** | 80 | 4 | 66.2 | 830 | 2.2 | 64.0 [96.1:3.9 = 24.5] |
| 4 | **4** | 80 | 4 | 54.2 | 680 | 5.3 | 48.9 [96.5:3.5 = 27.3] |

[a] α-Olefin (10 mmol), [Rh] (2 µmol, α-olefin:Rh = 5000), (additional free L):[Rh] = 9, $P(CO/H_2)$ = 20 bar, $V(CO):V(H_2)$ = 1:2. The conversions were determined by GC using decane (0.5 mL) as standard. [b] mol(conv. olefin)·mol(Rh)$^{-1}$·h$^{-1}$.

Table 4. *Solvent-free*, rhodium-catalysed hydroformylation of allyl benzyl ether using complexes **3** and **4**.[a]

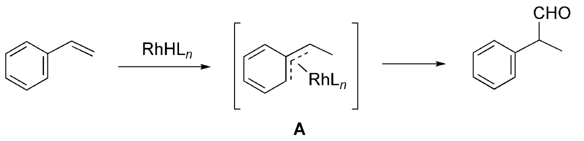
| Entry | [Rh] | $T$ | Time | Conversion | TOF[b] | Product distribution | | |
|---|---|---|---|---|---|---|---|---|
| | | (°C) | (h) | (%) | | By-product | | Aldehydes |
| | | | | | | Hyd. (%) | Iso (%) | (%) [l (%)/b (%) = l:b] |
| 1 | **3** | 120 | 4 | 100 | 1250 | 46.6 | traces | 53.4 [80.9:19.1 = 4.2] |
| 2 | **4** | 120 | 4 | 48.5 | 600 | 22.8 | 1.0 | 24.7 [84.1:15.9 = 5.3] |
| 3[c] | **3** | 120 | 4 | 92.1 | 1150 | 27.3 | 11.0 | 64.8 [87.6:12.4 = 7.1] |
| 4[c] | **4** | 120 | 4 | 42.8 | 530 | 8.7 | 6.6 | 27.5 [90.7:9.3 = 9.8] |

[a] $\alpha$-Olefin (10 mmol), [Rh] (2 µmol, $\alpha$-olefin:Rh = 5000), (additional free L)/[Rh] = 9, $P(CO/H_2)$ = 10 bar, $V(CO):V(H_2)$ = 1:2. The conversions were determined by GC using decane (0.5 mL) as standard and by $^1H$ NMR spectroscopy. [b] mol(conv. olefin)·mol(Rh)$^{-1}$·h$^{-1}$. [c] $V(CO):V(H_2)$ = 1:1.

*O*-allyl groups with respect to non-functionalised olefins. Furthermore, the linear aldehyde selectivity of this reaction was moderate (l:b ≈ 5) in comparison with the results presented above for 1-octene and 1-hexene. Reducing the partial hydrogen pressure decreased somewhat the amount of hydrogenated olefin and increased the regioselectivity. Thus, when applying a $CO/H_2$ ratio of 1:1, the l:b ratio raised up to 9.8 (Table 4, entries 3, 4).

## Hydroformylation of Styrene

It is well known that with conventional rhodium-phosphane catalysts, styrene hydroformylation leads mainly to the branched aldehyde, namely 2-phenylpropanal.[33] This result can be explained by the easy formation of a $\eta^3$-complex of type **A** (Scheme 3). As previously observed in organic and aqueous media, precatalysts **3** and **4** produce the linear aldehyde with high regioselectivities. Thus, operating at 50 °C in the absence of solvent under $CO/H_2$ (1:2, 10 bar), resulted in linear aldehyde selectivities of 82.0 and 84.7% with complexes **3** and **4**, respectively (at ca. 90% conversion) (Table 5, entries 2 and 4). Under these conditions the activities were about 7 times higher than in the experiments carried out in toluene.[23] Again, hydroformylation occurred faster with **3** than with **4** [TOF = 2080 (**3**) vs. 1690 (**4**) mol(converted styrene)·mol(Rh)$^{-1}$·h$^{-1}$; see Table 5, entries 1 and 3]. It is noteworthy that the regioselectivities remained constant during the whole catalytic process (Table 5, entries 1–4). Operating at 80 °C instead of 50 °C only slightly modified the catalytic outcome (Table 5, entries 5 and 6).



Scheme 3. $\eta^3$-Intermediate formed in the hydroformylation of styrene.

Table 5. *Solvent-free*, rhodium-catalysed hydroformylation of styrene using complexes **3** and **4**.[a]

| Entry | [Rh] | $T$ (°C) | Time (h) | Conv. (%) | TOF[b] | Aldehydes l (%) | b (%) | l:b |
|---|---|---|---|---|---|---|---|---|
| 1 | **3** | 50 | 1 | 41.6 | 2080 | 82.5 | 17.5 | 4.7 |
| 2 | **3** | 50 | 4 | 91.2 | 1140 | 82.0 | 18.0 | 4.5 |
| 3 | **4** | 50 | 1 | 33.9 | 1690 | 84.6 | 15.4 | 5.5 |
| 4 | **4** | 50 | 4 | 90.6 | 1130 | 84.7 | 15.3 | 5.5 |
| 5 | **3** | 80 | 4 | 91.9 | 1150 | 81.1 | 18.9 | 4.3 |
| 6 | **4** | 80 | 4 | 92.1 | 1150 | 83.4 | 16.6 | 5.0 |

[a] $\alpha$-olefin (10 mmol), [Rh] (2 µmol, $\alpha$-olefin:Rh = 5000), (additional free L):[Rh] = 4, $P(CO/H_2)$ = 10 bar, $V(CO):V(H_2)$ = 1:2. The conversions were determined by GC using decane (0.5 mL) as standard. [b] mol(conv. olefin)·mol(Rh)$^{-1}$·h$^{-1}$.

## Hydroformylation of 2-Vinylnaphthalene

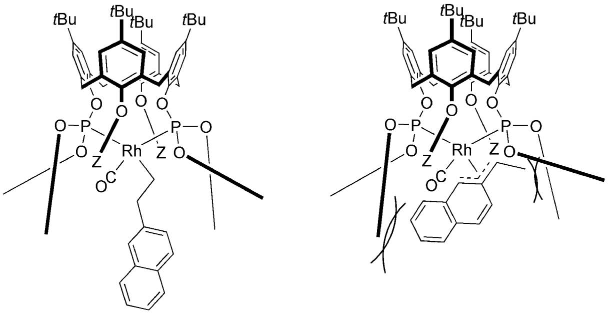
Runs with 2-vinylnaphthalene (melting point ca. 65 °C) were carried out at 80 °C under 10 bar $CO/H_2$ (1:2) in 4-hour experiments. From the literature it is known that hydroformylation of 2-vinylnaphthalene with conventional diphosphanes, mainly results, as for styrene, in the corresponding branched aldehyde.[34,35] Interestingly, we found that with catalysts **3** and **4** the linear aldehyde was the major regioisomer [linear selectivity: 67.9% (**3**), 72.0% (**4**); see Table 6, entries 1 and 2]. In these runs important amounts of hydrogenated substrate (2-ethylnaphthalene) were also produced. To prevent hydrogenation of the substrate we decided to reduce the partial hydrogen pressure. Thus, by using a $CO/H_2$ ratio of 1:1 instead of 1:2, the production of 2-ethylnaphthalene considerably dropped (19.2% vs. 47.1%; see Table 6, entries 1 and 3), without modifying the regioselectivity. A logical explanation for the

Table 6. *Solvent-free*, rhodium-catalysed hydroformylation of 2-vinylnaphthalene using complexes **3** and **4**.[a]

| Entry | [Rh] | $T$ | Time | Conversion | TOF[b] | Product distribution | |
|---|---|---|---|---|---|---|---|
| | | (°C) | (h) | (%) | | By-product | Aldehydes |
| | | | | | | Hydrogenation (%) | (%) [l (%)/b (%) = l:b] |
| 1 | **3** | 80 | 4 | 100 | 1250 | 47.1 | 52.9 [67.9:32.1 = 2.1] |
| 2 | **4** | 80 | 4 | 96.7 | 1200 | 27.0 | 69.7 [72.0:28.0 = 2.6] |
| 3[c] | **3** | 80 | 4 | 93.0 | 1160 | 19.2 | 73.8 [68.1:31.9 = 2.1] |

[a] $\alpha$-olefin (10 mmol), [Rh] (2 µmol, $\alpha$-olefin:Rh = 5000), (additional free L):[Rh] = 9, $P(CO/H_2)$ = 10 bar, $V(CO):V(H_2)$ = 1:2. The conversions were determined by $^1H$ NMR spectroscopy. [b] mol(conv. olefin)·mol(Rh)$^{-1}$·h$^{-1}$. [c] $V(CO):V(H_2)$ = 1:1.

formation of the linear aldehyde is the preferred formation with 2-vinylnaphthalene of an alkyl intermediate (Figure 2), rather than an allyl-type complex (of type **A**, Scheme 3), the latter coordination mode being prevented by strong steric interactions between the naphthyl fragment of the substrate and the pocket that hosts the metal. Our findings are a further confirmation that metal confinement may induce shape selectivity.



*favorable* *unfavorable*

Figure 2. Favorable and unfavorable intermediates in the hydroformylation of 2-vinylnaphthalene.

## Conclusions

The hydroformylation of non-functionalised α-olefins is efficiently catalysed in the absence of solvents by [Rh(acac)("1,3-calix-diphosphite")] complexes. It was shown that in all cases the reaction rate is considerably increased with respect to reactions performed in toluene. Furthermore, the catalysts display a high selectivity for linear aldehydes (except for allyl benzyl ether), a result which indicates that the ability of the hemispherical ligands to embrace the catalytic centre are not affected by the substrates studied nor by combinations of the latter with the aldehydes formed. A remarkable result was obtained in the hydroformylation of 1-octene with catalyst **3**, which resulted in a TOF as high as 17290 mol(converted 1-octene)·mol(Rh)$^{-1}$·h$^{-1}$, the linear aldehyde selectivity being 97.9% in this case. In comparison with our earlier study, in which the olefin was dissolved in toluene ($c$ = 0.7 M), this rate corresponds to an eightfold acceleration. Further studies on the rhodium catalysts presented in this work will focus on their possible recycling as well their use in domino reactions involving a hydroformylation step.

## 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 $^1$H NMR spectra (used in the determination of some conversions and selectivities) were recorded by using a Bruker AVANCE 300. $^1$H NMR spectra were referenced to residual protonated solvents ($\delta$ = 7.26 ppm for $CDCl_3$). The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm). 1,3-Calix-diphosphites **1** and **2** and the complexes **3** and **4** were prepared according to literature procedures.[23]

**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 under nitrogen with [Rh(acac)(1,3-calix-diphosphite)] (0.002 mmol) in olefin solution, free 1,3-calix-diphosphite dissolved in olefin (total amount of olefin: 10 mmol), and internal standard (decane, 0.5 mL), when required. Once closed, the autoclave was flushed twice with syngas ($CO:H_2$ = 1:1, v/v), pressurised with a $CO:H_2$ (1:2 or 1:1) mixture and heated. At the end of the run, the autoclave was cooled to room temperature before being depressurised. A sample was taken and analysed by GC or by $^1$H NMR spectroscopy.

## Acknowledgments

The authors wish to thank the French Agence Nationale de la Recherche (ANR) for financial support (ANR-MATCALCAT funding scheme). The University of Strasbourg is gratefully acknowledged for a grant to L. M. (Bourse Présidence).

---

[1] *Rhodium Catalyzed Hydroformylation* (Eds.: P. W. M. van Leeuwen, C. Claver), Kluwer, Dordrecht, **2000**.
[2] J. Falbe, *Carbon Monoxyde in Organic Synthesis*, Springer, Berlin, **1970**.
[3] F. J. Smith, *Platinum Met. Rev.* **1975**, *19*, 93–95.
[4] R. L. Pruett, J. A. Smith, U. S. Patent 3,527,809 to Union Carbide **1970**.
[5] R. L. Pruett, *Ann. N. Y. Acad. Sci.* **1977**, *295*, 239–248.
[6] R. Fowler, H. Connor, R. A. Baehl, *Chemtech* **1976**, 772–772.
[7] R. Fowler, H. Connor, R. A. Baehl, *Hydrocarbon Proc.* **1976**, *55*, 247–249.
[8] E. A. V. Brewester, *Chem. Eng.* **1976**, *83*, 90–91.
[9] C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney Jr., D. R. Powell, *J. Am. Chem. Soc.* **1992**, *114*, 5535–5543.
[10] P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741–2769.
[11] P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Acc. Chem. Res.* **2001**, *34*, 895–904.
[12] M.-N. Birkholz, Z. Freixa, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2009**, *38*, 1099–1118.
[13] R. Paciello, L. Siggel, M. Röper, *Angew. Chem. Int. Ed.* **1999**, *38*, 1920–1923.
[14] L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed.* **1999**, *38*, 336–338.
[15] L. A. van der Veen, P. H. Keeven, G. C. Schoemaker, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 872–883.
[16] W. Ahlers, M. Röper, P. Hofmann, D. C. M. Warth, R. Paciello, *WO 01/58589 (BASF)* **2001**.
[17] J. R. Briggs, G. T. Whiteker, *Chem. Commun.* **2001**, 2174–2175.
[18] R. P. J. Bronger, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **2003**, *22*, 5358–5369.
[19] A. van Rooy, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 835–847.
[20] L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1999**, *18*, 4765–4777.
[21] J. I. van der Vlugt, R. Sablong, P. C. M. M. Magusin, A. M. Mills, A. L. Spek, D. Vogt, *Organometallics* **2004**, *23*, 3177–3183.
[22] D. Sémeril, C. Jeunesse, D. Matt, L. Toupet, *Angew. Chem. Int. Ed.* **2006**, *45*, 5810–5814.
[23] D. Sémeril, D. Matt, L. Toupet, *Chem. Eur. J.* **2008**, *14*, 7144–7155.

[24] C. Kunze, D. Selent, I. Neda, R. Schmutzler, A. Spannenberg, A. Börner, *Heteroat. Chem.* **2001**, *12*, 577–585.

[25] C. Kunze, D. Selent, I. Neda, M. Freytag, P. G. Jones, R. Schmutzler, W. Baumann, A. Börner, *Z. Anorg. Allg. Chem.* **2002**, *628*, 779–787.

[26] L. Monnereau, D. Sémeril, D. Matt, L. Toupet, *Adv. Synth. Catal.* **2009**, *351*, 1629–1636.

[27] F. Shibahara, K. Nozaki, T. Hiyama, *J. Am. Chem. Soc.* **2003**, *125*, 8555–8560.

[28] D. I. Enache, W. Thian, D. Dumas, S. Ellwood, G. J. Hutchings, S. T. Taylor, S. Hawker, E. H. Stitt, *Catal. Today* **2007**, *128*, 18–25.

[29] M. L. Clarke, G. J. Roff, *Green Chem.* **2007**, *9*, 792–796.

[30] C. J. Cobley, D. D. Ellis, A. G. Orpen, P. G. Pringle, *J. Chem. Soc., Dalton Trans.* **2000**, 1109–1112.

[31] C. B. Dieleman, P. C. J. Kamer, J. N. H. Reek, P. W. N. M. van Leeuwen, *Helv. Chim. Acta* **2001**, *84*, 3269–3280.

[32] W. E. Smith, G. R. Chambers, R. C. Lindberg, J. N. Cawse, A. J. Dennis, G. E. Harrison, D. R. Bryant, *Catal. Org. React.* **1985**, *22*, 151–167.

[33] C. K. Brown, G. Wilkinson, *J. Chem. Soc. A* **1970**, 2753–2764.

[34] T. V. RajanBabu, T. A. Ayers, *Tetrahedron Lett.* **1994**, *35*, 4295–4298.

[35] E. Guimet, J. Parada, M. Diéguez, A. Ruiz, C. Claver, *Applied Catal. A: Gen.* **2005**, *282*, 215–220.

Received: February 23, 2010