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Bulky monophosphite ligands for ethene hydroformylation

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1. Introduction

The hydroformylation of olefins is a very important chemical reaction having considerable industrial impact. In particular, the rhodium-catalyzed hydroformylation is one of the world's largest homogeneously catalyzed processes in industry [1]. During the last decades, many efforts focused on the development of new catalytic systems able to provide simple, cheap, selective, and sustainable processes for the production of added-value chemicals: new ligands [2–4], biphasic catalytic systems [5–7], tandem reactions involving a hydroformylation step [8–18], asymmetric hydroformylation [19–23], catalysis in supercritical media [24–26], supramolecular catalysis [27–30], molecular-weight enlarged ligand for continuous reactions [31], bio-based catalysis [32], among others are some examples of the wide range of technologies used in the field of rhodium-catalyzed hydroformylation.

The hydroformylation of ethene, leading to propanal and *n*propanol, is a reaction of industrial interest since these chemical compounds can find many applications. Further to their direct use as solvents, they are also important intermediates for the production of propene, pesticides, pharmaceuticals, and fragrances. Unfortunately, this reaction often produces side products, such as ketones and even polyketone products [33,34]. Many examples, including heterogeneous catalytic systems, were reported. Notably, the group of Cole–Hamilton reported the excellent activity and

ABSTRACT

A wide range of monophosphite ligands was investigated in rhodium-catalyzed ethene hydroformylation. A stoichiometric gas mixture CO/H_2 /ethene 1:1:1 was used, the reaction being thus 100% atom economic. The reaction was found to be very selective and only propanal was formed under the reaction conditions studied. The most efficient catalytic system was **L1**-modified rhodium, and reaction parameters were optimized for this ligand. Under optimized catalytic conditions, reaction rates 10–15 times higher than those of the triphenylphosphine-modified system were obtained, demonstrating the high suitability of π -accepting ligands for this reaction. Stability tests, resistance toward water and acids in particular, showed the good stability of the selected phosphite **L1**. Notably, **L1** was more stable than cyclic phosphites **L6** and **L13**.

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selectivity toward *n*-propanol using a triethylphosphine modified rhodium catalyst, achieving turnover frequencies up to 54,000 h⁻¹ [35]. Lately, Rodríguez at Dow reported on the hydroformylation of diluted ethene using silica and resin-supported phosphines [36]. The mechanism and the kinetics of hydroformylation have been extensively studied in the last 20 years [37,38], and intermediate species such as [HRh(CO)₃(ethene)] [38] and [Rh(CH₃CH₂CO)(CO)₃(ethene)] [34] were detected, but to the best of our knowledge, no systematic study concerning ligand effects has been reported.

Van Leeuwen and co-workers have focussed since the mid 1970s on the application of bulky monophosphites in the hydroformylation reaction of alkenes [39-42]. Bulky phosphites performed much better than triphenylphosphine [43], which was especially important for otherwise unreactive alkenes. The electron-withdrawing effect of these ligands was shown to enhance CO dissociation in the complex $[HRh(CO)_{3}L]$ **1** (L being the phosphite ligand) and to favor the formation of the η^2 -alkene complex **2** (see Fig. 1). The rate limiting step now becomes the hydrogenolysis of the acyl complex 7. The important steric properties of these ligands enhance the formation of mono phosphite rhodium complexes in competition with CO, preventing the formation of less active [HRh(CO)₂L₂] or [HRh(CO)L₃] complexes [44]. For octene-1 TOFs of 160,000 mol mol⁻¹ h⁻¹ were obtained. Since steric factors dominate, it was thought that ethene might also give very high TOFs with the use of bulky phosphites.

One main drawback of phosphite ligands is their relative instability toward hydrolysis [45]. The P–O bond of phosphites is much weaker than the P–C bond of phosphines and phosphites may readily hydrolyze via metal or acid catalysis. In addition, alkyl



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Fig. 1. Mechanistic cycle of the rhodium-catalyzed hydroformylation of alkenes (equilibria omitted).

phosphites undergo Arbusov rearrangements via alkyl cation intermediates, which are catalyzed by metals, and for this reason, aryl phosphites are preferred, as formation of aryl cations is unlikely. On the other hand, phosphites are much less reactive toward molecular oxygen and the formation of phosphates is slower than the oxidation of phosphine to phosphine oxide. The present study will focus on the effect of various aryl phosphite ligands on the ethene hydroformylation rate and the hydrolytic stability of selected phosphites.

2. Phosphite ligand design

The design of phosphite ligands is based on several requirements. First only triaryl phosphites will be tested for their better stability and to avoid Arbuzov-type reactions. Second, an important steric bulk around the phosphorus atom is preferred, to favor the selective formation of monoligated rhodium species. Third, to investigate the electronic influence of the ligands on the catalytic activity, different functional groups will be introduced at the para position of the aryl group. Fourth, the influence of cyclic structures on the hydroformylation rate and stability will be studied. According to these four requirements, the 25 ligands described in Fig. 2 were prepared.

The library of ligands started with the syntheses of the well known bulky phosphite L1 and the UCC ligands L6 and L7 [46]. Analogs of L1 with different substituents in the para position of the aromatic rings were also prepared (L2, L3, L4, and L5). Similarly, L8 was prepared as a convenient analog of the UCC ligands in which the BHT (2,6-di-tert-butyl-4-methylphenoxy) unit was replaced by the 2,6-diphenylphenoxy moiety. C3-symmetric phosphite ligands L9-L12 were prepared, the 2,6-isopropylphenol and 2,6-diphenylphenol moieties (respectively ligands L9 and L10) bringing a very important steric bulk around the phosphorus atom. According to the literature, a linker between the arvloxy substituents in phosphite ligands increases their thermal stability [44]. To this end, the polycyclic phosphites L13 and L14 were synthesized. Finally, in order to evaluate the effect of the linker together with the electronic and steric factors of a single substituent within the same sub-class of phosphites, two different diols, 6,6'-methylenebis(2-tert-butyl-4-methylphenol) and 3,3',5,5'-tetra-tert-butyl[1,1'-biphenyl]-2,2'-diol, were selected as precursors for the two families of ligands L15–L21 and L22–L25, respectively.

3. Ligand screening conditions

The effect of the reported ligands in the rhodium-catalyzed hydroformylation of ethene was studied. An equimolar gas mixture of carbon monoxide, hydrogen, and ethene (1:1:1) was utilized during the reactions to keep the partial pressures of the three gases constant during the reaction. The catalytic tests were carried out in an AMTEC-SPR16 multireactor capable of maintaining the pressure of the gas mixture in each reactor and monitoring the gas uptake. In order to obtain reproducible results, all phosphites together with the rhodium precursor $[Rh(acac)(CO)_2]$ in toluene (5 mL) were subjected to an incubation period of 90 min at 80 °C under 20 bar of syngas to ensure the complete formation of the active $[HRh(CO)_x(L_{4-x}$ species prior to the addition of the substrate. After this period, the atmosphere of each reactor was replaced by 20 bar of the equimolar gas mixture $(CO/H_2/C_2H_4)$ and this pressure was kept constant while the reaction mixture was stirred at 80 °C for 90 min. Decane was utilized as internal standard, and the amount of propanal was determined by GC analysis using the previously calibrated propanal/decane response. After a few preliminary experiments, a concentration of rhodium of [Rh] = 0.25 mM and a metal to ligand ratio of L/Rh = 20 were selected as the best conditions to perform the screening of the 25 different phosphite ligands.

3.1. Ligand screening results and discussion

The results of the hydroformylation of ethene with rhodium/ phosphite catalysts are summarized in Figs. 3, 4 and 6–8. For each catalytic system, a minimum of three separate experiments were performed. The results are presented as averaged values.

For a matter of comparison, the same reaction was run using the conventional triphenylphosphine (PPh₃), which gave a turnover frequency of $2.23 \times 10^3 \text{ h}^{-1}$. According to these preliminary screening of ligands, phosphite ligands were found to be more active than PPh₃ in all cases except for ligands L9, L10, L13, L15, and L22. These five ligands present the maximum steric crowding around the phosphorus atom of the phosphite library, and it is believed that their low activity in ethene hydroformylation is due to their difficulty to form the ligated penta-coordinated Rh complexes under CO pressure. The formation of these active species during the incubation period was monitored *in situ* for selected ligands by high pressure infrared (HP-FTIR) spectroscopy. Experimentally, a cyclohexane solution of the appropriate ligand with the Rh



Fig. 4. Turnover frequencies for ligands L6–L8, L13, and L14.

precursor $[Rh(acac)(CO)_2]$ was heated to 80 °C while a syngas pressure was applied (20 bar) and the IR spectra of the carbonyl stretching range (2200–1600 cm⁻¹) was continuously monitored.

For ligands **L10**, **L13** and **L15**, a similar behavior was observed. Reaction of the rhodium precursor with the phosphite under an atmospheric pressure of argon resulted in the displacement of



Fig. 5. Expected and X-ray determined structures for **L14** (thermal ellipsoid probability level 50%; hydrogen atoms omitted for clarity).

one of the carbonyl ligands to give [Rh(acac)(CO)L], confirmed by a single strong absorption at 2011 and 2012 cm⁻¹, respectively. However, increasing the pressure of syngas to 20 bar resulted in the displacement of the phosphite ligand affording the

[Rh(acac)(CO)₂] precursor again, as indicated by the two characteristic bands at 2082 and 2013 cm⁻¹, instead of the active pentacoordinated hydride species. No other Rh-carbonyl complexes were observed in the IR spectra for 3 h until inactive Rh₄(CO)₁₂ and Rh₆(CO)₁₆ decomposition clusters started to appear. This behavior has been previously observed for bulky phosphine ligands under hydroformylation conditions [47]. We assume that the low catalytic activity found for ligands **L9** and **L22** is also due to this cluster carbonyl formation.

Nevertheless, most of the studied phosphites gave higher activity in ethene hydroformylation than triphenylphosphine, PPh₃. 2-*tert*-butylaryl phosphites (**L1–L5**) gave turnover frequencies up to $16.7 \times 10^3 h^{-1}$ (for **L1**, see Fig. 3).

Interestingly, the electronic character of the different substituents in the aromatic rings was found to have no predictable effect



Fig. 6. Turnover frequencies for ligands L9–L12.



Fig. 7. Turnover frequencies for ligands L15–L21.





on the catalytic performance of the ligands, and similar TOF values were obtained for those with *t*-butyl (**L2**) and Cl (**L5**) substituents in the *para* position of the rings and for those with H atoms (**L3**) and CF₃ groups (**L4**). The best results were obtained with **L1**, which possesses a methyl group in the *para* position of the aromatic rings.

The UCC ligands **L6–L8** gave higher TOFs with values up to $34.7 \times 10^3 h^{-1}$ (see Fig. 4). Similar performances were observed with binaphthol and biphenol moieties (**L6** vs. **L7**) and when the steric bulk was provided by phenyl rings instead of *tert*-butyl groups (**L7** vs. **L8**). Tricyclic ligands **L13** and **L14** showed very different behavior in catalysis; ligand **L14** provided a turnover frequency of $13.4 \times 10^3 h^{-1}$, whereas **L13** gave poor activity. This confirms the poor ability of this very bulky ligand [48] to form [RhH(CO)₃(**L**)] species under catalytic conditions [47]. Compared to **L13**, **L14** has two methylene linkers but lacks the *tert*-butyl groups in two directly linked aryl groups. This ligand was chosen because it was expected to adopt a partially open calix[3] rigid conformation allowing only coordination through the top of the cone (Fig. 5). However, its solid state structure revealed a totally different conformation.

As determined by single crystal X-ray diffraction, the structure of **L14** is not as crowded around the phosphorus atom as expected (the phenyl groups show an *up*, *down*, *up* configuration). Nevertheless, the activity of this ligand for ethene hydroformylation is very high and its polycyclic structure might be advantageous in terms of stability.

We mentioned before the poor activity of very bulky ligands **L9** and **L10**. Interestingly, the less sterically hindered C₃-symmetric tri-2-phenyl and trinaphthyl phosphites **L11** and **L12** were found to be very active with TOFs of 19.2×10^3 and 22.9×10^3 h⁻¹, respectively (Fig. 6).

The methylene-linked phosphite ligands, **L15–L21**, gave a wide distribution of results depending on the electronic and steric nature of the aryl substituents (Fig. 7). It is obvious that the activity of methylene-bridged phosphite ligands strongly depends on the steric and electronic nature of the aryl groups. HP-FTIR experi-

Table 1

Hydrolysis tests on selected ligands.^a

ments demonstrated that bulky ligand **L15** is not able to form the catalytically active species under the reaction conditions and consequently low TOF values are obtained with this ligand. Less steric crowding in the non-linked aryl substituent leads to higher activity as observed for the increasing TOF values for ligands **L15**, **L16**, and **L17**. At this point, the activity does not depend on steric factors as can be demonstrated with the similar TOFs obtained with **L17**, **L18**, and **L19**. However, electron-withdrawing groups in the non-linked aryl group can enhance the performance of this type of ligands increasing the TOFs up to 13×10^3 h⁻¹, as seen for ligands **L20** and **L21**.

Finally, the results from the hydroformylation experiments with the four phosphite ligands derived from 3,3',5,5'-tetra-tertbutyl[1,1'-biphenyl]-2,2'-diol (**L22–L25**) are summarized in Fig. 8. These results reveal the dependence of the catalytic activity on the nature of the third substituent in biphenyl-based ligands **L22–L25**. The behavior is really similar to that of ligands **L14– L21**; too much steric crowding leads to low TOFs and when sterics play no role (**L22**), electron-withdrawing substituents slightly improve the activity. However, for **L23–L25** ligands, the maximum TOFs were of $4.0 \times 10^3 h^{-1}$, just only slightly higher than the values obtained with PPh₃.

To choose the best ligand for this transformation among the ones described here, three criteria will be taken into account: (1) the activity presented above at 80 °C and 20 bar ethene-CO-H₂ 1:1:1 pressure, (2) the estimated cost of the ligand, important for industrial applications, and (3) the stability of the ligand.

In the next step of this investigation, stability tests will be performed, in particular toward water and acid that can often be present in industrial hydroformylation reactors and which are the main causes of phosphite decomposition [44].

3.2. Chemical stability of phosphite ligands

Being generally less susceptible to oxidation than phosphines, aryl phosphites mainly decompose via hydrolysis to afford





Ligand	%Decomposition (3 h)	%Decomposition (24 h)	%Decomposition (72 h)
P(OPh) ₃	78	99	100
L1	0	0	0
L6	6	17	18
L13	7	86	100
L14	8	20	100
L17	8	17	43

^a Experimental conditions: 0.1 mmol of ligand dissolved in 3 mL of acetone/dichloromethane and 0.1 mL of water. The mixture was heated to 60 °C and samples were analyzed by inverse gated decoupling ³¹P{¹H} NMR.

diarylphosphines or hetero-atom secondary phosphine oxides (HASPOs). In a large scale continuous system, water might be formed due to aldolcondensation of the aldehvde product. HASPOs add to aldehydes forming phosphonic acids, which act as a catalyst for hydrolysis [45]. Therefore, the study of the stability of the described phosphites toward hydrolysis will assess the suitability of the corresponding system for this transformation. The thermal stability of phosphites L6, L7, and L11 in the presence of aldehydes was studied by UCC many years ago to reveal that slight structural modifications such as the addition of linkers to form cyclic structures can improve the stability of these species [45,46]. More recently, Pringle and co-workers have reported a useful test to evaluate the stability of these compounds toward hydrolysis [4]. This experiment consists in taking a solution of the phosphite in a deliberately wet solvent and heating it to reflux while monitoring the formation of HASPOs by ³¹P NMR over time. The solvent of choice is a 1:1 mixture of acetone and dichloromethane. Solutions of selected phosphite ligands were prepared and water (3% w/w) was added. The homogeneous mixture was heated to 60 °C, and samples were taken and analyzed by inverse gated decoupling ³¹P{¹H} NMR in order to obtain quantitative analyses of the product distribution.

The effect of the linker between aryl groups in the stability toward hydrolysis of L1, L6, L13, L14, and L17 triaryl phosphites was studied (Table 1). Five different types of linkage were studied in addition to the non-linked phosphites with and without steric hindrance between the rings, L1 and P(OPh)₃. From the experimental results, it can be concluded that all of the ligands are more stable toward hydrolysis than triphenyl phosphite, but it seems that the stability improvement has nothing to do with the linkage between aryl groups. Polycyclic phosphites L13 and L14, expected to afford the highest stability, were totally hydrolyzed within 72 h. On the other hand, non-linked L1 remained intact after 3 days at 60 °C under the experimental conditions. Ligands bearing a single link between two of the aryl groups, L6 and L17, presented a moderate stability. It appears at this stage of the study that ligand L1 is very stable and is a very good candidate for this reaction, since it leads to very high catalytic activity (TOF of $16.7 \times 10^3 \text{ h}^{-1}$, Fig. 3) and is readily available and very cheap (it is an antioxidant for polypropylene).

An acidolysis test was then run on this ligand L1. Ligands L2, L3, and L4 were subjected to this test as well. For this purpose, aqueous hydrochloric acid (HCl) was deliberatively added to catalyze the hydrolysis of the bulky phosphites (Table 2). The ligands were first dissolved in the same mixture as previously described for the hydrolysis test and heated to 60 °C for 48 h. Then, concentrated HCl was added to the mixture which was stirred at 60 °C and the samples were analyzed by inverse gated decoupling.

Interestingly, all ligands, and especially **L1**, **L3** and **L4**, showed low levels of decomposition after 30 h. Moreover, only ca. 50% of ligand **L4** was hydrolyzed after 2 days under such harsh conditions. Nevertheless, the observed decomposition patterns need to be compared with conventional triphenylphosphine to show the better ability of our system for this transformation. The experimental conditions of the aqueous and acid hydrolysis tests presented above were reproduced with PPh₃ (See Table 3). As expected, in the absence of Rh, triphenylphosphine showed a much higher stability under these conditions than bulky phosphites.

The data for phosphites, though, shed some light on the key structural factors that improve phosphite stability. Steric bulk enhances the stability of the phosphite and all of the phosphites tested here are much more robust toward hydrolysis than triphenyl phosphite ($P(OPh)_3$). In addition, it has been demonstrated that the presence of a linker between the aryl groups does not directly lead to a positive effect on the stability of triaryl phosphites in spite of earlier reports of UCC [46].

Surprisingly, free ligand **L4** containing electron-withdrawing CF₃ groups in the *para* position is the most stable phosphite. This probably means that the hydrolysis starts with a protonation and not with a nucleophilic attack of water at the P-atom; of course, the acid catalysis already corroborated that. Thus, the electron poor ligand is more resistant to hydrolysis. This may reverse in a metal complex. **L4** gave a much slower catalyst than **L1** (see above). The very active catalytic system Rh-**L6** was not further investigated because of its lower stability and the expected higher ligand costs. Since **L1** seems to give the best results overall, this system was studied in more detail.

3.3. Hydroformylation of ethene using the rhodium-L1 system

In order to find the optimum catalytic conditions and to get high turnover frequencies, several reaction parameters were modified. For this purpose, the catalyst concentration was decreased to 0.1 mM in order to avoid formation of large amounts of propanal that could influence the reaction rate. Importantly, this change in catalyst concentration resulted in a significant decrease in the turnover frequencies (from 16.7×10^3 to 11.0×10^3 h⁻¹). This effect was even more pronounced when the catalyst concentration was decreased further. In this series of experiments, the Rh/L1 ratio was kept constant, and thus, if the competition between CO and L plays a role, lowering the ligand concentration will diminish the concentration of the active catalyst. Indeed, when the ligand to rhodium ratio was increased (see Fig. 9a), the high reaction rates were recovered until reaching a plateau at L:Rh of 40. Such high ratios are common in phosphite-modified rhodium hydroformylation,

Table 2

Acid-hydrolysis tests on selected ligands. Experimental conditions: 0.1 mmol of ligand dissolved in 3 mL of acetone/dichloromethane and 0.1 mL of water. The mixture was heated to 60 °C for 48 h and a sample was taken (t = 0 h). Then, 0.3 mmol of HCl_(aq) was added and samples were analyzed by inverse gated decoupling ³¹P NMR.



Ligand	%Decomposition (0 h)	% Decomposition (30 h)	% Decomposition (48 h)
L1	0	0	100
L2	9	27	100
L3	8	9	100
L4	0	0	53

Table 3

Aqueous and acid catalyzed decomposition tests with PPh₃. Experimental conditions: 0.1 mmol of PPh₃ dissolved in 3 mL of acetone/dichloromethane and 0.1 mL of water and 0.3 mmol of $HCl_{(aq)}$ (only in the acid test). The mixture was heated to 60 °C and samples were analyzed by inverse gated decoupling ³¹P NMR.

PPh ₃	%Decomposition (12 h)	%Decomposition (3 d)	%Decomposition (7 d)	%Decomposition (10 d)
3% H ₂ O	0	0	1.9	2.6
3% H ₂ O + 3 eq H ⁺	0	0	6.2	56.3

and this gradual increase in reaction rate is very likely due to more selective phosphite-coordinated species formation and emphasizes the coordination competition between the ligand and carbon monoxide [49].

The total pressure of the mixture H_2/CO /ethene 1:1:1 was then increased, keeping the ligand and rhodium concentrations constant (see Fig. 9b). Notably, although higher pressure could result in increased formation of non-phosphite-ligated species, the reaction rate increases with increasing pressure.

Kinetics for a hydroformylation reaction with a reaction scheme consisting of many reactions can be rather complex and relatively few publications deal with kinetics. Two major types of kinetics can be distinguished [49,50], both being an extreme case. In the first one (kinetics Type I), the rate limiting step is at the beginning of the cycle (Fig. 1), *viz.* either the coordination of the alkene $(2 \rightarrow 3)$ or the migratory insertion $(3 \rightarrow 4)$. This can kinetically not be distinguished and a ¹³C isotope effect study on only one particular system led to a draw between the two mechanisms [50]. The rate equation for this case reads:

$$v = \frac{A[Rh][alkene]}{B + C[CO]}$$
(1)



Fig. 9. Influence of (a) L1/Rh ratio; (b) pressure; (c) temperature.

Luckily though, many of the catalytic systems based on arylphosphines and phosphites and with the use of 1-alkenes as the substrate show kinetics close to Eq. (1). For other alkenes, the equation is more complicated; for styrene, the formation of the branched and linear aldehyde show different kinetics [42] and during a batch reaction it will even change [51]. For only one system, it has been shown that the backward reaction of **2** with CO is a hundred times faster than productive octene-1 coordination, thus showing that kinetic data are scarce [52]. The resting state of these catalytic systems is usually $HRh(CO)_2L_2$, in which L is an arylphosphine or phosphite of average electronic and steric properties [53,54]. For very high concentrations of triphenylphosphine, the resting state is $HRh(CO)L_3$ and in the first step dissociation of triphenylphosphine takes place.

The second kinetic scheme was first reported for ligand-free rhodium catalysts, that is, the ligand is CO [55], and extensively studied by Feng and Garland [56], albeit at room temperature rather than the usual conditions for catalysis. In this extreme case, the hydrogenolysis of 6 is the rate limiting step and thus complete equilibration between all species involved occurs. The rate Eq. (2) for this type of kinetics (Type II) reads:

$$\nu = \frac{\mathrm{D}[\mathrm{Rh}][\mathrm{H}_2]}{\mathrm{E} + \mathrm{F}[\mathrm{CO}]} \tag{2}$$

Thus, the alkene concentration does not show up in this equation. This kinetic scheme also holds for monophosphite rhodium catalysts that form when the phosphite [42] is very bulky or very electron poor [40]. A variant of this is a hydrogenolysis step that is bimolecular that takes place between a metal hydride and the metal acyl species as was first proposed for cobalt [57,58] and found by Garland also for Rh and heterometallic systems, for example, Rh acyl species (CO)₄RhC(O)R and hydrides of W, Mn, Re, and Co [59]. In general, the hydroformylation reaction will have a negative order in CO pressure. The response to total pressure changes maintaining the ratio the same should leave the rate unchanged, but at lower pressures, the rate does increase with pressure. We ascribe this to an incomplete formation of mononuclear catalyst species at lower pressure (vide infra) or a change in rate limiting step in this region. For the present system, Type II kinetics are expected and raising the H₂ pressure or lowering the CO pressure should lead to a faster reaction. In the system used, it was not possible to change the partial pressure of the reactants while feeding the gases in a 1:1:1 ratio and obtain reliable kinetic data.

The rate of hydrogenolysis of **6** (indirectly **7**, the resting state in Type II kinetics) should not depend on the length of the alkyl chain, be it ethyl or octyl, and thus the same rates might be expected for ethene and octene-1. However, the rates for ethene ($12-14 \times 10^3 h^{-1}$) are not as high as those obtained for octene-1 ($40 \times 10^3 h^{-1}$, 20 bar, 80 °C, 0.86 M at the start of the reaction [42]; in pure octene-1 and higher H₂ pressures much higher rates were obtained) [39]. At 80 °C, the concentration of ethene is estimated to be 0.86 and 1.79 M at, respectively, 10 and 20 bar [60]. Thus, accidentally at a total pressure of 30 bar, the initial concentrations are the same for both substrates (0.86 M), apart from changes of the solubility of ethene upon product formation. We explain this difference by the overall equilibrium between **1** + alkene and **7**, which for octene-1 is more favorable than for ethene for

entropy reasons. This may also result in incomplete formation of **7** at lower pressures.

Reaction temperatures ranging from 60 to 120 °C were then tested (see Fig. 9c). Strikingly, 80 °C is the temperature of choice since lower and higher temperatures led to lower reaction rates. While lower temperatures lead to slower reactions, the low rates observed at higher temperatures may well be due to catalyst decomposition. This effect is easily observable at 120 °C were the reaction starts very fast but slows down rapidly.

The concentration of Rh was kept low in our experiments to allow rate measurements with the equipment. In practice, the rhodium concentration could be raised, while the phosphite concentration can be kept at the same level. This increases the space-time yield and reduces the amount of phosphite used per rhodium.

As concerns a practical application, as a solvent propanal could be used (which leads to slightly higher pressures) or a condensation product of propanal. Interestingly, discarded in many cases, a stripping reactor could be considered for this reaction (requiring a recycle of the three reactant gases) [61].

4. Conclusions

Bulky phosphite **L1** turned out to be a fast and stable ligand for the rhodium-catalyzed hydroformylation of ethene. Two ligands, **L6** and **L7**, showed higher rates, but they were less stable in the tests conducted; of course, the higher rates might balance the higher ligand costs, but that is not the subject of this publication. Surprisingly, **L1** substituted with electron-withdrawing groups (**L4**) did not give a faster catalyst and thus other equilibria than the ones assumed in Fig. 1 must be involved. The rates obtained are lower than those reported for octene-1, but higher ethene pressure may reverse this. This interesting and cheap catalytic system based on bulky phosphites has thus a promising future in terms of industrial applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.11.031.

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