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Effects of ligands on the rhodium-catalyzed hydroformylation of acrylate

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In memory of Professor Eric Derouane, a great scientist, leader and friend.

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ABSTRACT

The hydroformylation of butyl acrylate in toluene was studied. Ligands were found to impact significantly on the reaction rates and selectivities. When combined with rhodium, ligands with large bite angles displayed higher activities. Whilst 1,4-bis(diphenylphosphino)butane (dppb) was found to be a best choice, a modified, electron-deficient dppb ligand led to considerably higher catalytic activities in comparison with the electron-rich analogues. Other parameters were also examined, including ligand/rhodium ratios, and concentrations of the catalyst and olefin.

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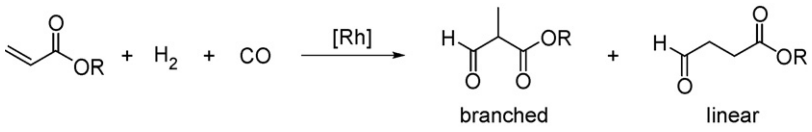
1. Introduction

Hydroformylation is mostly used for the preparation of bulk chemicals (e.g. butanol) and specialities (e.g. higher alcohols to be used as plasticizers). Its application in pharmaceutical and fine chemical synthesis remains to be fully investigated, however [1–3]. In particular, acrylates as substrate provide access to valuable building blocks for the preparation of bifunctional intermediates, which can be used for the synthesis of biologically active compounds, such as malonic acid, 1,4-dicarboxylic acids and lactones Eq. (1) [4,5]. However, the reaction generally suffers from a slow rate and formation of byproducts [6,7]. Thus, severe conditions may be necessary to accelerate the process. An example is seen in the hydroformylation of ethyl acrylate reported by Tanaka et al., where the reaction was carried out at 150 °C and 100 bar syngas pressure [8]. The chemoselectivity of the reaction depends on the metal complexes employed; among them, only rhodium complexes favour the hydroformylation and suppress the formation of undesired side reactions [9–11].

In the past one decade or so, efforts have been made to speed up the reaction and minimise undesired side products such as alkanes [12–14]. Much improved rates were obtained when the reaction is run under organo–aquo biphasic conditions or when a "supported aqueous phase" catalyst is used [12]. However, low solubilities of less hydrophilic acrylates in water limit the applicability of the biphasic systems and, in the case of the latter, it was shown that even a slight alteration in the water content in the supported aqueous phase could sharply reduce the activity of the catalyst. We recently reported that fast and selective hydroformylation of alkyl acrylates can readily be effected in supercritical CO_2 in the presence of $[Rh(acac)(CO)_2]$ and the fluoroalkylated phosphine ligand $P(p\text{-}C_6H_4C_6F_{13})_3$ [13,14]. We further demonstrated that electron-deficient monophosphine ligands enhance the hydroformylation rate in supercritical CO_2, affording the branched aldehyde exclusively. More recently, Clarke reported the hydroformylation of methyl acrylate with high turnover frequencies (TOF) (up to 4000 h^{-1}) using a caged phosphine (phosphaadamantane) in combination with rhodium



(1)

[15]. The reaction was performed at 75–80 bar and 75 °C, forming mainly the branched aldehyde.

In many aspects, 1,4-bis(diphenylphosphino)butane (dppb) has proven to be the best ligand for rhodium-catalyzed hydroformyla-

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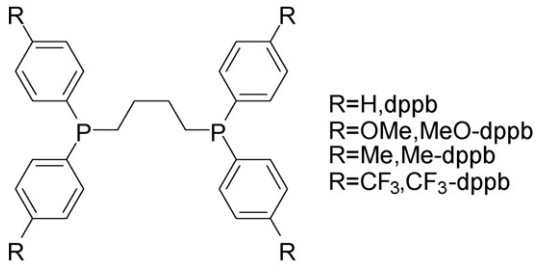


Scheme 1. Dppb and derivatives.

tion of these types of substrates [5–8,16,17]. However, it appears to be no study into how the steric and electronic properties of the dppb-type bidentate ligands may impact on the reaction rates and selectivities. In extending our work on the hydroformylation of acrylates previously studied in supercritical CO_2, we decided to examine the effects of ligands on the reaction in common solvents, using butyl acrylate as a model substrate. Herein we present our findings on the effect of ligands on the hydroformylation of butyl acrylate, in the hope to highlight the importance of ligand choice when running hydroformylation of this kind.

2. Experimental

2.1. General remarks

All reactions were carried out under a nitrogen or argon atmosphere with standard Schlenk techniques. All glasswares were oven-dried before use. Toluene was distilled under nitrogen atmosphere from sodium-benzophenone ketyl prior to use. The following chemicals were used as received from Aldrich: butyl acrylate, 1,4-bis(diphenylphosphino)butane (dppb), 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm), 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xanthphos), 1,1′-bisdiphenylphosphino)ferrocene (dppf), and sodium hydride (dry, 95%). The catalyst precursor Rh(acac)$(CO)_2$ was purchased from Strem and used as received. The CO/H_2 syngas mixture (1:1) was purchased from BOC Gases. The ligand MeO–dppb, Me–dppb and CF_3–dppb (Scheme 1) were synthesised according to the literature procedures [18,19]; (diethylamino)phosphinous dichloride was also synthesised according to the literature procedures [20]. Gas chromatography analysis was carried out on a Varian 3800 using a CP WAX 52 CB column (30 m × 0.53 mm) and a FID detector using toluene as external standard. The products were identified by NMR on a Bruker DRX-400 spectrometer with TMS as the internal standard and a TRIO-1000 GC–MS spectrometer using authentic samples.

2.2. General procedure for hydroformylation

All hydroformylation reactions were carried out in a 30 mL stainless steel autoclave. In a typical reaction, a glass liner containing a stirrer bar was charged with butyl acrylate (5.1 mmol), the catalyst precursor Rh(acac)$(CO)_2$ (3.9×10^{-3} mmol) and a ligand (0.03 mmol) in toluene (3 mL). Next, the vessel was sealed and degassed with syngas three times; 20 bar syngas was finally introduced. The autoclave was then placed into an oil bath preheated to 80 °C and stirred for a period of time given. After stopping the reaction and cooling down to room temperature with an ice bath, the syngas was carefully released and the resulting mixture was passed through a small column of silica. Conversion and selectivity were determined by gas chromatography using toluene as external standard. The products were identified by NMR and GC–MS.

3. Results and discussion

3.1. Optimization of the reaction conditions

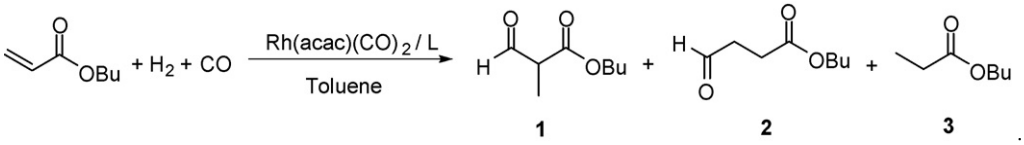
Before studying the ligand effect on the butyl acrylate hydroformylation, we initially decided to identify the optimal reaction conditions. In order to do this, dppb was chosen as the ligand. We examined the effect of ligand to rhodium (L/Rh) ratio, the catalyst concentration and the substrate concentration.

3.1.1. Effect of ligand to rhodium ratio

The optimization began with the examination of the effect of L/Rh on the catalytic activity/selectivity of the hydroformylation in the presence of Rh(acac)$(CO)_2$ and dppb. The hydroformylation was performed with a substrate to rhodium ratio (S/Rh) of 1314 at 20 bar syngas in 30 min at 80 °C. The results are summarised in Table 1.

It is shown that the activity of the Rh–dppb catalyst is improved if an excess of phosphine is employed, as judged by the increased conversion. The linear product **2** was not observed regardless of the L/Rh ratios, and as may be expected, increasing the L/Rh ratio ameliorates considerably the selectivity to the branched aldehyde **1** at the expense of the hydrogenation product **3**. A full conversion was reached in 30 min when L/Rh was above 7; still higher ratios led to better selectivity to **1**. Furthermore, it is worth noting that the catalyst was active even at a low L/Rh ratio of 1 (entry 1). Under these conditions, however, hydrogenation became significant. The exclusive formation of the branched products is in line with the

Table 1
Effect of L/Rh ratio on the hydroformylation[a].



Entry	L/Rh	Sel. [%][b] **1**	Sel. [%][b] **3**	Conv. [%][c]
1	1	84	16	8
2	2	85	14	76
3	5	89	11	95
4	7	90	10	100
5	10	95	5	100

[a] Conditions: [olefin] = 1.69 M, S/Rh = 1314 (mol/mol), 80 °C, 20 bar syngas, 30 min, in toluene (3 mL).
[b] Selectivity determined by GC; 2 was not detected.
[c] Conversion of the acrylate.

Table 2
Effect of catalyst concentration[a].

Entry	[Rh] [$\times 10^{-3}$ M]	Rh [mol%]	Sel. [%][b] **1**	Sel. [%][b] **3**	Conv. [%][c]	TOF [h^{-1}][d]
1	0.68	0.04	100	0	13	1292
2	1.29	0.08	94	6	24	1182
3	2.58	0.15	89	11	50	1166
4	3.87	0.23	85	15	78	1159

[a] Conditions: [olefin] = 1.69 M, L/Rh = 7, 80 °C, 20 bar syngas, 15 min, toluene (3 mL).
[b] Selectivity of the reaction shown in Table 1.
[c] Conversion of the acrylate.
[d] Turnover frequency based on 15 min conversion to 1.

literature when using dppb as ligand [6b]. Tanaka et al. reported similar results when using dppb and $[RhCl(CO)_2]_2$ as catalyst [8]. However, the current conditions allow for faster hydroformylation.

3.1.2. Effect of catalyst concentration

The effect of the catalyst concentration on the selectivity and reactivity was the next parameter studied, using a fixed olefin concentration and a fixed L/Rh ratio of 7; the results are shown in Table 2. As can be seen by comparing entries 1–4, the conversion is roughly proportional to [Rh]. A slight decrease in TOF to **1** was observed; this is accompanied by an increase in the concentration of the hydrogenation product. It thus appears that whist most of the catalyst are active in catalyzing the formation of **1** in the concentration range of 0.68×10^{-3} M to 3.87×10^{-3} M, a lower concentration benefits the chemoselectivity.

3.1.3. Effect of olefin concentration

The effect of the olefin concentration is seen in Table 3, where the catalyst concentration was kept constant. As can be seen, the selectivity to the branched aldehyde and the hydrogenation product do not depend on the [olefin]. They were the only products observed and their selectivity remained constant when varying the butyl acrylate concentration (entries 1–4). However the conversion was affected, decreasing from 58% to 11% when increasing the [olefin]. The TOF also varied, increasing with [olefin] at lower [olefin] but decreasing with [olefin] at higher [olefin]. This type substrate inhibition has been noted before [21] and in our case is partly due to the polymerisation of butyl acrylate at high [olefin].

3.2. Ligand steric effect

With the results above in hand, we then examined a range of bidentate ligands. The hydroformylation was performed using a combination of $Rh(acac)(CO)_2$ and 7 equiv. of a phosphine ligand in an autoclave at 80 °C and 20 bar syngas pressure, fixing the [olefin] at 1.69 M. All the reactions were run for 20 min to allow for comparison of catalytic activities, and in particular to inform if dppb is still the best ligand in terms of the production of branched aldehyde in comparison with other bidentate ligands such as dppf, Binap and Xanthphos. The results are summarised in Table 4. As can be seen, all the ligands afforded the branched aldehyde **1** as the major product, and only in the case of Xanthphos was the linear product **2** observed. The hydrogenation product **3** started to appear at higher conversions associated with dppf, dppb and Xanthphos. In terms of both TOF and selectivity to the branched aldehyde, it appears that dppb affords the best results.

As might be expected, an increase in the TOF was observed with increasing the ligand bite angle [22]. Thus, increasing the bite angle from $\beta = 85°$ to $\beta = 107°$ led to a remarkable increase in the TOF from 118 h^{-1} to 3052 h^{-1}, with the Xanthphos ligand showing the highest turnover frequency. Within the homologous series of α,ω-bis(diphenylphosphino)alkanes (entries 1–3 and 6), the catalytic activity is in the order of dppm < dppe < dppp < dppb. Similar results were observed by Tanaka et al. when studying the hydroformylation of various acrylic esters [8]. They showed that the bridge between the two phosphorus atoms, consisting of 2, 3 or 4 carbon atoms, of α,ω-bis(diphenylphosphino)alkanes was essential for high reactivity. A similar trend was also observed in platinum-catalyzed hydroformylation of 1-pentene [23]. Many other examples of bidentate phosphine ligands exist, where the chelating ring formed with the metal exerts a strong influence on the reactions [24–26].

The almost exclusive formation of the branched aldehyde with the various ligands may stem from an electronic control arising from the substrate. The strongly electron-withdrawing carbonyl group could render hydride transfer to the β carbon easier than to the α carbon. The appearance of the linear aldehyde **2** in the case of Xanthphos can at least be partly attributed to increased steric demanding from the ligand around the rhodium; this steric effect is expected to discourage the formation of Rh-(branched alkyl) responsible for **1**.

According to their bite angles, bidentate phosphines may coordinate to rhodium in equatorial–equatorial (ee) and axial–equatorial (ae) positions Eq. (2) [27,28]. In the previous work, bidentate ligands having bite angles around 90° show a preferential ae coordination mode [25,26,28,30,31]. Van Leeuwen's group studied the hydro-

Table 3
Effect of olefin concentration[a].

Entry	[olefin] [M]	Sel. [%][b] **1**	Sel. [%][b] **3**	Conv. [%][c]	TOF [h^{-1}][d]
1	0.85	94	6	58	1437
2	1.69	94	6	51	2512
3	2.12	94	6	24	1483
4	4.24	94	6	11	1359

[a] Conditions: [Rh] = 1.29×10^{-3} M, L/Rh = 7, 80 °C, 20 bar syngas, 15 min, toluene (3 mL).
[b] Selectivity of the reaction shown in Table 1.
[c] Conversion of the acrylate.
[d] Turnover frequency based on 15 min conversion to 1.

Table 4
Hydroformylation of butyl acrylate with various ligand[a].

Entry	Ligand	Bite angle [°]	Sel. [%][b]			Conv. [%][c]	TOF [h^{-1}][d]
			1	**2**	**3**		
1	Dppm	72	0	0	0	–	–
2	Dppe	85	100	0	0	3	118
3	Dppp	91	100	0	0	6	236
4	Binap	92	90	0	10	5	177
5	Dppf	96	95	0	5	23	861
6	Dppb	98	94	0	6	55	2038
7	Xanthphos	107	88	5	7	88	3052

[a] Conditions: [Olefin] = 1.69 M, S/Rh = 1314 (mol/mol), L/Rh = 7, 80 °C, 20 bar syngas pressure, 20 min, in toluene (3 mL). Bite angles taken from Ref. [25a].
[b] Selectivity of the reaction shown in Table 1.
[c] Conversion of the acrylate.
[d] Turnover of frequency based on 20 min conversion to 1.

Table 5
Influence of modified dppb on the hydroformylation of butyl acrylate[a].

Entry	Ligand	Sel. [%][b] **1**	Sel. [%][b] **3**	Conv. [%][c]	TOF [h^{-1}][d]
1	CF_3–dppb	95	5	95	4743
2	dppb	94	6	37	1828
3	Me–dppb	92	8	26	1257
4	MeO–dppb	92	8	20	967

[a] Conditions: [Olefin] = 1.69 M, S/Rh = 1314 (mol/mol), L/Rh = 7, 80 °C, 20 bar syngas, 15 min, in toluene (3 mL).
[b] Selectivity of the reaction shown in Table 1.
[c] Conversion of the acrylate.
[d] Turnover of frequency based on 15 min conversion to 1.

formylation of 1-octene and styrene using a class of rigid ligands of the Xanthphos type, which have bite angles between 102° and 131° [29,30]. Using spectroscopic methods, they found that these ligands showed a preference to ee coordination in RhH(diphosphine)$(CO)_2$ complexes, which afforded high linear-to-branched ratios. In the case of styrene using dppf-based catalyst, they suggested that the high selectivity to the branched aldehyde was due to a higher proportion of the ae isomers [31]. The existence of a mixture of two isomers of the active complex was earlier demonstrated by Brown et al. with monodentate ligands and extended later on by Casey et al. to bidentate ligands [27,28]. In the present study, if the Rh–Xanthphos complex adopts an ee mode, insertion of the olefin to give a branched alkyl species is likely to be sterically more demanding than a linear alkyl. The same would be true for the ae mode, but expectedly to a lesser degree. Thus, steric effects would encourage the formation of the linear aldehyde. However, the mechanistic details are undoubtedly more complicated, as indicated by the hydroformylation of acrylates reported previously [9].

(2)

3.3. Ligand electronic effects

Studies of the electronic effects of phosphine ligands on the activity and selectivity of rhodium-catalyzed hydrofomylation of alkenes, such as styrene and propene, have been reported for both monophosphines and chelating phosphines [1b,32]. A best way to investigate the electronic effect of phosphines is to use the same family of ligands having different electronic properties. Having confirmed that dppb is preferable for acrylate hydroformylation, we decided to synthesise analogous ligands possessing electron-donating and -withdrawing substituents at the *para* position of the phenyl rings of dppb (Scheme 1). Such substituents should alter the electronic properties of the ligand without affecting the steric environment in the immediate vicinity of the rhodium centre. These types of ligands have been reported by Leitner et al.; but they have not been used for hydroformylation [19].

With the MeO–dppb, Me–dppb and CF_3–dppb synthesized, we then carried out the hydroformylation of butyl acrylate under conditions similar to those above. The results of the studies are summarised in Table 5. As can be seen, the introduction of a strong electron-withdrawing CF_3 group on dppb led to a much faster reaction, whereas installing an electron-donating OMe slowed down the reaction considerably. Thus, the CF_3–dppb ligand afforded a high TOF of 4743 h^{-1}, whilst the MeO–dppb resulted in a TOF of less than 1000 h^{-1}, with dppb and Me–dppb displaying activities in between. However, the electronic properties of these ligands seem to have no impact on the regioselectivity and chemoselectivity, since all the ligands favour the same aldehyde **1**, and all produced only a small amount of hydrogenation product. From these results, it is clear that decreasing the phosphine basicity [33] increases the rate of acrylate hydroformylation, whilst increasing the phosphine basicity gives the opposite effect. Our previous results suggest that this is also true with monodentate phosphines [13].

Many examples exist in the literature, showing the beneficial effect of the ligand possessing electron-withdrawing group on the rate and on the selectivity of hydroformylation reactions [31,34–39]. Based on the previous studies, the introduction of electron-withdrawing group on a ligand may be expected to accelerate the rate of acrylate hydroformylation, as it would encourage CO dissociation. However, the low hydroformylation rate associated with acrylates is generally believed to stem from the formation of thermodynamically stable five- or six-membered rings *via* the coordination of the acrylate carbonyl group to rhodium, with the reaction rate determined by opening of the ring to give a coordinatively unsaturated intermediate [12d,17b]. An electron-deficient dppb might be expected to discourage this ring opening process, leading to a slower reaction. Clearly, the hydroformylation mechanism is more complicated than the arguments presented here and warrants more detailed studies.

4. Conclusions

The investigation of hydroformylation of butyl acrylate revealed some interesting results. When combined with rhodium, bidentate phosphines having large bite angles afforded fast reaction; however, too high a bite angle appears to erode the regioselectivity. In this context, dppb is a best compromise. Further studies showed that the hydroformylation can be significantly accelerated when dppb is made more electron-deficient, offering an easy way for enhancing the rate of acrylate hydroformylation.

Acknowledgment

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