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Crucial role of additives in iridium-catalyzed hydroformylation

Arno Behr[a,*], Alexander Kämper[a], Martin Nickel[a], Robert Franke[b,c]

[a] Department of Biochemical and Chemical Engineering, Chair of Technical Chemistry, Technische Universität Dortmund, Emil-Figge-Str. 66, 44227 Dortmund, Germany
[b] Evonik Industries AG, Advanced Intermediates, Paul-Baumann-Straße 1, 45772 Marl, Germany
[c] Chair of Theoretical Chemistry, Ruhr-Universität Bochum, 44780 Bochum, Germany

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ABSTRACT

This paper presents the new highly selective iridium-catalyzed hydroformylation of 1-octene with an Ir(cod)(acac)/PPh_3/salt catalyst system. The addition of inorganic salts such as LiCl suppresses the hydrogenation of 1-octene and increases the yield of desired hydroformylation products. Even low amounts of LiCl (LiCl/Ir = 2/1) significantly increase the chemoselectivity of aldehydes up to 94% with a 1-octene conversion of 90% within 7 h. This catalyst is applicable to other alkenes such as 1-pentene or 1-dodecene. The high selectivities and the remarkable activity of the optimized iridium catalyst are promising in terms of successfully implementing on an industrial scale in the future.

1. Introduction

In 1938, Otto Roelen discovered hydroformylation, also known as oxo-synthesis, during experiments on Fischer–Tropsch-synthesis. Generally, hydroformylation describes the catalytic addition of carbon monoxide (CO) and hydrogen (H_2) to C-C double bonds in order to form aldehydes (see example with 1-octene in Fig. 1) [1–7].

Aldehydes and their secondary products have many industrial applications in e.g., the production of solvents, plasticizers or odorants [4,6,8].

A wide range of starting compounds can be adapted for hydroformylation processes. In addition to the application of olefins such as propene, 1-butene or 1-octene, hydroformylation is also possible with styrene, 1,3-dienes or functionalized olefins, for example [4,6,9–12].

Using the example of short chain olefins such as propene, the historical development of the hydroformylation processes has seen new techniques for catalyst recycling and new catalytic systems. The BASF process was the first industrial application for producing butyraldehydes using unmodified cobalt-based catalysts and severe reaction conditions of up to 180 °C and 300 bars. In order to arrive at a more economical way of producing aldehydes via hydroformylation, an improvement of the reaction parameters was necessary. Therefore, with these goals in mind, new catalysts became the focus of research. This resulted for instance in the addition of phosphorous ligands such as PPh_3 (triphenyphosphine), represented by the homogeneous-catalyzed Shell process, or in the development of noble metal-based catalysts. With the discovery of rhodium-based catalysts, potential processes with very mild reaction conditions became possible such as the Union Carbide Company's low-pressure oxo process (LPO). The Ruhrchemie–Rhône–Poulenc process is another important hydroformylation process for converting propene into butyraldehydes with rhodium-based catalysts using an integrated liquid–liquid catalyst recycling concept [2,4,5,13].

Generally, the following order of activity for unmodified metals in hydroformylation has been assumed in the last decades [3,4,14].

$$Rh >> Co > Ir, Ru > Os > Pt > Pd > Fe > Ni$$

In spite of the high activity of rhodium and its widespread use in the industrial chemistry, it is among the scarcest metals on earth. Furthermore, apart from their use in chemical reactions, rhodium is in high demand within the automotive industry (ca. 80% of worldwide rhodium) for use in catalytic converters. With the increasing demand for rhodium on the market, the prize for this rare metal has increased significantly over time. Therefore, it has become necessary to look for alternative metals for hydroformylation reactions, such as iridium, platinum, ruthenium or iron [4,15–18].

* Corresponding author. Tel.: +49 231 755 2310; fax: +49 231 755 2311.
E-mail address: alexander.kaemper@bci.tu-dortmund.de (A. Behr).

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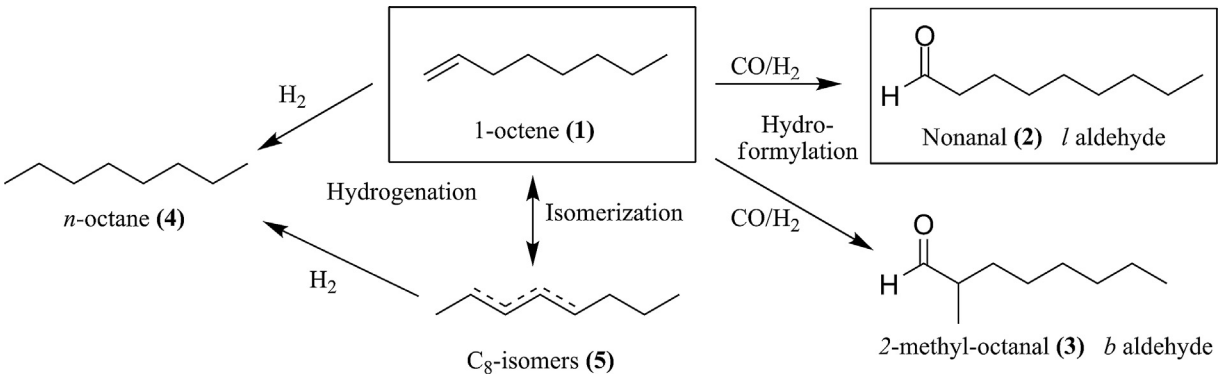

Fig. 1. Hydroformylation of 1-octene and side reactions.

Recent Beller research by Piras et al. [19] has shown that the old assumption concerning the activity of unmodified metals must be reexamined and corrected. Using iridium as an alternative metal, good results with homogeneous catalyzed hydroformylation are possible. Iridium complexes based on the precursor Ir(cod)(acac) and the ligand PPh_3 show good activity and high yields of aldehydes using a variety of substrates [16,19–21].

Iridium based catalysts are often typical hydrogenation catalysts. Haukka et al. [22] described the suppression of hydrogenation in the iridium-catalyzed hydroformylation of 1-hexene using $Ir_4(CO)_{12}$, $IrCl_3$ and $[Ir_3(CO)_3]_n$ based catalysts without ligands. In these experiments, the addition of inorganic salts such as LiCl, LiBr, NaCl and others decreased hydrogenation and increased the yield of hydroformylation products, significantly [22,23].

As a preliminary step towards the development of a process at a continuously operating miniplant scale, achieving high catalytic performance with high selectivities while keeping the amount of undesired hydrogenation products to a minimum is essential. Based on the results and findings of Beller et al. [19] and Haukka et al. [22], this paper describes the development of an appropriate catalyst system that ensures high reaction rates and aldehyde yields under mild conditions (p, T). An investigation and optimization of iridium-catalyzed hydroformylation of 1-octene was undertaken using an Ir(cod)(acac)/PPh_3 catalyst with the addition of salts and other additives. The influence of inorganic salts such as LiCl towards the chemoselectivity of hydroformylation was the focus of the investigation and optimization.

2. Experimental

2.1. Typical hydroformylation experiment

In a typical hydroformylation experiment, 0.0713 mmol of the precursor Ir(cod)(acac)-precursor (0.8 mol%; catalyst concentration refers to the molar amount of substrate), 0.1579 mmol PPh_3 (2.2/1; molar ratio of P/Ir) and 0.1415 mmol LiCl (2/1; molar ration of Li/Ir) were transferred to a 25 ml autoclave. Then 8.91 mmol 1-octene and 4 g *N*-Methyl-2-pyrrolidone (NMP) were added. The reaction was carried out at 100 °C, 30 bar (CO/H_2 = 2/1) and 700 min^{-1} for 16 h. A 300 ml *Parr* autoclave was used for kinetic experiments (Figs. 2 and 3. Thus the weighed portions were ten times higher (e.g., 9.81 mmol 1-octene) and a semi-continuous gas flow of 30 bar (CO/H_2 = 1/1) was ensured. After the reaction, the autoclave was left to cool, then depressurized and stripped with argon. The components were then prepared for analysis via gas chromatography (GC) (see Section 2.2).

2.2. Quantitative analysis via GC

For the quantitative analysis, 0.2 g of the reaction solution was weighted in a GC vial. 0.1 g decane (external standard) and 0.8 g isopropyl alcohol were added. The amount of substrate **1** and products **2–5** were determined using a gas chromatograph HP6890 from Agilent Technologies with an HP-INNOWAX column.

3. Results and discussion

The following results show the investigation and optimization of the iridium-catalyzed hydroformylation of 1-octene. We started our investigations with LiCl as an additive, which already showed the best performances in the results of Haukka et al. [22]. The variation of parameters such as catalyst concentration or additive amounts were optimized in order to show their influence on the suppression of the undesired hydrogenation product **4** and on the conversion (X) of 1-octene **1.** Our aim was to increase the yield (Y) and chemoselectivity (S) of aldehydes **2** and **3**. In terms of the linear/branched (*l:b*) ratio of the aldehydes, most experiments showed results of around 75:25.

3.1. Influence of LiCl and Ir(cod)(acac) concentrations

Table 1 shows the results of varying the catalyst concentration with and without LiCl as an additive. By increasing the catalyst concentration to 0.8 mol% the conversion as well as the chemoselectivity of **2 + 3** are heavily dependent on this variable. (Table 1, entries 1–5 and 6–10).

The addition of inorganic salts such as LiCl had a strong effect on the chemoselectivity of **2 + 3**. At a catalyst concentration of 0.8 mol% and an LiCl/Ir-ratio of = 2/1, optimal results with a chemoselectivity (**2 + 3**) of 94% and a conversion (**1**) of 86% were realized (Table 1, entry 9). The hydrogenation product **4** decreased from 12% (Table 1, entry 4) to 4% as well as the isomerization product **5** from 9% to 1%. The chemoselectivity of the desired aldehydes (**2 + 3**) increased from 77% to 94%. In comparing the corresponding catalyst concentration, increased chemoselectivity (**2 + 3**) and a decreased conversion of **1** were noted. Clearly, the desired hydroformylation catalyst intermediate was formed more selectively with the addition of LiCl, whereas the hydrogenation species was depressed.

The effect of LiCl as described above is demonstrated more precisely with the kinetic investigation's time curves shown in Figs. 2 and 3. Without the addition of LiCl, the chemoselectivity of **2 + 3** was approximately 60–65% whereas the yield of **4** (25%) and the conversion of **1** (90%) peaked after 4 h (Fig. 2). With addition of LiCl, the reaction was more selective towards the desired aldehydes though the reaction rate was slower (Fig. 3). After 8 h, yields of **2 + 3** and a conversion of **1** reached a maximum whereas

Table 1
Results of the variation of catalyst concentration.

Entry	$C_{catalyst}$ (mol%)	LiCl	X (%)	Y (%)			S (%)	*l:b*
			1	**2+3**	**4**	**5**	**2+3**	
1	0.2	–	54	18	25	11	33	75:25
2	0.4	–	77	44	22	11	57	77:23
3	0.6	–	84	63	13	9	75	79:21
4	0.8	–	93	72	12	9	77	78:22
5	1	–	86	72	7	7	84	79:21
6	0.2	+	23	10	8	5	43	75:25
7	0.4	+	38	32	3	2	86	77:23
8	0.6	+	83	78	4	1	94	76:24
9	0.8	+	86	81	4	1	94	76:24
10	1	+	77	73	3	2	95	76:24

8.91 mmol 1-octene, 4 g NMP, Ir(cod)(acac), PPh_3 (P/Ir = 2.2/1), LiCl/Ir = 2/1 (molar), 30 bar (CO/H_2 = 2/1), 100 °C, 16 h, 700 min^{-1}.
X = Conversion 1-octene, Y = Yield, S = Selectivity aldehydes **2+3**, *l:b* = regioselectivity, ratio of linear (**2**) to branched (**3**) aldehydes.

the chemoselectivity of **2+3** reached a maximum directly after the experiment began. Obviously, LiCl had a strong effect on the formation of the right catalyst intermediate for hydroformylation to occur at the beginning of the reaction.

The regioselectivity of linear to branched aldehydes is a very important aspect in industrial applications. The experimental investigations of iridium-catalyzed hydroformylation of 1-octene described here generally achieved linear to branched aldehydes in a ratio of approximately 75:25. Experiments with different ligands or additives showed no significant effects on regioselectivity [19].

3.2. Screening of catalyst precursor

It is assumed that the mechanism involved in iridium-catalyzed hydroformylation is very similar to rhodium based systems [6,24]. In order to form the desired C_9-oxo products it is necessary to form the proper Ir(I)-species with the appropriate hydrogen and carbon monoxide ligands in a configuration such as $IrHCO(PPh_3)_2$. Preforming this kind of iridium-complex may be possible using different Ir(I), Ir(III) and Ir(0) precursors other than Ir(cod)(acac). In Table 2 the results for the catalyst screening of different iridium precursors are shown with and without addition of LiCl.

Comparing the results of chapter 3.1 with the entries 1/1–4/2 of Table 2, the suppressed hydrogenation of **4** and improvement in the selectivity towards **2+3** was validated with other Ir(I) precursors as well. As mentioned in chapter 3.1, the addition of LiCl also resulted in a lower catalytic activity and conversion of 1-octene.

The Ir(I)-precursors in entries 5 and 6 already led to high chemoselectivities **2+3** of up to 94% without the addition of LiCl. The additions of LiCl showed no improvement or degradation in the chemoselectivities of **2+3**. The structures of the precursors in entry 5 and 6 already contain PPh_3 and CO and are similar to active rhodium complexes measured in the rhodium-catalyzed hydroformylation [6,24]. Therefore, the presence of LiCl causes a possible preforming effect for the appropriate coordination of these desired ligands. In chapter 3.4, this point will be discussed in more detail.

Experiments with Ir(III)-precursors (Table 2, entries 8 and 9) resulted in a low conversion of 1-octene but showed similar trends using LiCl in terms of improving the chemoselectivity of **2+3**. In this case reducing the Ir(III) into Ir(I) complexes was necessary in order to achieve sufficient catalytic activity, though this seemed to occur very slowly.

3.3. Variation of LiCl concentration

Fig. 4 shows another important aspect concerning the variation of the LiCl concentration.

Low amounts of LiCl had an increasing effect on the chemoselectivity of **2+3**. At a 1:1 molar ratio of LiCl/Ir, a maximum aldehyde selectivity of 95% and a conversion of **1** at 87% was possible. The application of higher LiCl concentrations caused no significant improvement and reduction in either the chemoselectivity of **2+3** and the conversion of 1-octene. It was therefore even possible to use low amounts of salts in order to increase catalytic performance. This finding is very important for potential use in industrial applications in order to avoid potential corrosive effects.

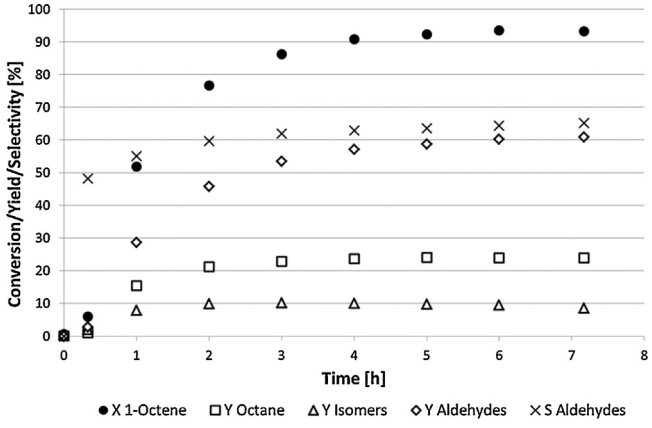

Fig. 2. Kinetic investigations of the 1-octene hydroformylation without addition of LiCl.
89.1 mmol 1-octene, 40 g NMP, 0.713 mmol Ir(cod)(acac), 1.579 mmol PPh_3, 30 bar (CO/H_2 = 2/1, contin. 1/1), 100 °C, 700 min^{-1}.

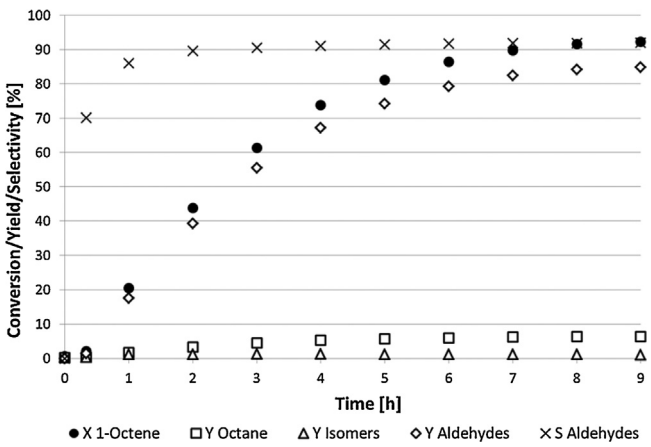

Fig. 3. Kinetic investigations of the 1-octene hydroformylation with addition of LiCl.
89.1 mmol 1-octene, 40 g NMP, 0.713 mmol Ir(cod)(acac), 1.579 mmol PPh_3, 1.415 mmol LiCl, 30 bar (CO/H_2 = 2/1, contin. 1/1), 100 °C, 700 min^{-1}.

Table 2
Catalyst screening.

Entry	Catalyst precursor	LiCl	X (%)	Y (%)			S (%)	*l:b*
			1	**2+3**	**4**	**5**	**2+3**	
1/1	Ir(cod)(acac)	–	93	72	12	9	77	78:22
1/2		+	86	81	4	1	94	76:24
2/1	Ir(cod)(hfacac)	–	99	72	18	9	73	74:26
2/2		+	63	57	3	3	90	76:24
3/1	$[Ir(cod)_2]BF_4$	–	73	49	9	15	67	75:25
3/2		+	53	49	2	2	92	74:26
4/1	$Ir(CO)_2(acac)$	–	87	41	32	13	47	75:25
4/2		+	69	65	4	<1	94	75:25
5/1	$IrCl(CO)(PPh_3)_2$	–	91	84	7	<1	92	75:25
5/2		+	69	64	5	<1	93	74:26
6/1	$IrH(CO)(PPh_3)_3$	–	96	90	6	<1	94	75:25
6/2		+	89	84	5	<1	94	75:25
7/1	$Ir_4(CO)_{12}$	–	45	18	16	11	40	73:27
7/2		+	45	17	16	12	38	73:27
8/1	$Ir(acac)_3$	–	15	3	6	6	20	71:29
8/2		+	<1	<1	0	<1	68	72:28
9/1	$IrCl_3x3H_2O$	–	3	2	1	<1	66	72:28
9/2		+	13	12	1	<1	92	73:27

8.91 mmol 1-octene, 4 g NMP, 0.0713 mmol Ir-precursor, 0.1579 mmol PPh_3, 0.1415 mmol LiCl, 30 bar (CO/H_2=2/1), 100 °C, 16 h, 700 min^{-1}.
X = Conversion 1-octene, Y = Yield, S = Selectivity aldehydes **2+3**, *l:b* = regioselectivity, ratio of linear (**2**) to branched (**3**) aldehydes.

Table 3
Experiments with different salts and other additives.

Entry	Additive	X (%)	Y (%)			S (%)	*l:b*
		1	**2+3**	**4**	**5**	**2+3**	
1	–	93	72	12	9	77	78:22
2	LiCl	86	81	4	1	94	76:24
3	LiBr	85	79	4	2	93	76:24
4	Li_2CO_3	78	73	4	1	94	76:24
5	NaF	86	72	10	4	87	76:24
6	NaCl	86	78	3	5	91	77:23
7	NaBr	82	76	5	1	92	76:24
8	KCl	88	77	8	3	88	77:23
9	CsCl	89	79	7	3	89	77:23
10	$MgCl_2$	67	59	5	3	88	74:26
11	$CaCl_2$	79	72	4	3	90	74:26
12	$FeCl_3$	68	64	3	1	94	76:24
13	$AlCl_3$	37	33	3	1	89	65:35

8.91 mmol 1-octene, 4 g NMP, 0.0713 mmol Ir(cod)(acac), 0.1579 mmol PPh_3, Additive/Ir = 2/1 (molar), 30 bar (CO/H_2 = 2/1), 100 °C, 16 h, 700 min^{-1}.
X = Conversion 1-octene, Y = Yield, S = Selectivity aldehydes **2+3**, *l:b* = regioselectivity, ratio of linear (**2**) to branched (**3**) aldehydes.

Table 4
Hydroformylation of alternative substrates.

Entry	Substrate	X (%)	Y (%)			S (%) aldehydes	*l:b*
			Aldehydes	Alkanes	Isomers		
1		86	81	4	1	94	76:24
2	ctene	17	16	<1	<1	94	1:99
3	1-pentene	79	75	3	1	95	74:26
4	2-pentene	42	39	3	1	93	1:99
5	1-dodecene	99	86	10	3	87	76:24
6	cyclohexene	10	9	<1	–	90	–
7	3,3-dimethyl-1-butene	59	57	2	–	97	95:5

8.91 mmol substrate, 4 g NMP, Ir(cod)(acac) = 0.8 mol% (substrate), PPh_3 (P/Ir = 2.2/1), LiCl/Ir = 2/1 (molar), 30 bar (CO/H_2 = 2/1), 100 °C, 16 h, 700 min^{-1}.
X = Conversion substrate, Y = Yield, S = Chemoselectivity, *l:b* = regioselectivity, ratio of linear to branched aldehydes.

3.4. Variation of additives

Another important aspect concerns the potential use of other salts and additives in iridium-catalyzed hydroformylation. Especially cheap additives such as NaCl are very interesting for an industrial application. However, it is also interesting to see the influence on the hydroformylation performance using additives with different anions and cations. Therefore, a thorough investigation was performed and is presented in Table 3.

The selectivities of the aldehydes **2+3** using LiCl, LiBr or Li_2CO_3 were nearly the same at a maximum of up to 94% (Table 3, entries 2–4). In the presence of these additives, it was possible to improve hydroformylation performance and suppress hydrogenation as described above. However, no significant differences in the chemoselectivities regarding the variety of anions were observed.

Experiments with Na-based systems showed similar behavior. The variation of anions from Cl^- to F^- or Br^- resulted in favorable hydroformylation outcomes with chemoselectivities of **2+3** at 87–92% and conversions of **1** at 86% (Table 3, entries 5–7).

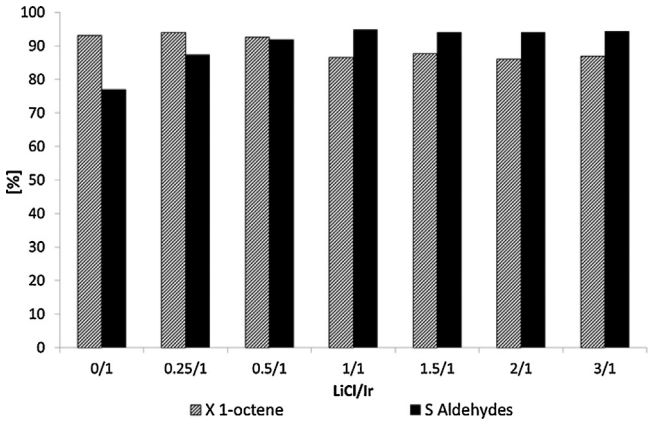

Fig. 4. Results of varying the LiCl concentration.
8.91 mmol 1-octene, 4 g NMP, 0.0713 mmol Ir(cod)(acac), 0.1579 mmol PPh_3, LiCl, 30 bar (CO/H_2 = 2/1), 100 °C, 16 h, 700 min^{-1}.

The use of NaCl, with its low price, could pose a particularly significant economic opportunity for potential industrial processes. Consequently, NaCl was chosen as an additive for further investigations besides LiCl. Furthermore, no significant dependence on different anions was observed, too. However, the strong effect and improvement on the chemoselectivity by addition of each salt can be validated very well.

Therefore, the presence of anions e.g., Cl^- in the solution is very important to achieve high hydroformylation performances. Based on the precursor Ir(cod)(acac), the presence of anions might have a strong preforming effect to the formation of the appropriate hydroformylation complex containing the desired ligands PPh_3, CO and even Cl^- or hydride. Especially, the chloride anion is able to coordinate to the iridium and prevents the formation of undesired hydrogenation species. The presence of chloride in an active iridium precursor can be seen with the Vaska complex ($IrCl(CO)(PPh_3)_2$) (chapter 3.2, Table 2, entry 5). In this case, good hydroformylation performances could be observed already without the addition of LiCl. This effect was also observed with $IrH(CO)(PPh_3)_3$, although this precursor contains no chloride. This could indicate, that the chloride only causes the preforming and coordination of the desired ligands PPh_3, CO and hydride to an appropriate intermediate as described above. Another possibility is the interaction with cationic effects. The cations Li^+, Na^+ and others may interact with Ir(cod)(acac) and effect the formation of an active hydroformylation complex as well.

Therefore, chlorine-based additives with different cations were investigated (Table 3, entries 8–13). The results showed high chemoselectivities **2 + 3** at about 90% with a maximum conversion of 89%. However, in some cases, e.g., with Al- and Fe-salts, the conversion was much lower than using alkali or alkaline earth metals. Thus, the best combination seems to use alkali salts with halogen ions such as Cl^- or Br^-.

Although, no strict dependency on different anions or cations could be figured out with our results, the crucial effect of additives on the hydroformylation performance was well validated. The positive influence on the chemoselectivity may be the result of adding both anions and cations to the reaction as already assumed by Haukka et al. [22]. In our further studies, we preferred the use of LiCl as an additive in the iridium-catalyzed hydroformylation due to the high selectivities of 94% and conversion of 86%. However, from an economical point of view the application of NaCl as an alternative additive should remain in mind.

3.5. Hydroformylation of alternative substrates

In order to draw further conclusions regarding the effects of using inorganic salts and additives in iridium-catalyzed hydroformylation, the effects of other potential substrates must be taken into consideration (Table 4).

In addition to 1-octene, terminal olefins such as 1-pentene or 1-dodecene provided similar results with aldehyde selectivities higher than 90% (Table 4, entries 1, 3 and 5). Experiments with internal olefins such as 4-octene and 2-pentene and cyclohexene afforded chemoselectivities up to 93% as well; however, the alkene conversion was low (Table 4, entries 2, 4 and 6). Iridium-catalyzed hydroformylation using internal olefins is thus very difficult to achieve. Experiments with 2-pentene and 4-octene produced an *l:b* ratio of 1:99 and did not result in isomerized hydroformylation. The use of other iridium precursors and the addition of ligands such as xantphos or biphephos did not result in any improvement in stimulating isomerized hydroformylation. With the substrate 3,3-dimethyl-1-butene, which is unable to isomerize, a *l:b*-ratio of 95:5 with a high aldehyde selectivity of 97% and a conversion of 59% was reached (Table 4, entry 7).

4. Conclusion

In summary, the addition of inorganic salts, e.g., LiCl, LiBr or NaCl, had strong effects on the suppression of hydrogenation products in iridium-catalyzed hydroformylation. Even small amounts of the additives were sufficient to achieve high chemoselectivities towards the desired aldehydes of up to 94%, which represents an improvement of more than 20%. Our investigations with different additives led to the assumption of a preforming effect caused by both a cationic and an anionic influence. First kinetic investigations resulted in high reaction rates and a conversion of 90% after only 7 h. In addition to using the precursor Ir(cod)(acac), also other Ir(I) complexes can be applied. The optimized catalyst concentration was in the range of 0.8 mol%. With optimized reaction parameters, converting other substrates such as 1-pentene, 1-dodecene and 3,3-dimethyl-1-butene to high yields of the desired aldehydes was also possible. Due to the high suppression of undesired alkanes, the described selective catalyst system for iridium-catalyzed hydroformylation was investigated on a continuously operated miniplant scale, too. The results of these experiments will be published in a separate paper soon.

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