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Promoted iridium complexes as catalysts in hydroformylation of 1-hexene

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Abstract

Iridium complexes $Ir_4(CO)_{12}$, $IrCl_3$, and $[IrCl(CO)_3]_n$ show activity toward hydroformylation of 1-hexene in the presence of inorganic salts as promoters. Use of promoters such as LiCl, Li_2CO_3, KCl, $CaCl_2$, and LiBr enhanced the catalytic activity and aldehyde selectivity considerably by suppressing the competing hydrogenation processes. The activity of the iridium compounds increases in the order $IrCl_3 < [IrCl(CO)_3]_n < Ir_4(CO)_2$. The role of the promoter and the effect of the reaction conditions are discussed.

Keywords: Iridium carbonyl; 1-Hexene; Hydroformylation; Promoter

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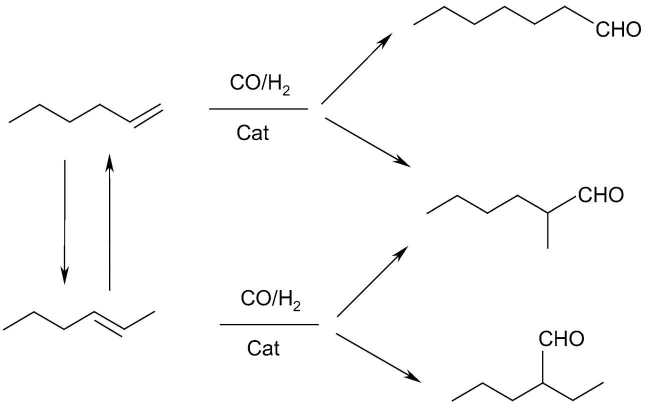
1. Introduction

Hydroformylation is an important industrial process. Several million tons of aldehydes and alcohols are produced annually by catalyzed oxo processes or oxo processes followed by hydrogenation [1] (Scheme 1).

The typical industrial catalysts are rhodium or cobalt carbonyls modified with ligands such as phosphanes [2] and phosphites [3]. Other metals and metal mixtures have also shown potential for hydroformylation. Bimetallic clusters of Re–Rh and Mn–Rh have been found to be active under mild conditions [4]. Ruthenium carbonyl derivatives with bulky diphosphine ligands exhibit good activity [5] and some palladium chlorides effectively improve the chemoselectivity for hydroformylation of internal alkynes [6]. Platinum complexes have produced 90% conversion to aldehydes in the presence of $SnCl_2$ [7].

In earlier studies on the influence of the ligand, modified cobalt carbonyl complexes have showed high activity related to their unmodified precursors [8] and improved the chemoselectivity. Likewise modified ruthenium carbonyl catalysts have shown better activity than pure $Ru_3(CO)_{12}$ [9,10]. Extensive studies related to ligand substitutions on rhodium catalysts have resulted in a wide range of modified complexes that enhance activity significantly, and products showed a good normal to branched ratio [11,12]. Recent studies suggest that the use of salts as promoters can improve the yields of products in hydroformylation [13] as well as in hydrogenation reactions [14].

Iridium compounds have been thoroughly studied as potential catalysts for hydroformylation. The hydroformylation activities have been at most moderate [15], largely due to competing hydrogenation activity under hydroformylation conditions [16–18].



Scheme 1.

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Although, the ligands are known to have considerable effects on the activities of iridium-containing catalysts, the strong tendency to hydrogenation is a noticeable feature regardless of the ligand environment. In general, the iridium compounds are better catalysts for hydrogenation than hydroformylation [19–29].

In the present work, we studied the catalytic behavior of $Ir_4(CO)_{12}$, $IrCl_3$, and $[IrCl(CO)_3]_n$ complexes in the hydroformylation of 1-hexene. The effect of pressure and the role of inorganic salts on the catalytic properties were investigated as well. The primary goal of our work was to improve the hydroformylation activity by suppressing the hydrogenation trough the addition of a suitable salt promoter.

2. Experimental

The gases CO and H_2 used in the experiments were of 99 and 99.99% purity, respectively. The solvent 1-methyl-2-pyrrolidone (Aldrich 99%) and the internal standard cyclohexane (Merck 99%) were used without further purification and degassed with nitrogen before use. Similarly, 1-hexene (99%) was degassed prior to use. $Ir_4(CO)_{12}$ (99%) and $IrCl_3$ (99%), were obtained from Strem Chemicals and $[IrCl(CO)_3]_n$ (99%) was from Across Organics. All catalysts were used without further purification. LiCl, LiBr, and KCl were obtained from Merck and Li_2CO_3, $CaCl_2$, and NaCl from J.T. Baker.

Gas chromatographic analyses of the product mixture were recorded on a Hewlett-Packard 5890 Series II chromatograph equipped with a Varian WCOT fused-silica 50 m × 0.53 mm column and temperature programming.

3. Methods

The hydroformylation reactions were performed in high-pressure autoclaves (100 ml Berghof) equipped with a Teflon liner. The autoclaves were charged in a glove box. In a typical experiment the solvent 1-methyl-2-pyrrolidinone (5 ml), the standard cyclohexane (0.5 ml), the olefin 1-hexene (0.2 ml), the catalyst ($Ir_4(CO)_{12}$, $IrCl_3$, or $[IrCl(CO)_3]_n$), and the promoter (LiCl, $LiCO_3$, etc.) were added to the autoclave, which was then pressurized. The total pressure was varied in the experiments from 20 to 60 bar with synthesis gas CO/H_2 1/1. The autoclave was heated at 150 °C for 17 h. The reaction was then stopped and the autoclave was rapidly cooled to room temperature and brought to atmospheric pressure, after which the liquid samples were analyzed. The product distribution is reported as weight percent.

4. Results and discussion

In the experiments, the hydroformylation activities of chloride, carbonyl, and carbonyl chloride compounds of iridium were studied at constant reaction temperature (150 °C) and reaction time (17 h). Similar conditions have been applied for several metal catalysts [30]. The H_2/CO pressure was varied from 20 to 60 bar in order to study the effect of pressure on the activity.

4.1. Iridium carbonyl complex $Ir_4(CO)_{12}$

The hydroformylation activity of the catalyst was studied under constant temperature varying the pressure. The results are summarized in Table 1.

The catalyst was active over the whole pressure range. For the first series of reactions where 0.3 mmol LiCl was used per reaction, aldehyde yield was lowest at 20 bar and highest at 40 bar (Table 1). The solubility of the iridium carbonyl cluster was considerably improved after addition of the salt promoter. Because of this the catalysis process was at least partially homogeneous. Furthermore, the IR spectrum of the recovered catalyst after hydroformylation reaction showed a completely different pattern than the original $Ir_4(CO)_{12}$ ($\nu(CO) = 1923$, 1959, 1979, 1987, and 2046 cm^{-1}).

The changes in the solubility and in carbonyl frequencies suggest that the halides may play an active role in the process leading to the formation of iridium carbonyl halides as the catalytically active species.

The effect of the pressure does not seem to be significant since there was virtually no variation in the conversion. However, increase in pressure appeared to reduce somewhat the side reactions of isomerization and hydrogenation, and a slight decrease was observed in n/i ratios of the products. According to these results, higher pressures seem to favor slightly the conversion of the terminal olefin to the branched products. In the second series of reactions where the amount of LiCl was increased to 0.6 mmol the same tendency was observed as in the previous experiment: the yield of aldehydes was lowest at 20 bar and highest at 40 bar and once again side products were formed. The presence of isomers is common in hydroformylation reactions because high pressures and temperatures allow shifting of the double bond in the olefin [31]. On the other hand, the production of hydrogenated products is directly associated with the well-known properties of carbonyl iridium compounds as hydrogenation catalysts [32]. The effect of LiCl promoter concentration on the products distribution is presented in Fig. 1.

As can be seen, where no promoter was used the reaction was dominated by hydrogenation, and when LiCl was added the amount of hydrogenated products decreased and the aldehydes increased. Above 0.4 mmol of LiCl, there was no appreciable enhancement of aldehyde yield. A relation between the amount of LiCl used and the distribution of

Table 1
Effect of total pressure on the hydroformylation selectivity of $Ir_4(CO)_{12}$ catalyst

1/1 CO/H_2 (bar)	Promoter (mmol)	Hexane (%)	Isomers[a] (%)	2-Me-hexanal (%)	1-Heptanal (%)	2-Me-hexanol (%)	1-Heptanol (%)	Aldehydes (n/i ratio)	Alcohols (n/i ratio)
20	0	72	15	–	–	4	9	–	2.2
	0.3 LiCl	35	14	15	34	0	0	2.2	
	0.6	36	16	14	34	0	0	2.4	
30	0	81	0	–	–	8	11		1.4
	0.3 LiCl	30	6	20	43	0	0	2.1	
	0.6	31	5	22	41	0	0	1.8	
40	0	81	0	–	–	9	10		1.1
	0.3 LiCl	30	4	21	45	0	0	2.1	
	0.6	24	3	25	48	0	0	1.9	
50	0	80	0	–	–	5	15		3.0
	0.1	70	0	10	12	4	5	1.2	1.3
	0.2	44	0	19	37	0	0	1.9	
	0.3 LiCl	35	0	22	43	0	0	1.9	
	0.4	34	0	22	44	0	0	2.0	
	0.6	28	0	21	48	0	0	2.2	
	0.3 NaCl	80	0	9	11	0	0	1.2	
	0.6	75	0	11	14	0	0	1.3	
	0.3 KCl	75	0	12	13	0	0	1.1	
	0.6	85	0	7	8	0	0	1.1	
	0.3 $CaCl_2$	47	0	19	34	0	0	1.8	
	0.6	51	0	19	30	0	0	1.5	
	0.3 Li_2CO_3	69	10	7	14	0	0	2.0	
	0.6	67	8	8	17	0	0	2.1	
	0.3 LiBr	49	0	20	31	0	0	1.5	
	0.6	52	0	19	29	0	0	1.5	
60	0	60	0	–	–	18	22		1.2
	0.3	32	4	21	42	0	0	2.0	
	0.6	33	2	20	45	0	0	2.2	

Reaction conditions: $T = 150\,^\circ C$; reaction time = 17 h; $n(\mathrm{Ir}) = 0.32$ mmol; $V(\text{solvent}) = 5$ ml 1-methyl-2-pyrrolidone; $V(\text{1-hexene}) = 0.5$ ml; $V(\text{standard}) = 0.2$ ml cyclohexane. Conversion = 100%.

[a] Isomers, 2-hexene and 3-hexene.

the products can be found. Thus, the selectivity toward aldehydes was also enhanced with increase in the amount of promoters.

Five other salts were investigated as promoters (see Table 1 and Fig. 2). The use of NaCl as promoter pushed the reaction in the hydrogenation direction and just a small yield of aldehydes was found amidst a large amount of hydrogenated products observed. The same effect was observed with use of KCl and Li_2CO_3 as promoters. With $CaCl_2$ as well as with LiBr the yield of aldehydes was moderately good and the amount of hydrogenated products was reduced accordingly.

Dombek [33] has shown that the addition of salts to solutions of ruthenium carbonyl clusters increases the activity for reduction of CO in comparison with the standard conditions. He investigated the cations of the salts in order to discern if they are involved into the catalytic cycle acting as a Lewis acid. The results of these experiments showed that the cation

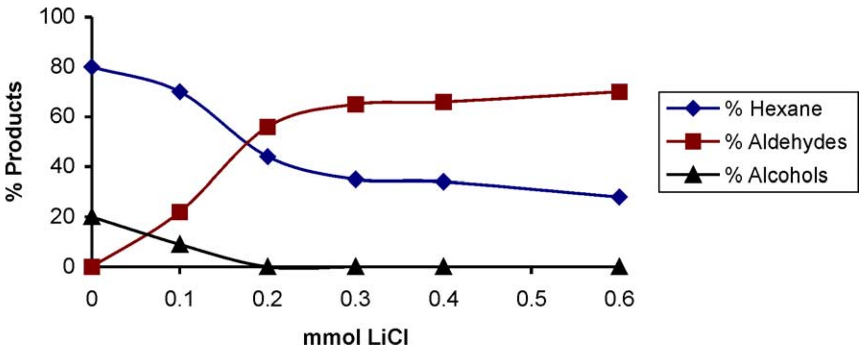

Fig. 1. Effect of promoter concentration on the product distribution with $Ir_4(CO)_{12}$ as catalyst.

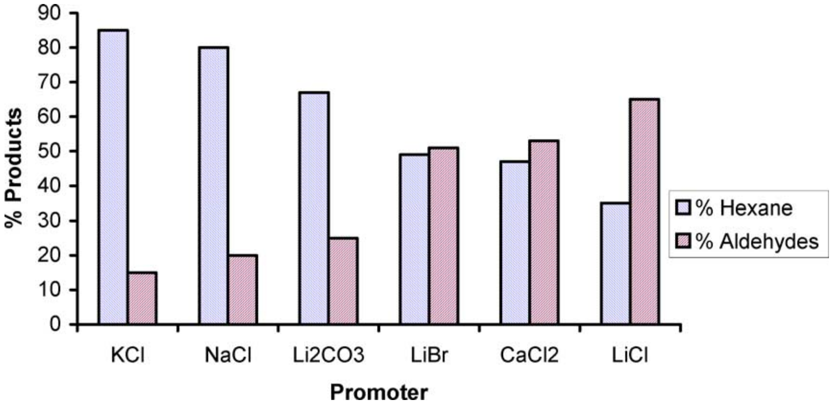

Fig. 2. Effect of promoters on the selectivity of the hydroformylation reaction with $Ir_4(CO)_{12}$ as catalyst.

had some role in the catalytic process under the experimental conditions. Our results suggested that the promotion effect is not exclusively due to anion or cation, but rather the results varied according to the nature of both. In our work the best promoter was LiCl. In order to evaluate the specific role of the ions, we varied cation and anion separately. An increase in the selectivity toward aldehydes was found to follow the order $K < Na < Ca < Li$. It seems that increase in the size of the cation decreases the yield of aldehydes even though the total conversion remains 100%. The anion was then varied while Li was retained as the best cation. The results showed an increase in the selectivity toward aldehydes in the following order: $CO_3^{2-} < Br^- < Cl^-$. Again these results suggest that the promoter effect is a combination of both anion and cation properties. The effect of the different promoters on the distribution of products can be seen in the Fig. 2.

It seems to be that the ionic nature of the salts and their solvation properties are significant and the promoting effect may be more related to these characteristics than to the properties of the ions separately. A relation between product yields and cation size is represented by Fig. 3. The covalent character of the bond in large ion salts like KCl, Li_2CO_3, and LiBr may be the reason for the less effective solvation and consequently poorer ionic promoting effect.

An earlier study [34] showed that the use of alkaline metal salts KBr, NaCl, KI, and NaI in hydrogenation reactions where $Ru_3(CO)_{12}$ was the catalyst enhanced the yield of products in the order $Cl^- < Br^- < I^-$. The authors attributed the effect to stabilization of the metal carbonyl complex by the halide, an effect that is greater with iodide than with bromide or chloride. This is in agreement with our results where the amount of hydrogenated product followed the same pattern. Conversely, the yield of aldehydes increased with the order $I^- < Br^- < Cl^-$.

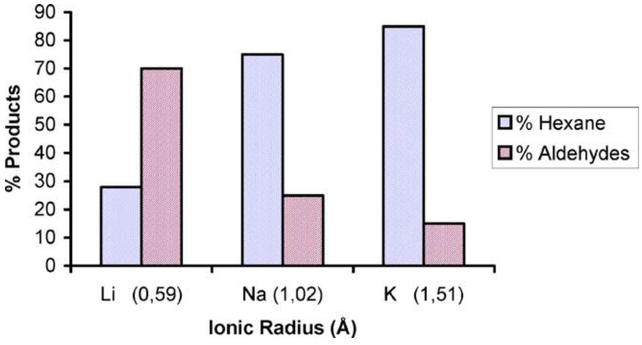

Fig. 3. Relation between ionic radius [38] of the promoter and the product distribution in reactions catalyzed by $Ir_4(CO)_{12}$.

4.2. *Iridium trichloride and iridium carbonyl chloride complexes*

The iridium chloride and iridium carbonyl chloride catalysts were studied under the standard reaction conditions. The results of the catalytic runs are summarized in Table 2.

In a previous study [29], use of iridium trichloride complex as catalyst for hydroformylation was reported to produce large amounts of hydrogenated olefin and isomers as additional products. In unpromoted reactions the strong hydrogenation capabilities of Ir compounds also favor formation of alcohols as the primary hydroformylation product, as can be seen in Table 2.

As in the case of $Ir_4(CO)_{12}$, the addition of the promoter improved the solubility of the Ir catalyst. This means that again, the catalysis process has at least a partially homogeneus nature. The recovered catalyst after hydroformylation showed a clear carbonyl patterns in both $IrCl_3$ and $IrCl(CO)_3$ cases ($\nu CO = 1921$, 1959, 1979, 1987, 2046 cm^{-1} and $\nu CO = 1961$, 2047, 2088 cm^{-1} for $IrCl_3$ and $IrCl(CO)_3$, respectively). This further supports the idea of some iridium carbonyl chloride species as active catalysts.

The use of LiCl promoter with $IrCl_3$ partially suppressed the hydrogenation, and aldehydes were obtained although in low yield. Use of Li_2CO_3 led to similar results but with formation of some additional alcohols indicating that the lithium carbonyl promoter is not able to completely block the hydrogenation of aldehydes even though it is reduces the hexane hydrogenation.

From these and the $Ir_4(CO)_{12}$ results (above) we can conclude that successful promotion effects require the presence of suitable anions such as halide, e.g., Cl^-, in one form or another. The $Ir_4(CO)_{12}/Li_2CO_3$ system, where there is no

Table 2
Catalytic activity of iridium trichloride and iridium carbonyl chloride catalyst

Catalyst	Promoter (mmol)	CO/H_2 1/1 (bar)	1-Hexene (%)	Hexane (%)	2-Me-hexanal (%)	1-Heptanal (%)	2-Me-hexanol (%)	1-Heptanol (%)	Conversion (%)	Aldehydes (n/i ratio)	Alcohols (n/i ratio)
$IrCl_3$	0[a]	50	0	37	0	0	17	18	100	1.0	1.0
	0.3 LiCl		43	43	6	8	0	0	57	1.3	
	0.6 LiCl		40	45	7	8	0	0	60	1.1	
	0.3 Li_2CO_3		48	33	6	6	3	4	52	1.0	1.3
	0.6 Li_2CO_3		49	29	6	7	4	5	51	1.1	1.3
$[IrCl(CO)_3]_n$	0[b]	50	0	40	0	0	12	16	100	1.3	1.3
	0.3 LiCl		43	0	24	33	0	0	57	1.4	
	0.6 LiCl		45	0	23	32	0	0	55	1.4	
	0.3 Li_2CO_3		36	0	23	41	0	0	64	1.8	
	0.6 Li_2CO_3		38	0	20	42	0	0	62	2.1	

Reaction conditions: $T = 150\,^\circ C$; reaction time = 17 h; $n(Ir) = 0.32$ mmol; $V(\text{solvent}) = 5$ ml 1-methyl-2-pyrrolidone; $V(\text{1-hexene}) = 0.5$ ml; $V(\text{standard}) = 0.2$ ml cyclohexane.

[a] 0 = 32% isomers in absence of promoters;

[b] 0 = 28% isomers in absence of promoter.

halide, the reaction goes in the hydrogenation direction and the yield of aldehydes is reduced from 70 to 45% (Table 1).

In systems where the chloride is included in the iridium complex, there is no marked difference between the activities of LiCl and Li_2CO_3-promoted reactions. Despite the overall similarity, there are nevertheless some differences in the effects of LiCl and Li_2CO_3 promoters. With IrCl, use of Li_2CO_3 led to the formation of some alcohols and with $[IrCl(CO)_3]_n$ the carbonate promoter gave somewhat better results than LiCl.

Iridium carbonyl chloride has been used as isomerization catalysts [35] and this reaction is totally blocked in the presence of promoter (see Table 2). Furthermore, the iridium carbonyl chloride complex in the presence of CO and H_2 forms a carbonyl species followed by the generation of a hydridocarbonyl complex [36]. This is a highly active complex for hydrogenation and isomerization [37] and these reactions in particular are suppressed in the presence of promoter.

Our results suggest that the main function of the promoters may be to produce active species by halide substitution onto the coordination sphere of the metal complex stabilized by the cation of the promoter or else to maintain the organometallic catalyst in the most active oxidation state.

5. Conclusions

The hydroformylation activity of the iridium complexes increases in the order $IrCl_3 < [IrCl(CO)_3]_n < Ir_4(CO)_{12}$. Pressure was found to be a more or less insignificant effect under our experimental conditions. High pressures slightly promote the appearance of undesirable side-reaction products, reducing the selectivity of the catalytic system.

The promoter seems to have an important role in the reaction in terms of the percentages of products obtained in comparison to those obtained without promoter. The active properties of the salt appear to be due to both anion and cation. Large cations such as Na^+ and K^+ reduce the active properties of the promoter and increase the amount of hydrogenated products. The same effect was observed when large anions like Br^- and $CO_3{}^{2-}$ were employed. The best results were achieved with LiCl and $CaCl_2$.

Only the $IrCl_3$ compound showed the same activity for the hydrogenation of aldehydes to alcohols in the presence of promoter. With $Ir_4(CO)_{12}$ and $[IrCl(CO)_3]_n$, alcohols were obtained only if the promoter was not present, suggesting that the catalytic mechanism differs with the catalyst.

Aldehyde selectivity was best with $[IrCl(CO)_3]_n$ and the highest aldehyde yields were obtained with $Ir_4(CO)_{12}$.

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