Hydroformylation

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A General and Efficient Iridium-Catalyzed Hydroformylation of Olefins**

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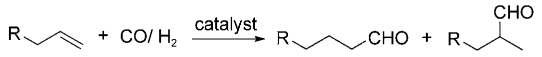
Hydroformylation is defined as the catalytic addition of a formyl group to olefins or alkynes to give linear and branched aldehydes with complete atom efficiency (Scheme 1).[1] Today, it is the most widely applied homogeneously catalyzed process in industry.[2] Annually more than 8 million tons of so-called oxo products are formed. These compounds are mainly converted into plasticizers and detergent alcohols.



Scheme 1. Formation of linear and branched aldehydes by the hydroformylation of terminal olefins.

This reaction of olefins with synthesis gas was discovered by Roelen as early as 1938 during investigations on the origin of oxygenated products obtained in cobalt-catalyzed Fisher–Tropsch reactions.[3] Until the early 1970s, when the first rhodium-based processes were commercialized, cobalt catalysts dominated academic and industrial hydroformylation chemistry. Since then, both in industry and in academic laboratories, the majority of studies have focused on rhodium-based catalysts.[4,5] Furthermore, comparably few investigations on asymmetric hydroformylation reactions with platinum catalysts have been carried out.[6] This limited interest in alternative hydroformylation catalysts is partially explained by the generally accepted order of activity of unmodified metal carbonyl complexes.[7] Thus, it has been established that rhodium is by far the most active system, followed by cobalt. Other metals, such as Ru, Ir, Os, Pt, Pd, Fe, and Ni, display significantly lower activities. However, such activities have been established under a fixed set of reaction conditions and might be changed by the use of other ligands and different reactions conditions. Owing to our interest in biphasic hydroformylation reactions,[8] we were recently attracted to the study of less common hydroformylation catalysts.[9]

Herein, we present a general and efficient iridium-catalyzed hydroformylation reaction of olefins that proceeds under mild conditions. Notably, competing hydrogenation side reactions can be suppressed.

Despite industrial applications, such as the Cativa process for the synthesis of acetic acid from methanol,[10] and economical advantages over rhodium, iridium catalysts have remained undeveloped in carbonylation reactions.[11,12] Owing to their significantly lower reactivity, iridium complexes have so far mostly been used as models in kinetic and mechanistic studies of hydroformylation reactions.[13] The major problem concerning the synthetic application of iridium-catalyzed hydroformylation reactions has been the competing hydrogenation activity of iridium complexes under hydroformylation conditions. Thus, large amounts of unwanted alkanes were produced, and low chemoselectivity was observed. Interestingly, Haukka and co-workers[12] reported that the addition of inorganic salts suppressed hydrogenation side reactions; however, only low catalyst activities (turnover frequency $< 0.5\ h^{-1}$) were observed for aldehydes.

In our initial studies, we tested different solvents and iridium precursors under a given set of conditions with 1-octene as the model olefin. All high-pressure experiments were performed in new uncontaminated autoclaves. In general, we used 0.2 mol% of the respective iridium precursor and 0.4 mol% of triphenylphosphane as the added ligand. The solvent has a significant influence on the chemoselectivity of the reaction (Table 1). In particular, polar solvents, such as THF, diglyme, and *N*-methylpyrrolidone

Table 1: Effect of the solvent and catalyst precursor on the iridium-catalyzed hydroformylation of 1-octene.[a]

Entry	Ir source	Solvent	Yield[b] [%]	*n*/*iso*	H[c] [%]	Octene isomers[d] [%]
1	[Ir(cod)acac]	THF	58	76:24	14	2
2	[Ir(cod)acac]	*o*-xylene	61	75:25	23	2
3	[Ir(cod)acac]	heptane	27	68:32	61	10
4	[Ir(cod)acac]	diglyme	57	75:25	17	2
5	[Ir(cod)acac]	toluene	50	75:25	33	5
6	[Ir(cod)acac]	NMP	74	74:26	9	1
7	$[\{Ir(cod)Cl\}_2]$	THF	30	71:28	47	10
8	$[Ir(cod)_2]BF_4$	THF	42	74:26	12	12

[a] Reaction conditions: 1-octene (5.1 mmol), 0.2 mol% Ir, PPh_3 (2.2 equiv), syngas (40 bar) introduced at room temperature, solvent (2 mL), 100 °C, 16 h. [b] The yield was determined by GC. [c] Yield of octane formed through hydrogenation. [d] Yield of isomers of 1-octene: 2-octene ≫ 3-octene. acac = acetylacetonate, cod = 1,5-cyclooctadiene.

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(NMP), favored the desired hydroformylation over hydrogenation of the olefin. [Ir(cod)acac] was found to be the best catalyst precursor in terms of chemoselectivity. As a result of its low cost and ease of handling, triphenylphosphane was chosen as the ligand for further investigations on the influence of pressure and temperature on the benchmark reaction (Table 2). Lowering of the synthesis-gas pressure generally resulted in higher reaction rates. Thus, when the reaction was carried out at 20 bar, the yield of aldehydes rose to 74% (Table 2, entry 5). An increase in the partial pressure of carbon monoxide improved the chemoselectivity further for formation of the aldehydes (Table 2, entries 7 and 8). While studying the effects of different partial pressures, we observed that the introduction of CO at room temperature and subsequent pressurization of the synthesis gas at 100 °C led to a significant increase in the desired chemoselectivity and promoted the carbonylation reaction over hydrogenation.

Table 2: Optimization of reaction conditions for the iridium-catalyzed hydroformylation of 1-octene.[a]

Entry	T [°C]	Pressure [bar]	Yield[b] [%]	*n*/*iso*	H[c] [%]	Octene isomers[d] [%]
1[e]	120	40 (CO/H_2 1:1)	70	71:29	29	1
2[e]	100	40 (CO/H_2 1:1)	69	74:26	20	2
3[e]	80	40 (CO/H_2 1:1)	13	75:25	3	–
4[e]	100	50 (CO/H_2 1:1)	62	74:26	17	1
5[e]	100	20 (CO/H_2 1:1)	74	75:25	20	3
6[e]	100	10 (CO/H_2 1:1)	72	75:25	23	5
7[f]	100	20 (CO/H_2 2:1)	73	75:25	14	3
8[g]	**100**	**20 (CO/H_2 2:1)**	**77**	**76:24**	**12**	**1**
9[h]	100	20 (CO/H_2 3:1)	71	76:24	8	1

[a] Reaction conditions: 1-octene (10.2 mmol), [Ir(cod)acac] (0.2 mol%), PPh_3 (2.2 equiv), THF (6 mL), 16 h. [b] The yield was determined by GC analysis. [c] Yield of octane. [d] Yield of isomers of 1-octene: 2-octene ≫ 3-octene. [e] Syngas was introduced when the reaction temperature had been reached. [f] CO (7 bar) and syngas (13 bar) were introduced at 100 °C. [g] CO (7 bar) was introduced at room temperature, and syngas (13 bar) was introduced at 100 °C. [h] CO (10 bar) was introduced at room temperature, and syngas (10 bar) was introduced at 100 °C.

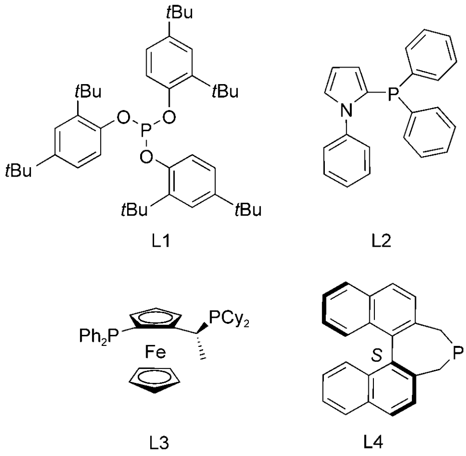
Since it is well-known that the ligand constitutes a key element in hydroformylation catalysts, we studied the influence of different ligands and the ligand concentration. The use of a higher concentration of the phosphine did not lead to an increase in the reaction rate (Table 3). Indeed, NMR spectroscopic investigations showed that only two phosphine ligands are bound to the iridium center under catalytic conditions. Among the various mono- and bidentate phosphorus ligands tested, PPh_3 was found to be optimal in terms of yield and selectivity (Table 3, entry 5). We also tested the defined hydridocarbonyltris(triphenylphosphane)iridium complex, which is expected to be formed from the catalyst precursor (Table 3, entry 6). This complex indeed showed similar performance to that of the catalyst formed in situ.

Interestingly, 2-(diphenylphospanyl)-1-phenyl-1H-pyrrole (**L2**) gave *n*-nonanal in the highest yield and octane in only 12% yield (Table 3, entry 10). Most of the ligands used (Scheme 2; Table 3) gave the linear/branched regioisomeric products in similar ratios of between 67:33 and 77:23. The sterically hindered ligand $((MeO)_3C_6H_2)_3P$ showed improved regioselectivity of 86:14 in favor of the linear aldehyde; however, an increased amount of octane was obtained with this ligand (Table 3, entry 7). Nevertheless, this regioselectivity is the highest reported so far for hydroformylation with any iridium catalyst. No significant amounts of isomerized octene products were detected in any of these reactions.

Table 3: Effect of the phosphine ligand on the iridium-catalyzed hydroformylation of 1-octene.[a]

Entry	Ligand (or complex)	L/Ir	Yield[b] [%]	*n*/*iso*	H[c] [%]
1[d]	–	–	30	52:48	65
2[d]	PPh_3	1	44	72:28	43
3[d]	PPh_3	4	61	76:24	13
4	PPh_3	3	81	76:24	12
5	**PPh_3**	**2.2**	**83**	**76:24**	**12**
6[e]	$[HIrCO(PPh_3)_3]$	–	80	76:24	13
7	$((MeO)_3C_6H_2)_3P$	2.2	43	86:14	37
8	L1	2.2	38	71:29	52
9	dppb	1	41	74:26	9
10	**L2**	**2.2**	**85**	**72:28**	**12**
11	PCy_3	2.2	26	67:33	55
12	L3	2.2	7	74:26	3
13	L4	2.2	58	77:23	16
14[f]	$[Ir_2(CO)_6(PPh_3)_2]$	–	46	74:26	41

[a] Reaction conditions: 1-octene (10.2 mmol), [Ir(cod)acac] (0.2 mol%), CO/H_2 (2:1, 20 bar), THF (6 mL), 100 °C, 20 h: CO (7 bar) was introduced at room temperature, and syngas was (13 bar) introduced at 100 °C. [b] The yield was determined by GC analysis. [c] Yield of octane. [d] Reaction time: 16 h. [e] $[HIrCO(PPh_3)_3]$ (0.2 mol%) was used as the catalyst. [f] $[Ir_2(CO)_6(PPh_3)_2]$ (0.2 mol%) was used as the catalyst. Cy = cyclohexyl, dppb = 1,4-bis(diphenylphosphanyl)butane.



Scheme 2. Ligands L1–L4.

When the reaction mixture was allowed to stand at 0–10 °C for several hours, precipitation of $[Ir_2(CO)_6(PPh_3)_2]$ was observed (Figure 1).[14] The use of this complex as a catalyst in the hydroformylation of 1-octene gave *n*-nonanal in 46% yield with a regioselectivity of 74:26 (Table 3, entry 14). Apparently, this complex readily forms the "real" active species. Clearly, the performance of the presented iridium catalyst system in the benchmark reaction under optimized conditions is superior to that of all previously reported

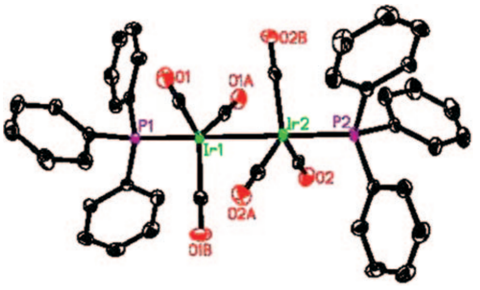


Figure 1. Molecular structure of the binuclear species $[Ir_2(CO)_6(PPh_3)_2]$. Thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity.

Table 4: Comparison of catalyst precursors containing different metals for the hydroformylation of 1-octene.[a]

Entry	Catalyst	Yield[b] [%]	*n*/*iso*	Octene isomers[c] [%]	H[d] [%]	TOF[e] [h^{-1}]
1[f]	[Ir(cod)acac] PPh_3 (8 equiv)	65	76:24	2	19	163
2[f]	$[Ru_3CO_{12}]$ PPh_3 (8 equiv)	–	–	–	–	–
3[g]	[Rh(cod)acac] PPh_3 (8 equiv)	75	60:40	21	3	1255

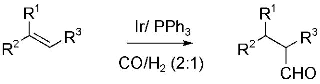
[a] Reaction conditions: 1-octene (10.2 mmol), metal precursor (0.02 mol%), PPh_3 (8 equiv), CO/H_2 (2:1, 20 bar), THF (6 mL), 120°C: CO (7 bar) was introduced at room temperature, then syngas (13 bar) was introduced at 100°C. [b] The yield was determined by GC. [c] Yield of isomers of 1-octene. [d] Yield of octane. [e] Turnover frequency based on the aldehyde yield. [f] Reaction time: 20 h. [g] Reaction time: 3 h.

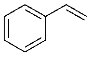
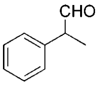
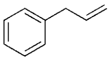
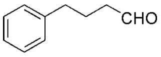
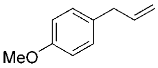
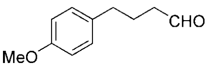
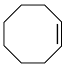
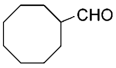
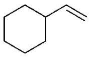
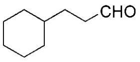
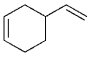
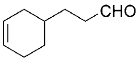
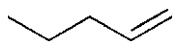
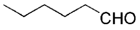
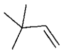
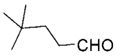
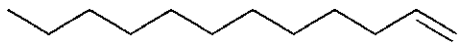
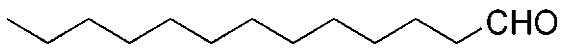
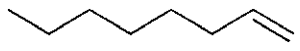
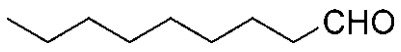
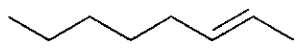
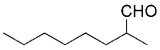
iridium catalyst systems. However, iridium-catalyzed hydroformylation reactions will only be of broader interest if the activity of the catalyst is competitive with that of rhodium-based catalysts and if the catalysts tolerate various substrates. Hence, we carried out rhodium- and ruthenium-catalyzed hydroformylation reactions in the presence of triphenylphosphane under identical reaction conditions (Table 4).

Whereas the ruthenium catalyst did not show any activity at all, the iridium and rhodium complexes performed similarly: $[Ir(cod)acac]/PPh_3$ gave the aldehyde products in 65% yield (*n*/iso 76:24), and $[Rh(cod)acac]/PPh_3$ gave the aldehydes in 75% yield with a regioselectivity of 60:40. The iridium catalyst showed an overall turnover frequency of 163 h^{-1}, which is only eight times lower than that of the rhodium/triphenylphosphane catalyst. However, prior to this study, rhodium catalysts were considered to be 10000 times faster than iridium catalysts.[15] If the price advantage of iridium, a factor of 5–10, is taken into account, iridium is clearly a promising metal for novel hydroformylation catalysts.[16]

Finally, after suitable process conditions had been established, we studied the scope and limitations of the present reaction protocol and found that the catalyst system is broadly applicable. Various aliphatic and aromatic olefins were hydroformylated in high yield (Table 5). To the best of our

Table 5: Scope and limitations of the iridium-catalyzed hydroformylation.[a]



Entry	Substrate	Product	*t* [h]	Yield[b] [%]	*n*/*iso*	H[c] [%]	Substrate isomers [%]
1		 CHO	24	62	26:74	6	–
2		 CHO	16	85	68:22	8	–
3	 MeO	 MeO, CHO	16	90[d]	68:22[d]	9[b]	<1
4[e]		 CHO	48	90	–	5	–
5		 CHO	16	90	84:16	7	2
6		 CHO	16	82	79:21	9	4
7		 CHO	20	71	75:25	5	2
8		 CHO	20[f]	69	96:4	9	–
			20	62	97:3	7	–
9[g]		 CHO	20	87	75:25	7	1
10		 CHO	16	89	76:24	6	1
11[f]		 CHO	20	14	4:96	2	2

[a] Reaction conditions: substrate (10.2 mmol), [Ir(cod)acac] (0.2 mol%), PPh_3 (2.2 equiv), NMP (6 mL), CO (7 bar), room temperature, then syngas (13 bar) introduced at 100°C. [b] The yield was determined by GC analysis. [c] Yield of the hydrogenated product ar 130°C. [d] The yield and *n*/*iso* product ratio were determined by NMR spectroscopy. [e] The reaction was carried out with [Ir(cod)acac] (0.4 mol%) in 130°C. [f] The reaction was carried out in THF. [g] The substrate contained dodecane (2%), ethyloctene (3%), and methyldodecene (2%).

knowledge, these are the highest aldehyde yields observed with iridium catalysts for all substrates shown. For example, the hydroformylation of 1-octene gave aldehydes in 89% yield (Table 5, entry 10), whereas the best yield observed previously was only 40% ([(cod)Ir(pnnp)Ir(cod)]BF$_4$ (2 mol%), 80°C, CO/H$_2$ (1:1, 30 bar), 6 h; pnnp = 3,5-bis(diphenylphosphanylmethyl)pyrazole).[17] Interestingly, no or very little isomerization occurred; thus, the catalyst system is highly selective for terminal olefins. In agreement with this observation, the hydroformylation of 2-octene gave the corresponding branched aldehyde in low yield (Table 5, entry 11). Cyclic olefins, such as cyclooctene, reacted well: cyclooctanecarbaldehyde was obtained in very good yield (90%; Table 5, entry 4). The hydroformylation of aromatic olefins[18] proceeded to give the branched aldehyde preferentially (Table 5, entry 1) owing to the increased thermodynamic stability of the intermediate benzyliridium complex.

In conclusion, we have demonstrated that iridium is a suitable metal for hydroformylation catalysts. Despite previous reservations, iridium/phosphine complexes form active hydroformylation catalysts under mild conditions. These catalysts promote the efficient hydroformylation of a variety of olefins. On the basis of our findings, we believe that iridium complexes will become more popular for this important transformation in organic synthesis and industrial chemistry.

Experimental Section

General procedure: The olefin (10.2 mmol) was added under argon to a solution of the metal precursor (0.2 mol% Ir) and the corresponding ligand (2.2 equiv) in THF or NMP (6 mL). The reaction mixture was transferred into an autoclave, which was then charged with CO and heated at the indicated reaction temperature. Syngas was then introduced. After the indicated reaction time, the autoclave was cooled to 0°C, and the pressure was released. The reaction mixture was analyzed immediately by gas chromatography; isooctane was used as an internal standard. The yield was determined by NMR spectroscopy with benzaldehyde as an internal standard.

X-ray crystal-structure analysis of [Ir$_2$(CO)$_6$(PPh$_3$)$_2$]: $C_{42}H_{30}Ir_2O_6P_2$, $M_r = 1077.00$, trigonal, space group $R\bar{3}$, $a = 15.2149(3)$, $c = 28.7461(6)$ Å, $V = 5763.0(2)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.862$ g cm^{-3}, $T = 200$ K; 30527 reflections measured, 2819 independent reflections ($R_{int} = 0.0289$), 2448 reflections observed ($I > 2\sigma(I)$); numerical absorption correction ($\mu = 7.05$ mm^{-1}, max./min. transmission: 0.4920/0.2372); final R indices ($I > 2\sigma(I)$): $R_1 = 0.0158$, $wR_2 = 0.0299$; R indices (all data): $R_1 = 0.0228$, $wR_2 = 0.0308$; 157 parameters. Data were collected on a STOE IPDS II diffractometer with graphite-monochromated Mo$_{K\alpha}$ radiation. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques on F^2 (SHELXL-97). XP (Bruker AXS) was used for graphical representation. CCDC 775742 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

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Keywords: aldehydes · alkenes · homogeneous catalysis · hydroformylation · iridium

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