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Rhodium versus Iridium Catalysts in the Controlled Tandem Hydroformylation–Isomerization of Functionalized Unsaturated Fatty Substrates

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The hydroformylation of 10-undecenitrile (**1**) and related unsaturated fatty substrates ($H_2C{=}CH(CH_2)_7CH_2R$; $R = CO_2Me$, CH_2Br, CHO) has been studied with rhodium, iridium, ruthenium, and palladium biphephos catalysts. The reactions proceeded effectively with all four systems, with high selectivities for the linear aldehyde (ratio of linear/branched aldehydes = 99:1). The biphephos-bis[chloro(cyclooctadiene)iridium] system showed a non-optimized hydroformylation turnover frequency (TOF_{HF}) of 770 h^{-1} that was only approximately 5 times lower than that of the rhodium-based system ($TOF_{HF} = 3320\ h^{-1}$); the palladium and ruthenium biphephos systems were less active ($TOF_{HF} =$ 210 and 310 h^{-1}, respectively). Upon recycling, remarkable productivities were achieved in both cases (TON ≈ 58 000 mol(**1**/**1**-*int*) mol(Ir)$^{-1}$ and 250 000 mol(**1**/**1**-*int*) mol(Rh)$^{-1}$, in which *int* = internal olefin). Competitive isomerization of terminal to internal olefins occurred with these catalysts. Iridium biphephos systems allowed slightly better control of the distribution of the internal isomers than the rhodium biphephos catalyst, with higher ratios of 9-/8-undecenitrile (**1**-*int*).

Introduction

Hydroformylation is the most widely applied homogeneously catalyzed process in industry; more than 10 million tons of aldehyde products are produced each year and converted mainly into plasticizers, solvents, and detergent alcohols.[1] The reaction, discovered by Roelen in 1938,[2] was initially performed with cobalt catalysts, which dominated academic and industrial hydroformylation chemistry for several decades. Nowadays, the majority of studies and some important industrial processes rely on rhodium-based catalysts, which are more active and allow a higher selectivity for the production of linear aldehydes with negligible quantities of alkanes.[3] However, the price of rhodium—a precious metal in high demand and limited supply—is quite high and extremely volatile.[4] There is thus a strong interest for catalysts based on more readily available metals to achieve hydroformylation.[5] Yet, in contrast to the extensive studies performed on cobalt and rhodium systems, other metals have received less attention, most likely because of their generally lower activity[5,6] (Rh ≫ Co > Ir, Ru > Os > Pt > Pd ≫ Fe > Ni, as established for unmodified metal carbonyl complexes)[7] and chemoselectivity in hydroformylation. Catalysts based on iridium, a metal cheaper than rhodium but also with a relatively volatile price,[4] have long remained underdeveloped in hydroformylation due to their tendency to promote side-hydrogenation under hydroformylation conditions.[8] Nonetheless, recent reinvestigations have demonstrated a good potential of this metal.[5,9] For instance, Beller and co-workers described the use of a triphenylphosphine-modified iridium catalyst that was only 8 times slower than its rhodium homologue in the hydroformylation of various olefins, with selectivities for linear aldehydes in the range 68–97 %.[9a] The potential of ruthenium catalysts in hydroformylation has been also investigated.[5,10] The groups of Drent and Beller have reported palladium phosphine catalysts modified with strong acids as co-catalysts that can afford aldehydes (sometimes in mixtures with alcohols) with modest activity but up to 95 % regioselectivity for the linear aldehydes.[11]

From economic and environmental point of views, one of the most challenging goals in current hydroformylation research is the selective conversion of internal olefins to linear aldehydes. The main obstacle is the isomerization process. This does not represent a huge problem for shorter alkenes but, for longer chain alkenes, internal isomers are present and/or formed in significant amounts and can eventually give access to a series of undesired branched aldehydes. To date, a few catalyst systems enable the selective conversion of internal alkenes towards terminal aldehydes.[12] Two strategies can be used. The first consists of dual hydroformylation–isomerization catalytic systems similar to those reported by the groups of Beller[13] and Nozaki,[14] relying on the use of a simple rhodium catalyst for hydroformylation and a ruthenium catalyst for

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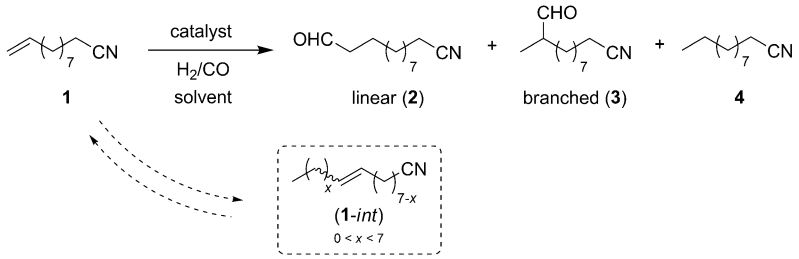
isomerization, albeit with relatively large loadings of the latter metal to achieve the isomerization–hydroformylation of 2-butene. Also, Reek et al. employed a combination of palladium triphenylphosphine and supramolecular rhodium bisphosphite catalysis for achieving the synthesis of α-methyl-branched aldehydes from terminal olefins.[15] The second—and likely most efficient strategy—remains the use of a single catalyst comprising a group VIII element and specific phosphorus-based ligands.[12] Hence, effective isomerization–hydroformylation of 2-olefins, such as 2-octene and 2-hexene, to linear aldehydes has been achieved with rhodium catalysts associated with bulky phosphite ligands of Union Carbide Corp. [ratio of linear/branched aldehydes (*l*/*b*) = 19 for 2-hexene][3b] and DuPont–DSM (*l*/*b* = 35 for 2-hexene),[16] Van Leuween's Xantphos derivatives (*l*/*b* = 9.5 for 2-octene),[3e-g] Börner's acylphosphite ligands (*l*/*b* = 2.2 for a mixture of octene isomers),[17] substituted Naphos-type ligands designed by Beller (*l*/*b* = 10.1 for 2-octene),[18] and Zhang's tetraphosphorous ligands (*l*/*b* = 362 for 2-hexene and 267 for 2-octene) (Figure 1).[19] Also, efficient Rh-based catalytic systems have been reported for the isomerization–hydroformylation of functional C_3–C_5 olefins such as pentenenitriles.[20]



Scheme 1. Hydroformylation and isomerization products arising from **1**.

In a previous study, we reported the use of an efficient (acetylacetonato)dicarbonylrhodium-biphephos catalyst system for the tandem isomerization–hydroformylation of the unsaturated fatty nitrile 10-undecenitrile (**1**, Scheme 1), as a potential route toward biosourced polyamide-12.[21] The reaction, which was also extended to related functionalized unsaturated fatty substrates, was performed at very high substrate/rhodium ratios (20 000–100 000) and allowed access to the desired linear aldehydes with high chemo- and regioselectivities up to 93 and 99%, respectively. However, these fatty C11 compounds could give access to significant amounts of undesired isomerization products [e.g., **1**-*int* (*int* = internal olefin) in the case of **1**] under the hydroformylation conditions, which eventually plagued both conversions and selectivities for the desired linear aldehydes (Scheme 1).

Herein, we report new results on the isomerization–hydroformylation of **1** and related functionalized unsaturated fatty substrates. Our objectives are two-fold: 1) to achieve hydroformylation with high regioselectivity, while controlling the distribution of the internal isomers formed; indeed, *cis*/*trans*-9-isomers produced from a 10-olefin can be valuable compounds for special applications, such as in the fragrance industry; and 2) to investigate alternative catalysts based on metals other than rhodium. Thus, the tandem isomerization–hydroformylation of a series of functionalized unsaturated fatty substrates has been performed with homogeneous rhodium, iridium, ruthenium, and palladium diphosphane catalysts. The conditions for achieving high selectivities and productivities, including an effective recycling of the hydroformylation catalyst, are described.

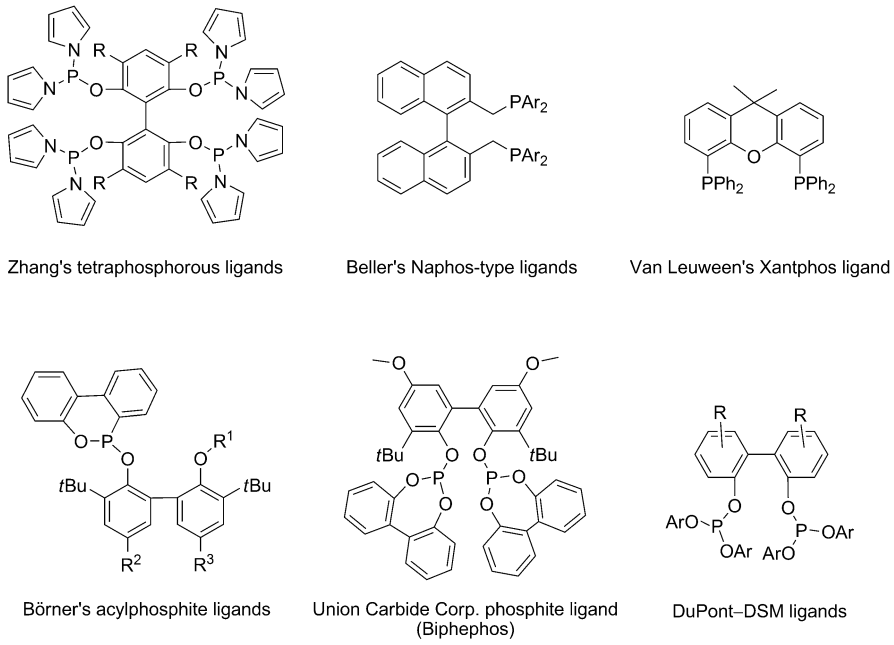


Figure 1. Typical phosphorus-based ligands associated to Rh for effective isomerization–hydroformylation of internal olefins.[12]

Results and Discussion

Single-batch hydroformylation of 1

Different Ir catalyst precursors were first evaluated in combination with biphephos under the conditions optimized previously in the Rh-biphephos-catalyzed hydroformylation of **1**,[21] chosen here as a model substrate. The results, summarized in Table 1 (see also Tables S1–S4), indicate

Table 1. Hydroformylation–isomerization of **1**/**1**-*int* promoted by Rh- and Ir-biphephos systems.[a]

Entry	Precursor [M]	$[\mathbf{1}]_0$/[M]	Solvent	**1**[b] [%]	**1**-*int*[b] [%]	9-/8-undec	**2**+**3**[b] [%]	**2**/**3**	**4**[b] [%]	Conv. **1**[c] [%]	HF[d] [%]
1[e]	$[Rh(acac)(CO)_2]$	20000	toluene	0	16	81/19	79	99/1	5	100	83
2	$[IrCl(cod)]_2$	20000	toluene	0	22	86/14	73	99/1	5	100	77
3	$[Rh(acac)(CO)_2]$	50000	toluene	0	21	89/11	75	99/1	4	100	79
4	$[IrCl(cod)]_2$	50000	toluene	8	22	92/8	65	99/1	5	92	75
5[f]	$[Rh(acac)(CO)_2]$	20000	toluene	45	7	98/2	46	97/3	2	53	92
6[f]	$[IrCl(cod)]_2$	20000	toluene	82	7	95/5	9	98/2	2	14	69
7	$[IrCl(cod)]_2$	20000	tetrahydrofuran	0	26	88/12	69	99/1	5	100	73
8	$[IrCl(cod)]_2$	20000	*N*-methyl-2-pyrrolidone	25	18	95/5	52	99/1	5	74	74
9	$[IrCl(cod)]_2$	20000	acetonitrile	1	20	92/8	75	99/1	4	99	80
10	$[IrCl(cod)]_2$	50000	acetonitrile	5	22	93/7	69	99/1	4	95	77
11	[Ir(acac)(cod)]	20000	toluene	3	21	92/8	64	99/1	12	97	70
12	[Ir(acac)(cod)]	50000	toluene	45	13	96/4	30	99/1	12	53	60
13	[Ir(acac)(cod)]	20000	acetonitrile	0	22	88/12	74	99/1	4	100	78
14	$[IrCp^{Me}(cod)]$	20000	toluene	16	18	90/10	62	99/1	4	83	78
15[g]	$Pd(acac)_2$	20000	toluene	0	19	88/12	76	99/1	5	100	76
16[h]	$[RuCl_2(PPh_3)_3]$	20000	toluene	2	21	93/7	73	99/1	4	98	75
18[i]	$[Rh(acac)(CO)_2]$	20000	bulk	1	20	84/16	75	99/1	4	99	80
19[i]	[Ir(acac)(cod)]	20000	bulk	8	16	94/6	72	99/1	4	92	83
20[i]	$[RuCl_2(PPh_3)_3]$	20000	bulk	4	19	92/8	72	99/1	5	96	80

[a] Reaction conditions unless otherwise stated: **1**/**1**-*int* (95:5, 5.0 mmol), $[biphephos]_0/[M] = 20$, solvent (5 mL), $P = 20$ bar CO/H_2 (1:1), $T = 120\,^{\circ}C$, $t = 5$ h (Rh), 20 h (Ir), 72 h (Ru, Pd). [b] Distribution [mol%] of remaining **1** and internal alkenes **1**-*int*, aldehydes **2** and **3**, and hydrogenation product **4**, as determined by NMR and GLC analyses. [c] Conversion of **1**. [d] Selectivity for hydroformylation products (**2**+**3**) vs. isomerization and hydrogenation. [e] Results from Ref. [21]. [f] With Xantphos as ligand. [g] $t = 72$ h. [h] $t = 48$ h. [i] A minimal amount (0.5 mL) of toluene (Rh and Ru) or acetonitrile (Ir) was used to introduce the catalyst precursors.

that the Ir biphephos system was less active than the Rh biphephos system (hence, the batch reactions were typically conducted over 5 h with Rh and 20 h with Ir), but not dramatically so. Indeed, the Ir biphephos system showed a non-optimized hydroformylation turnover frequency (TOF_{HF}) towards 12-oxododecanenitrile (**2**) of 770 mol(**2**) mol(Ir)$^{-1}$ h^{-1} (entry 2) that was only approximately 5 times lower than the TOF_{HF} of 3320 h^{-1} for the analogous Rh-based system (entry 1). As mentioned above, Beller et al. disclosed recently that an [Ir(cod)acac]PPh_3 (in which acac = acetylacetonato, cod = 1,5-cyclooctadiene) catalyst was no more than 8 times slower than a Rh catalyst in the hydroformylation of various olefins.[9a] Yet, the activity of Ir-based catalysts in the hydroformylation of **1** was very much dependent on the nature of the ligand: an experiment performed with Ir-Xantphos proceeded significantly more slowly ($TOF_{HF} = 97$ h^{-1}, entry 6) than that with the Rh-Xantphos system ($TOF_{HF} = 1950$ h^{-1}, entry 5). Notably, the $[Pd(acac)_2]$/biphephos and $[RuCl_2(PPh_3)_3]$/biphephos combinations also proved effective, although they proceeded more slowly than with Ir- and Rh-biphephos catalysts under the given conditions, with TOF_{HF} values of 210 mol(**2**) mol(Pd)$^{-1}$ h^{-1} (entry 15) and 310 mol(**2**) mol(Ru)$^{-1}$ h^{-1} (entry 16; see also Table S2 in the Supporting Information). For these reasons, further studies were focused on Ir and Rh systems.

Remarkably, the Ir- and Rh-biphephos catalysts performed similarly well in terms of chemo- and regioselectivity in hydroformylation. The linear aldehyde product **2** was obtained in 73% yield with $[IrCl(cod)]_2$/biphephos (entry 2) and in 79% yield with $[Rh(acac)(CO)_2]$/biphephos (entry 1), with *l*/*b* ratios [**2**/10-methyl-11-oxoundecanenitrile (**3**)] of 99:1 in both cases. These performances were only slightly affected after decreasing the catalyst loading to $[\mathbf{1}]_0$/[metal] up to 50000 (entries 1,2 vs. 3,4). In contrast, the nature of the solvent (entries 2 vs. 7–9) and catalyst precursor (entries 2, 11, and 14) appeared more important; in fact, significantly higher amounts of the hydrogenation product undecanenitrile (**4**)—the only side-product observed besides those from the isomerization of **1** (see the discussion below)—were observed with [Ir(acac)(cod)] as precursor, in contrast to $[IrCl(cod)]_2$ and $[IrCp^{Me}(cod)]$ as precursors, for reactions performed in toluene. Use of [Ir(acac)(cod)] as precursor gave better performance in acetonitrile (entries 11 vs. 13).

Both the Ir- and Rh-biphephos systems catalyzed the parallel isomerization of **1** and, at total conversion of the terminal olefin, induced formation of internal isomers (**1**-*int*) to a similar extent (≈15–25% yield). Remarkably, based on the results reported in Table 1, both the Rh- and Ir-biphephos systems controlled the distribution of the internal isomers formed, and eventually only 9-undecenitrile (major product) and 8-undecenitrile (minor product) were generated. The distribution of internal isomers of undecenitrile (**1**-*int*) was determined readily by NMR analysis of the crude reaction mixture. The typical signals for the internal isomers were observed in ^{1}H NMR ($CDCl_3$) spectra at $\delta = 5.20$–5.40 ppm for olefinic hydrogens and the presence of a distinct CH_3CH_2 triplet signal at $\delta = 1.05$ ppm evidenced isomerization products in which the double bond had migrated over at least two carbons from the terminal positions, that is 8-undecenitrile, 7-undecenitrile, and possibly other internal isomers (see Figure S5). Distinct alkene signals were also evidenced in $^{13}C\{^1H\}$ NMR spectra, enabling determination of the *trans*/*cis* configurations of the internal isomers (Figure 2, see also Figure S6).[22] As seen in Table 1, the Ir-biphephos system allowed for slightly but noticeably better control of the distribution of the internal isomers than the Rh-biphephos catalyst, with systematically higher ratios of 9-/8-undecenitrile, whatever the conditions used (entries 1,3 vs. 2,4). Thus, the internal olefins formed during the hydroformylation of **1** were typically comprised of 90–96% 9-undecenitrile with Ir-biphephos and 80–90% with Rh-biphephos.

A series of experiments were performed to evaluate the importance of the excess of ligand in the hydroformylation–isomerization reaction of **1**, regarding in particular the distribution of internal isomers **1**-*int*. The results are summarized in Table 2. With $[Rh(acac)CO_2]$, $[IrCl(cod)]_2$, and [Ir(acac)(cod)] as precursors, a slight but noticeable positive effect on the selectivity

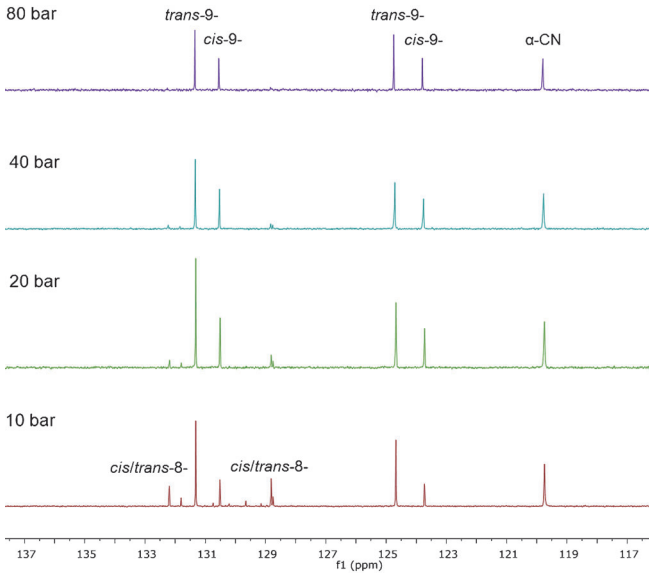


Figure 2. Detail of the olefinic region of the $^{13}C\{^1H\}$ NMR spectra (125 MHz, $CDCl_3$, 23 °C) of isomerization products (*cis*/*trans*-9- and 8-undecenitrile) isolated from the hydroformylation of **1** promoted by Rh-biphephos at 120 °C over 5 h at different pressures (Table 4, entries 1–4).

Table 2. Effect of ligand loading on the internal olefin distribution in hydroformylation–isomerization of **1**/**1**-*int* promoted by the Rh- and Ir-biphephos systems.[a]

Entry	Precursor	Biphephos $[equiv]_0$	**1**[b] [%]	**1**-*int*[b] [%]	9-/8-undec	**2** + **3**[b] [%]	**2**/**3**	**4**[b] [%]	Conv. **1**[c] [%]	HF[d] [%]
1	$[Rh(acac)(CO)_2]$	20	0	16	81/19	79	99/1	5	99	83
2	$[Rh(acac)(CO)_2]$	50	1	17	84/16	77	99/1	5	99	82
3	$[Rh(acac)(CO)_2]$	100	1	19	90/10	76	99/1	4	99	81
4	$[IrCl(cod)]_2$	20	0	22	86/14	73	99/1	5	100	77
5	$[IrCl(cod)]_2$	50	0	23	93/7	71	99/1	6	100	75
6	$[IrCl(cod)]_2$	100	18	16	100/0	60	99/1	6	81	78
7	[Ir(acac)(cod)]	20	3	21	92/8	64	99/1	12	97	70
8	[Ir(acac)(cod)]	100	36	13	95/5	43	99/1	8	62	73

[a] Reaction conditions unless otherwise stated: **1**/**1**-*int* (95:5, 5.0 mmol), $[\mathbf{1}/\mathbf{1}\text{-}int]_0/[M] = 20\,000$, toluene (5 mL), $P = 20$ bar CO/H_2 (1:1), $T = 120$ °C, $t = 5$ h (Rh) or 20 h (Ir). [b] Distribution [mol%] of remaining **1** and internal alkenes **1**-*int*, aldehydes **2** and **3**, and hydrogenation product **4**, as determined by NMR and GLC analyses. [c] Conversion of **1**. [d] Selectivity for hydroformylation products (**2** + **3**) vs. isomerization and hydrogenation.

for 9-undecenitrile was observed by increasing the biphephos/metal ratio from 20 to 100 (Table 2). Again, the control appeared better if Ir precursors were used (entries 1, 4, and 7). However, excess loading of ligand (i.e., 100 equiv) plagued the hydroformylation catalytic activity of the Ir systems (entries 6 and 8), which was not the case with the Rh-biphephos system (entries 1–3).

The results of the influence of the reaction temperature (100–140 °C) are summarized in Table 3. Whatever the solvent (toluene or acetonitrile) and precursor (Rh or Ir) used, the increase in reaction temperature resulted, as expected, in an increase in the global activity, both towards hydroformylation and isomerization (Table 3). The selectivity in favor of linear aldehydes was unaffected by the reaction temperature and, in all cases, 99% of linear aldehydes were observed. At high temperature, the distribution of the internal isomers was less controlled and larger amounts of the undesired hydrogenation product were formed.

The influence of the overall syngas pressure [20–80 bar (2–8 MPa), $CO/H_2 = 1:1$] was examined under conditions optimized specifically for Ir- and Rh-biphephos catalysts (see Table 4). Whatever the pressure used (20 or 80 bar), the activity and selectivity for linear aldehyde **2** were not significantly affected (Table 4). However, the rate of formation of internal olefins decreased with pressure. With both systems, high pressure—thus, a higher amount of CO—resulted in a better selectivity for hydroformylation, which was favored vs. isomerization; hence, better control over the distribution of internal isomers in favor of 9-undecenitrile was obtained (86–95% with Rh and 90–97% with Ir). This trend was clearly observed in the olefinic region of the ^{13}C NMR spectra of isomerization products (see Figure 2).

The influence of the CO/H_2 ratio is summarized in Table 5. With both Ir- and Rh-biphephos systems, an increase in the partial pressure of CO improved the chemoselectivity and thus the yield of aldehydes. Concomitantly, a slightly but noticeably improved control of the internal isomers distribution was observed.

The influence of total and partial CO pressure can be accounted for on the basis of the general dissociative catalytic cycle for olefin hydroformylation first proposed by Wilkinson and coworkers (Scheme 2).[23] Increase in the CO pressure shifts the conversion of alkyl metal intermediate **II** towards dicarbonyl species **III**, towards the corresponding acyl metal intermediate **IV** (and aldehyde), hence preventing β-H elimination from **II**, which eventually leads to isomerization via hydride intermediates of type **V**.

Substrate scope

The Ir- and Rh-biphephos systems both enabled the hydroformylation–isomerization of related functionalized fatty alkenes, such as methyl 10-undecenoate, 10-undecenal, 1-bromo-10-undecene, and the simple 10-undecene. Representative results obtained with these substrates under the reaction conditions optimized for **1** are summarized in Table 6. Good chemoselectivity and excellent regioselectivity for the linear aldehydes were observed in all cases. The relatively lower activity of Ir vs. Rh was apparent for all substrates: although the reactions with these other fatty alkenes were not optimized and no detailed kinetics were determined, a comparison of the apparent TOFs indicates that the Ir-biphephos system was approximately 2.5 ($R = CH_2Br$), 4 (CO_2Me), 7 (CH_3) or 10 (CHO) times less active

Table 3. Effect of the reaction temperature in hydroformylation–isomerization of **1**/**1**-*int* promoted by Rh- and Ir-biphephos systems.[a]

Entry	Precursor	Solvent	*T* [°C]	**1**[b] [%]	**1**-*int*[b] [%]	9-/8-undec	**2**+**3**[b] [%]	**2**/**3**	**4**[b] [%]	Conv. **1**[c] [%]	HF[d] [%]
1[e]	$[Rh(acac)(CO)_2]$	toluene	100	26	20	88/12	51	99/1	3	73	71
2[e]	$[Rh(acac)(CO)_2]$	toluene	120	2	21	79/21	72	99/1	5	98	77
3[e]	$[Rh(acac)(CO)_2]$	toluene	140	0	25	73/27	69	99/1	6	100	74
4	$[IrCl(cod)]_2$	toluene	100	70	7	98/2	21	99/1	2	26	84
5	$[IrCl(cod)]_2$	toluene	120	0	22	86/14	73	99/1	5	100	77
6	$[IrCl(cod)]_2$	toluene	140	0	28	90/10	66	99/1	6	100	70
7	$[IrCl(cod)]_2$	acetonitrile	100	65	9	98/2	24	99/1	2	32	80
8	$[IrCl(cod)]_2$	acetonitrile	120	1	20	92/8	75	99/1	4	99	80
9	$[IrCl(cod)]_2$	acetonitrile	140	0	25	80/20	69	99/1	6	100	73

[a] Reaction conditions unless otherwise stated: **1**/**1**-*int* (95:5, 5.0 mmol), $[\mathbf{1}/\mathbf{1}\text{-}int]_0/[M] = 20\,000$, $[biphephos]_0/[M] = 20$, solvent (5 mL), $P = 20$ bar CO/H_2 (1:1), $t = 4$ h (Rh) or 20 h (Ir). [b] Distribution [mol%] of remaining **1** and internal alkenes **1**-*int*, aldehydes **2** and **3**, and hydrogenation product **4**, as determined by NMR and GLC analyses. [c] Conversion of **1**. [d] Selectivity for hydroformylation products (**2**+**3**) vs. isomerization and hydrogenation. [e] Results from Ref. [21].

Table 4. Effect of the overall CO/H_2 pressure in hydroformylation–isomerization of **1**/**1**-*int* promoted by Rh- and Ir-biphephos systems.[a]

Entry	Precursor	H_2/CO [bar]	**1**[b] [%]	**1**-*int*[b] [%]	9-/8-undec	**9**-*trans*/**9**-*cis*	**2**+**3**[b] [%]	**2**/**3**	**4**[b] [%]	Conv. **1**[c] [%]	HF[d] [%]
1	$[Rh(acac)(CO)_2]$	10	0	37	86/14	75/25	58	99/1	5	100	60
2	$[Rh(acac)(CO)_2]$	20	0	21	89/11	68/32	75	99/1	4	100	79
3	$[Rh(acac)(CO)_2]$	40	0	18	93/7	62/38	78	99/1	4	100	82
4	$[Rh(acac)(CO)_2]$	80	0	15	95/5	58/42	82	99/1	3	100	86
5	[Ir(acac)(cod)]	10	2	35	90/10	65/35	58	99/1	5	98	63
6	[Ir(acac)(cod)]	20	1	20	92/8	62/38	75	99/1	4	99	80
7	[Ir(acac)(cod)]	40	2	21	95/5	61/39	73	99/1	4	97	79
8	[Ir(acac)(cod)]	80	3	17	97/3	59/41	77	99/1	3	97	84

[a] Reaction conditions unless otherwise stated: **1**/**1**-*int* (95:5, 5.0 mmol), $[\mathbf{1}/\mathbf{1}\text{-}int]_0/[Ir] = 20\,000$ and $[\mathbf{1}/\mathbf{1}\text{-}int]_0/[Rh] = 50\,000$, $[biphephos]_0/[M] = 20$, solvent (5 mL): toluene (Rh) or acetonitrile (Ir), $T = 120$ °C, $CO/H_2 = 1{:}1$, $t =$ 5 h (Rh) or 20 h (Ir). [b] Distribution [mol%] of remaining **1** and internal alkenes **1**-*int*, aldehydes **2** and **3**, and hydrogenation product **4**, as determined by NMR and GLC analyses. [c] Conversion of **1**. [d] Selectivity for hydroformylation products (**2**+**3**) vs. isomerization and hydrogenation.

Table 5. Effect of the CO/H_2 ratio in the hydroformylation–isomerization of **1**/**1**-*int* promoted by Rh- and Ir-biphephos systems.[a]

Entry	Precursor	CO/H_2	**1**[b] [%]	**1**-*int*[b] [%]	9-/8-undec	**2**+**3**[b] [%]	**2**/**3**	**4**[b] [%]	Conv. **1**[c] [%]	HF[d] [%]
1	$[Rh(acac)(CO)_2]$	1:1	0	18	93/7	78	99/1	4	100	82
2	$[Rh(acac)(CO)_2]$	1:3	0	20	85/15	71	96/4	9	100	74
3	$[Rh(acac)(CO)_2]$	3:1	0	16	94/6	81	99/1	3	100	85
4	[Ir(acac)(cod)]	1:1	2	21	95/5	73	99/1	4	97	79
5	[Ir(acac)(cod)]	1:3	18	22	90/10	54	97/3	6	81	70
6	[Ir(acac)(cod)]	3:1	52	9	96/4	38	99/1	1	45	88

[a] Reaction conditions unless otherwise stated: **1**/**1**-*int* (95:5, 5.0 mmol), $[\mathbf{1}/\mathbf{1}\text{-}int]_0/[M] = 20\,000$, $[biphephos]_0/[M] = 20$, solvent (5 mL): toluene (Rh) or acetonitrile (Ir), $P =$ 40 bar CO/H_2, $T = 120$ °C, $t = 5$ h (Rh) or 20 h (Ir). [b] Distribution [mol%] of remaining **1** and internal alkenes **1**-*int*, aldehydes **2** and **3**, and hydrogenation product **4**, as determined by NMR and GLC analyses. [c] Conversion of **1**. [d] Selectivity for hydroformylation products (**2**+**3**) vs. isomerization and hydrogenation.

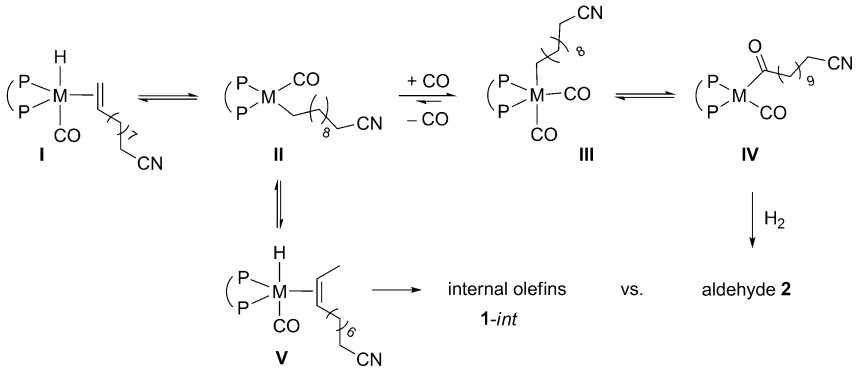
than the analogous Rh-based system, which was in line with the observed difference with **1** (Ir approximately 5 times less active than Rh).

Recycling of the hydroformylation catalyst

Even if Ir catalysts are usually cheaper than their Rh-based homologues, it is still essential for industrial perspectives to recycle the catalyst. For this purpose, we used a strategy based on vacuum distillation as reported in our previous study.[21] Vacuum distillation of the crude reaction mixture recovered in the hydroformylation–isomerization of **1**/**1**-*int* was readily achieved by using a Kugelrohr system [180 °C, 1 mm Hg (133 Pa), 5–15 min] to yield three different fractions containing respectively the internal isomers and the residual substrate, the pure aldehydes, and a liquid residue containing the catalyst. Notably, to avoid degradation of the catalyst and/or the ligand, the liquid residue was recycled in a controlled atmosphere (argon). Representative results obtained by using this procedure evidenced that it allowed a good chemo- and regioselectivity in favor of the linear aldehyde over at least 5 runs with the Rh-biphephos system and at least 3 runs with the Ir-biphephos system, simply by addition of a fresh charge of ligand after each run (i.e., $20 + 4 \times 5 = 40$ equiv total for Rh and $20 + 2 \times 5 = 30$ equiv total for Ir; see Table 7). Good chemo- and regioselectivity in favor of the linear aldehyde and 9-undecenitrile were obtained in the two systems. No accumulation of internal olefins was observed in the reaction, indicating that isomerization continued over the different runs. Just a slight decrease in selectivity for the linear aldehyde (with a slight increase in favor of hydrogenation) and an incomplete substrate conversion were observed, respectively, in the 5th (entry 5) and 3rd (entry 8) runs, indicating partial catalyst deactivation at these stages. Yet, remarkable productivities were achieved in both cases (TON $\approx 250\,000$ mol(**1**/**1**-*int*) mol(Rh)$^{-1}$ and 58 000 mol(**1**/**1**-*int*) mol(Ir)$^{-1}$).

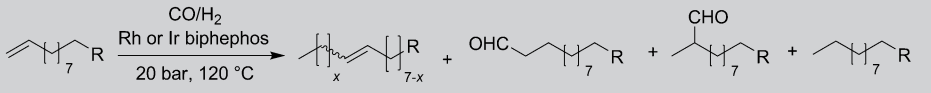
Conclusions

The combination of an iridium(I) precursor with biphephos ligand provides effective catalyst systems for the controlled hy-



Scheme 2. Simplified intermediates involved in the dissociative hydroformylation catalytic cycle, as proposed by Wilkinson and co-workers.[23]

Table 6. Hydroformylation–isomerization of functionalized and simple fatty alkenes promoted by the Ir- and Rh-biphephos systems.[a]



R = CN, CO_2Me, CHO, CH_2Br, CH_3

Entry	Precursor	R	*t* [h]	Subs[b] [%]	*int*[b] [%]	9-/8-*int*	Ald[b] [%]	Ald *l/b*	Hydrog[b] [%]	Conv. subs[c] [%]	HF[d] [%]
1[e]	[Rh(acac)(CO)$_2$]	CN	5	0	16	81/19	79	99/1	5	100	83
2	[Ir(acac)(cod)]	CN	20	0	22	88/12	74	99/1	4	100	78
3[e]	[Rh(acac)(CO)$_2$]	CO_2Me	5	0	11	80/20	82	99/1	7	100	86
4	[Ir(acac)(cod)]	CO_2Me	20	2	13	90/10	80	99/1	5	98	86
5[e]	[Rh(acac)(CO)$_2$]	CH_3	5	12	10	85/15	75	99/1	3	88	85
6	[Ir(acac)(cod)]	CH_3	20	47	5	95/5	45	99/1	3	53	85
			48	16	9	90/10	71	99/1	4	84	85
7[e]	[Rh(acac)(CO)$_2$]	CH_2Br	5	32	14	79/21	51	99/1	3	68	76
8	[Ir(acac)(cod)]	CH_2Br	20	51	6	91/9	41	99/1	2	49	84
			48	17	14	92/8	66	99/1	3	83	80
9[e]	[Rh(acac)(CO)$_2$]	CHO	5	15	10	90/10	71	99/1	4	85	84
10	[Ir(acac)(cod)]	CHO	20	39	5	90/10	53	99/1	3	61	88
			48	8	13	90/10	76	99/1	3	92	83

[a] Reaction conditions unless otherwise stated: substrate (5.0 mmol), [substrate]$_0$/[M] = 20 000, [biphephos]/[M] = 20, solvent (5 mL): toluene (Rh) or acetonitrile (Ir), T = 120 °C, P = 20 bar CO/H_2 (1:1). [b] Distribution [mol%] of remaining substrate, internal alkenes (residual or formed during the reaction), aldehydes (linear and branched) and hydrogenation product, as determined by NMR and GLC analyses. [c] Conversion of substrate. [d] Selectivity for hydroformylation products vs. isomerization and hydrogenation. [e] Results from Ref. [21].

droformylation–isomerization of simple and functionalized fatty 1-alkenes. In contrast with the open literature in which rhodium catalysts are usually considered much more active (i.e., by several orders of magnitude) than iridium catalysts, these iridium-biphephos catalysts are just only approximately 5 times less active than the corresponding rhodium-biphephos systems (730 vs. 3160 h^{-1} under similar reaction conditions). Reactions can be performed at a very high substrate/iridium molar ratio (20 000), yielding the desired linear aldehyde with 99% regioselectivity, whatever the precursor used. Interestingly, the iridium-biphephos system appears slightly less isomerizing than its rhodium analogue, allowing improved control of the distribution of internal olefins formed concomitantly during the hydroformylation step. Effective recycling of the iridium-biphephos catalyst by vacuum distillation in a controlled atmosphere is demonstrated over 3 runs.

Experimental Section

General

All reactions involving metal phosphine catalysts were performed in an inert atmosphere (Ar) by using standard Schlenk techniques. Solvents (toluene, tetrahydrofuran, and acetonitrile) were purified over alumina columns by using an MBraun system. NMP was used as received. [Rh(acac)(CO)$_2$] was provided by Umicore Co. and used as received. Ir, Ru, and Pd precursors and biphephos were purchased from Strem Chemicals and used as received. 10-Undecenitrile (**1**, 95%, containing 5% of 9- and other minor internal isomers), methyl 10-undecenoate, and undecenal were supplied by Arkema France. 11-Bromo-1-undecene was purchased from Sigma–Aldrich. All substrates were purified by passage through an alumina column and degassed thoroughly in freeze–thaw vacuum cycles.

^1H and ^{13}C NMR spectra were recorded on Bruker AC-300, AM-400, and AM-500 spectrometers. ^1H and ^{13}C chemicals shifts were determined by using residual signals of the deuterated solvents and were calibrated against $SiMe_4$. Signals were assigned by using 1D (^1H, $^{13}C\{^1H\}$) and 2D (COSY, HMBC, HMQC) NMR experiments. GLC-flame ionization detector analyses were recorded on a Shimadzu GC-2014 apparatus. Quantitative ^{13}C NMR spectra (Figure S6) were obtained in inverse gated experiments (pulse angle = 90°, delay = 10 s, acquisition time = 1.25 s, number of scans = 100–500).

Hydroformylation reactions

General procedure: In a typical experiment, **1** (826 mg, 5.0 mmol) was added in Ar to a solution of the metal precursor (0.25 μmol) and the corresponding ligand (5 μmol) in solvent (5 mL), pre-mixed in a Schlenk flask. The solution was transferred in Ar into a 100 mL stainless-steel autoclave, equipped with a magnetic stirrer bar. The reactor was sealed, flushed several times with CO/H_2 (1:1), charged with CO/H_2 at the desired pressure at RT, and heated in an oil bath

Table 7. Recycling of the Rh and Ir biphephos systems over 5 and 3 runs, respectively, in the hydroformylation–isomerization of **1**/**1**-*int*.[a]

Entry	Precursor	Cycle	Biphephos excess[e] [equiv]	**1**[b] [%]	**1**-*int*[b] [%]	9-/8-undec	**2**+**3**[b] [%]	**2**/**3**	**4**[b] [%]	Conv. **1**[c] [%]	HF[d] [%]
1	[Rh(acac)(CO)$_2$]	1	–	0	6	77/23	88	99/1	6	100	93
2		2	5	0	5	75/25	89	99/1	6	100	94
3		3	5	0	5	76/24	88	99/1	7	100	93
4		4	5	0	6	72/28	86	99/1	8	100	91
5		5	5	0	7	74/26	85	98/2	8	100	90
6	[Ir(acac)(cod)]	1	–	0	20	93/7	76	99/1	4	100	80
7		2	5	2	21	92/8	73	99/1	4	98	79
8		3	5	5	20	94/6	71	98/2	4	95	79

[a] Initial conditions: **1**/**1**-*int* (95:5, 5.0 mmol), [**1**/**1**-*int*]$_0$/[M] = 50 000 (Rh) or 20 000 (Ir), [biphephos]$_0$/[M] = 20, solvent (5 mL): toluene (Rh) or acetonitrile (Ir), P = 20 bar CO/H$_2$ (1:1), t = 72 h (Rh) or 24 h (Ir). [b] Distribution [mol%] of remaining **1**, internal alkenes **1**-*int* (residual or formed during the reaction), aldehydes **2** and **3**, and hydrogenation product **4**, as determined by NMR and GLC analyses. [c] Conversion of **1**. [d] Selectivity for hydroformylation products vs. isomerization and hydrogenation. [e] Added in each recycling run.

set at the desired temperature under magnetic stirring. During the reaction, aliquots were sampled at regular time intervals to monitor the conversion and selectivities by using NMR and GLC. After the appropriate reaction time, the reactor was cooled to RT and vented to atmospheric pressure. The solution was analyzed by using GLC and NMR (after evaporation of toluene). The linear/branched (**2**/**3**) regioselectivity of aldehydes was determined by using ^{1}H NMR spectroscopy, based on the aldehyde resonances. The distribution of internal isomers was determined by using ^{1}H and ^{13}C NMR spectroscopy.

Vacuum distillation of the hydroformylation reaction mixture and catalyst recycling

Typical procedure: The crude hydroformylation reaction mixture was transferred in an Ar atmosphere into a 50 mL flask. After removal of the solvent under reduced pressure at RT, the mixture was distilled in a Kugelrohr system at 180 °C at 1 mm Hg pressure. Two different fractions were thus obtained: the pure hydroformylation products, which were collected in the first flask, and the catalyst, recovered in solution with residual aldehydes and undecenitrile, in the boiler. This residual phase was collected in an inert atmosphere and reused, with or without addition of fresh ligand, for a subsequent hydroformylation run.

Supporting information

Representative 1D and 2D ^{1}H and ^{13}C{^{1}H} NMR spectra for organic compounds and additional catalytic data for Rh, Ir, and Ru-based systems are available in the Supporting Information.

Acknowledgements

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Keywords: hydroformylation · iridium · isomerization · P ligands · rhodium

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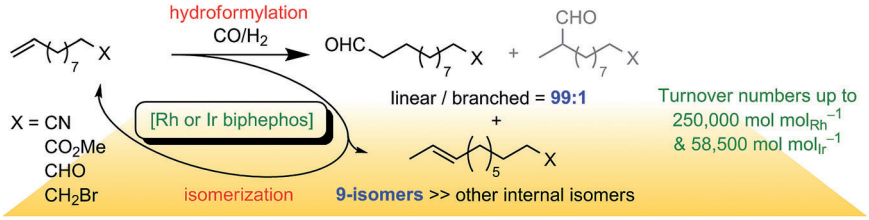

Place your bets now: Iridium-biphephos catalysts are highly effective in the controlled tandem isomerization–hydroformylation of 10-undecenitrile and related functionalized unsaturated fatty substrates.

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Rhodium versus Iridium Catalysts in the Controlled Tandem Hydroformylation–Isomerization of Functionalized Unsaturated Fatty Substrates