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Ruthenium-Catalyzed Hydroformylation/Reduction of Olefins to Alcohols: Extending the Scope to Internal Alkenes

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Supporting Information

ABSTRACT: In the presence of 2-phosphino-substituted imidazole ligands and $Ru_3(CO)_{12}$ or Ru(methylallyl)$_2$(COD) direct hydroformylation and hydrogenation of alkenes to alcohols takes place. In addition to terminal alkenes, also more challenging internal olefins are converted preferentially to industrially important linear alcohols in high yield (up to 88%) and regioselectivity (n:iso up to 99:1).

INTRODUCTION

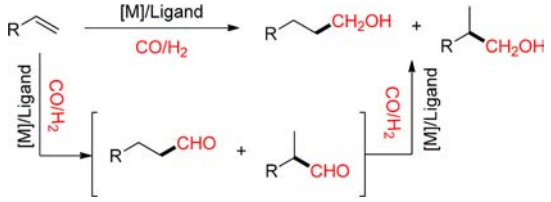
The so-called "oxo process", now known as hydroformylation,[1] was discovered by Otto Roelen in the course of the investigations of Fischer−Tropsch synthesis.[2] In general, these terms describe the reaction of alkenes and synthesis gas to give higher aldehydes and follow-up products. This transformation has become highly important for the chemical industry and represents currently the largest applied homogeneously catalyzed reaction, with more than 10 million tons of oxo compounds produced every year.[3]

Typically, aldehydes, which are the primary products of the hydroformylation of alkenes, are converted further to carboxylic acids, amines, or alcohols. Among these products, linear alcohols are widely employed as industrial solvents and raw materials for plasticizers and detergents, while branched alcohols are of some interest for the fine chemical and life science industries.[4] Today in industry, alcohols are mainly produced in two separate processes: regioselective hydroformylation and subsequent reduction of the formed aldehydes using molecular hydrogen.[5]

Due to the economic importance of alcohols, recently Krische,[6] Stahl,[7] Grubbs,[8] and Herzon[9] et al. developed alternative methods for their production. Despite these achievements, there is still great interest in the atom-economical and selective formation of linear alcohols. In this respect, the combination of hydroformylation and hydrogenation in a tandem sequence represents a straightforward approach (Scheme 1).

The first selective domino hydroformylation/hydrogenation sequence based on phosphine-modified cobalt catalysts was developed in 1966 by chemists from Shell Oil Company.[10] Since then, other catalyst systems based on Rh,[11] Pd,[12] and Ru[13] have been reported. In general, drawbacks of these catalyst systems were low regioselectivity and often harsh reaction conditions as well as the necessity to use high catalyst loading. To improve the selectivity, interesting approaches based on

Scheme 1. Hydroformylation/Reduction of Alkenes



cooperative ligands[11g] or bimetallic catalyst systems were performed.[13h] More recently, Breit and co-workers also reported on supramolecular catalysts;[14] the group of Nozaki developed a Rh/Ru dual catalyst system for the synthesis of alcohols from olefins.[15]

Though rhodium is the preferred catalyst for hydroformylation, its activity in the hydrogenation of the corresponding aldehyde is in general rather low in the presence of carbon monoxide. Therefore, the use of so-called "alternative hydroformylation catalysts" for a direct synthesis of alcohols from olefins is more interesting. On the basis of our continuing interests in hydroformylation[16] and application of less common metals,[17] we recently employed 2-phosphino-substituted imidazole ligands[18] (Figure 1) in the presence of Ru(0) in hydroformylation[19] and hydroaminomethylation reactions.[20] In the presence of LiCl and water also the synthesis of alcohols from alkenes was realized.[21] Here, lithium chloride is necessary

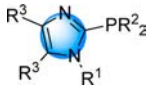


Figure 1. Ligand of choice for ruthenium-catalyzed hydroformylation/reduction of alkenes: 2-phosphino-substituted imidazole ligands.

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to promote the hydrogenation step and water suppressed the formation of aldol side products.

Although the transformation of terminal olefins proceeded well, internal olefins such as 2-octene provided a mixture of alcohols and aldehydes with low regioselectivity. However, the latter substrates represent an industrially favored feedstock due to the comparably lower price. In this regard, especially internal olefins in refinery mixtures constitute the most attractive starting materials for olefin valorizations.

In order to transform internal olefins to linear alcohols, the following requirements have to be met by the catalyst: (a) the hydroformylation of the terminal olefin has to be fast in comparison to the carbonylation reaction of the internal isomer, since only branched products are formed from internal olefins, (b) the regioselectivity (n:iso ratio) for the carbonylation reaction of the terminal olefin has to be very high, and (c) isomerizations of the internal olefins have to be fast in comparison to all hydroformylation reactions, as the thermodynamic mixture of olefins contains only minor amounts of the terminal alkene (typically <4%). In addition, the control of the chemoselectivity (oxo products vs alkane and also aldehyde vs alcohol) is challenging.

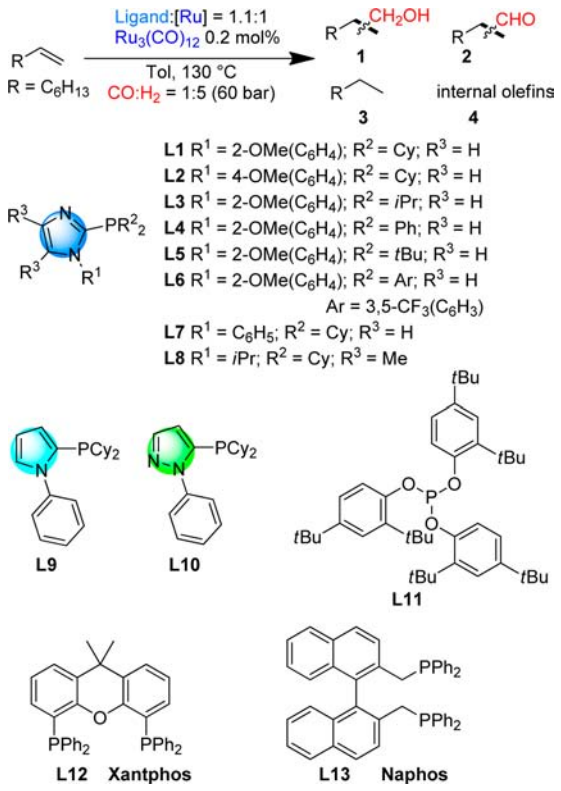
To the best of our knowledge, there exist only two catalyst systems from Shell researchers for the transformation of internal alkenes to linear alcohols. On the one hand, classic cobalt/alkylphosphine complexes have been applied under drastic conditions (>180 °C), while Drent and co-workers[12b] described halide anion dependent effects on the palladium-catalyzed hydroformylation reaction rate and its chemo- as well as regioselectivity. In their system, the addition of halide anions significantly reduced the amount of unwanted alkane (from 20% to 1%) and ketone (from 40% to 2%). Thus, the yield of alcohol was improved from 40% to 96% with 84% linear selectivity.

Herein, we report our new studies on the development of a linear selective ruthenium-catalyzed domino hydroformylation/reduction of alkenes. Investigations of the individual steps (hydroformylation and hydrogenation) and the influence of the ligand structure are discussed. In comparison to previous work, advantageously a convenient additive-free catalytic system is presented which allows extending the scope to internal alkenes.

RESULTS AND DISCUSSION

Development of the Catalyst System. Initial attempts of the domino hydroformylation/reduction sequence of 1-octene were carried out in the presence of $Ru_3(CO)_{12}$ and **L1**. This ligand was recently developed by us for ruthenium-catalyzed hydroformylation reactions.[19] In general, catalytic experiments were performed at 130 °C with 0.2 mol % of $Ru_3(CO)_{12}$ under 60 bar pressure of CO and H_2 (CO:H_2 = 1:5). To our delight, 1-nonanol was obtained smoothly from 1-octene as the main product in good yield and regioselectivity (87% yield, n:iso = 91:9). Interestingly, less than 1% of 1-nonanal was detected, which simplifies the purification and isolation of the desired products. To elaborate the influence of the ligand structure on the catalyst reactivity, 10 heterocycle-derived phosphine ligands were employed. Almost all of them afforded quantitative conversion of 1-octene, but the chemoselectivity was different. Ligands **L1**−**L3** and **L7** bearing cyclohexyl or isopropyl substituents on phosphorus as well as aromatic groups on the imidazole nitrogen atom provided alcohol **1** with high yields and regioselectivities (Table 1, entries 1−3 and 7). **L4** with a less basic phenyl substituent on the phosphorus displayed

Table 1. Ruthenium-Catalyzed Hydroformylation/Reduction of 1-Octene: Ligand Effect[a]



entry	ligand	yield (%)[b] 1 (n:iso)[c]	2 (n:iso)	3	4
1	**L1**	87 (91:9)	<1	9	
2	**L2**	83 (90:10)	<1	10	
3	**L3**	86 (91:9)	<1	9	
4	**L4**	3 (nd)	54 (94:6)	4	36
5	**L5**	3 (nd)	3 (nd)	47	47
6	**L6**	10 (80:20)	<1	22	65
7	**L7**	86 (91:9)	<1	11	
8	**L8**		7 (nd)	8	78
9	**L9**	15 (60:40)		52	32
10	**L10**	3 (nd)	26 (29:71)	45	20
11	PPh_3	3 (nd)	4 (nd)	29	54
12	**L11**			8	58
13	**L12**		7	12	33
14	**L13**		11 (79:21)	37	40

[a]Reaction conditions: 3.20 mmol of 1-octene (0.50 mL), 0.20 mol % of $Ru_3(CO)_{12}$ (0.60 mol % of [Ru]), 0.66 mol % of ligand, toluene 2.0 mL, CO 10 bar, H_2 50 bar, 130 °C, 20 h. [b]Determined by GC using isooctane (0.40 mL) as internal standard. [c]n:iso is the ratio of linear alcohol to all branched alcohols.

decreased hydrogenation activity and provided only 3% alcohol and 54% yield of nonanal (Table 1, entry 4). An electron-withdrawing aromatic group on the phosphorus led to a 65% yield of isomerized octenes and gave the alcohol in lower regioselectivity (Table 1, entry 6). Surprisingly, only 6% oxo product was obtained with the tBu_2P-substituted ligand. Again, 1-octene was converted mainly to octane and isomerized octenes (Table 1, entry 5). The 4,5-dimethylimidazole-based ligand **L8** gave an inferior result (Table 1, entry 8).

Pyrrole- and pyrazole-derived ligands did not provide significant carbonylations but displayed considerable activity

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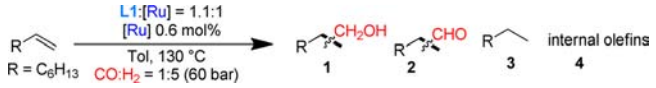
Table 2. Ruthenium-Catalyzed Hydroformylation/Reduction of 1-Octene: Catalyst Variation[a]



		yield (%)[b]			
entry	catalyst	**1** (n:iso)[c]	**2** (n:iso)	**3**	**4**
1	$Ru_3(CO)_{12}$	87 (91:9)	<1	9	
2	$RuH_2(CO)(PPh_3)_3$		2 (nd)		8
3	$RuCl_2(PPh_3)_3$			20	33
4	$Ru_2Cl_4(CO)_6$	13 (48:52)		45	31
5	$[CpRu(CO)_2]_2$				
6	$RuCl_3$	12 (41:59)	3	44	40
7	$[Ru(COD)Cl_2]_n$	15 (40:60)		43	40
8	$Ru(methylallyl)_2(COD)$	87 (92:8)	<1	9	
9	$[Rh(COD)_2]BF_4$	9 (65:35)	89 (55:45)	1	

[a]Reaction conditions: 3.20 mmol of 1-octene (0.50 mL), 0.60 mol % of [Ru] or [Rh], 0.66 mol % of **L1**, toluene 2.0 mL, CO 10 bar, H_2 50 bar, 130 °C, 20 h. [b]Determined by GC using isooctane (0.40 mL) as internal standard. [c]n:iso is the ratio of linear alcohol to all other alcohols.

in alkene hydrogenation (Table 1, entries 9 and 10). Next, the reactivity of our catalyst system was compared to that of several standard ligands known for rhodium-catalyzed hydroformylation. In all cases, only minor amounts (<11%) of oxo products were detected due to the low hydroformylation activity of these ligands in the presence of Ru(0) (Table 1, entries 11−14).

With the best ligand in hand, we studied the influence of ruthenium precatalysts in the domino hydroformylation/reduction reaction of 1-octene (Table 2). Here, ruthenium complexes in different oxidation states were examined. Among the tested complexes, Ru(II) and Ru(III) precursors either afforded isomerized olefins or octane (Table 2, entries 2−7). Apparently in all these cases, the assumed active $HRu(CO)_3L$ species cannot be formed under the reaction conditions. The $Ru(methylallyl)_2(COD)$ complex gave results comparable to those of $Ru_3(CO)_{12}$ (Table 2, entry 8). When rhodium ($[Rh(COD)_2]BF_4$) was applied instead of ruthenium in the presence of **L1** as ligand, the yield of aldehyde was high, but only 9% alcohol was formed with low regioselectivity. These results proved again that rhodium is not a good hydrogenation catalyst under hydroformylation conditions (Table 2, entry 9).

Investigations of the solvent scope revealed negligible dependence of the reaction outcome on the solvent (see the Supporting Information). The chemo- and regioselectivities were similar, except in the reaction with ethyl acetate, which yielded 7% aldehyde. Small amounts of side products (<2%) were detected in acetonitrile (condensation product) and methanol (dimethoxy acetal). Acetonitrile was chosen as solvent for the selective transformation of 1-octene to nonanal at lower temperature and reduced catalyst loading (see Supporting Information).

In order to understand the overall domino sequence in more detail, the individual reaction steps were studied using 1-octene as a model substrate. Interestingly, nonanal (76% yield; see the Supporting Information) is produced highly selectively at lower temperature (100 °C) and reduced catalyst loading (0.1 mol % [Ru]), which demonstrates that for the conversion of terminal olefins to linear alcohol the hydrogenation of the intermediate aldehyde is rate determining (see also Figure 3d).[19] The hydroformylation step (1-octene to nonanal) is highly solvent dependent. Hence, no carbonylation (nonanal) occurred when toluene was used as a solvent at low catalyst loading (0.1 mol % [Ru], 100 °C). Instead, in polar solvents such as acetonitrile and THF, the hydroformylation reaction proceeded well (Figure 2a).

A comparison of the hydroformylation (1-octene to nonanal) activity of the $Ru(methylallyl)_2(COD)$ complex with and without ligand **L1** is depicted in Figure 2b. In the absence of **L1** only 3% nonanal (see Supporting Information) was obtained

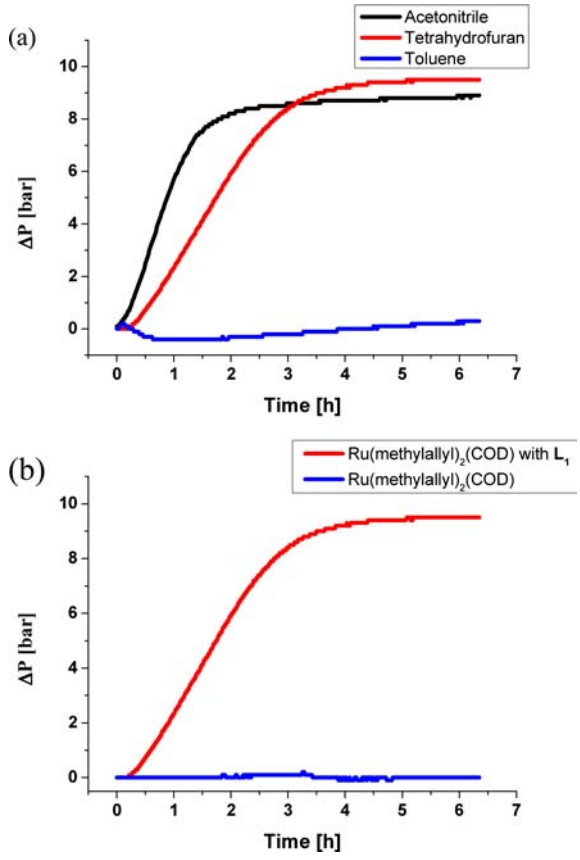


Figure 2. (a) Comparison of hydroformylation rates in different solvents. Reaction conditions: 20 mmol of 1-octene (3.14 mL), 0.10 mol % of [Ru], 0.11 mol % of **L1**, solvent 20 mL, CO 10 bar, H_2 50 bar, 100 °C, 7 h. (b) Ligand effects. Reaction conditions: 20 mmol of 1-octene (3.14 mL), 0.10 mol % of [Ru], 0.11 mol % of **L1**, acetonitrile 20 mL, CO 10 bar, H_2 50 bar, 100 °C, 7 h.

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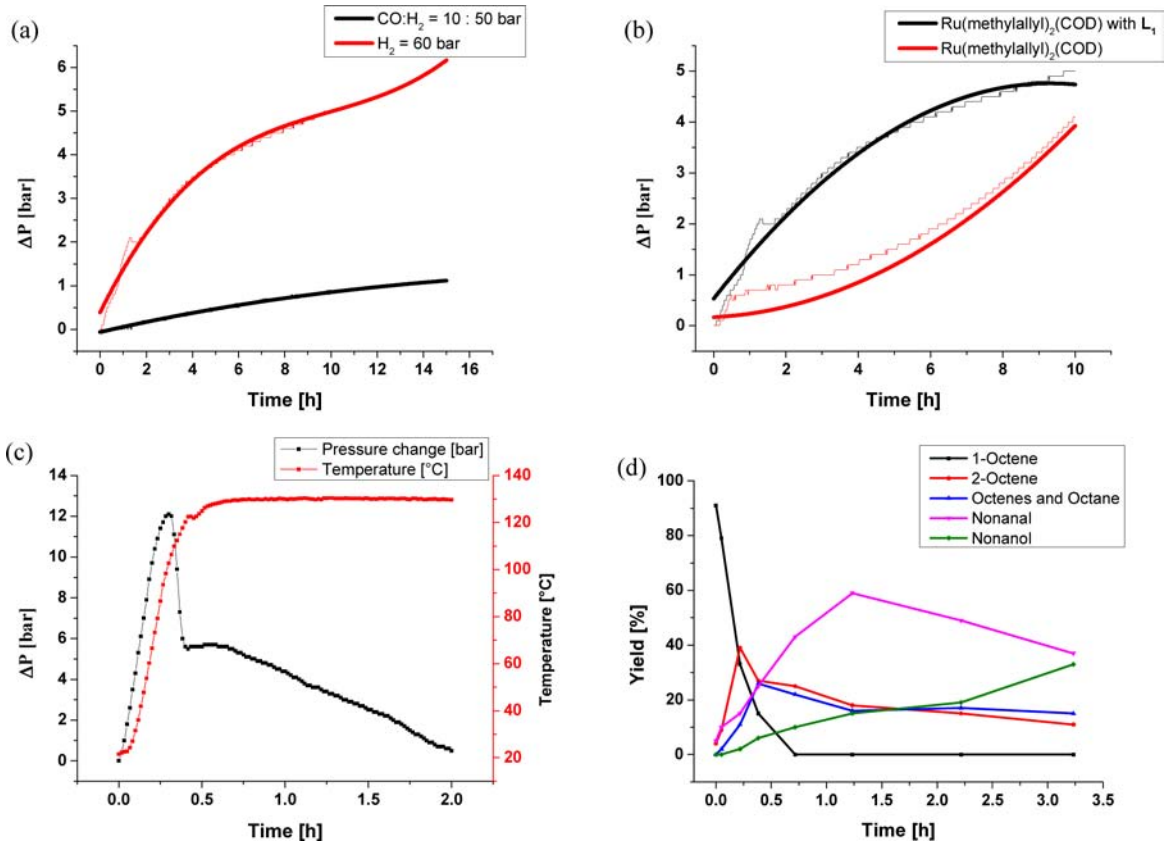
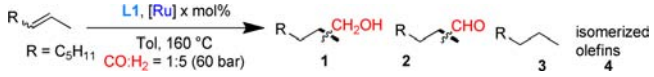


Figure 3. (a) Effect of CO in the reduction of 1-nonanal to 1-nonanol. Reaction conditions: 10 mmol of 1-nonanal (1.72 mL), 0.60 mol % of Ru(methylallyl)$_2$(COD), 0.66 mol % of **L1**, toluene 20 mL, CO 10 bar, H_2 50 bar, 130 °C, 16 h. (b) Effect of ligand in the reduction of 1-nonanal to 1-nonanol. Reaction conditions: 10 mmol of 1-nonanal (1.72 mL), 0.60 mol % of Ru(methylallyl)$_2$(COD), 0.66 mol % of **L1**, toluene 20 mL, CO 10 bar, H_2 50 bar, 130 °C, 16 h. (c) Pressure and temperature change curve. Reaction conditions: 20 mmol of 1-octene (3.14 mL), 0.60 mol % of Ru(methylallyl)$_2$(COD), 0.66 mol % of **L1**, toluene 20 mL, CO 10 bar, H_2 50 bar, 130 °C, 2 h. (d) Compound distribution of ruthenium-catalyzed hydroformylation/reduction. Reaction conditions: 20 mmol of 1-octene (1.72 mL), 0.60 mol % of Ru(methylallyl)$_2$(COD), 0.66 mol % of **L1**, toluene 20 mL, CO 10 bar, H_2 50 bar, 130 °C, 3.5 h.

Table 3. Ruthenium-Catalyzed Isomerization-Hydroformylation/Reduction of 2-Octene[a]



			yield (%)[b]			
entry	[Ru]; x (mol %)	**L1**:[Ru]	**1** (n:iso)[c]	**2** (n:iso)	**3**	**4**
1[d]	Ru(methylallyl)$_2$(COD); 0.6	1.1:1		50 (62:38)	19	3
2	$Ru_3(CO)_{12}$; 0.6	1.1:1	19 (79:21)	23 (74:26)	40	7
3	Ru(methylallyl)$_2$(COD); 0.6	1.1:1	22 (78:22)	20 (68:32)	40	5
4	Ru(methylallyl)$_2$(COD); 1.2	1.1:1	74 (86:14)	<1	23	3
5	Ru(methylallyl)$_2$(COD); 1.2	0:1	48 (63:37)	<1	51	
6	Ru(methylallyl)$_2$(COD); 1.2	2.2:1	82 (86:14)	<1	15	1
7[e]	Ru(methylallyl)$_2$(COD); 1.2	2.2:1	77 (83:17)	<1	18	2
8	$Ru_3(CO)_{12}$; 1.2	2.2:1	80 (85:15)	<1	16	2

[a]Reaction conditions: 3.20 mmol of 2-octene (0.50 mL), x mol % of [Ru], corresponding amount of **L1**, toluene 2.0 mL, CO 10 bar, H_2 50 bar, 160 °C, 24 h. [b]Determined by GC using isooctane (0.40 mL) as internal standard. [c]n:iso is the ratio of linear alcohol to all branched alcohols. [d]130 °C. [e]2 mol % AcOH added.

(0.1 mol % [Ru], 100 °C), which confirms the crucial role of the ligand in the hydroformylation step.

Next, the hydrogenation of nonanal to nonanol was investigated at higher temperature and catalyst loading (0.6 mol % [Ru], 130 °C). Similar to the case for rhodium-catalyzed reactions, the presence of CO reduces the hydrogenation rate of the ruthenium complex (Figure 3a). In fact, the reduction of nonanal takes place much more slowly in the presence of a CO/H_2 mixture than in pure H_2. The positive effect of the ligand **L1** on the reduction step is also shown in Figure 3b (0.6 mol % of [Ru], 130 °C).

Then, the reaction progress of the ruthenium-catalyzed hydroformylation/reduction of 1-octene to nonanol was examined under the optimized reaction conditions: 0.6 mol

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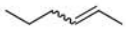
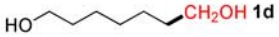
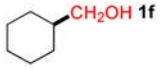
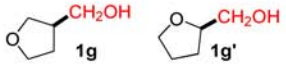
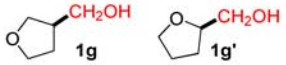
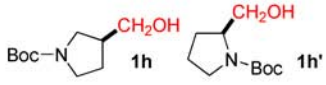
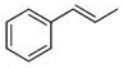
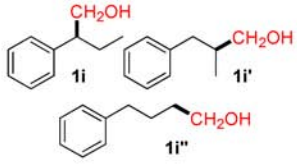
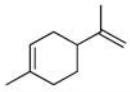
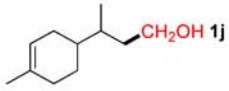
Table 4. Ruthenium-Catalyzed Synthesis of Higher Alcohols from Internal Alkenes[a]

Entry	Alkene	Major product	GC yield [%][b]	Isolated yield [%][d]	n/iso[b,c]
1			82	72	86:14
2			73	65	77:23
3			88	65	86:14
4			85	63	82:18
5			14	nd	57:43
6			72	69	83:17
7			50	40	53:47
8			81	51	-
9			78	71	67:33
10			66	60	33:67
11			47	43	89:11
12			88	72	62:8:30 1i:1i′:1i″
13			70	58	99:1

[a]Reaction conditions: 3.20 mmol of internal olefins, 1.20 mol % of Ru(methylallyl)$_2$(COD), 2.64 mol % of **L1**, toluene 2.0 mL, CO 10 bar, H_2 50 bar, 160 °C, 24 h. [b]Determined by GC using isooctane (0.40 mL) as internal standard, [c]n:iso is the ratio of main alcohol to all other isomers. [d]Isolated by column chromatography or bulb-to-bulb distillation.

% of Ru(methylallyl)$_2$(COD) and 1.1 equiv of ligand **L1** with 10 bar of CO and 50 bar of H_2 in toluene at 130 °C. As depicted in Figure 3c,d, the reaction is fast at the very beginning and then became much slower. This is explained by the fast hydroformylation of 1-octene to nonanal and the isomerization reactions to give internal octenes (quantitative conversion within 30 min). Subsequent isomerization/hydroformylation of the internal octenes to nonanal along with the reduction of nonanal to nonanol occur at a much lower rate.

Ruthenium-Catalyzed Hydroformylation/Reduction of Internal Alkenes. On the basis of the conditions for the transformation of terminal alkenes (0.6 mol % of Ru(methylallyl)$_2$(COD) and 1.1 equiv of ligand **L1** with 10 bar of CO and 50 bar of H_2 in toluene), the ruthenium-catalyzed sequential hydroformylation–hydrogenation reaction of 2-octene was investigated. When the reaction was performed under exactly the same conditions as for 1-octene, no alcohol was obtained. Instead, the corresponding aldehyde was obtained in 50% yield with moderate regioselectivity (Table 3, entry 1). At 160 °C the experiments showed preferential hydrogenation of the internal alkene and the regioselectivity was also unsatisfactory (Table 3, entries 2 and 3). However, applying higher catalyst loading and increasing the ligand:metal ratio to 2.2:1 resulted in suppressed hydrogenation of the

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alkene (Table 3, entry 6). Thus, to our delight the yield of C9-alcohols was improved to 82% and the regioselectivity to 86:14.

Next, the scope and limitations of this ruthenium-catalyzed isomerization/hydroformylation/reduction sequence were examined on 13 examples of industrially important aliphatic as well as various functionalized internal olefins (Table 4). We were pleased to find that simple internal alkenes (2-pentene, 2-hexene, 3-hexene) reacted well to give linear alcohols in high yield and regioselectivity (Table 4, entries 1−4). On the other hand, 4-octene gave only 14% yield with poor regioselectivity (Table 4, entry 5). Interesting building blocks for polymers were obtained in moderate to good yields from internal alkenes bearing hydroxyl or nitrile groups (Table 4, entries 6 and 7). Although cyclic olefins often show low reactivity in carbonylation reactions, a good result was obtained with cyclohexene as a substrate (Table 4, entry 8). Similarly, 2,5-dihydrofuran gave a good yield but only moderate regioselectivity (Table 4, entry 9). 2,3-Dihydrofuran, which represents an enol ether substrate, provided reverse regioselectivity in comparison to 2,5-dihydrofuran (Table 4, entry 10). Furthermore, the Boc-group-protected cyclic enamine was transformed to the product in moderate yield but good regioselectivity (Table 4, entry 11). With (1*E*)-1-propenylbenzene, a mixture of three different alcohols was obtained (Table 4, entry 12). When limonene was used as the substrate, the internal double bond remained intact and only the double bond in the side chain was selectively hydroformylated to the corresponding alcohol with good results (Table 4, entry 13).

Finally, the results obtained from the ruthenium-catalyzed isomerization/hydroformylation/reduction of internal alkenes prompted us to apply this system to an industrial mixture of octenes, which contains less than 4% of the terminal olefin. To our delight, nonanol was obtained in 68% yield with good regioselectivity (Scheme 2).

Scheme 2. Hydroformylation/Reduction of a Mixture of Octenes

CONCLUSION

The ruthenium-catalyzed conversion of terminal and internal alkenes to linear alcohols via a domino (isomerization)-hydroformylation/reduction reaction sequence has been presented. In comparison to our previous work, the novel protocol does not need any additives such as LiCl. Specifically, the combination of Ru(methylallyl)$_2$(COD) and 2-phosphino-substituted imidazole ligands allows for a general synthesis of linear alcohols from internal olefins, thereby expanding the scope of this interesting transformation to industrially relevant feedstocks.

ASSOCIATED CONTENT

Supporting Information

Text, tables, and figures giving synthetic details as well as ligand and product data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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