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Dual Rh-Ru catalysts for reductive hydroformylations of olefins to alcohols

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Abstract: An active and selective dual catalytic systems to promote domino hydroformylation/reduction reactions are described. Apart from terminal, di- and tri-substituted olefins for the first time also less active internal C-C double bond of tetra-substituted alkenes can be utilized. As an example, 2,3-dimethylbut-2-ene is converted to the corresponding *n*-alcohol with high yield (90%) as well as regio- and chemoselectivity (>97%). Key for this development is the use of a combination of Rh complexes with bulky monophosphites and the Ru-based Shvo's-complex. A variety of aromatic and aliphatic alkenes can be directly used to obtain mainly linear alcohols.

The functionalization of highly substituted olefins such as 2,3-dimethylbut-2-ene and the industrial feedstock dibutene *via* carbonylation reactions[1] is currently a topic of high industrial interest. Especially the efficient conversion of these substrates into high value linear alcohols is still a great challenge. Oxo alcohols are an important class of industrial products, which are currently produced by tandem hydroformylation/hydrogenation of olefins catalysed by several metal complexes[2] including Ru[3], Rh[4], and Pd[5]. The most prominent representative is the Shell Oil Co. process, which uses a cobalt-phosphine catalyst system to produce linear higher alcohols from regular internal higher olefins.[6] Nowadays, *n*-butanol, 2-ethylhexanol and isobutanol constitute main examples with an estimated market >12 Mio tons/a and growing *ca.* 4.4% until 2020.[7] In order to improve the synthesis of oxo alcohols, there exist a continuing interest in academia and industry to develop improved catalytic systems.[8] With respect to the principles of green chemistry, it is especially desirable to improve the step economy for these products.[9] In this respect, combination of hydroformylation and reduction – so-called hydrohydroxymethylation – would allow for a straightforward and atom efficient access to alcohols directly from easily available olefins and *syngas*. Due to the price of feedstocks, the selective conversion of mixtures of terminal and internal alkenes like for example refinery mixtures would be even more desirable.[10] In principle, combining the isomerization of internal to terminal olefins, followed by the *n*-selective hydroformylation, and subsequent hydrogenation of the obtained aldehyde allows for an ideal synthesis of *n*-alcohols. However, so far only few catalysts are known that promote the transformation of olefins directly to alcohols.[11] An important achievement was reported by Nozaki and co-workers in 2010, who described a tandem hydroformylation/hydrogenation of 1-decene to undecanol in over 90% yield using a bimetallic catalyst consisting of Rh-xantphos and Shvo´s-complex.[12] This complex is a well-known example of an hydrogenation catalyst that operates by an outer sphere mechanism.[13] Later in 2012, this group reported the scope and limitation of their dual catalyst

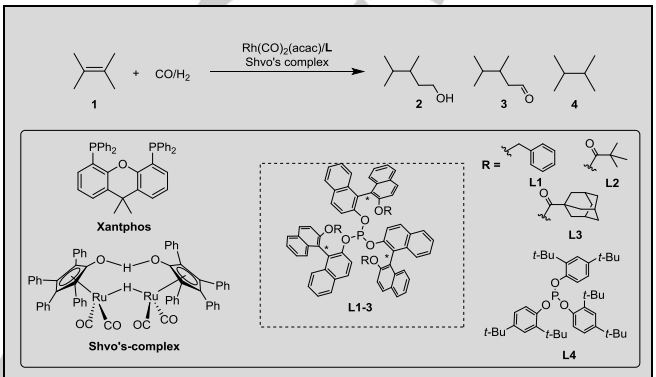

Table 1. Hydroformylation/reduction of 2,3-dimethylbut-2-ene **1** using dual catalyst systems.[a]

Entry	Ligand	Catalyst	Conv. (%)[b]	Yield (%)[b]		
				2	**3**	**4**
1	-	$Rh(CO)_2acac$	61	3	49	9
2	Xantphos	$Rh(CO)_2acac$	60	2	48	10
3	L1	$Rh(CO)_2acac$	84	4	77	3
4	L2	$Rh(CO)_2acac$	62	5	56	1
5	L3	$Rh(CO)_2acac$	82	4	75	3
6	L4	$Rh(CO)_2acac$	80	5	70	5
7	L1	$Rh(CO)_2acac$ + Shvo's catalyst	88	46	40	2
8	-	$Rh(CO)_2acac$ + Shvo's catalyst	65	42	14	9
9	-	Shvo's catalyst	29	11	6	12

[a] Reaction conditions: 2,3-dimethylbut-2-ene **1** (10.0 mmol), $[Rh(CO)_2acac]$ (7.7 µmol), **L** (15.4 µmol), Shvo's-complex (3.8 µmol), solvent: 30 mL of toluene, CO (12 bar) and H_2 (25 bar) at 120 °C for 20 h. [b] Determined by GC, using isooctane as external standard.

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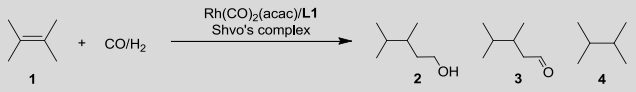


Table 2. Rhodium/phosphite/ruthenium-catalyzed hydroformylation/reduction of 2,3-dimethylbut-2-ene: Optimization of reaction conditions.[a]

Entry	p_{H2} (bar)	p_{CO} (bar)	T (°C)	$V_{Sol.}$ (mL)[c]	Conv. (%)[b]	Yield (%)[b] 2	3	4
1	10	10	120	30	71	28	38	4
2	20	10	120	30	75	44	31	0
3	30	10	120	30	81	77	0	4
4	50	10	120	30	97	91	0	6
5	30	10	80	30	10	0	9	1
6	30	10	100	30	24	0	24	0
7	30	10	120	20	93	90	0	3
8	30	10	120	5	90	88	0	2

[a] Reaction conditions: 2,3-dimethylbut-2-ene **1** (10.0 mmol), $[Rh(CO)_2acac]$ (7.7 µmol), **L1** (15.4 µmol), Shvo's-complex (3.8 µmol), solvent: toluene, 20 h. [b] Determined by GC, using isooctane as external standard. [c] For V_{Sol} = 5 mL a 40 mL autoclave was used instead of a 100 mL autoclave.

system for the production of linear α,ω-diols.[14] More recently, they developed a modified catalyst system (Rh/bisphosphite/Shvo´s-complex) for one-pot isomerization/hydroformylation/hydrogenation of internal alkenes to linear alcohols. Unfortunately, only moderate reaction rates (up to 36 h reaction time) were achieved and tri- and tetra-substituted olefins were not applied.[11c] In 2013, some of us described an alternative process to promote the domino hydroformylation/reduction of terminal and internal olefins to linear alcohols in the presence of ruthenium complexes with P-N ligands.[11a,11b,11d] Despite the lower price of ruthenium compared to rhodium, also this catalyst was limited to terminal olefins.

Taking into account the high activity and selectivity of Rh/phosphite catalysts in the hydroformylation of aliphatic and aromatic olefins,[15] herein we describe a new and practical Rh/Ru catalyst system for the selective functionalization of all kinds of olefins. Applying a combination of Rh/*tris*-binaphthyl-based helical monophosphites and Shvo's-complex,[16] promotes even the transformation of highly substituted olefins such as 2,3-dimethylbutene and the industrial feedstock dibutene.

To improve the known catalysts for a general synthesis of alcohols from olefins, the reaction of 2,3-dimethylbut-2-ene **1** to give 3,4-dimethylpentan-1-ol **2** was chosen as a model system. In general, test reactions were performed at 120 °C for 20 hours in the presence of 0.077 mol% of $[Rh(CO)_2acac]$ and 0.154 mol% of ligands under 12 bar CO and 25 bar H_2. In order to speed up the hydrogenation step, 0.038 mol% of the Shvo's-complex was added in some experiments. Initially, the effect of different ligands on activity and selectivity was evaluated. For this purpose reactions were carried out in the presence of $[Rh(CO)_2acac]$ and different *tris*-binaphthyl-based helical monophosphites **L1-L3** in comparison to Xantphos (Table 1). The latter ligand was previously applied by Nozaki and co-workers,[11c, 12, 14] while the former ligands were previously applied by some of us for highly regioselective rhodium-catalyzed hydroformylation reactions of internal olefins.[17]

As shown in Table 1 (entry 1), the hydroformylation in the absence of any phosphorous ligand gave 61% of conversion and 49% yield for aldehyde **3** as well as 3% of the desired alcohol **2.** Similarly, in the presence of Xantphos as ligand only tiny amounts (2%) of the desired alcohol **2** were obtained (60% conversion, 48% aldehyde **3**, 10% hydrogenated product **4**; Table 1, entry 2). The use of bulky phosphite π–acceptor ligands is known to increase significantly the activity and selectivity for the formation of aldehydes.[18] Hence, to improve the results of the Rh/Xantphos catalyst system, we employed phosphites as ligands.[17] Although *tris*-binaphthyl monophosphites **L1-L3** achieved improved conversion of 84%, 62% and 82%, respectively, the formation of the alcohol was still negligible (<5%; Table 1, entries 3-5). Moreover, for comparison with our system we also performed an experiment, according the conditions to entry 3-5 in Table 1, using tris(2,4-di-tert-butylphenyl) phosphite (**L4**) as ligand instead.

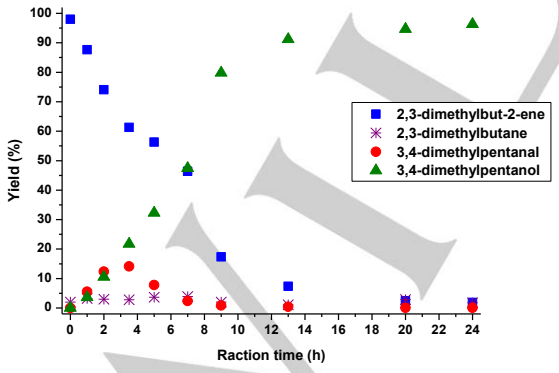
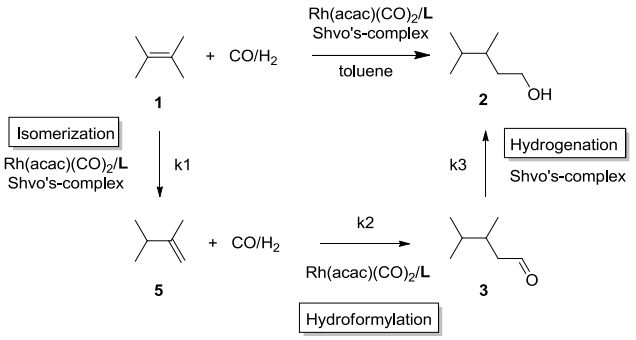


Figure 1. Reaction progress of hydroformylation/reduction of 2,3-dimethylbut-2-ene **1**: Substrate and product yield *vs*. time. Reaction conditions: **1** (40.0 mmol), $[Rh(CO)_2acac]$ (30.8 µmol), **L1** (61.6 µmol), Shvo's-complex (15.2 µmol), toluene (20 mL), with 40 bar initial pressure (p_{CO} = 10 bar, p_{H2} = 30 bar), reactor is connected to a constant feed of $CO:H_2$ (1:2) to keep pressure and ratio of *syngas* mixture constant during the reaction time, T = 120 °C. Yield determined by GC analysis, using isooctane as external standard.



Scheme 1. Proposed route for the conversion of olefin to desired alcohol.

Similar activity was obtained (80% conversion). Nevertheless selectivity for aldehyde **3** (70% yield) was lower while the yield of hydrogenated product **4** increased to 5% (Table 1, entries 6). To improve the final hydrogenation step of the aldehyde, 0.038 mol% of the Shvo's-complex was added to the Rh/**L1** system (Table 1, entry 7). To our delight, the application of this dual catalyst improved considerably the selectivity and did not reduce the overall activity (Table 1, entries 3 and 7). Hence, alcohol **2** was obtained as the major product in 46% yield. However, performing the reaction without **L1** (Table 1, entry 8) or without the **Rh/L1** combination (Table 1, entry 9) the conversion was significantly lower (65% and 29%). In the presence of only the Shvo´s-complex equal amounts of alcohol **2** and undesired alkane **4** were obtained. As expected, experiments performed in the absence of any metal in the presence or absence of ligand did not give any conversion.

Next, we investigated the reaction conditions (CO and H_2 total and partial pressure, temperature and reactant concentration) in more detail to improve this Rh-**L1**/Ru-Shvo's-complex further on (Table 2). Reducing the hydrogen content (1:1 CO/H_2 *syngas* mixture under 20 bar pressure) led to a conversion of 71% with aldehyde **3** being obtained as the major product (38%), and the desired alcohol **2** being formed in only 28% (Table 2, entry 1). Increasing the H_2 partial pressure (20, 30 and 50 bar) while keeping CO initial pressure at 10 bar, improved conversions to 75, 81 and 97%, respectively and led to better yields for the desired alcohol **2** (44, 77 and 91%, respectively) (Table 2, entries 2-4). In order to identify additional positive effects, all subsequent studies were performed using a *syngas* pressure of 40 bar (H_2/CO 3:1).

Despite the temperature-sensitive activity of Shvo's-complex, we searched for milder reaction conditions of the bimetallic system.[11c, 14] As expected, for lower temperatures (80 °C and 100 °C) conversions were significantly lower (10% and 24%), with almost exclusive formation of aldehyde **3** (Table 2, entries 3, 5-6). On the other hand, we were able to reduce the amount of solvent from 30 mL to 20 mL and 5 mL without decrease in activity or selectivity of desired alcohol **2** (Table 2, entries 3 and 7-8). This latter result demonstrates the potential viability of this catalytic system for industrial transposition. In addition we also evaluated the viability of the use of racemic **L1** counterpart as ligand in the previous best conditions and slightly lower activity was obtained (80% conversion) with the same alcohol selectivity (77% yield).

To understand the mechanism of this domino-reaction and to identify intermediates, the reaction progress was measured and aliquots were taken, at regular intervals, from the mixture within 24 h. The yield of corresponding products and remaining substrate is plotted in Figure 1.

As shown in Figure 1, the isomerized terminal olefin **5** (see also Scheme 1) is not detected. Hence, we conclude that the rate constant **k2** (hydroformylation of **5**) is significantly higher than **k1 (**isomerization of **1**). Along the first 3 h the built-up of the aldehyde occurs. After this period the aldehyde yield start to decrease suggesting the rate of the hydrogenation step is higher than the hydroformylation.

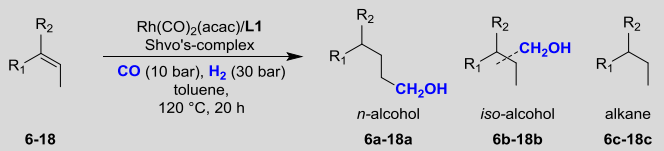
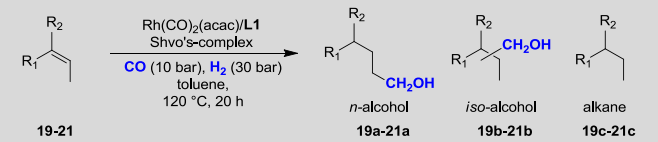


Table 3. Ruthenium/phosphite/rhodium-catalyzed hydroformylation/reduction of 2,3-dimethylbut-2-ene: Optimization of reaction conditions.[a]

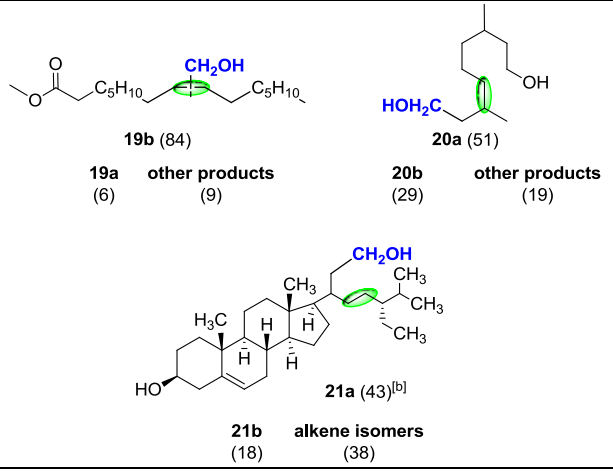
Entry	Substrate	Major product	Yield (%) Major Product [*n*/*i*]	Yield **c** (%)
1	**6**	**6a**	94 [99/1]	5
2	**7**	**7ba**	24 [25/75]	2
3	**8**	**8a**	88	10
4	**9**	**9a**	54	43
5	**10** mixture (1/1/0/1)	**10a**	37 [71/29]	48
6	**11**	**11a**	45 [87/13]	48
7	**12** diisobutylene (81% / 19%)	**12a**	95 [99/1]	5
8	dibutene[b] **13**	C_9-*n*-alcohols[c] **13a**	68 [70/30]	3
9	**14**	**14b**	37 [29/71]	16
10	**15**	**15a**	29 [55/45]	43
11	**16**[d]	**16b**	43 [33/67]	36
12	**17**	**17a**	45 [90/10]	50
13	**18**	**18b**	45 [35/65]	30

[a] Reaction conditions: alkene (4.0 mmol), [Rh(CO)$_2$acac] (3.1 µmol), **L1** (6.2 µmol), Shvo's-complex (1.5 µmol),CO (10 bar), H_2 (30 bar), solvent: toluene (2 mL), 20 h at 120 °C. Conversions were in all cases 98%. Determined by GC-MS. [b] Mixture of C_8-alkene which mainly consist of methyl-heptene (75%), 3,4-dimethyl-hexene (15%), octane (9%). [c] Corresponding C_9-*n*-alcohols of dibutene. [d] Alkene (3.0 mmol).



19-21 19a-21a 19b-21b 19c-21c

Scheme 2. Ruthenium/phosphite/rhodium-catalyzed hydroformylation/reduction of industrial/biological relevant substrates.[a]



[a] Reaction conditions: alkene (10.0 mmol), [Rh(CO)$_2$acac] (7.7 µmol), **L1** (15.4 µmol), Shvo's-complex (3.8 µmol), CO (10 bar), H_2 (30 bar), solvent: toluene (5 mL), 20 h at 120 °C. Conversions were in all cases 99%. Determined by GC-MS. [b] Reaction conditions: steroid (0.48 mmol), [Rh(CO)$_2$acac] (9.8 µmol), **L1** (19.6 µmol), Shvo's-complex (4.9 µmol), p(CO) = 10 bar, p(H_2) = 30 bar, solvent: toluene (3 mL), 48 h at 120 °C. Conversion determined by NMR analysis of the reaction crude. Conversions were, in all cases, 99%.

Finally, the applicability of this domino hydroformylation-hydrogenation methodology was evaluated for a series of aromatic and aliphatic olefins (Table 3). For the majority of substrates, good yields of the corresponding alcohols were obtained at 120 °C using 40 bar of synthesis gas (H_2/CO 3:1). Internal and terminal mono- and di-substituted aromatic olefins (Table 3, entries 1-4) as well as aliphatic di- and tri- substituted pure alkenes and mixtures of them (Table 3, entries 6-8) were successfully transformed to desired alcohols with the Rh/**L1**/Shvo's-complex. Except for substrates **9**-**11**, which gave significant amounts of the respective alkanes, very good alcohol yields were obtained. Interestingly, hydroformylation/reduction of 1,1-disubstituted as well as tri-substituted olefins leads in high regioselectivity to the linear oxo alcohol (Table 3, entries 1, 6-8). However, in the case of *trans*-1,2-disubstituted (*E*)-prop-1-en-1-ylbenzene **7** the branched alcohols **7b** (73% yield) were mainly obtained due to the thermodynamic stabilization of the intermediate rhodium benzyl complex (Table 3, entry 2). Noteworthy, the excellent chemoselectivity of 97% for alcohols is the result of the high activity of our bimetallic catalyst system. Next, under the same reaction conditions different functionalized olefins were investigated (Table 3, entries 9-13).

Similar to substrate **7**, 1-methoxy-4-propenylbenzene **14** gave the branched alcohols **14b** (*n*/*i* 29/71) as major products. In addition, alcohol **15a** is obtained by isomerization of *trans*-3-phenyl-2-propen-1-ol **15** with a regioselectivity of 55% (Table 3, entry 10). Besides, in this case direct hydrogenation of the double bond increased to 43%. Interestingly, imide and ester functionalities were well tolerated (Table 3, entries 11 and 12) and the corresponding alcohols were isolated in reasonable yields (63% and 50%, respectively). Finally, the reactivity of the unsaturated aldehyde **18** was tested. Gratifyingly, industrially relevant long chain alcohols and diols were formed exclusively (Table 3, entry 13).

Then, the substrate scope was extended to naturally occurring di- and tri-substituted olefins **19**-**21**. These transformations are of general interest in the context of valorisation of renewable feedstocks. As shown in Scheme 2 conversions were in all cases >99%. For methyl oleate **19** the hydroformylation/reduction of the internal double bond led to major formation of branched oxo alcohols **19b**, which are compounds with great relevance for industrial applications.[19] This observation is in agreement with previous results obtained using a Rh/bulky phosphite system for related hydroformylations.[20] Moreover, the tri-substituted terpene citronellol **20** was used as substrate. Here, chemoselective formation of alcohols was observed in 80% to give the linear oxo diol **20a**, resulting from the isomerization/hydroformylation/reduction, as the major product (51%, Scheme 2).

As an example of a bio-active steroid derivative, the reaction was extended to stigmasterol **21** leading to alcohols with 61% chemoselectivity. Here, the linear alcohol **21a** was identified by NMR spectroscopy as the major product in 43% yield.

Conclusion

In summary, we have developed an active and selective dual catalytic system to promote tandem hydroformylation/reduction reactions. Compared with previously known catalysts, our system promotes the direct hydroformylation/reduction of less active internal C-C double bonds. Hence, the conversion of highly substituted alkenes to mainly linear alcohols is possible for the first time. Key for this development is the use of a combination of Rh complexes with bulky monophosphites and the well-known Ru-based Shvo's-complex. The results presented here pave the way for more efficient preparation of value-added oxo alcohols from inexpensive industrial feedstocks or renewables.[21]

Experimental Section

General method for the hydroformylation/reduction of alkenes: A 100 mL steel autoclave was charged with [Rh(CO)$_2$acac] (1.98 mg, 7.7 µmol), *tris*[(*R*)-2'-(benzyloxy)-1,1'-binaphthyl-2-yl] phosphite ligand **L1** (17.8 mg 15.4 µmol) and Shvo's-complex (4.1 mg, 3.8 µmol). The autoclave was closed and the air was removed using a vacuum pump. Then, the desired amount of dry toluene and the alkene (10 mmol) were added through cannula. After flushing the autoclave with H_2/CO, it was pressurized with the desired amount of H_2/CO gas and heated to 120 °C with magnetic stirring. After 20 h, the autoclave was cooled with ice water and the pressure was released. The crude reaction mixture was diluted with toluene and analyzed by gas chromatography, using isooctane as external standard.

Non-commercially available products presented in the Table 3 and Scheme 2 were isolated by chromatography and the characterization data is presented in the SI.

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Keywords: hydroformylation • hydrogenation• linear alcohol• rhodium• ruthenium

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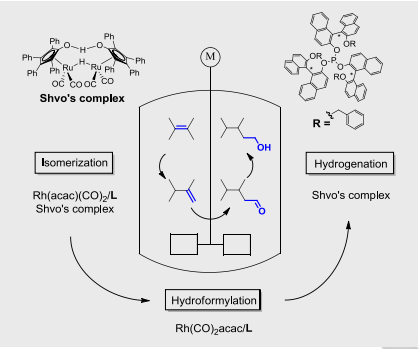
COMMUNICATION

Paving the way for more efficient preparation of value-added oxo alcohols: An active and selective dual catalytic system to promote one-pot hydroformylation/reduction reactions is described. The combination of Rh complexes with bulky monophosphites and the well-known Ru-based Shvo's-complex is the key for the high yield of oxo-alcohols.



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Dual Rh-Ru catalysts for reductive hydroformylations of olefins to alcohols