Cooperative Catalysis

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Tandem Rhodium-Catalyzed Hydroformylation–Hydrogenation of Alkenes by Employing a Cooperative Ligand System**

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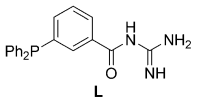
The hydroformylation of olefins is one of the largest industrial applications of homogeneous catalysis and results in the production of millions of tons of aldehydes per year.[1] These aldehydes constitute useful intermediates, but are rarely the final objective of the industrial chemist, because they are usually reduced to the corresponding alcohols. In particular linear alcohols have tremendous industrial applications as solvents but also as raw materials for plasticizers and detergents.[2] In most of the cases, these valuable materials are produced in two separate steps from the terminal alkenes, namely by a hydroformylation that employs syngas as an inexpensive one-carbon source, followed by a reduction step that uses molecular hydrogen and a second catalyst.[3] The cost of the alcohol is further increased by the requirement to purify the aldehyde.

Many approaches have been investigated in an attempt to shorten this sequence, ideally by designing a one-pot tandem hydroformylation/hydrogenation protocol, in which the alcohol would be directly isolated from the reaction mixture. In 1966, chemists from the Shell Oil Company pioneered such a process and reported the use of cobalt catalysts that are capable of converting alkenes into alcohols under CO/H_2 atmosphere.[4] The main limitations are the moderate yields and the somewhat harsh reaction conditions that are required.

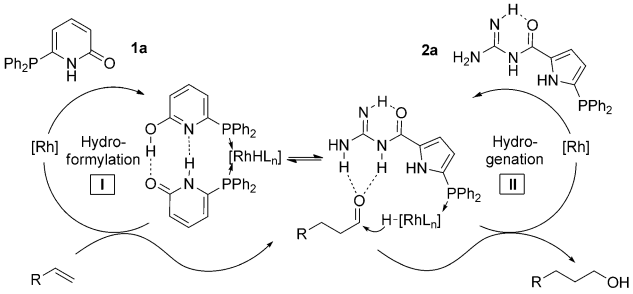
Many other catalytic systems that are composed of a ligand associated with a metal, such as Co,[5] Pd,[6] Rh,[7] or Ru,[8] have been reported as potential solution to this highly relevant industrial issue.[9] However, none of these systems operates with satisfying chemoselectivity (alcohol vs. alkane; the latter resulting from competing direct reduction of the alkene) and regioselectivity (linear/branched (l/b) regioisomers resulting from unselective hydroformylation). Recently, Nozaki and co-workers described an elegant approach that relies on the cooperative use of rhodium- and ruthenium-based catalysts and results in the formation of the desired linear alcohols with excellent linear/branched selectivities in good yields.[10] Our group also reported an example that fulfills these requirements by using a supramolecular rhodium catalyst based on the bifunctional ligand **L**. While the system showed high activity, its regioselectivity toward the linear alcohol product was not optimal.[11]



L

In recent years, the use of cooperative catalysis has enabled the development of many tandem processes or cascade reactions that combine the use of two or more separate catalytic systems, which work either in a cooperative or successive manner. Such tandem protocols can be the result of combining Lewis acid catalysis with Brønsted acid catalysis or Lewis base catalysis with Brønsted base catalysis, but also any other possible combination involving organometallic catalysis and organocatalysis.[12] For example, Cole-Hamilton and co-workers have reported an elegant approach for the synthesis of alcohols from alkenes by combining use of rhodium, Xantphos, and triethylphosphine.[13]

We herein report a unique multifunctional rhodium catalyst system that enables the simultaneous catalysis of two distinct transformations in a highly selective manner, controlled by the cooperative action of two different ligands **1a** and **2a** (Scheme 1). These ligands stem from two conceptually different supramolecular catalyst systems that were developed in our group.[14] Ligand **1a** (6-DPPon = 6-diphenylphosphanylpyridone) has been designed to self-assemble in the presence of a rhodium(I) center to form a chelating catalyst system that acts as a highly active and regioselective hydroformylation catalyst.[15] The acylguanidine ligand **2a**, which was also developed in our group, is an enzyme-inspired bifunctional ligand and enables highly chemoselective hydrogenation of aldehydes by relying on supramolecular aldehyde activation through hydrogen-bonding.[11] We report the combination of these two approaches in order to fulfill the following objectives:



Scheme 1. Ligand cooperation for tandem hydroformylation/hydrogenation of alkenes.

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1) one-pot conversion of alkenes to linear alcohols through hydroformylation/hydrogenation by using a single metallic catalyst;
2) high linear/branched regioselectivity;
3) simultaneous chemoselective reduction of the intermediate aldehyde with molecular hydrogen gas (no alkene hydrogenation).

For such a scenario to be successful, it is important that both complexes of type **I** and **II** exist in solution, and that the rate of hydroformylation with complex **I** is significantly faster than with any other rhodium complex present (Scheme 1). However, the rhodium/**1a** catalytic system is unable to reduce an aldehyde under hydroformylation conditions, and the hydrogenation step requires the presence of a rhodium catalyst of type **II**, which is modified with the acyl guanidine ligand **2a**. In other words, these complexes will have to be present in an equilibrium and the relative rates of hydroformylation and hydrogenation will have to be efficiently different and simultaneously balanced to allow an efficient and highly regioselective tandem process.

Initial experiments were carried out with 1-octene as a model substrate in toluene at 80 °C with 20 bar syngas pressure and a catalyst loading of 0.5 mol %. Employing both PPh_3 as well as ligand **1a** (6-DPPon) efficient hydroformylation with excellent regioselectivity for the 6-DPPon system in favor of the linear aldehyde was noted (Table 1). No traces of hydrogenation to the corresponding alcohols were detected (Table 1, entries 1 and 2).[15f] Conversely, nearly complete conversion to the alcohol was noted when a rhodium catalyst modified with the acylguanidine ligand **2a** was employed (Table 1, entry 3). However, the regioselectivity was low (81:19; Table 1, entry 3). Thus, neither the rhodium catalyst derived from **1a** nor that derived from **2a** could solve the chemo- and regioselectivity issues of the reaction on its own.

Interestingly, kinetic data from side-by-side experiments showed that hydroformylation was significantly faster with ligand **1a** than with **2a** (Figure 1). The situation is reversed for the reduction step, because **1a** is unable to initiate the reduction. These results suggested that a mix of both ligand types in the presence of a rhodium salt may result in a favourable cooperation between both catalyst systems, which may solve the problematic chemo- and regioselectivity issues of the desired transformation.

To our delight, the product was obtained in excellent yield (95 %, Table 1, entry 4) and with high regioselectivity (97:3)

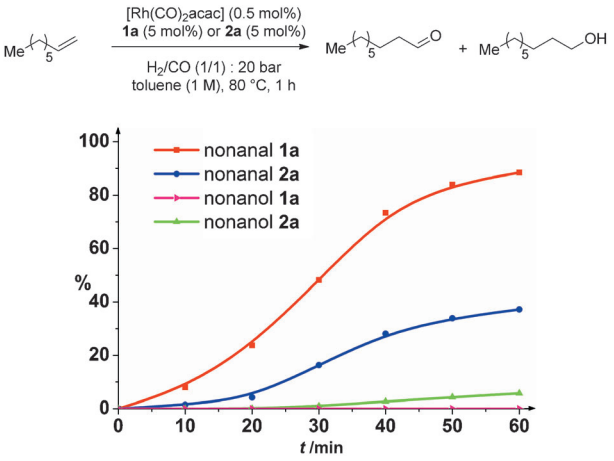


Figure 1. Kinetics of hydroformylation with ligand **1a** and **2a** independently.

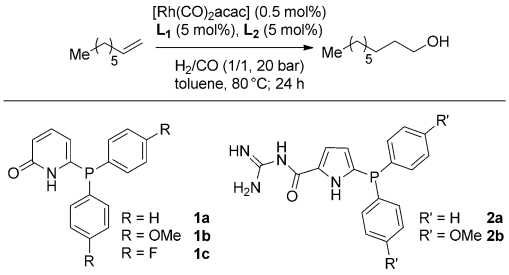
after 72 hours by using 0.5 mol % of rhodium catalyst and 5 mol % of both ligands **1a** and **2a**. Unfortunately, the overall reaction time to achieve quantitative conversion to the alcohol was too long.

Kinetic studies[16] of this tandem process by employing the ligand mixture **1a**/**2a** showed that hydrogenation is the rate limiting step, while hydroformylation is fast (90 % conversion after 3 h with **1a** (5 mol %), **2a** (5 mol %), $[Rh(CO)_2acac]$ (0.5 mol %), toluene (1 M), 80 °C).

A detailed analysis of the data showed that the hydrogenation rate for the **1a**/**2a** catalyst system is significantly slower compared to the activity of the rhodium/**2a** catalyst on its own. A reasonable explanation for this behavior is that the presence of the self-assembling ligand **1a** shifts the equilibrium between the different rhodium complexes toward complex **I**, thus reducing the concentration of catalyst **II** and resulting in a lower rate of hydrogenation (Scheme 1).

To solve this problem, we decided to tune the electronic properties of each ligand according to the following hypothesis. A reduction of the σ-donor strength and an increase of the π-acceptor abilities at the P donor of self-assembling ligand **1** should furnish a more active hydroformylation catalyst **I**.[17] Conversely, an increase of the σ-donor capabilities of the P donor of acylguanidine ligand **2** should increase both the binding constant toward rhodium(I) and the hydrogenation rate.[18] To test this hypothesis, both electron-rich and electron-poor 6-DPPon derivatives **1b** and **1c**, respec-

Table 1: Tandem hydroformylation/hydrogenation of 1-octene.



Entry	L_1	L_2	RCHO [%][a]	l:b[a]	ROH [%][a]	l:b[a]
1	PPh_3	–	99	82:18	0	–
2	**1a**	–	99	95:5	0	–
3	**2a**	–	2	–	98	81:19
4[b]	**1a**	**2a**	5	–	95	97:3
5	**1a**	**2b**	1	–	99	93:7
6	**1b**	**2b**	5	33:67	95	91:9
7	**1c**	**2b**	5	37:63	95	96:4

[a] Determined by GC analysis. [b] Reaction time was increased to 72 hours. acac = acetylacetonate.

tively, as well as the more electron-rich acylguanidine ligand **2b** were prepared (Table 1).[16]

Indeed, replacing **2a** in our **1a**/**2a** catalyst system with the more electron-rich pyrrole-derived phosphine **2b** led to complete conversion to the alcohol in less than 24 hours under standard conditions (Table 1). However, the regioselectivity dropped slightly to 93:7 (Table 1, entry 5). Use of a mixture of more electron-rich **1b** and **2b**, led to an even lower regioselectivity of 91:9 (Table 1, entry 6). However, by employing electron-poor ligand **1c** with electron-rich acylguanidine ligand **2b** in a 1:1 ratio, we observed nearly full conversion from the alkene to the desired alcohol in 24 hours (instead of 72 hours for the parent system **1a**/**2a**) with excellent regioselectivity in favor of the linear alcohol (96:4; Table 1, entry 7).

In order to gain deeper insight into the role of each ligand and the variety of complexes formed during the catalytic process, we performed kinetics studies by in situ ReactIR experiments as well as NMR experiments after pressurizing with syngas.

The reaction kinetics for rhodium catalysts derived from ligands **1c** and **2b** independently were studied (Figure 2). The rhodium catalyst derived from self-assembling ligand **1c** is a significantly faster hydroformylation catalyst than the rhodium catalyst derived from **2b**.[16]

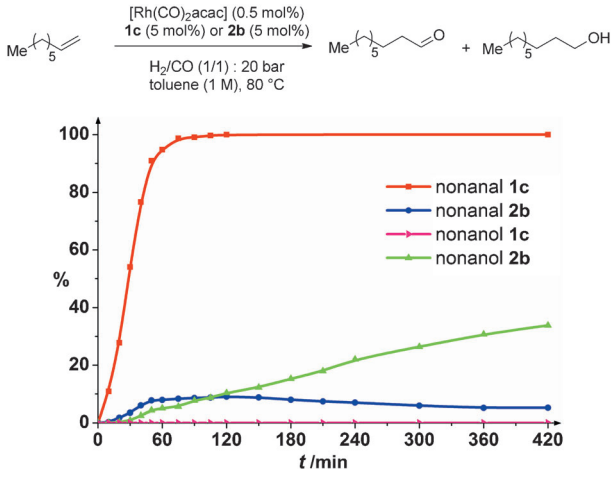


Figure 2. Kinetics of the tandem hydroformylation/hydrogenation of 1-octene with ligand **1c** and **2b** independently.

Conversely, by studying the hydrogenation step starting from *n*-nonanal, it becomes evident that the catalyst derived from **1c** is unable to reduce the aldehyde function (as with **1a**). However, the electron-rich acylguanidine **2b**/rhodium catalyst performed with significantly higher activity (turnover frequency after 50 min = 84 h^{-1}) than the parent system with **2a** (turnover frequency after 50 min = 40 h^{-1}), and thus, **2b** is so far the best ligand for this aldehyde hydrogenation step under hydroformylation conditions.[16]

Additionally, the reaction kinetics of the tandem process employing the **1c**/**2b** catalyst system was studied and the results are shown in Figure 3. Obviously, hydroformylation

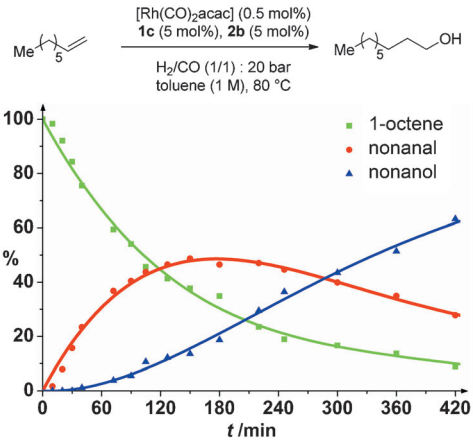


Figure 3. Kinetics of the tandem hydroformylation/hydrogenation of 1-octene with the optimal mixed **1c**/**2b** rhodium catalyst.

and hydrogenation operate simultaneously (after 5 h, 80% of octene was consumed, 40% aldehyde and 40% alcohol were formed), which proves the cooperate action of both ligand systems under these reaction conditions.[19]

That the self-assembled **1c**/rhodium catalyst is the kinetically competent hydroformylation catalyst became more obvious when the regioselectivities were studied during the course of the reaction. The mixed catalyst system operates with the same regioselectivity throughout the reaction, as observed for the single **1c**/rhodium catalyst (96/4 = l/b), compared to the low regioselectivity observed for the **2b**/rhodium catalyst (75/25 = l/b).[16,19]

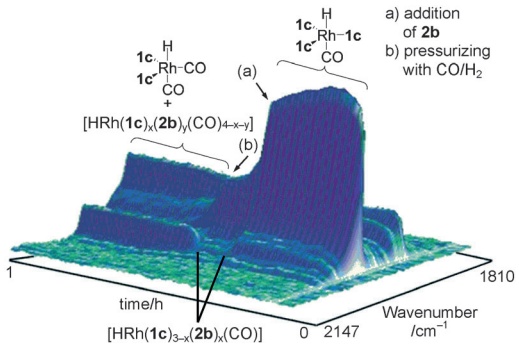
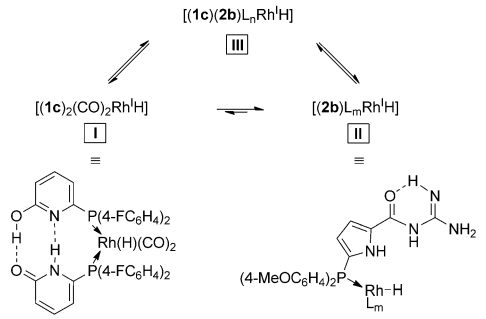


Figure 4. Complexes in the reaction of [HRh(**1c**)$_3$(CO)] with ligand **2b** under CO/H_2 pressure, observed by in situ IR spectroscopy.

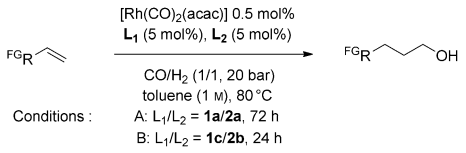
In situ IR spectroscopic experiments (Figure 4) corroborated by DFT calculations support the presence of an equilibrium between complexes **I**, **II**, and **III** (Scheme 2).[16] Therefore, we synthesized and isolated a [HRh(**1c**)$_3$(CO)] complex (characterized by ^{1}H and ^{31}P NMR spectroscopy). When this complex was dissolved in toluene, characteristic bands at 2025 cm^{-1} and 1936 cm^{-1} emerged. Interestingly, after **2b** (3 equiv) was added to the solution, the intensity of these bands decreased and a new band was detectable at 1996 cm^{-1}. This indicates the formation of a [HRh(**1c**)$_{3-x}$(**2b**)$_x$(CO)] complex. After the solution was pressurized with

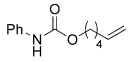
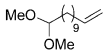


Scheme 2. Equilibrium of potential complexes formed in situ.

CO/H_2 (5 bar), five distinct absorptions were observed in the carbonyl area. To allow assignment of these five bands, we performed a control experiment in which the [HRh-(**1c**)$_3$(CO)] complex alone was pressurized with CO/H_2 (5 bar). Additionally, we computed the bands of the equatorial–equatorial (eq–eq) and axial–equatorial (ax–eq) conformers of the [HRh(**1c**)$_2$(CO)$_2$] complex by DFT calculations.[16] Four of the five bands observed after pressurizing the [HRh(**1c**)$_{3-x}$(**2b**)$_x$(CO)] with syngas can be assigned to the eq–eq and ax–eq conformer of the [HRh(**1c**)$_2$(CO)$_2$] complex. The band at 1952 cm^{-1} may arise from a [HRh(**1c**)$_x$-(**2b**)$_y$(CO)$_{4-x-y}$] complex. This supports our suggestion, which is based on the kinetic studies, that an independent [HRh-(**1c**)$_2$(CO)$_2$] complex is responsible for the outstanding hydroformylation activity of the ligand system presented herein, because such a complex was detectable by in situ IR spectroscopy in the presence of **2b**.

Table 2: Scope and limitations.



Entry	R	Cond.	ROH:RCHO[a]	l:b (ROH)[a]	Yield [%][b]
1	Me(CH$_2$)$_5$	A	95:5	97:3	94[c]
		B	95:5	96:4	94[c]
2	Me(CH$_2$)$_7$	A	95:5	93:7	94
		B	99:1	93:7	99
3		A	100:0	99:1	99[c]
		B	97:3	99:1	89[c]
4	HO(CH$_2$)$_4$	A	90:10	91:9	90[c]
		B	100:0	93:7	99[c]
5	THPO(CH$_2$)$_4$	A	96:4	94:6	94[c]
		B	98:2	96:4	90
6	BnO(CH$_2$)$_4$	A	100:0	92:8	98[c]
		B	100:0	93:7	97[c]
7	AcO(CH$_2$)$_4$	A	99:1	91:9	98
		B	99:1	96:4	99
8	TBSO(CH$_2$)$_9$	A	97:3	90:10	97[c]
		B	93:7	96:4	85
9		A	96:4	91:9	96
		B	99:1	85:15	99[c]
10		A	95:5	93:7	93
		B	97:3	96:4	87
11		A	90:10	89:11	70
		B	99:1	96:4	90
12		A	99:1	87:13	94[c]
		B	99:1	98:2	99[c]

[a] Determined by NMR analysis of the crude reaction mixture, except for entries 1 and 2, for which ratios were determined by GC analysis. [b] Yields of isolated products. [c] Yields determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard. Bn = benzyl, FG = functional group, TBS = *tert*-butyldimethylsilyl, THP = tetrahydropyranyl.

With the optimized reaction conditions in hand, we studied the scope of our method. For each substrate both catalyst combinations **1a**/**2a** and **1c**/**2b** were screened and compared. A wide range of substrates were evaluated, and many common functional groups were compatible with the reaction conditions (Table 2). Other aliphatic terminal alkenes, such as 1-decene, gave results identical to our model substrate, and undecen-1-ol was isolated in 99% yield and 93:7 regioselectivity after 24 hours with method B (Table 2, entry 2). An increased substitution at the allylic position provided the corresponding product with even higher selectivities (Table 2, entry 3). Acetals, esters, benzyl and silyl ethers, carbamates, and free hydroxyl groups are well tolerated (Table 2, entries 4–11). Furthermore, 1,2-disubstituted alkenes are completely unreactive under these reaction conditions because of high chemoselectivity for the terminal alkene in the hydroformylation step (Table 2, entry 12).

In conclusion, we have developed a unique multifunctional rhodium catalyst system that enables the simultaneous catalysis of two distinct transformations (hydroformylation of alkenes and aldehyde hydrogenation) in a highly selective manner controlled by the cooperative action of two different ligands **1** and **2** (Scheme 1). Thus, terminal alkenes are transformed into highly valuable C_1-chain-elongated linear alcohols in high yields and excellent selectivities. Even though this catalyst system relies on subtle hydrogen-bonding interactions to enable its performance, the system is compatible with a wide range of functional groups present in the alkenic substrate, thus rendering this method attractive for synthetic as well as industrial applications.

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