DOI: 10.1002/chem.201300899

Towards the Development of a Selective Ruthenium-Catalyzed Hydroformylation of Olefins

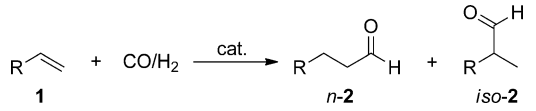
Ivana Fleischer,[a] Lipeng Wu,[a] Irina Profir,[a] Ralf Jackstell,[a] Robert Franke,[b, c] and Matthias Beller*[a]

Abstract: The ruthenium-catalyzed hydroformylation of 1- and 2-octene to give preferentially the corresponding linear aldehyde is reported. The catalyst system comprising of $Ru_3(CO)_{12}$ and an imidazole-substituted monophosphine ligand allows for high chemo- and regioselectivity. The hydroformylation proceeds with unprecedented rates for a ruthenium-based catalyst.

Keywords: aldehydes · carbonylation · hydroformylation · phosphine · ruthenium

Introduction

Homogeneously-catalyzed hydroformylation, also called oxo-synthesis, is a powerful, atom-efficient method for the synthesis of aldehydes from olefins with carbon monoxide and hydrogen (Scheme 1).[1] Originally, this reaction was discovered by Otto Roelen, who can be considered as a "pioneer of industrial homogeneous catalysis".[2,3] Nowadays, more than 10 million tons of oxo products are industrially produced by hydroformylation each year.



Scheme 1. Hydroformylation of olefins to aldehydes.

As depicted in Scheme 1, the formylation can in general occur at the terminal or internal carbon atom. Thus, mixtures of linear (*n*) and branched (*iso*) aldehydes can be obtained. Moreover, the double bond can isomerize and the following hydroformylation of internal olefins will increase the portion of branched regioisomers. Therefore, specific control of the regioselectivity is a very important issue for any application along with chemoselectivity and high catalyst activity. Although linear aldehydes are important intermediates for production of bulk chemicals, selectively produced branched aldehydes bearing a stereogenic center are of interest for the pharmaceutical industry, for instance.[4]

The early hydroformylation catalysts were based on cobalt complexes, but it was found in the 1970s that rhodium-based systems are superior in terms of catalytic activity and selectivity.[1,5] Since then, many efforts have been successfully put into the development of efficient rhodium catalysts. Other metals that are able to catalyze hydroformylation reactions display considerably lower activity than rhodium. However, the rough order of their catalytic activity (Rh > Co > Ir > Ru > Os > Pt > Pd > Fe > Ni) is simply based on the use of non-modified metal carbonyl complexes.[1a] Recently, we and others have shown that there exists a huge potential to utilize modified reaction conditions and ligands to improve the performance of so-called "alternative" hydroformylation catalysts, which might substitute the particularly expensive rhodium.[6,7]

Ever since the first ruthenium-catalyzed hydroformylation was reported by Evans, Osborn, Jardine, and Wilkinson in 1965,[8] several catalysts have been developed, but they could not compete with rhodium-based systems.[9] Notably, Takahashi, Yamashita, Tanaka, and Nozaki reported in 2012 a [Ru^{II}Cp*] complex with bidentate ligands for highly regioselective hydroformylation of propene and 1-decene.[10] The observed chemo- and regioselectivity is comparable to standard rhodium catalyst system, however, the catalytic activity was still significantly lower. More recently, a modified catalyst for domino hydroformylation/reduction was reported.[11]

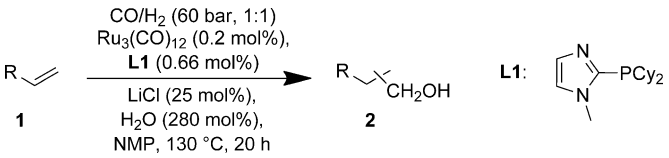
Our recent investigations in this field led to the development of a new hydroformylation/reduction catalyst system based on a Ru^0 carbonyl complex and the imidazoyl-substituted monophosphine ligand **L1** (Scheme 2).[12] Good activity, chemo- and regioselectivity were obtained in the domino hydroformylation of alkenes and subsequent reduction of the aldehydes to the corresponding alcohols. The scope of the reaction was demonstrated on terminal and internal ali-

[a] Dr. I. Fleischer, L. Wu, I. Profir, Dr. R. Jackstell, Prof. M. Beller
Leibniz Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-51113
E-mail: matthias.beller@catalysis.de

[b] Prof. Dr. R. Franke
Evonik Industries AG
Paul-Baumann-Strasse 1, 45772 Marl (Germany)

[c] Prof. Dr. R. Franke
Lehrstuhl für Theoretische Chemie
44780 Bochum (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300899.



Scheme 2. Ruthenium-catalyzed domino hydroformylation/reduction of alkenes to alcohols.

phatic, cyclic and araliphatic alkenes, 1,3-dienes and electron-poor methacrylic acid derivatives. In addition, the catalyst could be also applied to hydroaminomethylation reactions of various olefins and amines.[13] These reactions extend the scope of synthetically important Ru-catalyzed C–C bond forming reactions.[14,15]

Herein, we would like to present further investigations of the previously reported catalyst system and its application in the selective hydroformylation of alkenes to aldehydes.

Results and Discussion

In the course of our studies on hydroformylation/reduction of 1-octene that was carried out at 130 °C in a mixture of NMP (*N*-methyl-2-pyrrolidone) and H_2O as solvents, the formation of a mixture of alcohols and aldehydes was observed in the absence of lithium chloride (Table 1, entries 1 and 2). The selectivity towards aldehydes increased at lower reaction temperature demonstrating that the carbonyl reduction requires more drastic conditions (Table 1, entry 3). Next, the reaction conditions were further optimized in order to suppress the hydrogenation activity of the catalyst system further on and to improve its activity and regioselectivity.

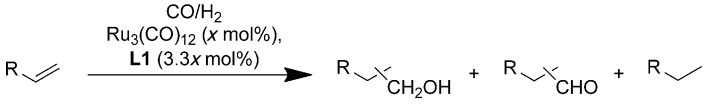
The following reactions were performed with a low catalyst loading of 0.1 mol% Ru and analyzed by GC after three hours. A minor yield of aldehyde and an undetectable amount of alcohol were obtained in NMP and PC (propylene carbonate) and their mixtures with water, respectively (Table 1, entries 4–6). However, increased partial hydrogen pressure led to a considerably higher aldehyde yield (79%, Table 1, entry 7) in propylene carbonate. Notably, the transformation proceeded with improved regioselectivity of 95:5, because hydroformylation of the internal olefins does not take place under these conditions. Applying the same pressure and varying solvents, inferior results were achieved (Table 1, entries 8–10). The catalyst system was active even at 0.05 mol% loading, which is, to the best of our knowledge, the lowest reported catalyst loading of any ruthenium complex in hydroformylation reactions (Table 1, entry 11). Furthermore, the reaction proceeded smoothly at 80 °C and even at 60 °C applying a longer reaction time (Table 1, entries 12 and 13). The contamination of the autoclave by other metals (e.g., rhodium) was excluded by a blank test (Table 1, entry 14).

In the following, the ligand structure was modified.[16] Decisive results are summarized in Scheme 3 and depicted in Figure 1. The alteration of the nitrogen substituent revealed an ameliorative effect of aromatic groups, in particular of the electron-rich *ortho*-anisyl substituent (**L2**). Further variations were conducted on the phosphorus atom. The gas consumption curves shown in Figure 1 provide a clear and direct representation of activities of the respective catalyst systems. Whereas the *iso*-propyl- and cyclohexyl- substituted ligands **L2** and **L6** exhibit highest reactivity, bulkier *tert*-butyl and adamantyl-derived ligands **L5** and **L7** were entirely inactive. Slightly diminished aldehyde yield and lower regioselectivity were obtained with the less basic **L8**. Benzimidazol-based ligands **L9–10** were less active than their imidazole analogs and required longer reaction times. By comparison, pyrrole-derived ligand **L11** was not active under the standard reaction conditions. The same result was obtained with a ligand-free system.

Using $Ru_3(CO)_{12}$/**L2**, nonanal was isolated in 59% yield by extraction with heptane and bulb-to-bulb distillation. Unfortunately, a small amount of propylene carbonate was found in the isolated material. The lower isolated yield was caused by the partial oxidation of the aldehyde in the presence of ruthenium catalyst.

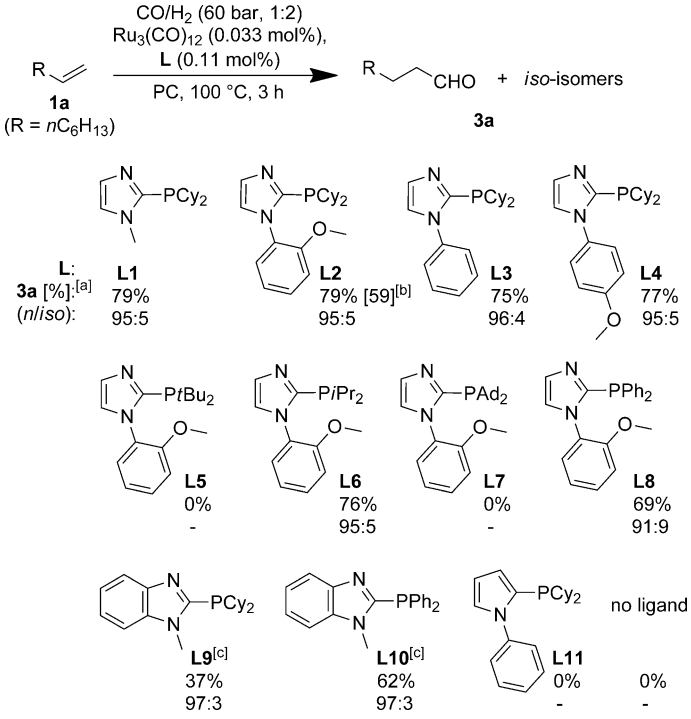
In order to demonstrate the unique activity of our ruthenium catalyst, the hydroformyla-

Table 1. Reaction of 1-octene with synthesis gas: Optimization of reaction conditions.[a]



	T [°C]	CO/H_2 [bar]	Solvent	*t* [h]	*x* [mol%]	Yield [%][d] **2a** (*n*/*i*)	**3a** (*n*/*i*)
1[b,c]	130	30/30	NMP/H_2O	20	0.2	90 (88:12)	1[d]
2[b]	130	30/30	NMP/H_2O	20	0.2	37 (95:5)	54 (85:15)
3	100	30/30	NMP/H_2O	20	0.2	6 (95:5)	83 (89:11)
4	100	30/30	NMP/H_2O	3	0.033	0	23 (92:8)
5	100	30/30	PC/H_2O	3	0.033	0	10 (94:6)
6	100	30/30	PC	3	0.033	0	32 (94:6)
7	100	20/40	PC	3	0.033	<1	79 (95:5)
8	100	20/40	NMP	3	0.033	0	60 (95:5)
9	100	20/40	PhMe	3	0.033	0	11 (95:5)
10	100	20/40	THF	3	0.033	0	<1
11	100	20/40	PC	8	0.0167	0	74 (95:5)
12	80	20/40	PC	15	0.033	0	79 (95:5)
13	60	20/40	PC	72	0.033	0	80 (94:6)
14	100	20/40	PC	20	0	0	0

[a] 50.0 mmol 1-octene, $Ru_3(CO)_{12}$, **L1**, 25 mL solvent, CO/H_2, 100 mL autoclave. [b] Performed in 25 mL autoclave with 20.0 mmol 1-octene. [c] With LiCl (25 mol%). [d] Determined by GC with isooctane as internal standard.



Scheme 3. Hydroformylation of 1-octenes: Ligand variation. [a] Determined by GC with isooctane as internal standard. [b] Isolated yield is given in brackets. [c] 24 h.

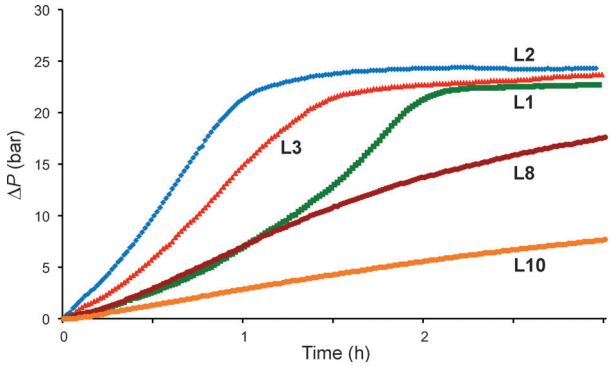


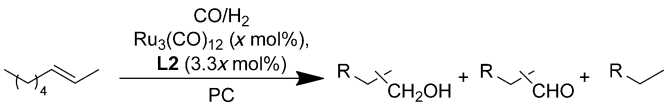
Figure 1. Gas consumption curves in the hydroformylation of 1-octene with varying ligands.

tion of 1-octene was carried out at 130 °C in the presence of ligands **L1** and **L2** and 0.017 mol % of the ruthenium precursor (0.05 mol % in Ru). After 40 min, the aldehyde **3a** was formed in 60 (**L1**) and 68 % yield (**L2**), which corresponds to a turnover-frequency of 1800 and 2040 h^{-1}, respectively. With 1-butene as substrate and only 0.025 mol % of Ru, a turnover-frequency of 2400 h^{-1} was achieved at 130 °C. Notably, the obtained values are much closer to the activities of rhodium catalysts as it was ever expected for any ruthenium catalyst in hydroformylations.

A considerably more challenging transformation is the hydroformylation of internal olefins to linear aldehydes, which proceeds through isomerization of the internal double bond and the subsequent regioselective hydroformylation. Several rhodium-based systems were developed in industry and academia for this demanding reaction.[17] Thus, the ruthenium-catalyzed hydroformylation of 2-octene was also investigated (Table 2). Unfortunately, no conversion was obtained by applying the standard reaction conditions developed for terminal alkenes (100 °C, 0.1 mol % Ru; Table 2, entry 1). However, activity was observed at 130 °C and 70 % yield of C9-aldehydes was achieved (Table 2, entry 2). At this temperature, the isomerization of 2-octene occurred and the obtained regioselectivity for aldehydes was 72:28. Though, the aldehyde was partially reduced to the corresponding alcohol. In order to suppress this sequential hydrogenation, the reaction was performed with a 1:1 CO/H_2 mixture (Table 2, entry 3). Indeed, no alcohol was observed, however, the overall activity and selectivity diminished. Further experiments were performed with higher catalyst loading at 100 °C under constant pressure of carbon monoxide and hydrogen (5/20 bar). A higher partial hydrogen pressure was applied in order to facilitate the isomerization of the double bond. Indeed, these conditions led to an aldehyde yield of 75 % and *n*/*iso* selectivity of 81:19 (Table 2, entry 4).

Slightly higher regioselectivity was observed by employing a more diluted reaction mixture (Table 2, entry 5). Low aldehyde yield (12 %) was obtained, when non-isobaric conditions were used (Table 2, entry 6). The variation of partial pressures revealed that the CO/H_2 5:20 mixture represents the optimum ratio for this reaction (Table 2, entries 7–10). However, the present catalyst system has to be further optimized in order to achieve higher activity and improved che-

Table 2. Reaction of 2-octene with synthesis gas: Optimization of reaction conditions.[a]



	T [°C]	CO/H_2 [bar]	5 [mmol]	t [h]	x [mol %]	Yield [%][b] 2a (n/i)	3a (n/i)
1	100	20/40	50	6	0.033	0	0
2	130	20/40	50	40	0.033	13 (79:21)	70 (72:28)
3	130	30/30	50	40	0.033	0	37 (67:33)
4	100	5/20 const.[c]	50	20	0.1	5 (33:67)	75 (81:19)
5	100	5/20 const.[c]	20	20	0.1	5 (30:70)	75 (83:17)
6	100	5/20	20	20	0.1	<1	12 (88:12)
7	100	2.5/22.5 const.[c]	20	20	0.1	2	54 (87:13)
8	100	3.5/21.5 const.[c]	20	20	0.1	5 (30:70)	67 (86:14)
9	100	8.5/16.5 const.[c]	20	20	0.1	<1	36 (84:16)
10	100	12.5/12.5 const.[c]	20	20	0.1	0	29 (83:17)

[a] 2-Octene, $Ru_3(CO)_{12}$, **L2**, 25 mL PC, CO/H_2, 100 mL autoclave. [b] Determined by GC with isooctane as internal standard. [c] Performed under constant pressure in autoclave connected to a burette filled with CO/H_2 1:1.

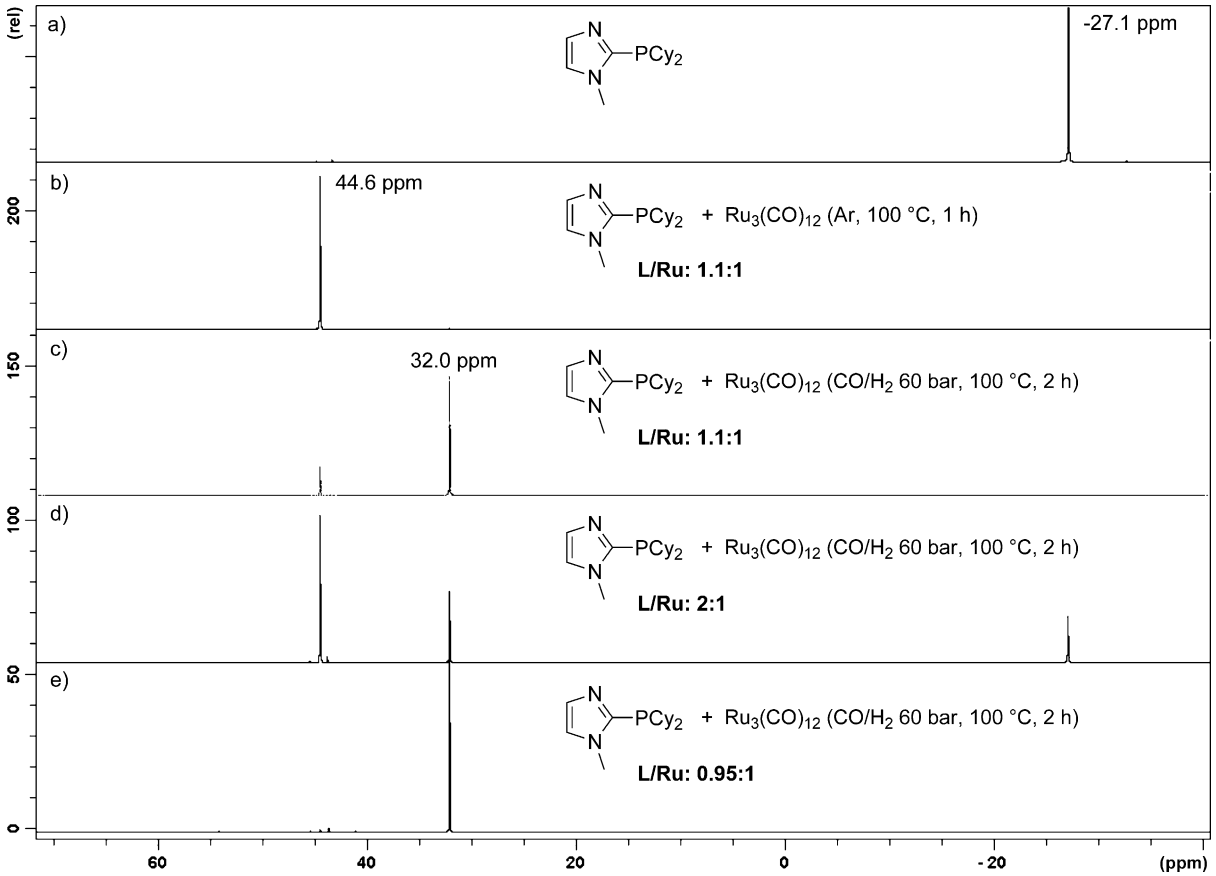
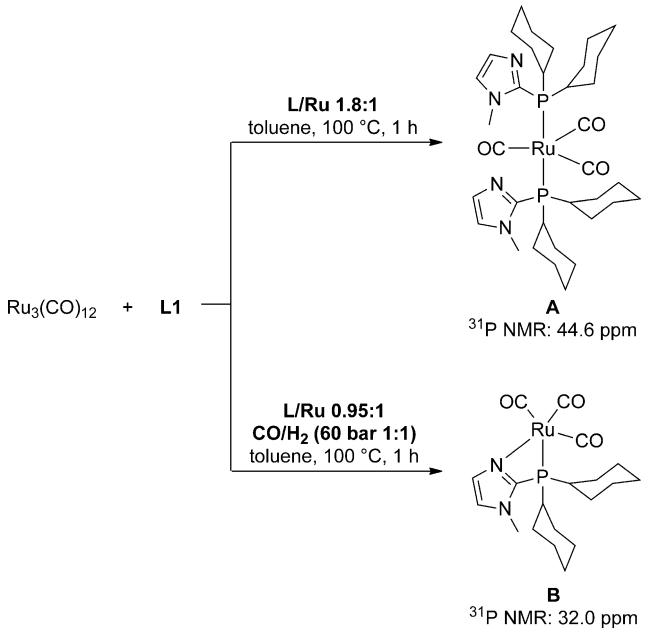


Figure 2. ^{31}P NMR spectra of **L1**/$Ru_3(CO)_{12}$ mixtures: a) Ligand **L1**. b) **L1**/$Ru_3(CO)_{12}$ (1.1:1) (Table 2, entry 6) stirred at 100 °C under argon atmosphere for 1 h. c) **L1**/$Ru_3(CO)_{12}$ (1.1:1) stirred in autoclave at 100 °C with CO/H_2 (1:1, 60 bar) for 2 h. d) As c), with **L1**/$Ru_3(CO)_{12}$ (2:1). e) As c), with **L1**/$Ru_3(CO)_{12}$ (0.95:1).

moselectivity for industrially important olefin mixtures. Also, the conversion of challenging 4-octene was not successful under the reaction conditions.

Comparable to our original work,[12] the formation of defined complexes was studied by ^{31}P NMR spectroscopy (Figure 2). When a toluene solution of ligand **L1** and triruthenium dodecacarbonyl was heated to 100 °C under argon, a new complex showing a signal at 44.6 ppm was mainly obtained (Figure 2b). On the other hand, the same reaction performed under synthesis gas pressure (60 bar, CO/H_2 1:1) gave an additional signal at 32.0 ppm (Figure 2c). The variation of the amount of the ligand and Ru revealed that these two signals correspond to complexes with different Ru/L ratio (Figure 2c–e). Signal at 44.6 ppm is dominant when excess ligand is used, whereas only one complex with signal at 32.0 ppm is formed with equimolar L/Ru ratio.

These results were adopted for the synthesis of the defined complexes after careful optimization of the conditions (Scheme 4). The complex with signal at 44.6 ppm was prepared by heating of a toluene mixture of **L1** and $Ru_3(CO)_{12}$ (L/Ru 1.8:1) to 100 °C for 1 h and isolated in a pure form after removal of the solvent by precipitation with heptane. The particularly stable mononuclear complex **A** bearing two ligands was characterized by NMR, HRMS, and X-ray anal-

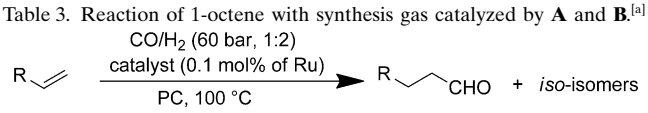


Scheme 4. Synthesis and structures of ruthenium–ligand **L1** complexes **A** and **B**.

ysis. On the other hand, complex **B** was obtained as a toluene solution. It was synthesized in analogy to the preparation of complex **A** with different L/Ru ratio (0.95:1) under synthesis gas pressure (60 bar, CO/H_2 1:1). Due to its instability, an X-ray characterization was not successful. However, NMR and HRMS analysis suggest formation of the mononuclear complex **B** with one ligand that should bind in a bidentate mode. This kind of structure is known in the literature.[16]

In contrast to the successful rhodium-based hydroformylation catalysts, the catalysis performed by the herein presented system is suppressed in the presence of higher excess of the ligand (>2 equivalents to Ru). Hence, we suggest complex **B** to be responsible for the catalysis. It can be detected in the crude mixture after the reaction as the major phosphorus-containing component. To test its catalytic performance, the hydroformylation of 1-octene was carried out with the freshly prepared solution of **B** in toluene and compared to the result of reaction catalyzed by the standard in situ catalytic system and complex **A** (Table 3, Figure 3). As expected, the hydroformylation reaction catalyzed by **A** was slower than the standard system, contrary to the performance of **B**, which was similar to the in situ catalyst.

Table 3. Reaction of 1-octene with synthesis gas catalyzed by **A** and **B**.[a]



1a (R = nC_6H_{13}) **3a**

	Catalyst	t [h]	**3a** Yield [%][b]	n/i[b]
1	**L1**/$Ru_3(CO)_{12}$ (L/Ru 1.1:1) in situ	3	79	95:5
2	**A**	20	75	95:5
3	**B**[c]	10	77	95:5

[a] 50.0 mmol 1-octene, catalyst (0.1 mol% of Ru), 25 mL solvent, CO/H_2 (1:2, 60 bar), 100 °C, 100 mL autoclave. [b] Determined by GC with isooctane as internal standard. [c] Performed with a solution of **B** in toluene (0.114 M).

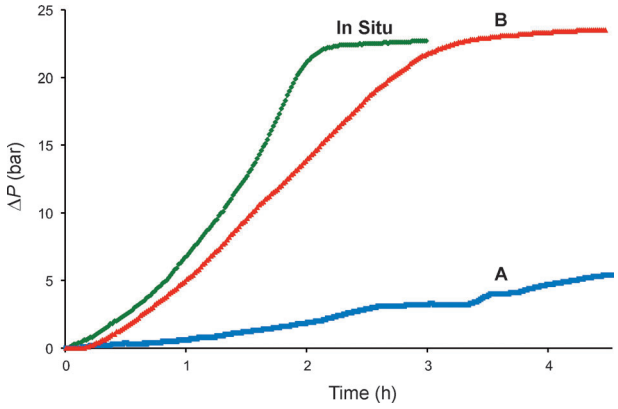


Figure 3. Gas consumption curves in the hydroformylation of 1-octene: **L1**/$Ru_3(CO)_{12}$ (L/Ru 1.1:1).

Conclusion

In summary, we have developed a highly active ruthenium-based catalyst for hydroformylation of aliphatic olefins. The catalyst system consisting of $Ru_3(CO)_{12}$ and imidazoyl-substituted phosphine ligand exhibited excellent activity in the *n*-selective hydroformylation of 1-octene. The transformation of challenging internal olefins was demonstrated with 2-octene, although this tandem isomerization/hydroformylation sequence required more forcing reactions conditions. In addition, a complex responsible for the catalysis was identified. We expect this catalyst to broaden the scope of hydroformylation reactions and offer an interesting alternative to rhodium-based carbonylation chemistry.

Experimental Section

General procedure, Ligand synthesis: In a three-necked 100 mL round-bottomed flask equipped with a reflux condenser, the corresponding substituted *1H*-imidazole (13.5 mmol) was dissolved in THF (30 mL) under argon and cooled to −30 °C. *n*BuLi (1.6 M in hexane, 8.4 mL, 13.5 mmol) was added and the reaction mixture was stirred at −30 °C for 30 min. A solution of the corresponding dialkylchlorophosphine (14.8 mmol in 10 mL of THF) was slowly added through a dropping funnel at −30 °C. The reaction mixture was slowly warmed to 50 °C and stirred for 60 min. After cooling with an ice bath, degassed aqueous NH_4Cl-solution was added, stirred for a few minutes, and the organic phase was separated. The aqueous layer was extracted with toluene (2×20 mL) and the combined organic layers were concentrated under vacuum. The product was recrystallized from diethyl ether to give the pure ligand as a colorless solid.

Hydroformylation of 1-octene: A 100 mL autoclave was charged with $Ru_3(CO)_{12}$ (10.7 mg, 16.7 μmol), ligand **L2** (20.4 mg, 55.0 μmol), 25 mL propylene carbonate and 7.8 mL 1-octene (5.6 g, 50 mmol). Then 40 bar of synthesis gas (CO/H_2 1:1) and 20 bar H_2 were introduced before the autoclave was heated to 100 °C. The reaction was stopped by cooling down and releasing the pressure. Water (25 mL) was added and the crude product was extracted with heptane (4×50 mL). The collected organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The product was isolated by bulb-to-bulb distillation (75–80 °C, 20 mbar) as a 14:1:2 mixture of nonanal, 2-methyloctanal and propylene carbonate (59% yield).

Nonanal: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.71 (t, $^3J_{HH}$ = 1.9 Hz, 1H, C*H*O), 2.37 (dt, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 1.9 Hz, 2H, CH_2CHO), 1.58 (p, $^3J_{HH}$ = 7.3 Hz, 2H, CH_2CH$_2$CHO), 1.36–1.13 (m, 10H, CH_2), 0.83 ppm (t, $^3J_{HH}$ = 6.7 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.7 (*C*HO), 43.8 (*C*H$_2$CHO), 31.7 (*C*H$_2$), 29.2 (*C*H$_2$), 29.0 (*C*H$_2$), 29.0 (*C*H$_2$), 22.5 (*C*H$_2$), 22.0 (*C*H$_2$), 13.9 ppm (*C*H$_3$); MS (EI): m/z (%): 141 [M−H]$^+$, 124, 114, 109, 98, 81, 70, 57, 55, 43, 41 (100), 29.

CCDC939937 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We are particularly grateful to the Bundesministerium für Bildung und Forschung (the German Federal Ministry of Education and Research) for financial support under the PROFORMING project (no. 03X3559). We also thank the Deutsche Forschungsgemeinschaft (Leibniz-price), Swiss National Science Foundation (grants for I.F.), Chinese Scholarship Council (grants for L.W.) and the analytical department at LIKAT.

[1] For recent reviews on hydroformylation, see: a) R. Franke, D. Selent, A. Börner, *Chem. Rev.* **2012**, *112*, 5675–5732; b) K.-D. Wiese, D. Obst, in *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Berlin Heidelberg **2010**, pp. 1–33; c) C. P. Casey, J. Hartwig, in *Organotransition Metal Chemistry: From Bonding to Catalysis*, Palgrave Macmillan, **2009**, pp. 751–769; d) P. W. N. M. Van Leeuwen, C. Claver, *Rhodium Catalyzed Hydroformylation*, Springer, Berlin Heidelberg **2008**; e) B. Breit, in *Metal Catalyzed Reductive C-C Bond Formation* (Ed.: M. Krische), Springer, Berlin Heidelberg **2007**, pp. 139–172.

[2] O. Roelen, *Chem. Abstr.* **1944**, *38*, 550 (DE 849548; US 1217066).

[3] B. Cornils, W. A. Herrmann, M. Rasch, *Angew. Chem.* **1994**, *106*, 2219–2238; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2144–2163.

[4] For selected reviews on branched-selective hydroformylations, see: a) J. Klosin, C. R. Landin, *Acc. Chem. Res.* **2007**, *40*, 1251–1259; b) M. L. Clarke, *Curr. Org. Chem.* **2005**, *9*, 701–718; c) B. Breit, *Acc. Chem. Res.* **2003**, *36*, 264–275; d) F. Agbossou, J.-F. Carpentier, A. Mortreux, *Chem. Rev.* **1995**, *95*, 2485–2506.

[5] D. Evans, J. A. Osborn, G. Wilkinson, *J. Chem. Soc. A* **1968**, *208*, 3133–3142.

[6] For a review on "alternative" hydroformylation catalysts, see: J. Pospech, I. Fleischer, R. Franke, S. Buchholz, M. Beller, *Angew. Chem.* **2013**, *125*, 2922–2944; *Angew. Chem. Int. Ed.* **2013**, *52*, 2852–2872.

[7] For selected examples on Pd- and Ir-catalyzed hydroformylations, see: a) R. Jennerjahn, I. Piras, R. Jackstell, R. Franke, K.-D. Wiese, M. Beller, *Chem. Eur. J.* **2009**, *15*, 6383–6388; b) M. Baya, J. Houghton, D. Konya, Y. Champouret, J.-C. Daran, K. Q. Almeida Leñero, L. Schoon, W. P. Mul, A. B. v. Oort, N. Meijboom, E. Drent, A. G. Orpen, R. Poli, *J. Am. Chem. Soc.* **2008**, *130*, 10612–10624; c) E. Drent, P. H. M. Budzelaar, *J. Organomet. Chem.* **2000**, *593–594*, 211–225; d) I. Piras, R. Jennerjahn, R. Jackstell, A. Spannenberg, R. Franke, M. Beller, *Angew. Chem.* **2011**, *123*, 294–298; *Angew. Chem. Int. Ed.* **2011**, *50*, 280–284; e) M. A. Moreno, M. Haukka, T. A. Pakkanen, *J. Catal.* **2003**, *215*, 326–331; f) G. Franciò, R. Scopelliti, C. G. Arena, G. Bruno, D. Drommi, F. Faraone, *Organometallics* **1998**, *17*, 338–347.

[8] D. Evans, J. A. Osborn, F. H. Jardine, G. Wilkinson, *Nature* **1965**, *208*, 1203–1204.

[9] For selected examples, see: a) P. Frediani, M. Bianchi, A. Salvini, L. C. Carluccio, L. Rosi, *J. Organomet. Chem.* **1997**, *547*, 35–40; b) T.-A. Mitsudo, N. Suzuki, T. Kondo, Y. Watanabe, *J. Mol. Catal. A: Chem.* **1996**, *109*, 219–225; c) M. M. T. Khan, S. B. Halligudi, S. H. R. Abdi, *J. Mol. Catal.* **1988**, *48*, 313–317; d) J. F. Knifton, *J. Mol. Catal.* **1988**, *47*, 99–116; e) T. Hayashi, Z. H. Gu, T. Sakakura, M. Tanaka, *J. Organomet. Chem.* **1988**, *352*, 373–378; f) G. Süss-Fink, G. F. Schmidt, *J. Mol. Catal.* **1987**, *42*, 361–366; g) I. Ojima, K. Kato, M. Okabe, T. Fuchikami, *J. Am. Chem. Soc.* **1987**, *109*, 7714–7720.

[10] K. Takahashi, M. Yamashita, Y. Tanaka, K. Nozaki, *Angew. Chem.* **2012**, *124*, 4459–4463; *Angew. Chem. Int. Ed.* **2012**, *51*, 4383–4387.

[11] K. Takahashi, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2012**, *134*, 18746–18757.

[12] I. Fleischer, K. M. Dyballa, R. Jennerjahn, R. Jackstell, R. Franke, A. Spannenberg, M. Beller, *Angew. Chem.* **2013**, *125*, 3021–3025; *Angew. Chem. Int. Ed.* **2013**, *52*, 2949–2953.

[13] L. Wu, I. Fleischer, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 3989–3996.

[14] For selected reports on $Ru_3(CO)_{12}$-catalyzed C–C bond forming reactions, see: a) N. Chatani, M. Tobisu, T. Asaumi, Y. Fukumoto, S. Murai, *J. Am. Chem. Soc.* **1999**, *121*, 7160–7161; b) M. Tobisu, N. Chatani, T. Asaumi, K. Amako, Y. Ie, Y. Fukumoto, S. Murai, *J. Am. Chem. Soc.* **2000**, *122*, 12663–12674; c) N. Hasegawa, V. Charra, S. Inoue, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, *133*, 8070–8073; d) J. C. Leung, L. M. Geary, T.-Y. Chen, J. R. Zbieg, M. J. Krische, *J. Am. Chem. Soc.* **2012**, *134*, 15700–15703.

[15] For a review on Ru-catalyzed hydroacylation reactions, see: a) J. Moran, M. J. Krische, *Pure Appl. Chem.* **2012**, *84*, 1729–1739; for selected reports, see: b) P. Isnard, B. Denise, R. P. A. Sneeden, J. M. Cognion, P. Durual, *J. Organomet. Chem.* **1982**, *240*, 285–288; c) T. Kondo, M. Akazome, Y. Tsuji, Y. Watanabe, *J. Org. Chem.* **1990**, *55*, 1286–1291; d) F. Shibahara, J. F. Bower, M. J. Krische, *J. Am. Chem. Soc.* **2008**, *130*, 14120–14122; e) S. Omura, T. Fukuyama, J. Horiguchi, Y. Murakami, I. Ryu, *J. Am. Chem. Soc.* **2008**, *130*, 14094–14095; f) J. R. Zbieg, E. Yamaguchi, E. L. McInturff, M. J. Krische, *Science* **2012**, *336*, 324–327.

[16] For recent reviews, see: a) D. B. Grotjahn, *Pure Appl. Chem.* **2010**, *82*, 635–647; b) D. B. Grotjahn, *Dalton Trans.* **2008**, 6497–6508; for selected examples, see: c) C. R. Larsen, D. B. Grotjahn, *J. Am. Chem. Soc.* **2012**, *134*, 10357–10360; d) J. P. Lee, Z. Ke, M. A. Ramírez, T. B. Gunnoe, T. R. Cundari, P. D. Boyle, J. L. Petersen, *Organometallics* **2009**, *28*, 1758–1775; e) D. B. Grotjahn, C. R. Larsen, J. L. Gustafson, R. Nair, A. Sharma, *J. Am. Chem. Soc.* **2007**, *129*, 9592–9593; f) V. Díez, G. Espino, F. A. Jalón, B. R. Manzano, M. Pérez-Manrique, *J. Organomet. Chem.* **2007**, *692*, 1482–1495; g) D. B. Grotjahn, Y. Gong, L. Zakharov, J. A. Golen, A. L. Rheingold, *J. Am. Chem. Soc.* **2006**, *128*, 438–453; h) D. B. Grotjahn, D. A. Lev, *J. Am. Chem. Soc.* **2004**, *126*, 12232–12233; i) S. Harkal, F. Rataboul, A. Zapf, C. Fuhrmann, T. Riermeier, A. Monsees, M. Beller, *Adv. Synth. Catal.* **2004**, *346*, 1742–1748.

[17] For selected recent examples, see: a) C. Cai, S. Yu, G. Liu, X. Zhang, X. Zhang, *Adv. Synth. Catal.* **2011**, *353*, 2665–2670; b) Y. Yan, X. Zhang, X. Zhang, *J. Am. Chem. Soc.* **2006**, *128*, 16058–16061; c) H. Klein, R. Jackstell, M. Beller, *Chem. Commun.* **2005**, 2283–2285; d) D. Selent, D. Hess, K.-D. Wiese, D. Röttger, C. Kunze, A. Börner, *Angew. Chem.* **2001**, *113*, 1739–1741; *Angew. Chem. Int. Ed.* **2001**, *40*, 1696–1698; e) H. Klein, R. Jackstell, K.-D. Wiese, C. Borgmann, M. Beller, *Angew. Chem.* **2001**, *113*, 3505–3508; *Angew. Chem. Int. Ed.* **2001**, *40*, 3408–3411; f) L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Angew. Chem.* **1999**, *111*, 349–351; *Angew. Chem. Int. Ed.* **1999**, *38*, 336–338; g) L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1999**, *18*, 4765–4777.

Received: May 13, 2013
Published online: July 4, 2013

