Carbonylation

DOI: 10.1002/ange.201207133

From Olefins to Alcohols: Efficient and Regioselective Ruthenium-Catalyzed Domino Hydroformylation/Reduction Sequence**

*Ivana Fleischer, Katrin Marie Dyballa, Reiko Jennerjahn, Ralf Jackstell, Robert Franke, Anke Spannenberg, and Matthias Beller**

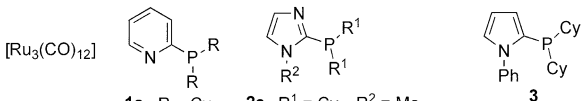
Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

Carbonylation reactions of olefins are among the most important industrially applied homogeneous catalytic transformations.[1] Nowadays, especially, lower aliphatic olefins are converted on a million-ton scale by hydroformylation into aldehydes,[2,3] and further on into aliphatic alcohols, which are used as major components of solvents, plasticizers, speciality chemicals, etc. In general, the linear products are preferred for such large-scale applications, whereas branched aldehydes and alcohols are of interest for the fine chemical and life-science industries.[4] By far the most utilized catalysts for hydroformylation reactions both in industry and academia are based on rhodium; cobalt catalysts are also highly utilized, in particular for the functionalization of higher aliphatic olefins. Other metal catalysts have not received much attention in the past.[5]

During our ongoing research in the field of hydroformylation,[6] we became interested in the activities of alternative hydroformylation catalysts. Notably, the accepted order of catalyst activity (Rh > Co > Ir > Ru > Os > Pt > Pd > Fe > Ni) is solely based on fixed reaction conditions and the use of unmodified metal carbonyl complexes.[2a] More recently, we have demonstrated that metals such as palladium[6c] and iridium[6a] can be successfully applied in the hydroformylation of olefins, as they show improved activity under modified reaction conditions. In the case of iridium, for example, the addition of the required amount of hydrogen at the appropriate reaction temperature proved crucial for the prevention of the undesired competitive hydrogenation of the substrate.

Among all the available noble metals used in catalysts for carbonylation reactions, ruthenium is the least expensive metal, and is also becoming increasingly important in homogeneous catalysis.[7] For hydroformylations, the relative activity of ruthenium carbonyl complexes is assumed to be lower by a factor of 10^5 compared with similar rhodium complexes. Although the first ruthenium-catalyzed hydroformylation, which employed $[Ru(CO)_3(PPh_3)_3]$ as a catalyst, was reported as early as 1965 by Evans, Osborn, Jardine, and Wilkinson,[8] only a few selective Ru-based catalysts have been described in the decades since then.[9] In general, only a narrow substrate scope could be realized with these systems and the reactions were very often carried out under harsh conditions with high catalyst loadings. Typically, mixtures of aldehydes and alcohols were obtained, with higher temperatures preferred for obtaining the alcohols. In addition, hydrogenation and/or isomerization of the olefin occurred as side reactions. Hence, none of these systems was of practical relevance. Notably, very recently Takahashi, Yamashita, Tanaka, and Nozaki demonstrated a highly regioselective catalytic system based on a specific [RuCp*] complex and bidentate ligands for the transformation of olefins to aldehydes.[10] However, the activity of the reported catalysts is considerably lower than that of rhodium-based catalysts.

Herein, we present a novel active ruthenium catalyst system based on $[Ru_3(CO)_{12}]$ and bifunctional ligands of type **1** or **2**.[11] Our system allows for hydroformylation/hydrogenation of olefins to provide selectively linear aliphatic alcohols under reaction conditions typically used in industrial hydroformylations. The resulting products are important intermediates for the chemical industry.[12]



In the initial studies, 1-octene was subjected to the hydroformylation reaction conditions, including $[Ru_3(CO)_{12}]$ (0.6 mol% [Ru]) in *N*-methylpyrrolidone (NMP) at 160 °C, in the presence of synthesis gas (CO/H_2 1:1; 60 bar). Water was employed as an additive because Kalck et al. showed that it

[*] Dr. I. Fleischer, Dr. K. M. Dyballa, Dr. R. Jennerjahn, Dr. R. Jackstell, Dr. A. Spannenberg, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-51113
E-mail: matthias.beller@catalysis.de
Homepage: http://www.catalysis.de
Dr. K. M. Dyballa, Prof. Dr. R. Franke
Evonik Industries AG
Paul-Baumann-Str. 1, 45772 Marl (Germany)
Prof. Dr. R. Franke
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum
44780 Bochum (Germany)

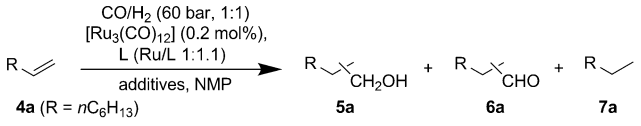
[**] This work has been funded by the Deutsche Forschungsgemeinschaft (Leibniz price), the Swiss National Science Foundation (SNSF, grants for I.F.), and Evonik Oxeno GmbH. We thank Dr. C. Fischer, S. Buchholz, S. Schareina, S. Smyczek, I. Stahr, A. Koch, and Dr. W. Baumann for their technical and analytical support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207133.

facilitates the production of a catalytically active ruthenium hydride species from carboxylato ruthenium complexes.[13] To suppress unwanted hydrogenation of the alkene, we added 0.25 equivalents of LiCl to the reaction mixtures.[14]

Around 20 different mono- and bidentate phosphines and N ligands were tested under these reaction conditions; selected results are shown in Table 1.[15] To our delight, particular bifunctional P,N ligands generated active catalyst

Table 1: Reaction of 1-octene with synthesis gas: Ligand screening.[a]



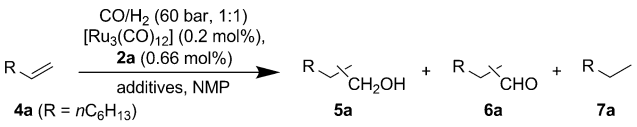
Entry	L	Yield [%][b]		
		5a (*n*/*i*)	**6a** (*n*/*i*)	**4**+**7a**[c]
1	**1a**	52 (58:42)	2[d]	26
2	**1b**	15 (73:27)	20 (60:40)	44
3	**2a**	76 (86:14)	<0.5[d]	7 (**7a**)[e]
4	**2b**	32 (63:37)	17 (35:65)	10
5	**2c**	74 (84:16)	<0.5[d]	5 (**7a**)[e]
6	**2d**	75 (67:33)	3[d]	15
7	**3**	80 (63:37)	<0.5[d]	8 (**7a**)[e]
8	–	21 (71:29)	46 (50:50)	19
9[f]	**2a**	0	0	98 (**4a**)

[a] Reaction conditions: 1-octene (20.0 mmol), $[Ru_3(CO)_{12}]$ (40.0 μmol), LiCl (5.00 mmol), L (132 μmol), H_2O (0.5 mL), NMP (4 mL), CO/H_2 (1:1; 60 bar), 160 °C, 5 h. [b] Determined by GC with 2.0 mL of isooctane as internal standard. [c] **4a**, its isomers, and **7a**. [d] *n*/*i* ratio was not determined. [e] Only *n*-octane (**7a**) was obtained. [f] Without $[Ru_3(CO)_{12}]$. L = ligand.

systems. For example, when ligand **1a** (L/[Ru] 1.1:1) was used the desired C9-alcohols were obtained after 5 h, in 52% yield with *n*/*i* selectivity of 58:42. The use of the less basic ligand **1b** led to higher regioselectivity, but the activity was diminished (Table 1, entry 2). The use of a ligand with an *N*-methylimidazoyl moiety instead of the pyridyl had a surprising effect on both yield (76% yield of C9-alcohols) and regioselectivity (86:14 *n*/*i*; Table 1, entry 3). This bifunctional ligand structure seems to be required to obtain high regioselectivity, as the corresponding phenyl derivatives, for example, phenyldicyclohexyl phosphine, gave only a 60:40 mixture of isomers. Similarly, ligand **3**, which lacks one nitrogen atom in comparison with **2a**, also provided the alcohols in good yield, though with considerably lower regioselectivity (Table 1, entry 7). As expected, the ligand-free system gave inferior results (Table 1, entry 8) and a control reaction performed in the absence of $[Ru_3(CO)_{12}]$ ruled out the possibility of contamination in the autoclave by other hydroformylation active metals (Table 1, entry 9).

The reaction parameters were further optimized for the reaction employing ligand **2a** (Table 2). Here, the aim was to find milder reaction conditions and to minimize side reactions (aldol condensation, etc.), which were observed in the cases when aldehyde reduction was slow. First, the effect of water was studied in more detail.[9a,c,13,16] In the absence of water the yield of the oxo products as well as the *n*/*i* ratio decreased (Table 2, entry 2). However, when the reaction in the absence

Table 2: Reaction of 1-octene with synthesis gas: Optimization of reaction conditions.[a]



Entry	*T* [°C]	*t* [h]	H_2O [mol%]	Yield [%][b]		
				5a (*n*/*i*)	**6a** (*n*/*i*)	**4**+**7a**[c]
1	160	5	140	76 (86:14)	<0.5[d]	7 (**7a**)[e]
2	160	5	0	44 (77:23)	4 (50:50)	14
3	160	5	280	87 (90:10)	2[d]	8 (**7a**)[e]
4	160	5	560	74 (92:8)	3 (67:33)	14
5	130	20	280	90 (88:12)	1[d]	3 (**7a**)[e]
6	120	22	280	78 (90:10)	5 (80:20)	3 (**7a**)[e]
7[f]	130	20	280	37 (95:5)	54 (85:15)	7
8[g]	160	5	0	77 (88:12)	<0.5[d]	5 (**7a**)[e]
9[g]	160	5	140	88 (86:14)	<0.5[d]	5 (**7a**)[e]
10[h]	130	20	280	68 (90:10)	8 (75:25)	6

[a] Reaction conditions: 1-octene (20.0 mmol), $[Ru_3(CO)_{12}]$ (40.0 μmol), LiCl (5.00 mmol), **2a** (132 μmol), H_2O (0.5—2 mL), NMP (3–4 mL), CO/H_2 (1:1; 60 bar). [b] Determined by GC with 2.0 mL isooctane as internal standard. [c] **4a**, its isomers, and **7a**. [d] *n*/*i* ratio was not determined. [e] Only *n*-octane (**7a**) was obtained. [f] No LiCl. [g] Performed with CO/H_2 (1:2; 60 bar). [h] With 0.1 mol% of $[Ru_3(CO)_{12}]$.

of water was carried out with an increased partial pressure of H_2 (CO/H_2 1:2), the yield of the alcohol improved (Table 2, entry 8). Nevertheless, according to GC–MS measurements, aldol condensation side products were formed. With a 1:1 gas mixture, the optimum amount of water was found to be 2.8 equivalents (Table 2, entry 3). Thus, we can conclude that the addition of a suitable amount of water suppresses the formation of side products.

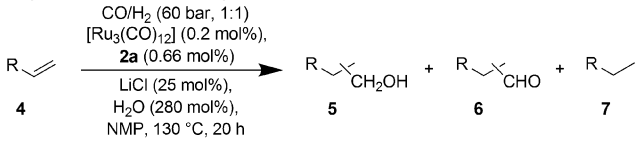
Next, the temperature was lowered to 130 °C (Table 2, entry 5), a temperature that is more common for industrial hydroformylations. Below this temperature, the overall reaction became slower (Table 2, entry 6), which was also the case in the absence of lithium chloride (Table 2, entry 7). Hence, a mixture of aldehydes and alcohols was formed in the absence of lithium chloride. Reduction of the catalyst loading to 0.3 mol% ([Ru]) resulted in lower yield and formation of side products (Table 2, entry 10).

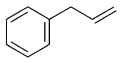
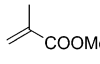
Thus, the optimum performance of the catalyst system was observed at 130 °C in the presence of 0.25 equivalents of LiCl and 2.8 equivalents of water (Table 2, entry 5). The reaction progress was closely examined under these conditions.[15] Gas consumption started at approximately 80 °C. Surprisingly, after 30 min, the reaction rate decreased. To understand this phenomenon, samples were taken out of the reaction mixture and analyzed. The decrease of gas uptake is explained by the slower reduction of the terminal aldehyde and the hydroformylation of the internal olefins compared with the initial hydroformylation of terminal olefin. Remarkably, the initial TOF for the hydrofomylation step reached 200 h^{-1} after 30 min.

Next, the substrate scope and limitations were examined under the optimized reaction conditions (Table 3). Both short- and long-chained terminal alkenes **4a–f** provided the corresponding alcohols in good to excellent yields and with

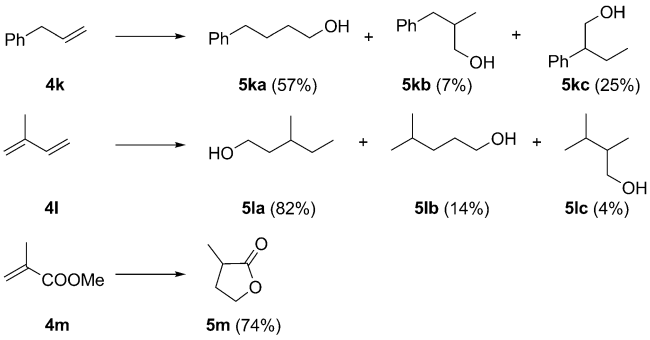
high chemo- and regioselectivities (Table 3, entries 1–6). The lower *n*/*i* ratio of aldehydes can be explained by the faster reduction of *n*-aldehyde. Furthermore, two cyclic alkenes were tested; cyclohexylmethanol was obtained in 79% yield (Table 3, entry 7), whereas cyclooctylmethanol was surprisingly obtained in lower yield (Table 3, entry 8). The more challenging internal alkene, 2-octene (**4i**), was transformed to C9-alcohols in 59% yield and 66:34 *n*/*i* selectivity (Table 3, entry 9). In this case, the conversion of **4i** was not complete and the reduction of aldehydes to alcohols was relatively slower. As a result of the stabilization of the in situ generated benzylic ruthenium complex, lower or even inverted regioselectivity was observed with aryl-substituted alkenes **4j** and **4k** (Table 3, entries 10 and 11; Scheme 1). When isoprene (**4l**) was employed as a substrate, one double bond was hydroformylated and the corresponding aldehyde reduced, whereas the second double bond was hydrogenated (Table 3, entry 12; Scheme 1).

Table 3: Ruthenium-catalyzed domino hydroformylation/hydrogenation sequence: Substrate scope.[a]



Entry	Substrate		5[c] (*n*/*i*)	6 (*n*/*i*)	4[d]	7
			Yield [%][b]			
1		**4a**	90 [81] (88:12)	1[e]	0	3
2		**4b**	82 [75] (89:11)	2[e]	–[f]	–[f]
3		**4c**	85 [83] (89:11)	4 (75:25)	2	6
4		**4d**	88 [81] (89:11)	3 (67:33)	3	6
5[g]		**4e**	83 (85:15)	15 (73:27)	–[f]	–[f]
6		**4f**	>99 [87] (>99:1)	0	–[f]	–[f]
7		**4g**	79 [76]	3	1	0
8		**4h**	28	8	41	2
9		**4i**	59 (66:34)	14 (57:43)	10	5
10		**4j**	83 [80] (40:60)	0	0	10
11[h]		**4k**	89 [85] (64:36)	0	0	9
12[h]		**4l**	>99 [80] (96:4)	0	–[f]	–[f]
13[h]		**4m**	74 [55]	0	0	–[f]

[a] Reaction conditions: lkene(20.0 mmol), $[Ru_3(CO)_{12}]$ (40.0 μmol), LiCl (5.00 mmol), **2a** (132 μmol), H_2O (56 mmol), NMP (3 mL), CO/H_2 (1:1; 60 bar) at 130°C for 20 h. [b] Determined by GC with 2.0 mL of isooctane as internal standard. [c] Yield of the isolated alcohols is given in square brackets. [d] All isomers. [e] *n*/*i* ratio was not determined. [f] Compound(s) not detectable by GC. [g] Performed with 1-butene (103 mmol), $[Ru_3(CO)_{12}]$ (200 μmol), LiCl (25.0 mmol), **2a** (660 μmol), H_2O (275 mmol), NMP (15 mL), under constant pressure CO/H_2 (1:1; 60 bar) at 130°C for 20 h. [h] For products, see Scheme 1.

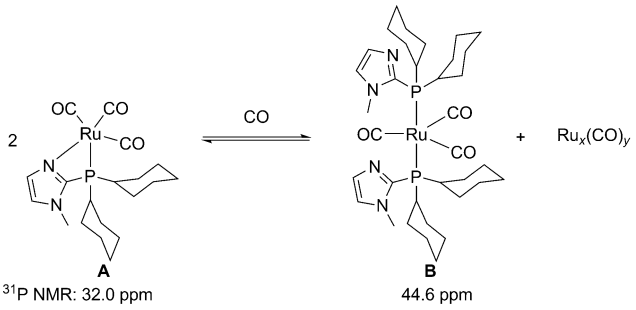


Scheme 1. Hydroformylation/reduction of alkenes **4k**, **4l**, and **4m**. Reaction conditions: alkene (20.0 mmol), $[Ru_3(CO)_{12}]$ (40.0 μmol), LiCl (5.00 mmol), **2a** (132 μmol), H_2O (56 mmol), NMP (3 mL), and CO/H_2 (1:1; 60 bar) at 130°C for 20 h.

Finally, the reaction was carried out with methyl methacrylate (**4m**), which bears an electron-poor double bond. The corresponding lactone **5m** was obtained in good yield (Table 3, entry 13; Scheme 1). This result represents an efficient catalytic synthesis of γ-lactones by a domino hydroformylation/reduction/transesterification reaction sequence.[17]

To investigate the active ruthenium complex involved in the catalysis, a sample of the crude reaction mixture was analyzed by ^{31}P NMR spectroscopy. Two main signals were observed, a major one at 32.0 ppm (**A**) and a minor one at 44.6 ppm (**B**). The same species were obtained when $[Ru_3(CO)_{12}]$ and **2a** were stirred in $[D_8]$toluene at 100°C for 2 h under 30 bar of synthesis gas. As the ratio of signals of **A** and **B** depended on the ratio of [Ru] and **2a**, we assumed that the L/Ru ratio was 1:1 for complex **A** and 2:1 for **B** (Scheme 2). Indeed, we were able to isolate both complexes separately and perform an X-ray analysis of complex **B**. Complex **B** is stable under ambient conditions and contains two P ligands and three CO molecules.[15] On the other hand, complex **A** is unstable in the absence of a CO atmosphere, but its NMR and HRMS analysis show that it contains of only one phosphorous ligand, which likely coordinates in a bidentate fashion.[18]

All attempts to recrystallize complex **A** led to isolation of crystals of **B**. Thus, we propose an equilibrium between **A** and **B**, depending on the presence of carbon monoxide. We



Scheme 2. Structures of ruthenium/**2a** complexes and the proposed equilibrium between them.

believe complex **A** is responsible for the performance of the present catalytic system.

In summary, we have developed an active and selective ruthenium-based catalyst system for the conversion of terminal and internal aliphatic and araliphatic alkenes to linear alcohols by a domino hydroformylation/reduction reaction sequence. Although ruthenium complexes have been largely neglected for carbonylations, this work demonstrates that ruthenium can be an appropriate and promising metal for such reactions. The results presented here constitute a useful alternative to the recently reported rhodium-catalyzed domino hydroformylation/reduction reactions.[19]

Experimental Section

General method for the optimized hydroformylation/reduction of alkenes: A 25 mL steel autoclave was charged under argon atmosphere with $[Ru_3(CO)_{12}]$ (25.6 mg, 40.0 μmol), **2a** (36.7 mg, 132 μmol) and LiCl (212 mg, 5.00 mmol). Then, NMP (3 mL), H_2O (1.0 mL, 1.0 g, 56 mmol), and alkene (20.0 mmol) were added. The autoclave was pressurized with 60 bar CO/H_2 and heated to 130 °C for 20 h. After the reaction time, the autoclave was cooled with ice water and the pressure was released. The crude reaction mixture was analyzed by gas chromatography with isooctane (2.0 mL) as internal standard. For isolation of selected compounds, the solvent was removed by washing the crude reaction mixture with water. Subsequent bulb-to-bulb distillation afforded the desired product.

Received: September 3, 2012
Published online: February 12, 2013

Keywords: alcohols · domino reactions · homogeneous catalysis · hydroformylation · ruthenium

[1] For recent reviews and compendia on carbonylation reactions, see: a) J. Hartwig in *Organotransition Metal Chemistry*, University Science Books, Sausalito, **2010**, pp. 745 – 824; b) *Modern Carbonylation Methods* (Ed.: L. Kollár), Wiley-VCH, Weinheim, **2008**; c) *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Heidelberg, **2006**; d) B. Gabriele, G. Salerno, M. Costa, *Synlett* **2004**, 2468 – 2483; e) *Applied Homogeneous Catalysis with Organometallic Compounds* (Eds.: B. Cornils, W. A. Herrmann), Wiley-VCH, Weinheim, **2002**.

[2] For recent reviews on hydroformylations, see: a) K.-D. Wiese, D. Obst in *Catalytic Carbonylation Reactions* (Ed.: M. Beller), Springer, Heidelberg, **2010**, pp. 1 – 33; b) C. P. Casey, J. Hartwig in *Organotransition Metal Chemistry: From Bonding to Catalysis*, Palgrave Macmillan, **2009**, pp. 751 – 769; c) B. Breit in *Metal Catalyzed Reductive C–C Bond Formation* (Ed.: M. Krische), Springer, Heidelberg, **2007**, pp. 139 – 172; d) P. W. N. M. Van Leeuwen, C. Claver, *Rhodium Catalyzed Hydroformylation*, Springer, Heidelberg, **2000**.

[3] O. Roelen, DE 849548, **1938/1952**; O. Roelen, US 2327066, **1943** (*Chem. Abstr.* **1944**, 3631).

[4] For selected reviews on hydroformylations selective for branched products, 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] For selected recent examples, see: a) M. Gottardo, A. Scarso, S. Paganelli, G. Strukul, *Adv. Synth. Catal.* **2010**, *352*, 2251 – 2262; b) M. Rosales, J. A. Duran, A. Gonzalez, I. Pacheco, R. A. Sanchez-Delgado, *J. Mol. Catal. A* **2007**, *270*, 250 – 256; c) D. Konya, K. Q. Almeida Lenero, E. Drent, *Organometallics* **2006**, *25*, 3166 – 3174; d) E. Mieczyńska, A. M. Trzeciak, J. J. Ziółkowski, I. Kownacki, B. Marciniec, *J. Mol. Catal. A* **2005**, *237*, 246 – 253; e) M. A. Moreno, M. Haukka, A. Turunen, T. A. Pakkanen, *J. Mol. Catal. A* **2005**, *240*, 7 – 15.

[6] For selected examples from our research group, see: a) 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; b) I. Piras, R. Jennerjahn, R. Jackstell, W. Baumann, A. Spannenberg, R. Franke, K.-D. Wiese, M. Beller, *J. Organomet. Chem.* **2010**, *695*, 479 – 486; c) R. Jennerjahn, I. Piras, R. Jackstell, R. Franke, K. D. Wiese, M. Beller, *Chem. Eur. J.* **2009**, *15*, 6383 – 6388; d) R. Jackstell, H. Klein, M. Beller, K.-D. Wiese, D. Röttger, *Eur. J. Org. Chem.* **2001**, 3871 – 3877; e) H. Klein, R. Jackstell, K.-D. Wiese, M. Beller, *Angew. Chem.* **2001**, *113*, 3505 – 3508; *Angew. Chem. Int. Ed.* **2001**, *40*, 3408 – 3411.

[7] For compendia on ruthenium-catalyzed reactions, see: a) *Ruthenium Catalysts and Fine Chemistry*, (Eds.: C. Bruneau, P. H. Dixneuf), Springer, Heidelberg, **2004**; b) S.-I. Murahashi, *Ruthenium in Organic Synthesis*, Wiley-VCH, Weinheim, **2004**.

[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* **1996**, *109*, 219 – 225; c) M. M. Taqui 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] 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) D. B. Grotjahn, C. R. Larsen, J. L. Gustafson, R. Nair, A. Sharma, *J. Am. Chem. Soc.* **2007**, *129*, 9592 – 9593; e) V. Díez, G. Espino, F. A. Jalón, B. R. Manzano, M. Pérez-Manrique, *J. Organomet. Chem.* **2007**, *692*, 1482 – 1495; f) D. B. Grotjahn, Y. Gong, L. Zakharov, J. A. Golen, A. L. Rheingold, *J. Am. Chem. Soc.* **2006**, *128*, 438 – 453; g) D. B. Grotjahn, D. A. Lev, *J. Am. Chem. Soc.* **2004**, *126*, 12232 – 12233; h) S. Harkal, F. Rataboul, A. Zapf, C. Fuhrmann, T. Riermeier, A. Monsees, M. Beller, *Adv. Synth. Catal.* **2004**, *346*, 1742 – 1748.

[12] J. Falbe, H. Bahrmann, W. Lipps, D. Mayer in *Ullmann's Encyclopedia of Industrial Chemistry*, electronic release, *7th ed.*, Wiley-WCH, Weinheim, **2009**.

[13] P. Kalck, M. Siani, J. Jenck, B. Peyrille, Y. Peres, *J. Mol. Catal.* **1991**, *67*, 19 – 27.

[14] a) M.-L. Kontkanen, L. Oresmaa, M. A. Moreno, J. Jänis, E. Laurila, M. Haukka, *Appl. Catal. A* **2009**, *365*, 130 – 134; b) V. K. Srivastava, P. Eilbracht, *Catal. Commun.* **2009**, *10*, 1791 – 1795; c) K.-i. Tominaga, *Catal. Today* **2006**, *115*, 70 – 72; d) K.-I. Tominaga, Y. Sasaki, *J. Mol. Catal. A* **2004**, *220*, 159 – 165; e) M. A. Moreno, M. Haukka, T. A. Pakkanen, *J. Catal.* **2003**, *215*, 326 – 331; f) S. Jääskeläinen, M. Haukka, *Appl. Catal. A* **2003**, *247*, 95 – 100; g) K.-I. Tominaga, Y. Sasaki, *Catal. Commun.* **2000**, *1*, 1 – 3.

[15] For more details, see the Supporting Information.

[16] For ruthenium-catalyzed carbonylations in the presence of water, see: a) J. Jenck, P. Kalck, E. Pinelli, M. Siani, A. Thorez, *J. Chem. Soc. Chem. Commun.* **1988**, 1428 – 1430;

b) H. C. Kang, C. H. Mauldin, T. Cole, W. Slegeir, K. Cann, R. Pettit, *J. Am. Chem. Soc.* **1977**, *99*, 8323 – 8325.

[17] Rhodium-catalyzed synthesis of γ-lactones from homoallylic alcohols by hydroformylation and subsequent oxidation was reported by Grünanger and Breit: C. U. Grünanger, B. Breit, *Angew. Chem.* **2008**, *120*, 7456 – 7459; *Angew. Chem. Int. Ed.* **2008**, *47*, 7346 – 7349.

[18] For evidence on bidentate coordination mode of ligand **2a**, see Ref. [11].

[19] a) D. Fuchs, G. Rousseau, L. Diab, U. Gellrich, B. Breit, *Angew. Chem.* **2012**, *124*, 2220 – 2224; *Angew. Chem. Int. Ed.* **2012**, *51*, 2178 – 2182; b) O. Diebolt, C. Müller, D. Vogt, *Catal. Sci. Technol.* **2012**, *2*, 773 – 777; c) K. Takahashi, M. Yamashita, T. Ichihara, K. Nakano, K. Nozaki, *Angew. Chem.* **2010**, *122*, 4590 – 4592; *Angew. Chem. Int. Ed.* **2010**, *49*, 4488 – 4490; d) I. I. F. Boogaerts, D. F. S. White, D. J. Cole-Hamilton, *Chem. Commun.* **2010**, *46*, 2194 – 2196; e) L. Diab, T. Smejkal, J. Geier, B. Breit, *Angew. Chem.* **2009**, *121*, 8166 – 8170; *Angew. Chem. Int. Ed.* **2009**, *48*, 8022 – 8026.

