Amine Synthesis

DOI: 10.1002/anie.201402368

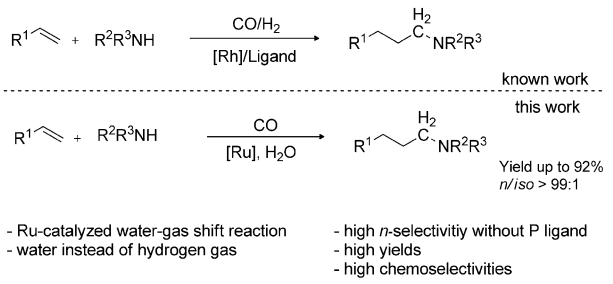
Phosphine- and Hydrogen-Free: Highly Regioselective Ruthenium-Catalyzed Hydroaminomethylation of Olefins**

*Samet Gülak, Lipeng Wu, Qiang Liu, Robert Franke, Ralf Jackstell, and Matthias Beller**

Abstract: *A highly regioselective ruthenium-catalyzed hydroaminomethylation of olefins is reported. Using easily available tririutheniumdodecacarbonyl an efficient sequence consisting of a water-gas shift reaction, hydroformylation of olefins, with subsequent imine or enamine formation and final reduction is realized. This novel procedure is highly practical (ligand-free, one pot) and economic (low catalyst loading and inexpensive metal). Bulk industrial as well as functionalized olefins react with various amines to give the corresponding tertiary amines generally in high yields (up to 92 %), excellent regioselectivities (n/iso > 99:1), and full chemoselectivity in favor of terminal olefins.*

Amines and their derivatives are of substantial importance in the chemical industry and are produced on a multimillion ton scale per year.[1] In particular, aliphatic amines constitute valuable compounds which are used as solvent-free coatings, civil engineering compounds (flooring, patch repair), chemical-resistant tank linings, adhesives, composites, castings, moldings as well as dyes and agrochemicals.[2] Because of their importance many methodologies have been developed for the synthesis of all kinds of amines. Traditionally, nucleophilic substitution reactions of alkyl halides, hydrocyanation/reduction reactions,[3] and reductive amination of carbonyl compounds are the most common routes to aliphatic amines.[4] Despite all the known processes, there is continuing interest in the development of more efficient catalytic routes to this class of products.[5] One of the most promising catalytic syntheses of amines in terms of atom-efficiency, selectivity, and operational practicability is the so-called hydroaminomethylation (HAM) of olefins. This effective domino sequence consists of an initial hydroformylation of alkenes to aldehydes,[6] condensation with amines, and subsequent reduction step. Since its seminal discovery by Reppe in 1949,[7] the past decades have witnessed several developments especially by the groups of Eilbracht[5a,8] and Zhang,[9] as well as ourselves.[10]

Despite all achievements, most of the known catalytic procedures require expensive rhodium catalysts in which the *n*-selectivity is ensured by using a large excess of bidentate phosphine ligands like Naphos and Xantphos derivatives. Hence, it is of interest that recent examples of ruthenium-catalyzed C–C bond-formation reactions[11] were reported and showed their potential in hydroformylation reactions.[12] Nevertheless, powerful alternatives to rhodium-catalyzed HAMs have been rarely reported.[13] Last year our group presented a general protocol for a highly *n*-selective ruthenium-catalyzed HAM using syngas.[14] Here, the use of special imidazole-substituted phosphine ligands was essential for achieving high yields and regioselectivites. Based on our continuing interest in the development of practical and economic procedures for the synthesis of amines, we herein present a general hydrogen-free ruthenium-catalyzed HAM system (Scheme 1). Notably, excellent regioselectivities are obtained without any phosphine ligands present.[15]



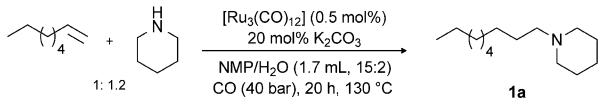
Scheme 1. Selective ruthenium-catalyzed HAM with water as the hydrogen source.

Our initial studies were carried out with 1-octene and piperidine as a model reaction and the results are summarized in Table 1.[16] Notably, HAM reactions proceeded similarly well when using either syngas or CO in water. To our surprise the regioselectivity for 1-nonylpiperidine under water-gas shift conditions were outstanding. The use of various P ligands did not additionally improve the *n*-selectivity. A moderate product yield was obtained with NMP (NMP = *N*-methyl-2-pyrrolidone) as the solvent and 0.5 mol % $[Ru_3(CO)_{12}]$ in the presence of 20 mol % K_2CO_3 as the base (entry 1). Other solvents and solvent mixtures led to lower yields (entries 2 and 3). The amount of base can be reduced to

[*] Dr. S. Gülak,[+] L. Wu,[+] Dr. Q. Liu, Dr. R. Jackstell, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e. V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: matthias.beller@catalysis.de
Prof. Dr. R. Franke
Evonik Industries AG
Paul-Baumann-Strasse 1, 45772 Marl (Germany)
and Lehrstuhl für Theoretische Chemie, 44780 Bochum (Germany)
[+] These authors contributed equally to this work.

[**] We are particularly grateful to the Bundesministerium für Bildung und Forschung for financial support under the PROFORMING project (No. 03X3559) and the Chinese Scholarship council (grants for L.W.). Q.L. thanks the Alexander von Humboldt Foundation for financial support. We thank Dr. C. Fischer, S. Buchholz, S. Schareina, A. Koch, Dr. W. Baumann, Dr. N. Rockstroh, and P. Bartels for their technical and analytical support.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402368.

Table 1: Variation of reaction parameters.[a]



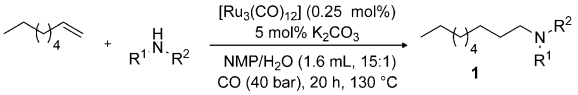
Entry	$[Ru_3(CO)_{12}]$ [mol%]	Variation from standard conditions	Yield [%][b]	*n*/*iso*[b]
1	0.5	–	61	97:3
2	0.5	Tol/MeOH/H_2O (8:8:2)	34	97:3
3	0.5	MeCN/H_2O (15:2)	55	98:2
4	0.5	without water	10	96:4
5	0.5	without K_2CO_3	49	97:3
6	0.5	5 mol% K_2CO_3	60	97:3
7	–	5 mol% K_2CO_3	0	–
8	0.5	5 mol% K_2CO_3, 1:1.3[c]	63	97:3
9	0.5	5 mol% K_2CO_3, 1.3:1[c]	75	97:3
10	0.5	5 mol% K_2CO_3, 1.3:1,[c] NMP/H_2O (15:1)	81	97:3
11	0.25	5 mol% K_2CO_3, 1.3:1,[c] NMP/H_2O (15:1)	**81**, 53[d] 71,[e] 45[f]	**97:3**

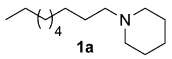
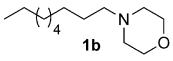
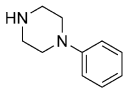
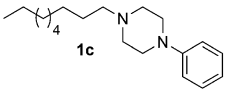
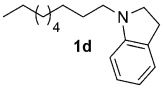
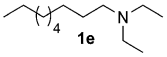
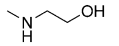
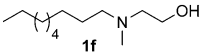
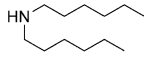
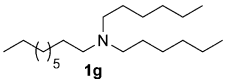
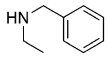
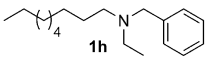
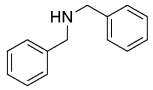
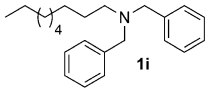
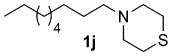
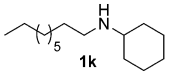
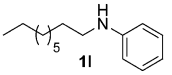
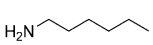
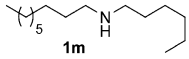
[a] Reaction conditions: $[Ru_3(CO)_{12}]$ (0.5 mol%), 1-octene (1 mmol), piperidine (1.2 mmol) in THF/H_2O (15:2 v/v, 1.7 mL), K_2CO_3 (20 mol%), CO (40 bar), 130°C, 20 h. [b] Determined by GC. [c] 1-octene/piperidine. [d] 20 bar CO. [e] 140°C. [f] 100°C.

5 mol% (entry 6). Control experiments showed that the ruthenium catalyst and water are essential for the reaction (entries 4 and 7). Notably, the reaction without base showed lower, but still significant activity (entry 5).[17] This activity is explained by the presence of the basic amines which also serve as organic bases in the reaction.[18] Considering the fact that internal olefins barely react under these reaction conditions and 1-octene slowly underwent isomerization, it was beneficial to use a slight excess of the olefin (entry 9), whereas an excess of piperidine led to a lower yield (entry 8).[19] The water concentration in the reaction is of relevance, too. By lowering the amount of water, the yield was increased to 81% (entry 10). It is worth noting that higher catalyst loadings (1 mol%) did not increase the yields, and lowering the catalyst loading (0.25 mol%) led to the same result (entry 11). Neither the variation of the CO pressure nor the temperature could improve upon the reaction (entry 11).

With the optimized reaction conditions in hand, we explored the substrate scope and potential applications of our protocol (Table 2). First, reactions of 1-octene with various secondary and primary amines were studied. With cyclic secondary amines like piperidine, morpholine, 1-phenylpiperazine, and 2,3-dihydroindole as starting materials, high yields (72–82%) and excellent regioselectivities (*n*-selectivity up to 97%) were achieved (entries 1–4). Acyclic amines like diethylamine, more bulky amines like dibenzylamine, and the alcoholic substrate (2-methylamino)ethanol led to similar yields (72–80%) and regioselectivities (entries 5–9). However, primary amines such as aniline, 1-hexaneamine, or cyclohexylamine gave somewhat lower yields (22–45%; entries 11–13). GC analysis indicated a selectivity problem resulting from consecutive reactions of the secondary amine products. In all cases mixtures of the secondary and tertiary amines were observed. Our efforts to

Table 2: Hydroaminomethylations of 1-octene with various amines.[a]



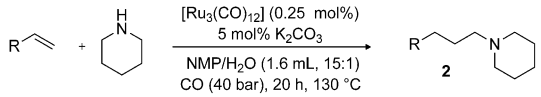
Entry	Amines	Major product	Yield [%][b]	*n*/*iso*[b]
1		 **1a**	82	97:3
2		 **1b**	76	96:4
3		 **1c**	72[c]	97:3
4		 **1d**	75	97:3
5		 **1e**	80[c]	97:3
6		 **1f**	72	98:2
7		 **1g**	75	97:3
8		 **1h**	73[c]	97:3
9		 **1i**	77[c]	98:2
10		 **1j**	0	–
11		 **1k**	44	95:5
12		 **1l**	45	95:5
13		 **1m**	24	95:5

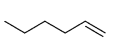
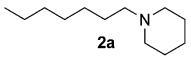
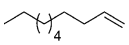
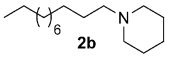
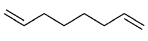
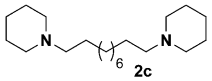
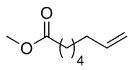
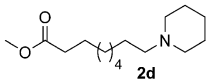
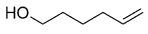
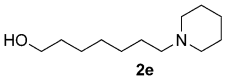
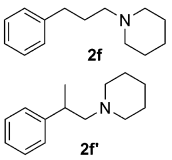
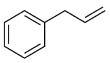
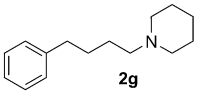
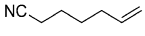
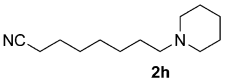
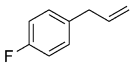
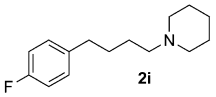
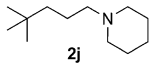
[a] Reaction conditions: $[Ru_3(CO)_{12}]$ (0.25 mol%), 1-octene (1.3 mmol), amine (1.0 mmol) in THF/H_2O (15:1 v/v, 1.6 mL), K_2CO_3 (5 mol%), CO (40 bar), 130°C, 20 h. [b] Determined by GC. [c] Yield of isolated product.

increase the selectivity towards the tertiary or the secondary product, by variation of the olefin to amine ratio (olefin to amine 1:1 or 2.6:1), did not give superior results. Nevertheless the *n*-selectivity is still high.

Then, the reactions of bulk industrial as well as functionalized olefins with piperidine were studied (Table 3). Substituted linear terminal olefins like 1-hexene and higher analogues gave generally high yields and *n*-selectivities (entries 1 and 2). A double HAM of 1,7-octadiene gave an interesting diamine in a similar manner (entry 3). Various functionalized linear olefins were tested, too. Olefins containing ester, alcohol, and nitrile groups were efficiently converted into the amines (73–86%; entries 4, 5, and 8). Interestingly, in these cases excellent chemoselectivity is obtained and no amide formation or alcohol amination is observed. Styrene provided a 70:30 mixture of amine isomers but a very high overall yield (entry 6). It is expected that

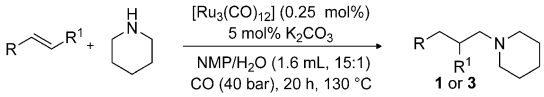
Table 3: Hydroaminomethylations of various alkenes with piperidine.[a]

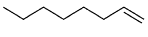
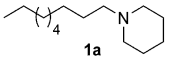
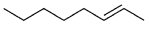
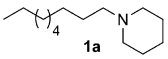
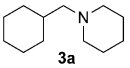
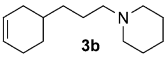
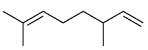
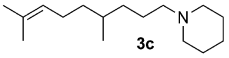


Entry	Alkene	Major product	Yield [%][b]	*n*/*iso*[b]
1		 **2a**	81	97:3
2		 **2b**	80	97:3
3		 **2c**	70[d]	93:7
4		 **2d**	73	98:2
5		 **2e**	83	97:3
6		 **2f** **2f'**	92[e]	30:70
7		 **2g**	92	90:10
8		 **2h**	86[c]	95:5
11		 **2i**	90[c]	90:10
12		 **2j**	82[c]	>99:1

[a] Reaction conditions: $[Ru_3(CO)_{12}]$ (0.25 mol%), alkene (1.3 mmol), piperidine (1.0 mmol), THF:H_2O (15:1 v/v, 1.6 mL), K_2CO_3 (5 mol%), CO (40 bar), 130°C, 20 h. [b] Determined by GC. [c] Yield of isolated product. [d] 1,7-octadiene (1.3 mmol), piperidine (2 mmol). [e] Combined yield.

Table 4: Selective hydroaminomethylations of terminal and internal olefins.[a]



Entry	Alkene	Major product	Yield [%][b]	*n*/*iso*[b]
1		 **1a**	82	97:3
2		 **1a**	10 11[e]	85:15 86:14
3		 **3a**	<2	–
4		 **3b**	90[c]	>99:1[d]
5		 **3c**	77[c]	>99:1[d]

[a] Reaction conditions: $[Ru_3(CO)_{12}]$ (0.25 mol%), 1-octene (1.3 mmol), amine (1.0 mmol) in THF/H_2O (15:1 v/v, 1.6 mL), K_2CO_3 (5 mol%), CO (40 bar), 130°C, 20 h. [b] Determined by GC. [c] Yield of isolated product. [d] Greater than 99% chemoselectivity in favor of the terminal alkene. [e] 0.5 mol% $[Ru_3(CO)_{12}]$ and 1 mol% 2-(dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole.

styrene forms a π-allyl intermediate stabilized by ruthenium, and results in lower *n*-selectivity. However, allylbenzene and the fluoro-substituted analogue gave comparable yields to that of styrene, but with much higher *n*-selectivies (entries 7 and 11). As an example of a sterically hindered substrate, neohexene led to the corresponding amine in excellent yield with greater than 99% *n*-selectivity (entry 12).

After achieving good activity with various terminal alkenes, we turned our attention to the HAM of internal olefins and dienes. As shown before, internal olefins barely react under the optimized reaction conditions. Hence, 2-octene gave significantly lower yields than 1-octene (Table 4, entries 1 and 2). Surprisingly, the *n*-selectivity is still comparably high. To promote the formation of the more reactive terminal olefin by isomerization, we decided to use 2-(dicyclohexylphosphino)-1-phenyl-1*H*-pyrrole as a ligand, which is known to promote isomerization reactions.[20] Unfortunately, this attempt did not result in a higher yield of the amine; instead larger amounts of internal olefins were detected. In accordance with these results, cyclic olefins like cyclohexene gave a low yield of the amine product (entry 3). Gratifyingly, the poor reactivity of internal olefins allows the chemoselective transformation of olefins containing both internal and terminal double bonds. Thus, highly chemoselective HAMs in favor of the terminal double bond were possible with 4-vinylcyclohexene and β-citronellene (entries 4 and 5). In both cases the linear amine products were formed exclusively in high yields and excellent *n*-selectivities.

Finally, some mechanistic experiments were performed. To get more insight into the domino sequence, we analyzed the composition of the reaction solution and the gas phase. The ruthenium-catalyzed water-gas shift reaction produces carbon dioxide and hydrogen. The latter is used initially in the ruthenium-catalyzed hydroformylation reaction. After base-promoted condensation reaction with the amine the corresponding imine/enamine intermediate is formed. Subsequent hydrogenation led to the final product. At no period of the reaction could we detect the aldehyde or the imine/enamine intermediate, thus indicating that the hydroformylation step is rate determining. This assumption is supported by the detection of excess amounts of hydrogen and carbon dioxide in the gas phase after 3 hours.

In conclusion, we have developed the first general protocol for a hydrogen-free ruthenium-catalyzed HAM reaction. Contrary to established hydroformylation methodologies this reaction provides high yields (up to 92%) and

excellent regioselecitvities (*n/iso* > 99:1) without the use of any P ligands. The broad applicability is demonstrated by the conversion of various alkenes into structurally interesting linear amines. The reactions display tolerance of alcohol, ester, nitrile, and halide substituents. Moreover, chemoselective HAMs of terminal olefins can be achieved in the presence of internal double bonds, thus allowing the selective conversion of multiple unsaturated substrates, even alkene mixtures. Additionally, this novel protocol is an operationally simple, economical, and practical one-pot procedure.

Experimental Section

General procedure: Experiments were carried out in 4 mL reaction vials which were placed in a Parr stainless steel autoclave. The reaction vial was charged with $[Ru_3(CO)_{12}]$ (0.25 mol%), alkene (1.3 mmol), amine (1.0 mmol), degased water (0.1 mL), and NMP (1.5 mL) under argon atmosphere. The autoclave was pressurized with 40 bar CO 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 as an internal standard. For isolation the product was extracted with diethyl ether from the mixture and NMP was removed by washing with water. After drying and removing the solvent the crude raction mixture was purified by column chromatography on silica gel (gradient elution using hexanes/ethyl acetate).

Received: February 13, 2014
Published online: May 23, 2014

Keywords: amines · chemoselectivity · homogeneous catalysis · ruthenium · synthetic methods

[1] *Chem. Mark. Rep.* **1998**, December, 7.
[2] S. A. Lawrence, *Amines: Synthesis, Properties and Applications*, Cambridge University Press, Cambridge, **2004**.
[3] a) A. P. V. Göthlich, M. Tensfeldt, H. Rothfuss, M. E. Tauchert, D. Haap, F. Rominger, P. Hofmann, *Organometallics* **2008**, *27*, 2189 – 2200; b) L. Bini, C. Müller, J. Wilting, L. von Chrzanowski, A. L. Spek, D. Vogt, *J. Am. Chem. Soc.* **2007**, *129*, 12622 – 12623; c) T. V. RajanBabu, A. L. Casalnuovo, *J. Am. Chem. Soc.* **1996**, *118*, 6325 – 6326.
[4] a) O.-Y. Lee, K.-L. Law, D. Yang, *Org. Lett.* **2009**, *11*, 3302 – 3305; b) R. I. Storer, D. E. Carrera, Y. Ni, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2006**, *128*, 84 – 86; c) T. Gross, A. M. Seayad, M. Ahmad, M. Beller, *Org. Lett.* **2002**, *4*, 2055 – 2058.
[5] a) P. Eilbracht, C. L. Kranemann, L. Bärfacker, *Eur. J. Org. Chem.* **1999**, 1907 – 1914; b) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675 – 703.
[6] a) X. Jia, Z. Wang, C. Xia, K. Ding, *Chem. Eur. J.* **2012**, *18*, 15288 – 15295; b) O. Diebolt, C. Muller, D. Vogt, *Catal. Sci. Technol.* **2012**, *2*, 773 – 777; c) D. Crozet, M. Urrutigoïty, P. Kalck, *ChemCatChem* **2011**, *3*, 1102 – 1118; d) E. Zuidema, L. Escorihuela, T. Eichelsheim, J. J. Carbo, C. Bo, P. C. Kamer, P. W. van Leeuwen, *Chem. Eur. J.* **2008**, *14*, 1843 – 1853; e) A. Polo, C. Claver, S. Castillon, A. Ruiz, J. C. Bayon, J. Real, C. Mealli, D. Masi, *Organometallics* **1992**, *11*, 3525 – 3533.
[7] a) W. Reppe, H. Vetter, *Liebigs Ann. Chem.* **1953**, *582*, 133 – 163.
[8] a) M. Beigi, S. Ricken, K. S. Müller, F. Koç, P. Eilbracht, *Eur. J. Org. Chem.* **2011**, 1482 – 1492; b) M. A. Subhani, K.-S. Müller, P. Eilbracht, *Adv. Synth. Catal.* **2009**, *351*, 2113 – 2123; c) F. Koç, M. Wyszogrodzka, P. Eilbracht, R. Haag, *J. Org. Chem.* **2005**, *70*, 2021 – 2025.
[9] a) G. Liu, K. Huang, B. Cao, M. Chang, S. Li, S. Yu, L. Zhou, W. Wu, X. Zhang, *Org. Lett.* **2012**, *14*, 102 – 105; b) G. Liu, K. Huang, C. Cai, B. Cao, M. Chang, W. Wu, X. Zhang, *Chem. Eur. J.* **2011**, *17*, 14559 – 14563.
[10] a) M. Ahmed, R. P. J. Bronger, R. Jackstell, P. C. J. Kamer, P. W. N. M. van Leeuwen, M. Beller, *Chem. Eur. J.* **2006**, *12*, 8979 – 8988; b) M. Ahmed, A. M. Seayad, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2003**, *125*, 10311 – 10318; c) A. Seayad, M. Ahmed, H. Klein, R. Jackstell, T. Gross, M. Beller, *Science* **2002**, *297*, 1676 – 1678.
[11] a) E. L. McInturff, J. Mowat, A. R. Waldeck, M. J. Krische, *J. Am. Chem. Soc.* **2013**, *135*, 17230 – 17235; b) B. Y. Park, T. P. Montgomery, V. J. Garza, M. J. Krische, *J. Am. Chem. Soc.* **2013**, *135*, 16320 – 16323; c) D. C. Schmitt, J. Lee, A.-M. R. Dechert-Schmitt, E. Yamaguchi, M. J. Krische, *Chem. Commun.* **2013**, *49*, 6096 – 6098; d) J. R. Zbieg, E. Yamaguchi, E. L. McInturff, M. J. Krische, *Science* **2012**, *336*, 324 – 327; e) S. Omura, T. Fukuyama, J. Horiguchi, Y. Murakami, I. Ryu, *J. Am. Chem. Soc.* **2008**, *130*, 14094 – 14095; f) F. Shibahara, J. F. Bower, M. J. Krische, *J. Am. Chem. Soc.* **2008**, *130*, 14120 – 14122; g) T. Kondo, M. Akazome, Y. Tsuji, Y. Watanabe, *J. Org. Chem.* **1990**, *55*, 1286 – 1291; h) P. Isnard, B. Denise, R. P. A. Sneeden, J. M. Cognion, P. Durual, *J. Organomet. Chem.* **1982**, *240*, 285 – 288.
[12] For ruthenium-catalyzed hydroformylation, see: a) K. Takahashi, M. Yamashita, Y. Tanaka, K. Nozaki, *Angew. Chem.* **2012**, *124*, 4459 – 4463; *Angew. Chem. Int. Ed.* **2012**, *51*, 4383 – 4387; b) K. Takahashi, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2012**, *134*, 18746 – 18757; c) for hydroformylation/reduction, see: I. Fleischer, K. M. Dyballa, R. Jennerjahn, R. Jackstell, R. Franke, A. Spannenberg, M. Beller, *Angew. Chem. Int. Ed.* **2013**, *52*, 2949 – 2953; *Angew. Chem.* **2013**, *125*, 3021 – 3025; d) L. Wu, I. Fleischer, R. Jackstell, I. Profir, R. Franke, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 14306 – 14312.
[13] H. Schaffrath, W. Keim, *J. Mol. Catal. A* **1999**, *140*, 107 – 113.
[14] L. Wu, I. Fleischer, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 3989 – 3996.
[15] a) F. Jachimowicz, J. W. Raksis, *J. Org. Chem.* **1982**, *47*, 445 – 447; b) Y. Chen, F. Zhang, C. Xu, J. Gao, D. Zhai, Z. Zhao, *J. Phys. Chem. A* **2012**, *116*, 2529 – 2535.
[16] For full screening data see the Supporting Information.
[17] For references on WGSR applications: a) A. Tlili, J. Schranck, H. Neumann, M. Beller, *Chem. Eur. J.* **2012**, *18*, 15935 – 15939; b) R. B. King, *J. Organomet. Chem.* **1999**, *586*, 2 – 17; c) P. C. Ford, *Acc. Chem. Res.* **1981**, *14*, 31 – 37; d) C. Ungermann, V. Landis, S. A. Moya, H. Cohen, H. Walker, R. G. Pearson, R. G. Rinker, P. C. Ford, *J. Am. Chem. Soc.* **1979**, *101*, 5922 – 5929; e) R. B. King, C. C. Frazier, R. M. Hanes, A. D. King, Jr., *J. Am. Chem. Soc.* **1978**, *100*, 2925 – 2927.
[18] P. Aguirre, S. A. Moya, R. Sariego, H. Le Bozec, A. J. Pardey, *Appl. Organomet. Chem.* **2002**, *16*, 597 – 600.
[19] Around 30% of the isomerized octenes were observed. See the Supporting Information.
[20] R. Jennerjahn, I. Piras, R. Jackstell, R. Franke, K.-D. Wiese, M. Beller, *Chem. Eur. J.* **2009**, *15*, 6383 – 6388.

