ChemPubSoc Europe

DOI: 10.1002/chem.201502982

CHEMISTRY A European Journal Communication

Organic Chemistry

Efficient Domino Hydroformylation/Benzoin Condensation: Highly Selective Synthesis of α-Hydroxy Ketones

Kaiwu Dong,[a] Rui Sang,[a, b] Jean-Francois Soule,[b] Christian Bruneau,[b] Robert Franke,[c, d] Ralf Jackstell,[a] and Matthias Beller*[a]

Abstract: An improved domino hydroformylation/benzoin condensation to give α-hydroxy ketones has been developed. Easily available olefins are smoothly converted into the corresponding α-hydroxy ketones in high yields with excellent regioselectivities. Key to success is the use of a specific catalytic system consisting of a rhodium/phosphine complex and the CO_2 adduct of an N-heterocyclic carbene.

Hydroformylation reactions, which produce aliphatic aldehydes from olefins and syngas, constitute the most important homogeneous transition-metal-catalyzed processes in the chemical industry.[1] Due to the versatile chemistry of the aldehyde group,[2] in recent decades this transformation has been combined with other reactions in a one-pot manner.[3–7] Such tandem sequences follow a general trend in green chemistry considering the advantageous step economy.[4] In this respect, the development of productive novel or improved domino hydroformylation reactions has a great appeal for organic chemists. In fact, hydroformylation/reduction (hydrohydroxymethylation),[5] hydroformylation/reductive amination (hydroaminomethylation),[6] and hydroformylation/aldol condensation[7] have become powerful synthetic methods in organic synthesis.

Combination of hydroformylation and benzoin condensation would allow for a straightforward and atom-efficient access to α-hydroxy ketones directly from easily available olefins and CO/H_2. The resulting products constitute important organic intermediates which can be further functionalized to valuable amines, diols, epoxides, or deoxygenated compounds.[8] In order to realize a domino hydroformylation/benzoin condensation sequence, the development of a suitable catalyst system is crucial. While hydroformylations are known to be catalyzed in the presence of various rhodium, cobalt, ruthenium, and palladium complexes, benzoin condensations are known to be catalyzed by bases or carbenes. Since the first isolation by Arduengo and co-workers in 1991,[9] N-heterocyclic carbenes (NHCs) have not only become versatile ligands in organometallic chemistry,[10] but also used as organocatalysts in various organic transformations such as benzoin condensation,[11] the Stetter reaction,[12] cyanosilylation,[13] transesterification,[14] and other reactions.[15, 11c] Owing to their sensitivity,[16] NHCs are generally in situ produced from the corresponding (dihydro)imidazolium salts by deprotonation with a strong base. Unfortunately, this method is not applicable for base-sensitive substrates/products in most cases. Therefore, more stable NHC adducts with haloalkanes,[17] alcohols,[18] silver,[19] CO_2,[20] and H_2CO_3[21] have been developed to liberate NHCs on demand under base-free conditions. Among these masked NHCs, zwitterionic (dihydro)imidazolium-2-carboxylates ((H_2)IMes-CO_2) gain much attention owing to their accessibility, good stability, and easy generation of the respective free NHCs.[13b, 14b, 20c]

A general problem for the use of NHCs in domino hydroformylation/benzoin condensations is the competitive coordination of such δ-donor ligands to the transition-metal catalyst, for example, Rh^I or Ru^{II}, needed for the hydrofomylation step. Very recently, Vorholt and co-workers reported the first tandem hydroformylation/benzoin reaction using the rhodium/BiPhePhos and vitamin B_1 (in situ generated from its corresponding hydrochloride salt and Et_3N) as the catalytic system.[22] Herein, we present a more general combination of a specific rhodium/phosphine complex and H_2IMes-CO_2, which allow for hydroformylation/benzoin condensation of various aliphatic olefins, providing linear α-hydroxy ketones in high yields with excellent regioselectivities (Scheme 1).

In cooperation with industry, we demonstrated earlier on that H_2IMes-CO_2 adduct **C1** is an efficient organocatalyst for benzoin condensations of various aldehydes under base-free conditions.[23] Consequently, in our initial studies we investigated the domino hydroformylation/benzoin condensation of 1-octene (**1a**) with **C1** and [Rh(acac)$(CO)_2$] (acac = acetylacetone) in the presence of different phosphine ligands (Table 1, entries 2–8). Under standard conditions (80 °C, 20 h, THF), without phosphine ligand no conversion of **1a** was observed (entry 1).

[a] Dr. K. Dong,[+] R. Sang,[+] Dr. R. Jackstell, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: Matthias.Beller@catalysis.de

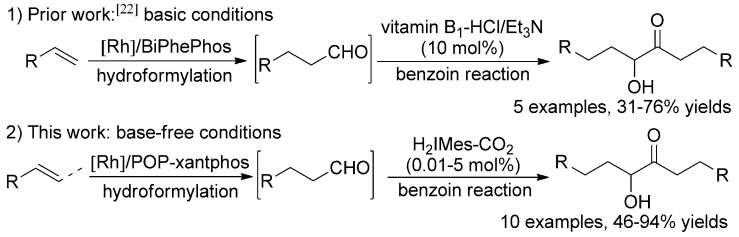
[b] R. Sang,[+] Prof. Dr. J.-F. Soule, Prof. Dr. C. Bruneau
Institut Sciences Chimiques de Rennes, UMR 6226
CNRS-Université de Rennes "Organométalliques: Matériaux et Catalyse"
Campus de Beaulieu, 35042 Rennes (France)

[c] Prof. Dr. R. Franke
Evonik Performance Materials GmbH
Paul-Baumann-Str. 1, 45772 Marl (Germany)

[d] Prof. Dr. R. Franke
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum
44780 Bochum (Germany)

[+] These authors contributed equally to this work.

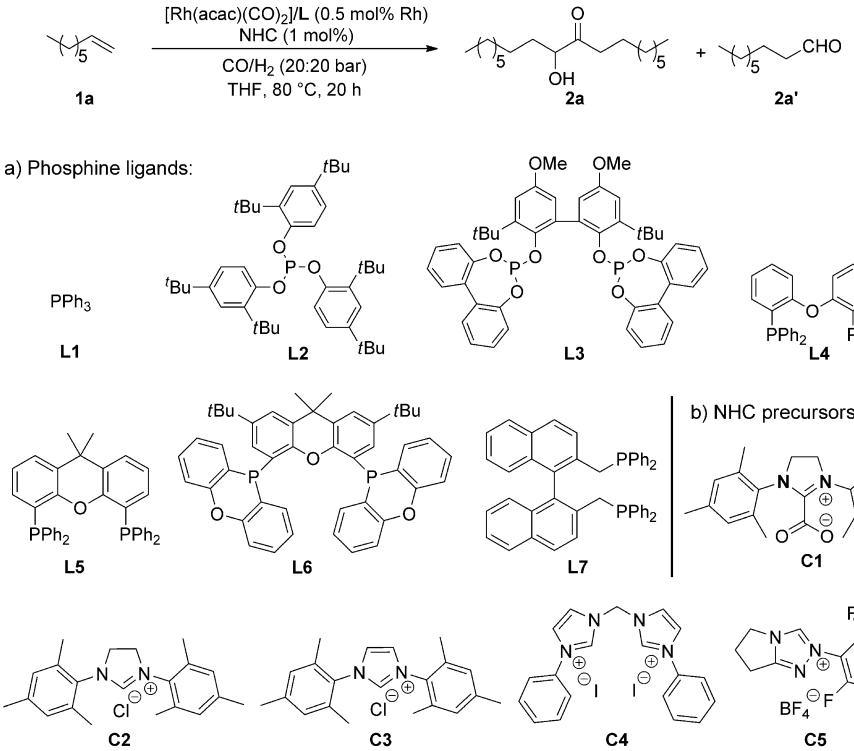
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/chem.201502982.



Scheme 1. Domino hydroformylation/benzoin condensations of olefins.

Applying triphenylphosphine **L1** afforded the benzoin product **2a** in poor yield, while using a standard phosphite ligand (tris(2,4-di-*tert*-butylphenyl) phosphite) **L2** only gave the aldehyde product **2a'** (Table 1, entries 2 and 3). Gratefully, the yields of **2a** were improved significantly in the presence of bidentate phosphines (Table 1, entries 4–8, **L3**–**L7**). For example, applying bulky and electron-poor ligand **L3** (BiPhePhos) provided the desired product **2a** in 57% yield with 96:4 regioselectivity (entry 4), which is in agreement with the recent results from Vorholt and co-workers.[22] Notably, bulky and electron-rich ligand **L6** (POP-xantphos) showed better performance (entry 7, 76% yield, 98:2 *n*/*iso*). With other bidentate ligands, such as **L4** (DPEphos), **L5** (Xantphos), and **L7** (Naphos), the benzoin product **2a** was achieved in moderate yields (entries 5, 6, and 8). There is no obvious effect when the ratio of [Rh(acac)(CO)$_2$]/**L6** was

Table 1. Domino hydroformylation/benzoin condensation: Investigation of phosphine ligands and NHC precursors.[a]



Entry	L	NHC	**2a** (yield [%], *n*/*iso*)	**2a′** (yield [%], *n*/*iso*)
1	0	**C1**	0	0
2	**L1**	**C1**	6 (90:10)	32 (53:47)
3	**L2**	**C1**	0	89 (57:43)
4	**L3**	**C1**	57 (96:4)	12 (83:17)
5	**L4**	**C1**	26 (93:7)	41 (73:27)
6	**L5**	**C1**	58 (93:7)	16 (82:18)
7	**L6**	**C1**	76 (98:2)	18 (76:24)
8	**L7**	**C1**	67 (96:4)	17 (70:30)
9	**L6**	**C1**	77 (97:3)	16 (76:24)
10[b]	**L6**	**C1**	86 (97:3)	5 (11:89)
11[b]	**L6**	**C2**/DBU (1:8)	40 (86:14)	40 (72:28)
12[b]	**L6**	**C3**/DBU (1.8)	29 (83:17)	50 (77:23)
13[b]	**L6**	**C4**/DBU (1:8)	77 (94:6)	2 (0:100)
14[b]	**L6**	**C5**/DBU (1:8)	76 (94:6)	2 (0:100)

[a] Reaction conditions: [Rh(acac)(CO)$_2$] (2.5 mg, 0.5 mol%), **L1**–**L2** (2.0 mol%) or **L3**–**L7** (1.0 mol%), **C1** (7 mg, 1.0 mol%) or **C2**–**C5**/DBU (1/8 mol%), **1a** (0.32 mL, 2.0 mmol), CO/H$_2$ (20/20 bar), THF (2.0 mL), 80 °C, 20 h. The yields and regioselectivities of **2a** and **2a′** were determined by GC analysis using isooctane as an internal standard. [b] Heptane (2 mL) was used instead of THF (2 mL). DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

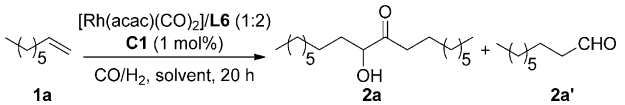
changed from 1:1 to 1:2 (entry 9). Considering these results, especially the different catalytic activities between monodentate and bidentate ligands, we assume that the carbene ligand competes with the phosphine ligand in the coordination to the Rh^{I} center. Apparently, the resulting Rh^{I}/carbene complexes show only poor activity in this domino reaction.

With the optimal metal catalyst [Rh(acac)$(CO)_2$]/**L6** in hand, the influence of other NHC precursors on the domino hydroformylation/benzoin condensation was investigated (Table 1, entries 11–14). By contrast, with H_2IMes-chloride **C2** as organocatalyst instead of **C1** (H_2IMes-CO_2 adduct), the yield of the benzoin product **2a** decreased dramatically (entry 10 vs. 11). This is also true for **C3**. However, applying biimidazolium iodide **C4** or triazolium tetrafluoroborate **C5** as the organocatalyst afforded the product **2a** in high yields with very high regioselectivities (entries 13 and 14).

To improve the yield of **2a** further on, additional reaction parameters, such as solvent, reaction temperature, and the pressure of syngas, were varied in the presence of [Rh(acac)$(CO)_2$]/**L6** and **C1** (Table 2). In addition to THF, the reaction proceeded smoothly in other nonprotonic solvents including toluene, ethyl acetate, and heptane, and the product **2a** was obtained in good yields (Table 2, entries 1–4, 70–86% yields and 97:3—98:2 *n/iso*). On the other hand, no product **2a** was detected when methanol was used as the solvent (entry 5). The yield of **2a** was not affected when this domino sequence was carried out at 60–100 °C (entries 7 and 8). However, below 40 °C hydroformylation of 1-octene **1a** did not proceed (entry 6), while above 120 °C the organocatalyst is deactivated (entry 9). The pressure of syngas was also examined and no obvious effect was observed on the domino hydroformylation/benzoin condensation of **1a** (entry 10). Notably, even in the presence of 0.1 mol% of Rh^{I} complex and 0.2 mol% of **C1** the product **2a** could be achieved in 80% yield and 98:2 regioselectivity (entry 11).

Next, the compatibility and limitations of olefins in our domino hydroformylation/benzoin condensations were examined. Besides the model substrate **1a**, important bulk olefins such as ethylene **1b** and propylene **1c** also reacted smoothly, affording the corresponding products **2b** and **2c** in good yields (Table 3, entries 3 and 4). For ethylene (gramscale), the

Table 2. Domino hydroformylation/benzoin coupling reaction: Investigation of reaction conditions.[a]

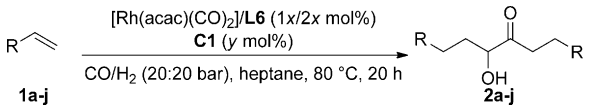


1a 2a 2a'

Entry	Solvent	*T* [°C]	**2a** (yield [%], *n/iso*)	**2a**′ (yield [%], *n/iso*)
1	THF	80	76 (98:2)	18 (76:24)
2	toluene	80	80 (98:2)	10 (41:58)
3	EA	80	70 (97:3)	15 (46:54)
4	heptane	80	86 (97:3)	5 (11:89)
5	MeOH	80	0	57 (90:10)
6	heptane	40	0	0
7	heptane	60	83 (98:2)	3 (0:100)
8	heptane	100	83 (97:3)	12 (16:84)
9	heptane	120	73 (98:2)	25 (42:58)
10[b]	heptane	80	85 (98:2)	5 (10:90)
11[c]	heptane	80	80 (98:2)	6 (12:88)

Reaction conditions: [a] [Rh(acac)$(CO)_2$] (2.5 mg, 0.5 mol%), **L6** (14.4 mg, 1.0 mol%), **C1** (7 mg, 1.0 mol%), **1a** (0.32 mL, 2.0 mmol), CO/H_2 (20:20 bar), solvent (2.0 mL), 20 h. The yields and regioselectivities of **2a** and **2a**′ were determined by GC analysis using isooctane as an internal standard. [b] CO/H_2 (10:10 bar). [c] [Rh(acac)$(CO)_2$] (0.1 mol%), **L6** (0.2 mol%), **C1** (0.2 mol%), **1a** (20 mmol), heptane (10 mL). EA = ethyl acetate.

Table 3. Domino hydroformylation/benzoin condensation of olefins.[a]



1a-j 2a-j

Entry	Olefin **1a–j**	*x*, *y*	product **2a–j**	**2a–j** (yield [%], *n/iso*)
1	**1a**	0.5, 1		**2a** (85, 98:2)
2[b]	**1a**	0.1, 0.2		**2a** (80, 98:2)
3[c]	**1b**	0.01, 0.1		**2b** (84, –)
4[d]	**1c**	0.1, 0.3		**2c** (86, 93:7)
5	**1d**	0.5, 1		**2d** (80, 99:1)
6	**1e**	0.5, 1		**2e** (84, 95:5)
7	**1f**	0.5, 1		**2f** (86, 99:1)
8	**1g**	0.5, 1		**2g** (94, 97:3)
9	**1h**	0.5, 1		**2h** (88, 96:4)
10	**1i**	0.5, 1		**2i** (61, 97:3)
11[e]	**1j**	2, 5		**2j** (46, 93:7)

Reaction conditions: [a] [Rh(acac)$(CO)_2$]/**L6** (1*x*/2*x* mol%), **C1** (*y* mol%), **1** (2.0 mmol), CO/H_2 (20:20 bar), heptane (2.0 mL), 80 °C, 20 h. Isolated yields. The regioselectivities were determined by GC analysis. [b] **1a** (20 mmol), heptane (10 mL), the yield was determined by GC analysis using isooctane as an internal standard. [c] **1b** (54 mmol), heptane (20 mL). [d] **1c** (80 mmol), heptane (20 mL). [e] [Rh(acac)$(CO)_2$] (2 mol%), **L3** (4 mol%) was used instead of **L6** (1 mol%), **C1** (5 mol%), 80 °C, 20 h.

Rh^{I} and **C1** catalyst loading can be decreased to as low as 0.01 and 0.1 mol%, which demonstrated the efficiency of these reactions. *tert*-Butyl-substituted ethylene **1d** was well-tolerated and gave **2d** in good yield with excellent linear selectivity (entry 5). Applying allylbenzene **1e** and olefins containing functional groups such as silyl, chloro, and dimethyl acetal the corresponding products **2e**–**i** were achieved in moderate to good yields with very good regioselectivities (entries 6–10). Interestingly, 2-octene **1j** also worked with our catalytic system using **L3** instead of **L6** with higher catalyst loading, and the product **2j** was obtained in 46% yield with 93:7 regioselectivity for the linear product (entry 11). To the best of our knowledge, this is the first example of a selective domino isomerization/hydroformylation/benzoin condensation sequence.

In order to get some mechanistic information on the rate of the individual steps of this domino transformation, the hydroformylation/benzoin condensation of the benchmark system (1-octene (**1a**)) was investigated in more detail. As shown in Figure 1, the time–yield plot of this reaction provides useful information. 90% of 1-octene (**1a**) was consumed within 4 h. Although the yield of nonanal, hydroformylation product of **1a**, increased during the first 0.5 h to 8%, it is reduced afterwards due to the relatively faster benzoin condensation. In fact, after 1.5 h, only 1% yield of nonanal is detected. These observations clearly indicate that the hydroformylation of **1a** is the rate-determining step in this domino sequence.

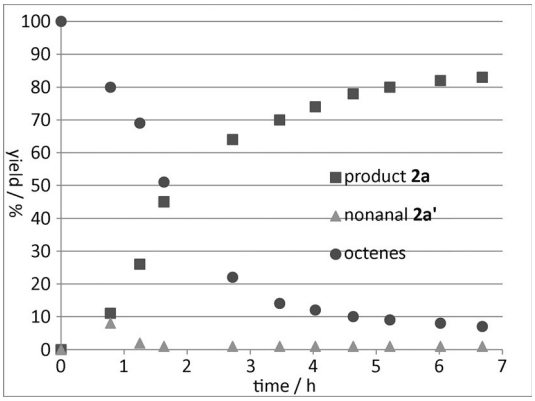


Figure 1. Compound distribution in the domino hydroformylation/benzoin condensation of 1-octene (**1a**). Reaction conditions: [Rh(acac)(CO)$_2$] (0.1 mol%), **L6** (0.2 mol%), **C1** (0.5 mol%), **1a** (20 mmol), isooctane (3.0 mL), CO/H$_2$ (20/20 bar), heptane (20 mL), 80 °C.

In conclusion, we developed a general and efficient domino hydroformylation/benzoin condensation of aliphatic olefins. In the presence of [Rh(acac)(CO)$_2$]/**L6** and an organocatalyst (**C1**, H$_2$IMes-CO$_2$), various readily available olefins are converted into the desired α-hydroxy ketones in good yields with excellent regioselectivities for the linear products. Apart from the selectivity, the high atom-efficiency and the low catalyst loading make this domino transformation attractive for organic synthesis and might allow for potential applications in industry.

Experimental Section

General procedure for Table 3

Under an argon atmosphere, vial (4 mL) was charged with [Rh(acac)(CO)$_2$] (2.5 mg, 0.5 mol%), **L6** (14.4 mg, 1.0 mol%), **C1** (7.0 mg, 1.0 mol%), and a stirring bar. Then heptane (2.0 mL) and **1** (2.0 mmol) were injected by the syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H$_2$ 1:1) three times, and then pressurized with syngas to 40 bar. The reaction was performed at 80 °C for 20 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. The regioselectivity was measured by GC analysis. After removing the solvent under vacuum, the residue was directly purified by flash chromatography on silica gel (eluent: heptane/ethyl acetate = 10:1) to give the desired product **2**.

Acknowledgements

This work has been funded by Evonik Industries and the BMBF (Germany). We thank Dr. C. Fischer and her colleagues for their technical and analytical support. K. Dong thanks the Shanghai Institute of Organic Chemistry-Zhejiang Medicine joint fellowship for financial support. R. Sang thanks Fondation Rennes 1 for financial support.

Keywords: benzoin condensation · catalysis · domino reactions · hydroformylation · olefins

[1] a) M. Beller, B. Cornils, C. D. Frohning, C. W. Kohlpaintner, *J. Mol. Catal. A* **1995**, *104*, 17–85; b) P. W. N. M. van Leeuwen, C. Claver, *Rhodium Catalyzed Hydroformylation*, Springer, Berlin, **2000**; c) B. Breit in *Metal Catalyzed Reductive C–C Bond Formation* (Ed.: M. Krische), Springer, Berlin, **2007**, pp. 139–172; d) R. Franke, D. Selent, A. Börner, *Chem. Rev.* **2012**, *112*, 5675–5732.

[2] S. Patai, *The Chemistry of the Carbonyl Group*, Wiley, New York, **1966**, **1970**.

[3] a) B. Breit, S. K. Zahn, *Angew. Chem. Int. Ed.* **1999**, *38*, 969–971; *Angew. Chem.* **1999**, *111*, 1022–1024; b) P. Eilbracht, L. Bärfacker, C. Buss, C. Hollmann, B. E. Kitsos-Rzychon, C. L. Kranemann, T. Rische, R. Roggenbuck, A. Schmidt, *Chem. Rev.* **1999**, *99*, 3329–3366; c) B. Breit, S. K. Zahn, *Angew. Chem. Int. Ed.* **2001**, *40*, 1910–1913; *Angew. Chem.* **2001**, *113*, 1964–1967; d) P. Eilbracht, A. M. Schmidt, *Top. Organomet. Chem.* **2006**, *18*, 65–95; e) J. Stiller, A. J. Vorholt, K. A. Ostrowski, A. Behr, M. Christmann, *Chem. Eur. J.* **2012**, *18*, 9496–9499; f) K. Dong, X. Fang, R. Jackstell, M. Beller, *Chem. Commun.* **2015**, *51*, 5059–5062.

[4] a) T.-L. Ho, *Tandem Organic Reactions*, Wiley, New York, **1992**; b) L. F. Tietze, U. Beifuss, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–163; *Angew. Chem.* **1993**, *105*, 137–170; c) R. A. Bunce, *Tetrahedron* **1995**, *51*, 13103–13159; d) L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115–136.

[5] a) 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; b) L. Wu, I. Fleischer, R. Jackstell, I. Profir, R. Franke, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 14306–14312; c) Y. Yuki, K. Takahashi, Y. Tanaka, K. Nozaki, *J. Am. Chem. Soc.* **2013**, *135*, 17393–17400; d) Q. Liu, L. Wu, I. Fleischer, D. Selent, R. Franke, R. Jackstell, M. Beller, *Chem. Eur. J.* **2014**, *20*, 6888–6894; for recent "noncarbonylative" protocols of hydrohydroxymethylation and hydroaminomethylation, see: e) B. Sam, B. Breit, M. J. Krische, *Angew. Chem. Int. Ed.* **2015**, *54*, 3267–3274; *Angew. Chem.* **2015**, *127*, 3317–3325; f) S. Oda, B. Sam, M. J. Krische, *Angew. Chem. Int. Ed.* **2015**, *54*, 8525–8528; *Angew. Chem.* **2015**, *127*, 8645–8648.

[6] a) B. Zimmermann, J. Herwig, M. Beller, *Angew. Chem. Int. Ed.* **1999**, *38*, 2372 – 2375; *Angew. Chem.* **1999**, *111*, 2515 – 2518; b) A. Seayad, M. Ahmed, H. Klein, R. Jackstell, T. Gross, M. Beller, *Science* **2002**, *297*, 1676 – 1678; c) M. Ahmed, A. M. Seayad, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2003**, *125*, 10311 – 10318; d) D. Crozet, M. Urrutigoity, P. Kalck, *ChemCatChem* **2011**, *3*, 1102 – 1118; e) G. Liu, K. Huang, B. Cao, M. Chang, S. Li, S. Yu, L. Zhou, W. Wu, X. Zhang, *Org. Lett.* **2012**, *14*, 102 – 105; f) L. Wu, I. Fleischer, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2013**, *135*, 3989 – 3996.

[7] a) X. Fang, R. Jackstell, A. Börner, M. Beller, *Chem. Eur. J.* **2014**, *20*, 15692 – 15696; b) X. Fang, R. Jackstell, R. Franke, M. Beller, *Chem. Eur. J.* **2014**, *20*, 13210 – 13216.

[8] a) W. Adam, M. Lazarus, C. R. Saha-Möller, P. Schreier, *Acc. Chem. Res.* **1999**, *32*, 837 – 845; b) J. G. Uranga, A. F. Chiosso, A. N. Santiago, *RSC Adv.* **2013**, *3*, 11493 – 11497.

[9] a) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361 – 363; b) A. J. Arduengo, *Acc. Chem. Res.* **1999**, *32*, 913 – 921.

[10] a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290 – 1309; *Angew. Chem.* **2002**, *114*, 1342 – 1363; b) R. H. Crabtree, *Coord. Chem. Rev.* **2007**, *251*, 595 – 896; c) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122 – 3172; *Angew. Chem.* **2008**, *120*, 3166 – 3216; d) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561 – 3598; e) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940 – 6952; *Angew. Chem.* **2010**, *122*, 7094 – 7107.

[11] a) D. Enders, U. Kallfass, *Angew. Chem. Int. Ed.* **2002**, *41*, 1743 – 1745; *Angew. Chem.* **2002**, *114*, 1822 – 1824; b) Y. Hachisu, J. W. Bode, K. Suzuki, *J. Am. Chem. Soc.* **2003**, *125*, 8432 – 8433; c) D. M. Flanigan, F. Romanov-Michailidis, N. A. White, T. Rovis, *Chem. Rev.* **2015**, DOI: 10.1021/acs.chemrev.5b00060.

[12] a) M. S. Kerr, J. Read deAlaniz, T. Rovis, *J. Am. Chem. Soc.* **2002**, *124*, 10298 – 10299; b) M. Christmann, *Angew. Chem. Int. Ed.* **2005**, *44*, 2632 – 2634; *Angew. Chem.* **2005**, *117*, 2688 – 2690.

[13] a) G. M. Pawar, M. R. Buchmeiser, *Adv. Synth. Catal.* **2010**, *352*, 917 – 928; b) M. Fèvre, P. Coupillaud, K. Miqueu, J.-M. Sotiropoulos, J. Vignolle, D. Taton, *J. Org. Chem.* **2012**, *77*, 10135 – 10144.

[14] a) P. U. Naik, L. Petitjean, K. Refes, M. Picquet, L. Plasseraud, *Adv. Synth. Catal.* **2009**, *351*, 1753 – 1756; b) J. Pinaud, J. Vignolle, Y. Gnanou, D. Taton, *Macromolecules* **2011**, *44*, 1900 – 1908.

[15] a) D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606 – 5655; b) N. Marion, S. Díez-González, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 2988 – 3000; *Angew. Chem.* **2007**, *119*, 3046 – 3058; c) X. Bugaut, F. Glorius, *Chem. Soc. Rev.* **2012**, *41*, 3511 – 3522.

[16] a) M. K. Denk, J. M. Rodezno, S. Gupta, A. J. Lough, *J. Organomet. Chem.* **2001**, *617*, 242 – 253; b) O. Hollóczki, P. Terleczky, D. Szieberth, G. Mourgas, D. Gudat, L. Nyulászi, *J. Am. Chem. Soc.* **2011**, *133*, 780 – 789.

[17] a) T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 2546 – 2558; b) M. S. Viciu, F. K. Zinn, E. D. Stevens, S. P. Nolan, *Organometallics* **2003**, *22*, 3175 – 3177; c) G. W. Nyce, S. Csihony, R. M. Waymouth, J. L. Hedrick, *Chem. Eur. J.* **2004**, *10*, 4073 – 4079.

[18] a) D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021 – 1023; *Angew. Chem.* **1995**, *107*, 1119 – 1122; b) J. P. Morgan, R. H. Grubbs, *Org. Lett.* **2000**, *2*, 3153 – 3155; c) M. S. Viciu, G. A. Grasa, S. P. Nolan, *Organometallics* **2001**, *20*, 3607 – 3612; d) O. Coulembier, A. P. Dove, R. C. Pratt, A. C. Sentman, D. A. Culkin, L. Mespouille, P. Dubois, R. M. Waymouth, J. L. Hedrick, *Angew. Chem. Int. Ed.* **2005**, *44*, 4964 – 4968; *Angew. Chem.* **2005**, *117*, 5044 – 5048; e) S. Csihony, D. A. Culkin, A. C. Sentman, A. P. Dove, R. M. Waymouth, J. L. Hedrick, *J. Am. Chem. Soc.* **2005**, *127*, 9079 – 9084.

[19] A. C. Sentman, S. Csihony, R. M. Waymouth, J. L. Hedrick, *J. Org. Chem.* **2005**, *70*, 2391 – 2393.

[20] a) H. A. Duong, T. N. Tekavec, A. M. Arif, J. Louie, *Chem. Commun.* **2004**, 112 – 113; b) A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2007**, *129*, 12834 – 12846; c) H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu, X.-B. Lu, *J. Org. Chem.* **2008**, *73*, 8039 – 8044; d) B. R. Van Ausdall, J. L. Glass, K. M. Wiggins, A. M. Aarif, J. Louie, *J. Org. Chem.* **2009**, *74*, 7935 – 7942.

[21] M. Fèvre, J. Pinaud, A. Leteneur, Y. Gnanou, J. Vignolle, D. Taton, K. Miqueu, J.-M. Sotiropoulos, *J. Am. Chem. Soc.* **2012**, *134*, 6776 – 6784.

[22] K. A. Ostrowski, T. A. Faßbach, A. J. Vorholt, *Adv. Synth. Catal.* **2015**, *357*, 1374 – 1380.

[23] R. Jackstell, I. Jovel, M. Beller, M. Hateley, C. Weckbecker, K. Huthmacher, PCT Int. Appl., WO 2008019927A1 20080221, **2008**.

Received: July 29, 2015
Published online on October 27, 2015