Angewandte
International Edition Chemie

VIP Homogeneous Catalysis Very Important Paper

DOI: 10.1002/anie.201400456

Towards a Sustainable Synthesis of Formate Salts: Combined Catalytic Methanol Dehydrogenation and Bicarbonate Hydrogenation**

*Qiang Liu, Lipeng Wu, Samet Gülak, Nils Rockstroh, Ralf Jackstell, and Matthias Beller**

Abstract: *Formate salts are important chemicals widely used in everyday products. The current industrial-scale manufacture of formates requires CO at high pressure and harsh reaction conditions. Herein, we describe a new process for these products without the utilization of hazardous gases and chemicals. By application of ruthenium pincer complexes, a simultaneous methanol dehydrogenation and bicarbonate hydrogenation reaction proceeds, which provides a green synthesis of formate salts with excellent TON (>18000), TOF (>1300 h^{-1}), and yield (>90%).*

Formate salts are widely applied in various industrial processes and represent important products of our daily life. For example, sodium formate is frequently used in fabric dyeing and printing processes. It is also employed as a buffering reagent for strong mineral acids, as a drilling fluid, and as a food additive as well.[1] Moreover, potassium formate is considered to be a more environmentally benign de-icing salt.[2] Currently, the industrial-scale production of sodium formate proceeds by absorbtion of carbon monoxide under high pressure in solid sodium hydroxide at 160°C [Scheme 1, Eq. (1)].[3] Clearly, this process relies on the use of hazardous and flammable carbon monoxide, which is also difficult to transport on a bulk scale. On a small scale, sodium formate has been prepared by reacting chloroform or chloral hydrate with sodium hydroxide in alcoholic solution [Scheme 1, Eq. (2)]. Salt formation and the use of toxic substrates restrict the further application of this process on a large scale. More recently, in the context of the development of hydrogen-storage materials,[4] formate salts have been also obtained through the hydrogenation of bicarbonates[5] or carbon dioxide in hydroxide solution[6] [Scheme 1, Eqs. (3) and (4)]. In principle, these protocols represent a green process for the synthesis of formate salts, in which only water is generated as the by-product. Notably, excellent catalyst turnover numbers (TONs) were achieved for the hydrogenation of carbon dioxide in hydroxide solution as well.[6] However, the yields of these reactions are usually below 80%. As a result, it is difficult to isolate pure formate salts from the reaction mixtures. In addition, hydrogen (and carbon dioxide in some cases) at high pressures is needed to facilitate the desired reaction. Hence, the development of novel and more efficient processes for formate synthesis remains highly desired.

$$\mathrm{NaOH + CO \xrightarrow{160\,^{\circ}C} HCOONa} \qquad (1)$$

$$\mathrm{CHCl_3 + 4\,NaOH \longrightarrow HCOONa + 3\,NaCl + 2\,H_2O} \qquad (2)$$

$$\mathrm{NaHCO_3 + H_2 \xrightarrow{[M]} HCOONa + H_2O} \qquad (3)$$

$$\mathrm{NaOH + CO_2 + H_2 \xrightarrow{[M]} HCOONa + H_2O} \qquad (4)$$

$$\mathbf{2\,MHCO_3 + MeOH + MOH \xrightarrow{[Ru]} 3\,HCOOM + 2\,H_2O} \qquad \mathbf{(5)}$$

M = Na, K

This work

Scheme 1. Various synthetic routes to formate salts.

Very recently, we developed the first ruthenium-catalyzed alkoxycarbonylation of alkenes with carbon dioxide and alcohols. In this reaction carbon dioxide is reduced by the alcohols through transfer hydrogenation to carbon monoxide.[7] Moreover, ruthenium-pincer-complex-catalyzed dehydrogenation of methanol[8] and dehydrogenative transformation of alcohols to carboxylic acid salts[9] in basic aqueous solution were developed by our group and Milstein's group, respectively. Inspired by these achievements, we envisioned that the transfer hydrogenation of bicarbonate with methanol should be feasible. In our concept bicarbonate constitutes an ideal hydrogen acceptor for the methanol dehydrogenation to formate since the same product (formate) can be formed from bicarbonate hydrogenation and methanol dehydrogenation. Herein, we describe the first ruthenium-based PNP-pincer-complex-catalyzed reaction combining methanol dehydrogenation and bicarbonate hydrogenation [Scheme 1, Eq. (5)], which provides a green process for the sustainable synthesis of formate salts with excellent TON (>18000), TOF (>1300 h^{-1}), and yield (>90%).

The Ru-MACHO complex **1**[10] (the structure is shown in Table 2, entry 1) catalyzes the dehydrogenation of methanol under basic conditions. In an open reaction system three molecules of hydrogen and one molecule of carbonate salt are generated.[8] For the preparative synthesis of formates the dehydrogenation sequence has to be selectively stopped at this intermediate and carefully controlled.[11] Thus, at the start of our investigations, the dehydrogenation reaction of methanol was studied in the presence of sodium hydroxide at 100°C in a closed system (100 mL autoclave). Under such

---

[*] Dr. Q. Liu, L. Wu, Dr. S. Gülak, Dr. N. Rockstroh, Dr. R. Jackstell, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: matthias.beller@catalysis.de

[**] This research was funded by the State of Mecklenburg-Vorpommern, the BMBF, and the DFG (Leibniz Prize). We thank Dr. W. Baumann, Dr. C. Fischer, S. Buchholz, S. Schareina, A. Koch, and S. Rossmeisl (all at LIKAT) for their excellent technical and analytical support. Q.L. thanks the Alexander von Humboldt Foundation for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201400456.

conditions the dehydrogenation of formate should be more difficult due to the in situ generated hydrogen pressure. Indeed, the desired product, sodium formate, was produced with a TON of 130 (Table 1, entry 1). The TON was further increased to 746 when sodium bicarbonate was introduced as a hydrogen acceptor (Table 1, entry 2). These results demonstrated the feasibility of our concept [Scheme 1, Eq. (5)]. To our delight, the catalytic activity is retained after addition of water to the reaction system (Table 1, entry 3). From a practical point of view it is important to note that the tolerance of water will not only improve the solubility of larger amounts of substrates, but also ensure the possibility of methanol recycling without a drying process to remove the water generated in this reaction.

Table 1: Synthesis of sodium formate through the dehydrogenation of methanol.[a]

$$\mathrm{NaHCO_3} + \mathrm{NaOH} + \mathrm{MeOH} \xrightarrow[100\,^{\circ}\mathrm{C},\ 20\ \mathrm{h}]{\text{Ru-MACHO}} \mathrm{HCOONa}$$

Entry	*n* ($NaHCO_3$) [mmol]	*n* (NaOH) [mmol]	*V* (MeOH/H_2O) [mL]	TON[b]
1	0	30	30/0	130
2	20	30	30/0	746
3	20	30	25/5	769

[a] Reaction conditions: 100 mL autoclave, Ru-MACHO complex (10 μmol), 100 °C, 20 h. [b] TON = mmol HCOONa/mmol Ru catalyst.

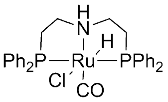
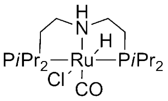
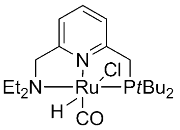
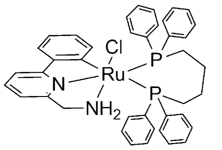
To further prove that sodium bicarbonate can act as a hydrogen acceptor and generate sodium formate in this reaction, the Ru-MACHO-catalyzed hydrogenation of sodium bicarbonate in methanol under 10 bar of hydrogen at 100 °C was performed [Scheme S1 in the Supporting Information, Eq. (1)]. A TON of 1420 is obtained after 20 h. Additionally, under the same conditions, no sodium formate is formed in the absence of H_2 [Scheme S1, Eq. (2)]. When THF is used as the solvent instead of methanol, a TON of 758 is acquired as well [Scheme S1, Eq. (3)]. These results indicate that the hydrogenation of sodium bicarbonate proceeds smoothly in our designed sodium formate synthesis by methanol reforming.

In recent years, a variety of ruthenium pincer complexes have been proven to be efficient catalysts for the dehydrogenation of alcohols.[8,12] Therefore, a selection of different ruthenium pincer complexes was tested for their activities in the target reaction. We found that HPNP^{iPr}/Ru complex **2**,[12d] Milstein's catalyst **3**,[13] and Baratta's catalyst **4**[14] also showed activity, albeit somewhat lower than that of the Ru-MACHO complex **1** (Table 2, entries 1–4). Other ruthenium catalysts known to be efficient for the hydrogenation of bicarbonates and carbon dioxide had much lower activity (Table 2, entries 5–7). The blank reaction without ruthenium catalyst did not lead to any conversion under the given reaction conditions (Table 2, entry 8).

Based on the reaction conditions from entry 3 in Table 1, we screened other reaction parameters to improve the efficiency of this transformation to a more practical level (Table 3). Reducing the catalyst loading from 10 to 5 μmol resulted in an increased TON of 880, however only with 9 % yield (Table 3, entry 1). Better TONs were observed with higher amounts of sodium bicarbonate and/or sodium hydroxide (Table 3, entries 2–4). The best catalyst TON was obtained at a NaOH/$NaHCO_3$ ratio of 1:3 (Table 3, entry 3). Additional sodium bicarbonate prevents the generation of desired product because the methanol dehydrogenation is less effective at lower pH (Table 3, entry 4). Additionally, increasing the reaction temperature resulted in improved TONs (Table 3, entries 5 and 6). A TON of 3266 with 20 % yield was achieved at 150 °C (Table 3, entry 6).

Table 2: Synthesis of sodium formate from sodium bicarbonate, sodium hydroxide, and methanol: Variation of ruthenium catalysts.[a]

$$\mathrm{NaHCO_3} + \mathrm{NaOH} + \mathrm{MeOH} \xrightarrow[100\,^{\circ}\mathrm{C},\ 20\ \mathrm{h}]{\text{Ru-Catalyst}} \mathrm{HCOONa}$$

Entry	Ru catalyst		TON[b]
1		**1**	746
2		**2**	190
3		**3**	183
4		**4**	302
5	[$RuCl_2$(benzene)]$_2$/dppm		0
6	[$RuCl_2$(benzene)]$_2$/dppe		103
7	Ruh(OAc)(PPh_3)$_3$		0
8	no catalyst		0

[a] Reaction conditions: 100 mL autoclave, Ru-MACHO complex (10 μmol), $NaHCO_3$ (20 mmol), NaOH (30 mmol), MeOH (30 mL), 100 °C, 20 h. [b] TON = mmol HCOONa/mmol Ru catalyst.

Table 3: Synthesis of sodium formate from sodium bicarbonate, sodium hydroxide and methanol: Variation of reaction parameters.[a]

$$\mathrm{NaCO_3} + \mathrm{NaOH} + \mathrm{MeOH} \xrightarrow[100\,^{\circ}\mathrm{C},\ 20\ \mathrm{h}]{\text{Ru-MACHO}} \mathrm{HCOONa}$$

Entry	*n* ($NaHCO_3$) [mmol]	*n* (NaOH) [mmol]	TON[b]	Yield [%][c]
1	20	30	880	9
2	60	30	1647	9
3	20	60	2568	16
4	60	60	1498	6
5[d]	20	60	2611	16
6[e]	20	60	3266	20

[a] Reaction conditions: 100 mL autoclave, Ru-MACHO complex (5 μmol), MeOH/H_2O (25/5 mL), 100 °C, 20 h. [b] TON = mmol HCOONa/mmol Ru-catalyst. [c] Yield = mmol HCOONa/mmol ($NaHCO_3$ + NaOH). [d] The reaction temperature is 130 °C. [e] The reaction temperature is 150 °C.

Performing the reaction for the potassium formate synthesis indicated that the catalyst TON was dramatically increased to 12380 with 77% yield (Table 4, entry 1) under the same reaction conditions as in entry 6 of Table 3. In the early stages of the reaction, a TOF of 1346 h^{-1} (after 4 h) is reached (Table 4, entry 2). As shown in entry 3 of Table 4, a lower reaction temperature resulted in considerably lower yield and TON (28% and 4481, respectively). Decreased TONs and yields were gained with lower amounts of potassium bicarbonate, which illustrates its important role as a hydrogen acceptor to promote this transformation (Table 4, entries 4 and 5). However, a greater amount of potassium bicarbonate decreased the reaction efficiency as well due to the lower pH value of the reaction system as mentioned above (Table 4, entries 6 and 7). Most significantly, a combination of 20 mmol potassium bicarbonate and 80 mmol potassium hydroxide afforded a TON of 18422 with up to 92% yield in aqueous methanol (Table 4, entry 5). The ^{13}C NMR spectrum of the final product indicates that there is no potassium bicarbonate remaining and no potassium carbonate generated after reaction (Figure S3). To the best of our knowledge, this result is superior to any reported example for the direct catalytic hydrogenation of bicarbonates to formates even under high pressure of hydrogen gas.

Table 4: Synthesis of potassium formate from potassium bicarbonate, potassium hydroxide, and methanol: Variation of reaction parameters.[a]

$$KHCO_3 + KOH + MeOH \xrightarrow[150\,^{\circ}C,\ 20\ h]{\text{Ru-MACHO}} HCOOK$$

Entry	*n* ($KHCO_3$) [mmol]	*n* (KOH) [mmol]	TON[b]	Yield [%][c]
1	20	60	12380	77
2	20	60	5384 (4 h)	33
3[d]	20	60	4481	28
4	0	60	8108	68
5	10	60	10185	73
6	40	60	9523	48
7	60	60	9428	39
8[e]	**20**	**80**	**18422**	**92**

[a] Reaction conditions: 100 mL autoclave, Ru-MACHO complex (5 μmol), MeOH/H_2O (25/5 mL), 150°C, 20 h. [b] TON = mmol HCOOK/mmol Ru catalyst. [c] Yield = mmol HCOOK/mmol ($KHCO_3$ + KOH). [d] The reaction temperature is 130°C. [e] The reaction time is 36 h.

Interestingly, carbon dioxide serves also as a suitable hydrogen acceptor for this transformation (Table 5). Hence, 80 mmol of potassium hydroxide reacted with 5 bar (about 20 mmol) carbon dioxide affording high TON and yield (Table 5, entries 1 and 2). Under otherwise identical conditions, additional carbon dioxide suppressed this transformation (Table 5, entry 3). The reaction was completely shut down by almost equal amounts of carbon dioxide and potassium hydroxide (Table 5, entry 4).

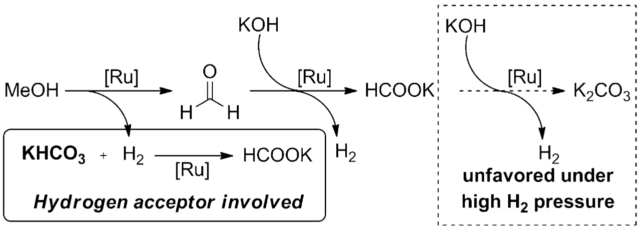
Based on these observations, we propose the reaction pathway of our transformation as shown in Scheme 2. Previous studies on methanol dehydrogenation at ambient pressure indicated the following sequential processes, including the initial dehydrogenation of methanol to hydrogen and formaldehyde, the base-promoted dehydrogenation of formaldehyde to formate and hydrogen, and the final dehydrogenation of formate to hydrogen and carbonate.[8] The last step in this reaction sequence is rate limiting when the Ru-MACHO complex is used. With increased hydrogen pressure this step is further slowed down. Actually, the pressure of the in situ generated hydrogen under the optimized conditions (Table 4, entry 8) for the potassium formate synthesis was > 30 bar after the reaction had been cooled to room temperature. In addition, an analysis of the gas phase revealed that only hydrogen was produced in the reaction. In this case, the formate dehydrogenation step was completely prevented. Meanwhile, bicarbonate acts as a hydrogen acceptor or undergoes transfer hydrogenation[15] with methanol to afford the formate product as well, which also facilitates the methanol dehydrogenation process.

Table 5: Synthesis of potassium formate from carbon dioxide, potassium hydroxide, and methanol.[a]

$$CO_2 + KOH + MeOH \xrightarrow[150\,^{\circ}C,\ 20\ h]{\text{Ru-MACHO}} HCOOK$$

Entry	CO_2 pressure [bar]	*n* (KOH) [mmol]	TON[b]	Yield [%][c]
1	0	80	10882	68
2	5	80	12308	77
3	10	80	8024	50
4	20	80	0	0

[a] Reaction conditions: 100 mL autoclave, Ru-MACHO complex (5 μmol), MeOH/H_2O (25/5 mL), 150°C, 20 h. [b] TON = mmol HCOOK/mmol Ru catalyst. [c] Yield = mmol HCOOK/mmol (KOH).



Scheme 2. Proposed reaction pathway.

In summary, we have developed the first combined catalytic process consisting of methanol dehydrogenation and bicarbonate hydrogenation to give formate salts. This industrially relevant reaction allows for a straightforward and cost-efficient synthesis of formate salts, which also produces hydrogen as an additional valuable product. When the commercially available $HPNP^{ph}$/Ru pincer complex was applied, a high product yield (> 90%) of potassium formate with a TON exceeding 18000 was realized. Studies on the detailed reaction mechanism and application of non-noble-metal catalysts for this transformation are currently underway in our laboratory.

Experimental Section

Synthesis of potassium formate: $KHCO_3$ (20 mmol), KOH (60 mmol), and Ru-MACHO complex **1** (5 μmol) were placed in an autoclave (100 mL) and MeOH (25 mL)/H_2O (5 mL) was added under an argon atmosphere. The reaction mixture was stirred (400 rpm) at 150°C. After 20 h, the autoclave was cooled with ice water and the pressure was slowly released. The reaction mixture was fully evaporated in a rotary evaporator and the potassium formate content (white in color) was measured through ^1H NMR spectroscopy in D_2O with THF as the internal standard at a relaxation delay of 20 s.

Received: January 16, 2014
Revised: March 3, 2014

Keywords: dehydrogenation · formates · hydrogen acceptors · methanol · ruthenium

[1] a) A. van Dijk, *Kraftfutter* **2009**, *92*, 20–22; b) V. P. Danilov, E. A. Frolova, D. F. Kondakov, L. I. Avdushkina, A. V. Bykov, V. T. Orlova, *Theor. Found. Chem. Eng.* **2012**, *46*, 528–535.

[2] a) R. C. Steven, W. G. Steven, G. Bowman, G. F. Greg, D. R. Troy, *Environ. Sci. Technol.* **2009**, *43*, 40–46; b) J. S. Willemsen, J. C. M. van Hest, F. P. J. T. Rutjes, *Chem. Commun.* **2013**, *49*, 3143–3145.

[3] K. Weissermel, H. J. Arpe, *Industrial Organic Chemistry, Important Initial and Intermediate Products*, Wiley-VCH, Weinheim, **1976**.

[4] A. Boddien, F. Gaertner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, M. Beller, *Angew. Chem.* **2011**, *123*, 6535–6538; *Angew. Chem. Int. Ed.* **2011**, *50*, 6411–6414.

[5] a) J. Elek, L. Nádasdi, G. Papp, G. Laurenczy, F. Joó, *Appl. Catal. A* **2003**, *255*, 59–67; b) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy, M. Beller, *Angew. Chem.* **2010**, *122*, 9971–9974; *Angew. Chem. Int. Ed.* **2010**, *49*, 9777–9780; c) C. Federsel, R. Jackstell, M. Beller, *Angew. Chem.* **2010**, *122*, 6392–6395; *Angew. Chem. Int. Ed.* **2010**, *49*, 6254–6257; d) C. Federsel, R. Jackstell, A. Boddien, G. Laurenczy, M. Beller, *ChemSusChem* **2010**, *3*, 1048–1050; e) C. Federsel, C. Ziebart, R. Jackstell, W. Baumann, M. Beller, *Chem. Eur. J.* **2012**, *18*, 72–75; f) C. Ziebart, C. Federsel, P. Anbarasan, R. Jackstell, W. Baumann, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* **2012**, *134*, 20701–20704; g) S. Gowrisankar, C. Federsel, H. Neumann, C. Ziebart, R. Jackstell, A. Spannenberg, M. Beller, *ChemSusChem* **2013**, *6*, 85–91.

[6] a) Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga, *Organometallics* **2004**, *23*, 1480–1483; b) Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, K. Kasuga, *Organometallics* **2007**, *26*, 702–712; c) R. Tanaka, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 14168–14169; d) Y. Himeda, S. Miyazawa, T. Hirose, *ChemSusChem* **2011**, *4*, 487–493.

[7] L. Wu, Q. Liu, I. Fleischer, R. Jackstell, M. Beller, *Nat. Commun.* **2014**, *5*, 3091.

[8] M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller, *Nature* **2013**, *495*, 85–89.

[9] E. Balaraman, E. Khaskin, G. Leitus, D. Milstein, *Nat. Chem.* **2013**, *5*, 122–125.

[10] W. Kuriyama, T. Matsumoto, Y. Ino, O. Ogata, WO 2011048727 A1, **2011**.

[11] a) A. Boddien, D. Mellmann, F. Gaertner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science* **2011**, *333*, 1733–1736; b) X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita, Q. Xu, *J. Am. Chem. Soc.* **2011**, *133*, 11822–11825; c) G. Papp, J. Csorba, G. Laurenczy, F. Joó, *Angew. Chem.* **2011**, *123*, 10617–10619; *Angew. Chem. Int. Ed.* **2011**, *50*, 10433–10435; d) Q.-Y. Bi, X.-L. Du, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *J. Am. Chem. Soc.* **2012**, *134*, 8926–8933; e) M. Grasemann, G. Laurenczy, *Energy Environ. Sci.* **2012**, *5*, 8171–8181; f) M. Yadav, T. Akita, N. Tsumori, Q. Xu, *J. Mater. Chem.* **2012**, *22*, 12582–12586; g) M. Yadav, A. K. Singh, N. Tsumori, Q. Xu, *J. Mater. Chem.* **2012**, *22*, 19146–19150; h) J. H. Barnard, C. Wang, N. G. Berry, J. Xiao, *Chem. Sci.* **2013**, *4*, 1234–1244; i) W. Gan, D. J. M. Snelders, P. J. Dyson, G. Laurenczy, *ChemCatChem* **2013**, *5*, 1126–1132; j) S. Zhang, Ö. Metin, D. Su, S. Sun, *Angew. Chem.* **2013**, *125*, 3769–3772; *Angew. Chem. Int. Ed.* **2013**, *52*, 3681–3684.

[12] a) B. Gnanaprakasam, J. Zhang, D. Milstein, *Angew. Chem.* **2010**, *122*, 1510–1513; *Angew. Chem. Int. Ed.* **2010**, *49*, 1468–1471; b) S. Musa, I. Shaposhnikov, S. Cohen, D. Gelman, *Angew. Chem.* **2011**, *123*, 3595–3599; *Angew. Chem. Int. Ed.* **2011**, *50*, 3533–3537; c) M. Nielsen, A. Kammer, D. Cozzula, H. Junge, S. Gladiali, M. Beller, *Angew. Chem.* **2011**, *123*, 9767–9771; *Angew. Chem. Int. Ed.* **2011**, *50*, 9593–9597; d) M. Bertoli, A. Choualeb, A. J. Lough, B. Moore, D. Spasyuk, D. G. Gusev, *Organometallics* **2011**, *30*, 3479–3482; e) M. Nielsen, H. Junge, A. Kammer, M. Beller, *Angew. Chem.* **2012**, *124*, 5809–5811; *Angew. Chem. Int. Ed.* **2012**, *51*, 5711–5713; f) D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem.* **2012**, *124*, 2826–2829; *Angew. Chem. Int. Ed.* **2012**, *51*, 2772–2775; g) R. Kawahara, K.-i. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 3643–3646; h) C. Gunanathan, D. Milstein, *Science* **2013**, *341*, 249.

[13] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840–10841; b) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790–792.

[14] a) W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zanette, E. Zangrando, P. Rigo, *Angew. Chem.* **2005**, *117*, 6370–6375; *Angew. Chem. Int. Ed.* **2005**, *44*, 6214–6219; b) W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, *Organometallics* **2005**, *24*, 1660–1669; c) W. Baratta, G. Bossi, E. Putignano, P. Rigo, *Chem. Eur. J.* **2011**, *17*, 3474–3481.

[15] a) S. Sanz, M. Benítez, E. Peris, *Organometallics* **2010**, *29*, 275–277; b) S. Sanz, A. Azua, E. Peris, *Dalton Trans.* **2010**, *39*, 6339–6343; c) A. Azua, S. Sanz, E. Peris, *Chem. Eur. J.* **2011**, *17*, 3963–3967; d) Z. Shen, Y. Zhang, F. Jin, *RSC Adv.* **2012**, *2*, 797–801.