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Ruthenium Catalysts for Hydrogenation of Aromatic and Aliphatic Esters: Make Use of Bidentate Carbene Ligands

Felix A. Westerhaus, Bianca Wendt, Andreas Dumrath, Gerrit Wienhöfer, Kathrin Junge, and Matthias Beller*[a]

The generation of alcohols through the reduction of esters belongs to the key synthetic methodologies in organic chemistry.[1] In general, this transformation is still performed by using stoichiometric reducing agents such as $LiAlH_4$ or $NaBH_4$.[2] The disadvantages of such reagents are clear, that is, generation of large amounts of waste, safety concerns, low functional group tolerance, and sensitivity because of high reactivity of the metal hydride. A more environmentally benign approach is to use catalytic hydrogenations, which result in only the respective alcohol as the main product. Industrially, fatty acid ester hydrogenations are accomplished by using heterogeneous copper chromite catalysts. Unfortunately, this system requires high temperatures (> 200 °C) and pressures (200 bar), while the substrate scope and functional group tolerance are limited.[3] Moreover, the rather harsh conditions are relatively energy consuming. Because of these drawbacks, the development of alternative and milder methods that omit these drawbacks and limitations is desirable for both industry and academic research.

Several homogeneous catalyst systems for the hydrogenation of esters, acids, or amides have been reported.[4] First attempts of homogeneous hydrogenations of esters were accomplished by using hydridoruthenate salts or ruthenium–carbonyl clusters.[5] Further improvements were achieved by using an in situ-generated catalyst synthesized from [Ru(acetylacetonate)$_3$] and a tridentate phosphine ligand.[6] Recently, more active systems for ester hydrogenation were disclosed by Milstein[7] and Saudan.[8] In addition, other groups have also contributed to this topic during recent years.[9] As an example, our group reported a catalyst system for ester hydrogenation based on imidazolyl–phosphine–ruthenium complexes.[10] Although the existing methods exhibit high efficiencies, they are still troubled by a number of limitations: a) functional group tolerance is still restricted, and b) nearly all active ruthenium catalysts require phosphorous ligands, which are sometimes expensive and/or difficult to modify and handle.

Based on our general interest in the selective reduction of carboxylic acid derivatives,[11] we set a goal to develop improved catalytic systems, which should not be based on traditional phosphines. More specifically, we proposed that carbenes constitute promising alternative ligands for ester hydrogenation. In comparison to phosphines, carbenes are less easily oxidized and their electronic and steric properties allow for easy fine-tuning. However, so far the use of solitary carbene ligands for ester hydrogenation remains elusive.

Initially, two commercially available imidazolium salts, **1** and **2**, were tested in combination with the ruthenium precursor $[Ru(p\text{-cymene})Cl_2]_2$ for the hydrogenation of methyl benzoate. Despite numerous attempts, the yield of benzyl alcohol never exceeded 7% (Table 1, entries 1 and 2). We then tested bidentate imidazolium salts **3**–**8** because the corresponding bidentate carbenes offered a stronger binding mode (Figure 1).[12]

Table 1. Reactivity of different carbine–ruthenium catalysts.[a]

Entry	Ligand	Conversion [%][b]	Yield [%][c]
1	**1**	41	7
2	**2**	43	6
3	**3**	78	38
4	**4**	95	65
5	**5a**	99	**82**
6[d]	–	79	39
7	**5a**[e]	98	65
8[f]	**5a**	90	58
9[g]	**5a**	95	64
10	**5b**	99	77
11	**5c**	99	75
12	**6**	99	72
13	**7**	83	47
14	**8**	67	34

[a] Conditions: 0.5 mmol methyl benzoate, 0.5 mol% $[Ru(p\text{-cymene})Cl_2]_2$, 2 mol% ligand **1**–**8**, 30 mol% KO*t*Bu, 2 mL 1,4-dioxane, 100 °C, 50 bar H_2, 6 h. [b] Conversion was determined by using GC with hexadecane as the internal standard. [c] Yield was determined by using GC with hexadecane as the internal standard. For ligands **1**–**3** between 4–5% benzylbenzoate were formed. [d] Isolated complex [Ru(*p*-cymene)(**5**)Cl]Cl was used. [e] Isolated complex [Ru(*p*-cymene)(**5**)Cl]Cl + **5a** was used. [f] Ru/Ligand = 1:1. [g] Ru/Ligand = 1:4.

The imidazolium salts were prepared through the dimerization of commercially available N-substituted imidazoles with dihalomethanes.[13] This straightforward synthetic pathway offered numerous variations at the substituted nitrogen atoms in the 4- and 5-positions of the imidazole backbone, which were also used for the exchange of corresponding halides (Scheme 1).

Until now, these chelating bisimidazolium salts have mainly been reported for cross-coupling reactions[14] and C–H activation processes;[15] however, they have scarcely been used in catalytic hydrogenations.[16] Here, ruthenium catalysts were applied for the reduction of olefins, aldehydes, and ketones by

[a] F. A. Westerhaus, B. Wendt, A. Dumrath, G. Wienhöfer, Dr. K. Junge, Prof. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Straße 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de

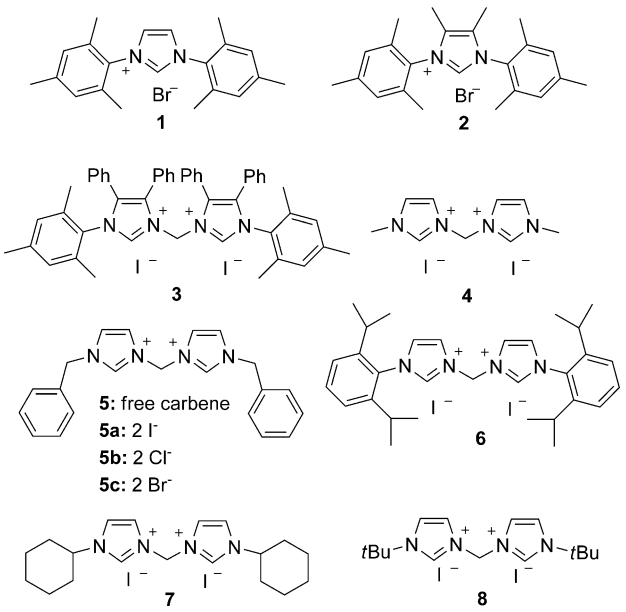
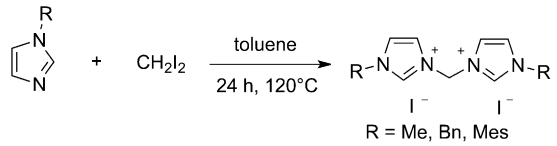


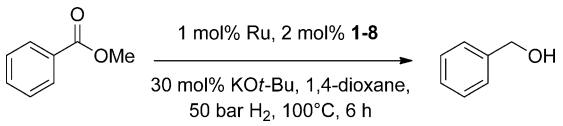
Figure 1. Selection of carbene ligands that were used in this study.



Scheme 1. Synthesis of imidazolium salts **3**–**8**, which serve as precursors for the carbene ligands.

using similar carbene ligands.[17] Bidentate carbenes have been tested in combination with palladium, iridium, or rhodium for catalytic transformations,[18] and a number of complexes bearing different metals centers have also been characterized.[19] With respect to ester reduction reactions, only catalysts containing a carbene moiety in the ligand backbone have been reported, but solitarily carbene ligands have not been successful for this transformation.[20]

When we applied ligand precursors **3**–**8** to the hydrogenation of methyl benzoate, improved reduction to the corresponding alcohol was observed (Table 1, entries 3–14). By using optimized conditions (1 mol% catalyst loading; ruthenium-to-ligand ratio 1:2, 100 °C, 6 h, 30 mol% base), the conversion and yields were significantly higher than for monodentate ligand precursors **1** and **2**. Among the different bidentate imidazolium salts, the benzyl-substituted derivative **5a** presented the best results (Table 1, entry 5). Testing different Ru/ligand ratios (Table 1; entries 5, 8, and 9) demonstrated an optimum at 1:2. Furthermore, the defined ruthenium biscarbene complex [Ru(*p*-cymene)(**5**)Cl]Cl, bearing only one ligand (**5**), was isolated. Positive ion ESIMS analysis of the isolated complex showed a peak at $m/z = 599$ for [Ru(*p*-cymene)(**5**)Cl]$^+$ and the characteristic isotopic distribution for one ruthenium atom.[21] This complex was used for the model reaction; however, only 39% yield of benzyl alcohol was obtained (see



Scheme 2. Model reaction for the catalytic hydrogenation of carboxylic acid ester.

Scheme 2 and Table 1, entry 6). When a second equivalent of ligand **5a** was added to the [Ru(*p*-cymene)(**5**)Cl]Cl isolated complex, the catalytic activity was improved (Table 1, entry 7).

Next, the most active catalyst system was used for different types of aromatic esters. As shown in Table 2, good to excellent yields of the corresponding benzylic alcohols were obtained. Different alcohols in the ester moiety resulted in slight to moderate changes in the yield (Table 2, entries 1 and 2; Table 3, entries 6 and 7). Here, primary and secondary alcohols were tolerated in the ester function (Table 2, entries 1 and 2; Table 3, entries 1–3), as well as a number of diverse functional groups, including halogens (Table 2, entries 7–9). Moreover, diesters were easily reduced to the corresponding diols (Table 2, entry 3). The reactivity of the catalyst was not significantly affected by the presence of electron-donating (Table 2, entries 4–6) or electron-withdrawing groups on the aromatic ring (Table 2, entries 7 and 9).

Aliphatic esters are generally considered to be more challenging substrates for this transformation. Interestingly, our catalytic system obtained moderate to good yields, even when primary and secondary aliphatic esters were used as substrates (Table 3, entry 10).

Homobenzylic as well as aliphatic esters were converted into the corresponding alcohols in good to excellent yield, in which the presence of conjugated double bonds resulted in complete hydrogenation (Table 3, entries 5 and 9). In addition, lactones could also be reduced (Table 3, entries 11 and 13). Finally, levulinic acid, which constitutes an interesting intermediate that is easily available from biomass, was reduced and yielded up to 80% γ-valerolactone (Table 3, entry 12). Notably, this reaction worked well at 15 mol% base concentration (Figure 2), and ligand screening demonstrated that the best result was

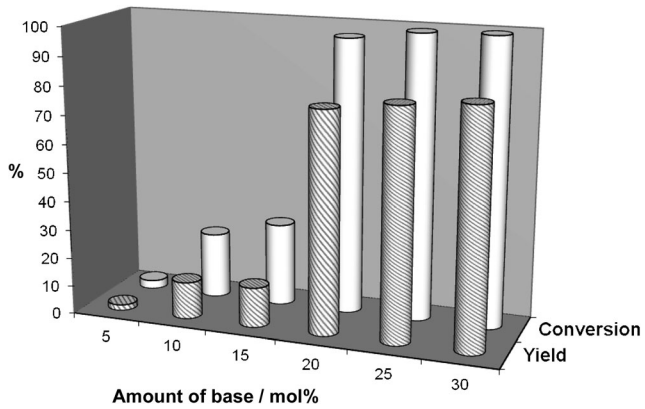
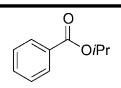
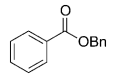
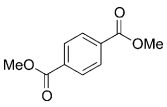
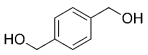
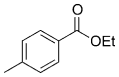
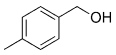
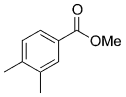
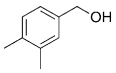
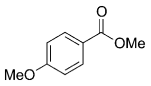
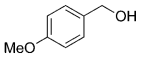
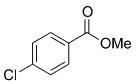
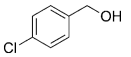
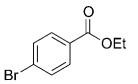
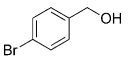
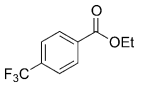
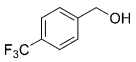
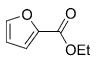


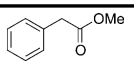
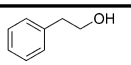
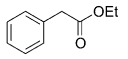
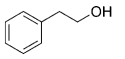
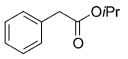
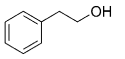
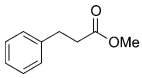
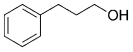
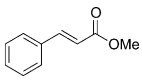
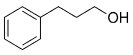
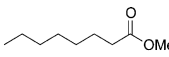
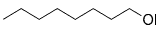
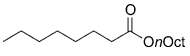
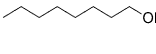
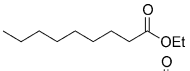
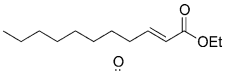
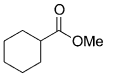
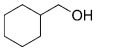
Figure 2. Screening of different concentrations of KO*t*Bu for the catalytic reduction of methyl benzoate with [Ru(*p*-cymene)Cl$_2$]$_2$**5a**.

Table 2. Ruthenium-catalyzed hydrogenation of aromatic esters.[a]

Entry	Ester	Alcohol	Yield [%][b]
1			78
2			92
3			60
4			74
5			85
6			74
7			77 40
8			72
9			63
10			70

[a] Conditions: 0.5 mmol ester, 0.5 mol% [Ru(*p*-cymene)Cl_2]$_2$, 2 mol% ligand **5a**, 30 mol% KO*t*Bu, 2 mL 1,4-dioxane, 100 °C, 50 bar H_2, 6 h. [b] Yield was determined by using GC with hexadecane as the internal standard.

Table 3. Catalytic hydrogenation of aliphatic esters.[a]

Entry	Ester	Alcohol	Yield [%][b]
1			67
2			77
3			50
4			89
5			65
6			88 77[c]
7			90
8			89
9			75
10			83
11			59
12			62 75[d] 80[e]
13			32 54[f]

[a] Conditions: 0.5 mmol ester, 0.5 mol% [Ru(*p*-cymene)Cl_2]$_2$, 2 mol% ligand **5a**, 30 mol% KO*t*Bu, 2 mL 1,4-dioxane, 100 °C, 50 bar H_2, 6 h. [b] Yield was determined by using GC with hexadecane as the internal standard. [c] 20 mol% KO*t*Bu. [d] 1 mol% Ru, 2 mol% ligand **5c**, 15 mol% KO*t*Bu. [e] 1 mol% Ru, 2 mol% ligand **7**, 15 mol% KO*t*Bu. [f] 1 mol% Ru, 2 mol% ligand **5b**, 15 mol% KO*t*Bu. Most of the catalytic experiments were realized by using 30 mol% of KO*t*Bu to reach high yields and full conversion within a reasonable time (Figure 2).

achieved with the cyclohexyl-substituted bisimidazol ligand **7**. Furthermore, the corresponding lactone was reduced to 1,4-pentanediol in good yield (Table 3, entry 13).

Conclusions

For the first time ruthenium biscarbene catalysts are described for the straightforward homogeneous hydrogenation of esters. Key to their success is the application of bidentate carbene ligands. The ligand precursors are easily synthesized through the dimerization of N-substituted imidazoles with diiodomethane. The synthesis is straightforward and highly modular, and as such offers multiple positions at which the ligand can be modified. The most active catalyst is generated in situ from [Ru(*p*-cymene)Cl_2]$_2$ and biscarbene **5a**, showing broad applicability for the hydrogenation of aromatic as well as aliphatic carboxylic acid esters.

Experimental Section

General procedure for the catalytic hydrogenation of esters: A mixture of [Ru(*p*-cymene)Cl_2]$_2$ (1 mol% of Ru), ligand **1**–**8** (2 mol%), KO*t*Bu (30 mol%), and hexadecane as an internal standard was added into the reaction vial, sealed, and purged with argon. The liquid ester (0.5 mmol) was then added together with 1,4-dioxane. If a solid ester was used, it was placed directly into the reaction vial. The reaction vials (up to 6) were placed into a 300 mL autoclave. The autoclave was flushed with hydrogen twice (ca. 20 bar) and pressurized to 50 bar hydrogen. It was then placed into an aluminum block that had been preheated to 100 °C, and stirred for the indicated time (6 h). After the reaction was complete, the autoclave was cooled to room temperature and the hydrogen was released. The crude reaction mixture was filtered through silica gel and analyzed by using GC. The yield was determined by using hexadecane as an internal standard.

Synthesis of [Ru(*p*-cymene)(**5**)Cl]Cl: **5a** or **5b** (300 mg, 0.75 mmol) in THF (10 mL) was placed in a Schlenk flask at −78 °C and *n*BuLi (600 μL, 2.5 M, 2 eq.) was added dropwise. The mixture was warmed to rt over 2 h and was then filtered through Celite. A suspension of [Ru(*p*-cymene)Cl_2]$_2$ (0.5 eq.) in THF (5 mL) was added at

−78 °C to the filtrate and stirred overnight. Finally, the solvent of the suspension was evaporated to yield a red brown solid. The precipitation was washed with diethyl ether and dried in a vacuum. Yield: 45%. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.53$ (s, 4H, $CH_2C_6H_5$), 7.42–7.22 (m, 10H, $CH_2C_6H_5$), 7.33 (d, 2H, CH_{imid}), 6.72 (d, 2H, CH_{imid}), 5.70–5.54 (m, 2H, HCH_2N), 5.46–5.28 (dd, 2H, $CH_{arom.}$, *p*-cymene), 5.04–4.94 (dd, 2H, $CH_{arom.}$, *p*-cymene), 2.95 [m, 1H, $(CH_3)_2CH$, *p*-cymene], 2.07 (s, 3H, CH_3, *p*-cymene), 1.33–1.27 ppm [dd, 6H, $(CH_3)_2CH$, *p*-cymene]; ^{13}C NMR ($CDCl_3$, 300 MHz): $\delta = 173.1$ (C–Ru), 137.2; 129.1; 128.1; 127.3 ($C_{aromt.}$; $CH_2C_6H_5$), 123.5; 123.3 (CH_{imid}), 109.3; 98.6; 86.5 (d); 82.1 (d, $C_{aromt.}$; *p*-cymene); 63.0 ($CH_2C_6H_5$); 54.8 (NCH_2N); 30.8 [$(CH_3)_2CH$, *p*-cymene], 23.4 (CH_3, *p*-cymene), 21.7; 19.0 ppm [$(CH_3)_2CH$, *p*-cymene]. HRMS (EI): calcd. for $C_{31}H_{34}N_4ClRu$ [M^+] 599.1515, found 599.1513.

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Keywords: alcohols · carbenes · homogeneous catalysis · hydrogenation · ruthenium

[1] a) P. N. Rylander, *Catalytic Hydrogenation in Organic Syntheses*; Academic Press, **1979**; b) *Handbook of Heterogeneous Hydrogenation for Organic Synthesis* (Ed.: S. Nishimura), Wiley, New York, **2001**; c) *Handbook of Homogeneous Hydrogenation* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**; d) P. G. Andersson, I. J. Munslow, *Modern Reduction Methods*, Wiley, New York, **2008**.

[2] a) M. J. Jorgenson, *Tetrahedron Lett.* **1962**, *3*, 559–562; b) H. C. Brown, N. M. Yoon, *J. Am. Chem. Soc.* **1966**, *88*, 1464–1472.

[3] Y. Pouilloux, F. Autin, J. Barrault, *Catal. Today* **2000**, *63*, 87–100.

[4] a) M. Bianchi, G. Menchi, F. Francalanci, F. Piacenti, U. Matteoli, P. Frediani, C. Botteghi, *J. Organomet. Chem.* **1977**, *141*, 107–111; b) M. Bianchi, G. Menchi, F. Francalanci, F. Piacenti, U. Matteoli, P. Frediani, C. Botteghi, *J. Organomet. Chem.* **1980**, *188*, 109–119; c) D. He, N. Wakasa, T. Fuchikami, *Tetrahedron Lett.* **1995**, *36*, 1059–1062; d) A. A. Núñez Magro, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* **2007**, 3154–3156.

[5] a) A. R. Grey, G. P. Pez, A. Wallo, J. Corsi, *Chem. Commun.***1980**, 783–784; b) A. R. Grey, G. P. Pez, A. Wallo, *J. Am. Chem. Soc.* **1981**, *103*, 7536–754; c) U. Matteoli, G. Mechi, M. Bianchi, F. Piacenti, *J. Organomet. Chem.* **1986**, *299*, 233–238; d) U. Matteoli, G. Mechi, M. Bianchi, F. Piacenti, *J. Mol. Catal.*, **1988**, *44*, 347–355; e) U. Matteoli, G. Mechi, M. Bianchi, F. Piacenti, S. Ianelli, M. Nardelli, *J. Organomet. Chem.* **1995**, *498*, 177–186.

[6] a) Y. Hara, H. Inagaki, S. Nishimura, K. Wada, *Chem. Lett.* **1992**, 1983–1986; b) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1997**, 667–668; c) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1998**, 1367–1367; d) K. Nomura, H. Ogura, Y. Imanishi, *J. Mol. Catal., A* **2001**, *166*, 345–349; e) K. Nomura, H. Ogura, Y. Imanishi, *J. Mol. Catal., A* **2001**, *166*, 345–349; f) M. C. Van Engelen, H. T. Teunissen, J. G. de Vries, C J. Elsevier, *J. Mol. Catal., A* **2003**, *206*, 185–192; g) M. J. Hanton, S. Tin, B. J. Boardman, P. Miller, *J. Mol. Catal., A* **2011**, *346*, 70–78.

[7] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131–1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115; b) E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon, D. Milstein, *Organometallics* **2011**, *30*, 3826–3833; c) E. Balaraman, E. Fogler, D. Milstein, *Chem. Commun.* **2012**, *48*, 1111–1113.

[8] L. A. Saudan, C. M. Saudan, C. Debieux, P. Wyss, *Angew. Chem.* **2007**, *119*, 7617–7620; *Angew. Chem. Int. Ed.* **2007**, *46*, 7473–7476.

[9] a) M. L. Clarke, M. B. Diaz-Valenzuela, A. M. Z. Slawin, *Organometallics* **2007**, *26*, 16–19; b) H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horvath, *Top. Catal.* **2008**, *48*, 49–54; c) W. Kuriyama, Y. Ino, O. Ogata, N. Sayo, T. Saito, *Adv. Synth. Catal.* **2010**, *352*, 92–96; d) F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, *Angew. Chem.* **2010**, *122*, 5642–5646; *Angew. Chem. Int. Ed.* **2010**, *49*, 5510–5514; e) M. Ito, T. Ootsuka, R. Watari, A. Shiibashi, A. Himizu, T. Ikariya, *J. Am. Chem. Soc.* **2011**, *133*, 4240–4242; f) F. M. A. Geilen, B. Engendahl, M. Hölscher, J. Klankermayer, W. Leitner, *J. Am. Chem. Soc.* **2011**, *133*, 14349–14358; g) I. Carpenter, S. C. Eckelmann, M. T. Kuntz, J. A. Fuentes, M. B. France, M. L. Clarke, *Dalton Trans.* **2012**, *41*, 10136–10140; h) W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo, T. Saito, *Org. Process Res. Dev.* **2012**, *16*, 166–171.

[10] K. Junge, B. Wendt, F. A. Westerhaus, A. Spannenberg, H. Jiao, M. Beller, *Chem. Eur. J.* **2012**, *18*, 9011–9018.

[11] a) S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, *Angew. Chem.* **2009**, *121*, 9671–9674; *Angew. Chem. Int. Ed.* **2009**, *48*, 9507–9510; b) S. Zhou, D. Addis, S. Das, K. Junge, M. Beller, *Chem. Commun.* **2009**, 4883–4885; c) S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, *Org. Lett.* **2009**, *11*, 2461–2464; d) S. Das, D. Addis, S. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 1770–1771; e) S. Das, S. Zhou, D. Addis, S. Enthaler, K. Junge, M. Beller, *Top. Catal.* **2010**, *53*, 979–984; f) D. Addis, S. Das, K. Junge, M. Beller, *Angew. Chem.* **2011**, *123*, 6128–6135; *Angew. Chem. Int. Ed.* **2011**, *50*, 6004–6011; g) S. Das, K. Möller, K. Junge, M. Beller, *Chem. Eur. J.* **2011**, *17*, 7414–7417; h) S. Das, D. Addis, L. R. Knöpke, U. Bendrup, K. Junge, A. Brückner, M. Beller, *Angew. Chem.* **2011**, *123*, 9346–9359; *Angew. Chem.* **2011**, *123*, 9346–9350; *Angew. Chem. Int. Ed.* **2011**, *50*, 9180–9184; i) S. Das, D. Addis, K. Junge, M. Beller, *Chem. Eur. J.* **2011**, *17*, 12186–12192; j) S. Das, B. Join, K. Junge, M. Beller, *Chem. Commun.* **2012**, *48*, 2683–2685.

[12] N-Heterocyclic carbenes in Transition metal catalysis: *21 (Topics in Organometallic Chemistry)* (Ed.: F. Glorius), Springer, Berlin, **2007**.

[13] a) R. E. Douthwaite, D. Haussinger, M. L. H. Green, P. J. Silcock, P. T. Gomes, A. M. Martins, A. A. Danopoulos, *Organometallics* **1999**, *18*, 4584–4590; b) B. K. Avery, W. G. Devine, C. M. Kormos, N. E. Leadbeater, *Tetrahedron Lett.* **2009**, *50*, 2851–2853; c) E. Fuchs, O. Molt, (BASF AG), WO2008000727 (A1), 2008-01-03.

[14] a) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239–2246 and references therein; b) J. A. Mata, M. Poyatos, E. Peris, *Coord. Chem. Rev.* **2007**, *251*, 841–859; c) C.-F. Fu, C.-C. Lee, Y.-H. Liu, S.-M. Peng, S. Warsink, C. J. Elsevier, J.-T. Chen, S.-T. Liu, *Inorg. Chem.* **2010**, *49*, 3011–3018; d) F.-T. Luo, H.-K. Lo, *J. Organomet. Chem.* **2011**, *696*, 1262–1265; e) G. Nan, B. Rao, M. Luo, *ARKIVOC* **2011**, 29–40; f) M. Micksch, T. Strassner, *Eur. J. Inorg. Chem.* **2012**, DOI: 10.1002/ejic.201200940.

[15] a) M. Muehlhofer, T. Strassner, W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1817–1819; *Angew. Chem. Int. Ed.* **2002**, *41*, 1745–1747; b) T. Strassner, M. Muehlhofer, A. Zeller, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2004**, *689*, 1418–1424; c) S. Ahrens, A. Zeller, M. Taige, T. Strassner, *Organometallics* **2006**, *25*, 5409–5415.

[16] For Ru-catalyzed hydrogenation of styrene see: a) C. Gandolfi, M. Heckenroth, A. Neels, G. Laurency, M. Albrecht, *Organometallics* **2009**, *28*, 5112–5121. For Ir and Rh catalyzed transfer hydrogenation see: b) M. Albrecht, R. H. Crabtree, J. Mata, E. Peris, *Chem. Commun.* **2002**, 32–33; c) M. Albrecht, J. R. Miecznikowski, A. Samuel, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 3596–3604; d) E. Mas-Marzá, M. Poyatos, M. Sanau, E. Peris, *Organometallics* **2004**, *23*, 323–325; e) J. R. Miecznikowski, R. H. Crabtree, *Organometallics* **2004**, *23*, 629–631.

[17] a) M. Poyatos, J. Mata, E. Falomir, R. Crabtree, E. Peris, *Organometallics* **2003**, *22*, 1110–1114; b) D. Gnanamgari, E. Sauer, N. Schley, C. Butler, C. Incarvito, R. Crabtree, *Organometallics* **2009**, *28*, 321–325.

[18] a) W. Herrmann, C.-P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93–96; b) J. Schwarz, V. Böhm, M. Gardiner, M. Grosche, W. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780; c) D. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. Crabtree, *J. Am. Chem. Soc.* **2007**, *129*, 12834–12846; d) M. Poyatos, W. McNamara, C. Incarvito, E. Clot, E. Peris, R. Crabtree, *Organometallics* **2008**, *27*, 2128–2136; e) A. da Costa, J. Mata, B. Royo, E. Peris, *Organometallics* **2010**, *29*, 1832–1838; f) A. Azua, S. Sanz, E. Peris, *Organometallics* **2010**, *29*, 3661–3664; g) A. Azua, J. Mata, E. Peris, *Organometallics* **2011**, *30*, 5532–5536; h) A. Azua, S. Sanz, E. Peris, *Chem. Eur. J.* **2011**, *17*, 3963–3967.

[19] a) U. Kernbach, M. Ramm, P. Luger, W. Fehlhammer, *Angew. Chem.* **1996**, *108*, 333–335; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 310–312; b) R. Fränkel, J. Kniczek, W. Ponikwar, H. Nöth, K. Polborn, W. Fehlhammer, *Inorg. Chim. Acta* **2001**, *312*, 23–39; c) R. Fränkel, C. Birg, U. Kern-

bach, T. Habereder, H. Nöth, W. Fehlhammer, *Angew. Chem.* **2001**, *113*, 1961 – 1964; *Angew. Chem. Int. Ed.* **2001**, *40*, 1907 – 1910; d) M. Poyatos, E. Mas-Marza, M. Sanau, E. Peris, *Inorg. Chem.* **2004**, *43*, 1793 – 1798.

[20] a) Y. Sun, C. Koehler, R. Tan, V. T. Annibale, D. Song, *Chem. Commun.* **2011**, *47*, 8349 – 8351; b) D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem.* **2012**, *124*, 2826 – 2829; *Angew. Chem. Int. Ed.* **2012**, *51*, 2772 – 2775; c) D. Spasyuk, D. G. Gusev, *Organometallics* **2012**, *31*, 5239 – 5242.

[21] The defined ruthenium complex [Ru(*p*-cymene)(**5**)Cl]Cl was prepared from [Ru(*p*-cymene)Cl_2] and the free carbene (**5**), which was generated from **5a** or **5b** by addition of *n*BuLi.

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*F. A. Westerhaus, B. Wendt, A. Dumrath, G. Wienhöfer, K. Junge, M. Beller**

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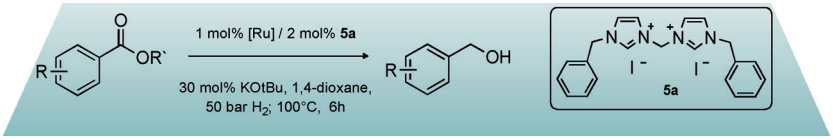
Ruthenium Catalysts for Hydrogenation of Aromatic and Aliphatic Esters: Make Use of Bidentate Carbene Ligands



Committed carbenes: The convenient application of bidentate carbene ligands is described for the hydrogenation of carboxylic acid esters. The ligand precursors are easily synthesized through the dimerization of N-substituted imidazoles with diiodomethane. The catalyst is generated in situ and exhibits good activity and functional group tolerance for the hydrogenation of aromatic and aliphatic carboxylic acid esters.