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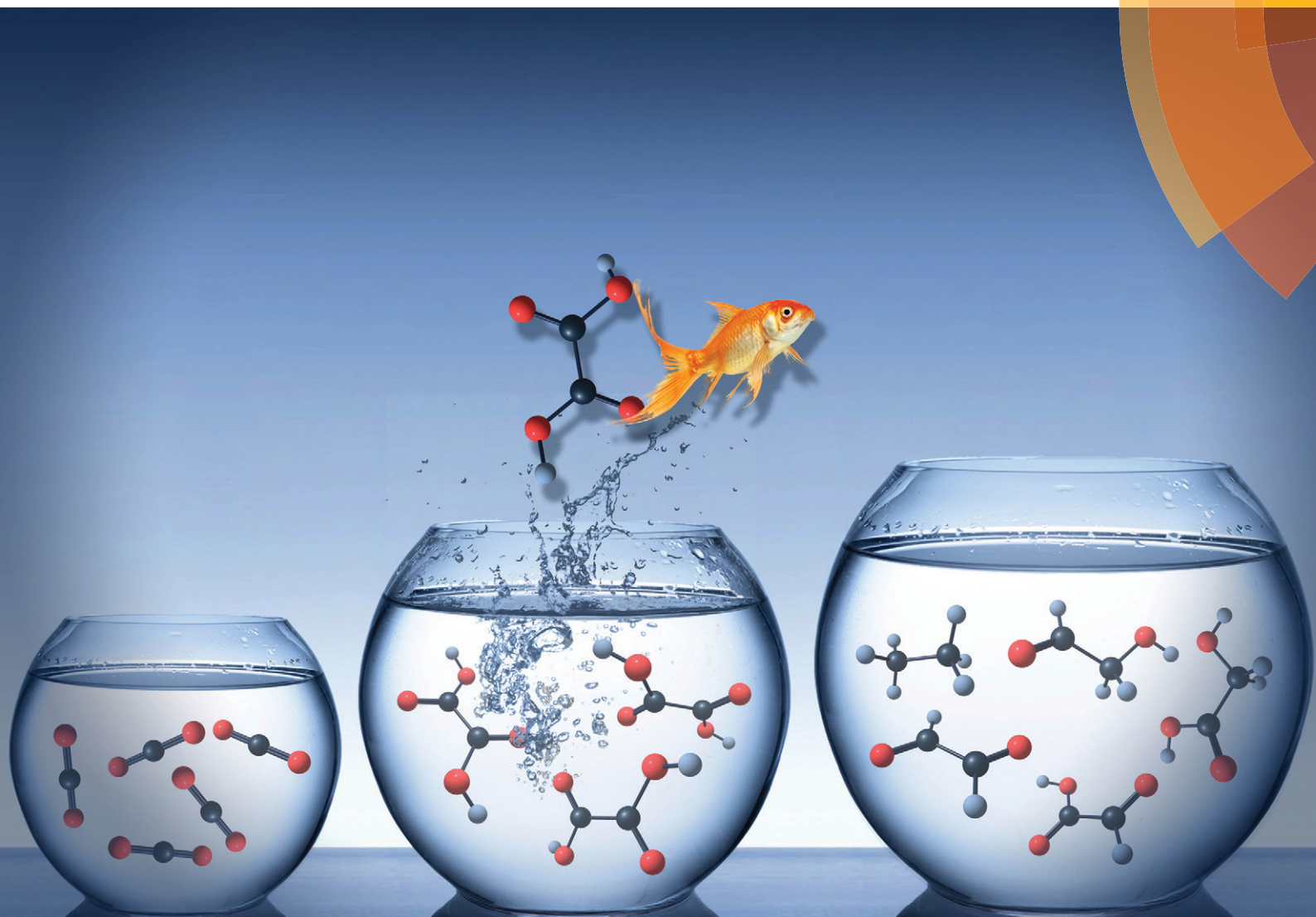
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Catalytic hydrosilylation of oxalic acid: chemoselective formation of functionalized C₂-products†

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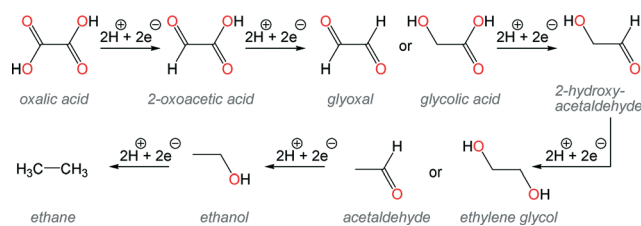
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Oxalic acid is an attractive entry to functionalized C₂-products because it can be formed by C–C coupling of two CO₂ molecules under electrocatalytic reduction. Herein, we describe the first attempts to reduce oxalic acid by catalytic hydrosilylation. Using B(C₆F₅)₃ as a Lewis acidic catalyst, oxalic acid can be converted to reduced C₂-molecules, with high chemoselectivity, under mild reaction conditions.

Because it has a low toxicity and a low cost, CO₂ is an attractive carbon source in organic chemistry.¹ Beyond the industrial applications utilizing CO₂ for the production of urea, carbonates and salicylic acid,^{1a,c} novel methodologies have been developed over the past few years to use CO₂ as a C₁-building block in the formation of formic acid, formaldehyde, methanol, formamides, formamidines, imines and methylamines.² These advances were facilitated on the one hand by the design of efficient hydrogenation catalysts which are able to convert CO₂-H₂ mixtures to reduced C₁ compounds.^{2a,f-h,3} On the other hand, the utilization of polarized reductants, such as hydrosilanes and hydroboranes, enabled the development of efficient reduction processes for the conversion of CO₂ at low temperature and low pressure.^{2b-e,j-m,4} Key examples of this development include the efficient hydrogenation of CO₂ to methanol^{2a} and the reductive functionalization of CO₂ to methylamines, using organometallic catalysts.^{2c,i,5} Nonetheless, these novel transformations are limited to the formation of C₁-products.

In 2012, Sabo-Etienne, Bontemps *et al.* showed that the ruthenium catalyzed hydroboration of CO₂ to methoxyborane generated a C₂-intermediate.^{2k-m} The pinB–OCH₂–OCHO compound (pinB = 4,4,5,5-tetramethyl-1,3,2-dioxaboryl) results

from the C–O bond coupling of two CO₂ molecules, *via* the transient formation of formaldehyde.^{2l} So far, oxalic acid, HO₂CCO₂H, is the main C₂-product accessible by reduction of CO₂. In fact, selective electrocatalysts have been developed to promote the C–C bond coupling of CO₂ with high Faradaic efficiency.⁶ In this context, the reduction of oxalic acid could provide novel routes to the conversion of CO₂ to C₂-compounds. While oxalic acid is mostly utilized as a ligand in the extraction of rare earth elements,⁷ the reduction chemistry of this simple dicarboxylic acid remains a largely unexplored area. In fact, the two C^{III} atoms of oxalic acid can each undergo six-electron reduction to yield ethane and the sequential two-electron reduction of oxalic acid is a potential entry to a variety of functionalized C₂-molecules. As depicted in Scheme 1, these include glyoxal, glycolic acid, ethylene glycol, acetaldehyde and ethanol. Yet, to the best of our knowledge, glycolic acid and glyoxal are the only products available from the reduction of oxalic acid. The conversion of oxalic acid to glycolic acid can be achieved either with powdered magnesium or electrochemical reduction at a Hg cathode;⁸ LiAlH₄ favors the formation of glyoxal.⁹ Importantly, catalytic hydrosilylation reactions have shown superior chemoselectivity to classical reduction methods involving metal-hydrides for the reduction of a wide range of carbonyl groups, including carboxylic acids.¹⁰ Herein, we report the first attempts to reduce oxalic acid under hydrosilylation conditions and



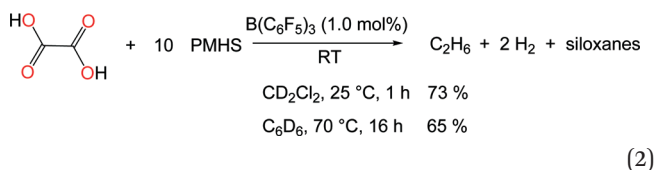
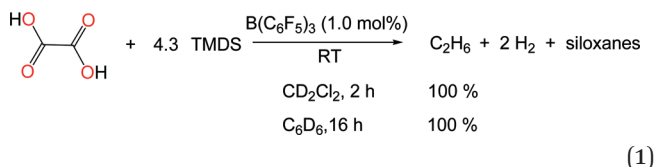
Scheme 1 Product distribution for the sequential 2-electron reduction of oxalic acid to ethane.

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describe the selective conversion of oxalic acid to ethane and silylated derivatives of 2-oxoacetic acid, glyoxal, glycolic acid and glycolaldehyde.

With the recent development of highly active and selective molecular catalysts, hydrosilylation reactions have found compelling success in the reduction of esters, carboxylic acids, amides and ureas, which are reluctant substrates in hydrogenation transformations.^{10d,11} Striking examples include the design of iron and ruthenium catalysts able to promote the hydrosilylation of esters to alcohols or aldehydes selectively.^{11c,e} Notably, the Lewis acid $B(C_6F_5)_3$ is a potent hydrosilylation catalyst for the reduction of carbonyl derivatives, alcohols and ethers¹² and it has been recently utilized for the reduction of lignin models and cellulose.¹³ In addition, this metal-free catalyst can also convert polymethylhydrosiloxane ($Me_3Si(OSiMeH)_nOSiMe_3$, PMHS) and tetramethyldisiloxane ($Me_2SiHOSiHMe_2$, TMDS), which are cost-efficient (2–5 € per mole), non-toxic and moisture stable by-products of the silicone industry.^{2d,14} Thus, the complete reduction of oxalic acid was first undertaken in CH_2Cl_2 , using 4.3 equiv. TMDS, which has a slight excess of Si–H functionalities. Catalyst $B(C_6F_5)_3$ promotes the reduction of oxalic acid to ethane within 2 h at 25 °C, with a low catalyst loading of 1.0 mol% (eqn (1)). The quantitative formation of ethane and hydrogen was monitored by 1H NMR and GC analyses. This transformation represents the first example of the reduction of oxalic acid to ethane. It is noteworthy that the solvent plays an important role in the reduction of oxalic acid and the reaction is significantly slower in benzene. Ethane was also successfully produced in the presence of PMHS (eqn (2)). Nonetheless, the conversion yield was somewhat limited (<73%), presumably because of the concomitant formation of siloxane gels which precluded the full conversion of the Si–H functionalities. Overall, this reaction chemistry exemplifies the ability of $B(C_6F_5)_3$ to promote the reduction of the different functional groups involved in the 12-electron reduction of oxalic acid to ethane, namely esters, acetals and ethers. Although ethane is a valuable fuel or chemical for the production of ethylene, its formation from oxalic acid (or CO_2) is clearly not competitive with its extraction from fossil feedstocks. The partial reduction of oxalic acid was thus explored, so as to preserve chemical functional groups in the products.



No intermediate could be observed in the reduction of oxalic acid to ethane with TMDS or PMHS (eqn (1) and (2)) and, using a default amount of the reductant, ethane was still obtained as the sole organic product, with limited conversion. Nevertheless, we have observed previously that Et_3SiH presents a lower reactivity, compared to TMDS and PMHS, in the electrophilic hydrosilylation of lignin model compounds.^{13a} The sequential reduction of oxalic acid was therefore carried out with increasing amounts of Et_3SiH . Addition of 3 equiv. Et_3SiH to a CH_2Cl_2 solution of anhydrous oxalic acid, in the presence of 1.0 mol% $B(C_6F_5)_3$, resulted in the rapid formation of **1** in 61% yield (eqn (3)). This reaction is consistent with previous findings by Brookhart *et al.*, who demonstrated the efficient conversion of carboxylic acids to their silylacetals by $B(C_6F_5)_3$ -catalyzed hydrosilylation.¹⁵ Reduction of oxalic acid to **1** is accompanied with H_2 evolution (observed by 1H NMR), resulting from the dehydrogenative silylation of the acidic O–H groups. The silylation of the carboxylic functionalities likely precedes the reduction of oxalic acid, although the putative bis(triethylsilyl)oxalate intermediate could not be detected. In fact, pre-activation of the substrate can be achieved independently by reacting oxalic acid with two equivalents of Me_3SiCl to prepare oxalate **3** in quantitative yield. The 1H and ^{13}C NMR spectra of **3** are in agreement with the reported data and its crystal structure was determined by X-ray diffraction (Fig. 1).[†] As depicted in eqn (3) and (4), with the $B(C_6F_5)_3$ catalyst, reduction of **3** with 1 equiv. Et_3SiH mimics the chemical behaviour of oxalic acid in the presence of 3 equiv. Et_3SiH , thereby confirming the involvement of a silyloxalate intermediate in the formation of **1**. From a mechanistic perspective, previous investigations by Piers' group have established that the $B(C_6F_5)_3$ -catalyzed hydrosilylation of carbonyl groups involves the formation of an ion pair, in which the carbonyl functionality is activated by coordination to a silylium cation while the active reductant is the $HB(C_6F_5)_3^-$ anion.^{12b} It is likely that the formation of this ion pair is favoured by a polar solvent, therefore accounting for the enhanced reaction rates in dichloromethane ($\epsilon = 8.9$) compared to benzene ($\epsilon = 2.3$). It is thus expected that reduction of **3** to **1** follows this scheme (Scheme 2).

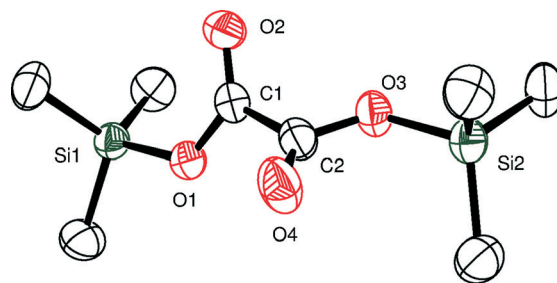
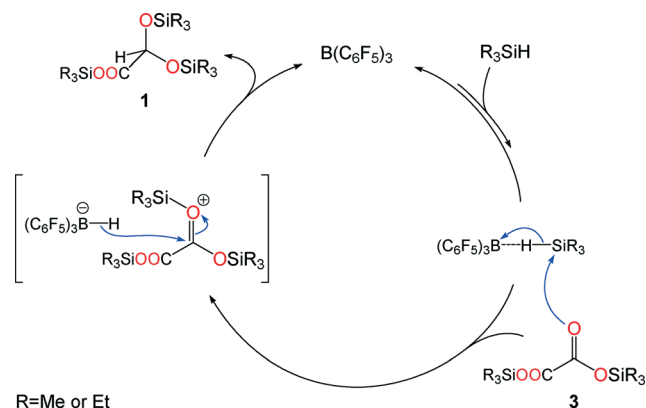
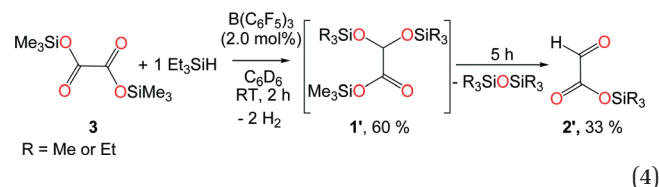
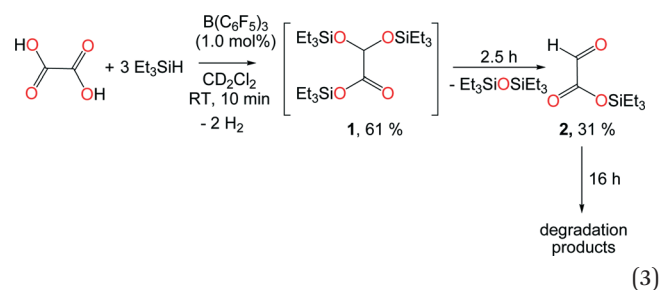


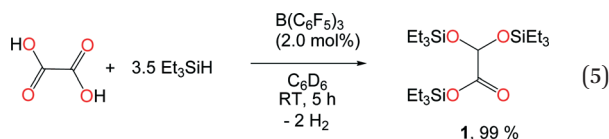
Fig. 1 X-ray crystal structure of **3**, with displacement ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: C2–O4 1.197 (2), C1–O2 1.200 (2), C1–C2 1.524 (2), Si1–O1 1.720 (1), Si2–O3 1.721 (1); C1–C2–O4 122.12 (13), C2–C1–O2 122.29 (13), C1–C2–O3 111.91 (12), C2–C1–O1 111.63 (12), Si2–O3–C2 124.38 (10), Si1–O1–C1 123.96 (9).



Scheme 2 Proposed mechanism for the reduction of **3** to **1** based on mechanistic studies carried out by Piers *et al.*

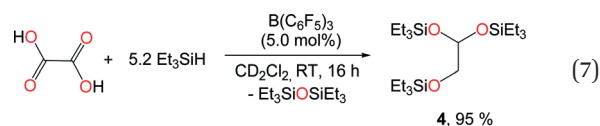


Importantly, **1** is a reactive intermediate in the reduction of oxalic acid and it rearranges to triethylsilyl 2-oxoacetate **2** in 31% yield, after 2.5 h at room temperature (eqn (3) and (4)). **1** and **2** are silylated derivatives of 2-oxoacetic acid and their formation by reduction of oxalic acid exemplifies the potential of catalytic hydrosilylation in promoting the controlled reduction of oxalic acid. Although **2** is unstable and degrades to unidentified products in CH_2Cl_2 , **1** could be successfully prepared in quantitative yield from the catalytic reduction of oxalic acid and 3.5 equiv. Et_3SiH , in benzene (eqn (5)).



Formally, the 4-electron reduction of oxalic acid can lead to two isomers, namely glyoxal or glycolic acid (Scheme 1). Using 4 equiv. Et_3SiH , the hydrosilylation of oxalic acid produces **1** in quantitative yield, within 1 h at 25 °C. The reaction

mixture then evolves slowly, until the reductant is fully consumed, to yield a ~1 : 1 mixture of **1** and **4**, over 16 h (eqn (6)). Compound **4** was fully characterized by ^1H and ^{13}C NMR spectroscopy. **4** is a silylated form of 2-hydroxyacetaldehyde and, thus, a 6-electron reduction product of oxalic acid. In addition, using 5.2 equiv. Et_3SiH and a greater loading of $\text{B}(\text{C}_6\text{F}_5)_3$ (5.0 mol%), **4** was obtained in quantitative yield by reduction of oxalic acid in CH_2Cl_2 , within 1 h at RT (eqn (7)). This reaction chemistry therefore reveals that, in CH_2Cl_2 , the hydrosilylation of **1** with Et_3SiH affords an intermediate with an increased reactivity towards reduction, leading to the accumulation of **4**. In fact, **4** is the end-product in the hydrosilylation of oxalic acid with Et_3SiH and no evolution of ethane (nor ethoxysilane) was observed when oxalic acid was reacted with excess Et_3SiH (>15 equiv.) and 5.0 mol% $\text{B}(\text{C}_6\text{F}_5)_3$, even after 48 h at 100 °C.



Because the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed hydrosilylation of oxalic acid is much slower in benzene, a different chemoselectivity can also be expected when replacing CH_2Cl_2 with this latter solvent. Indeed, **5** was formed in 90% yield, after 50 h at RT, when oxalic acid was reduced with 4.2 equiv. Et_3SiH and 7.5 mol% $\text{B}(\text{C}_6\text{F}_5)_3$ (eqn (8)). Yet, in the reaction mixture, **5** is unstable and it converts slowly to the more stable **6**, with concomitant elimination of $\text{Et}_3\text{SiOSiEt}_3$ siloxane (eqn (8)). Both **5** and **6** are formally 4-electron reduction products of oxalic acid and silylated forms of glyoxal and glycolic acid, respectively. The redox tautomerism at play in the conversion of **5** to **6** is therefore unusual, since both glyoxal and glycolic acid are stable compounds and they do not interconvert at 100 °C. Interestingly, glyoxal conversion to glycolic acid was reported, for the first time, by Mondelli, Pérez-Ramírez *et al.* in 2014.¹⁶ The authors showed that, using zeolites as Lewis acid catalysts, glyoxal could undergo a Meerwein–Ponndorf–Verley reduction/Oppenauer oxidation sequence (MPV/O) to produce glycolic acid at 90–100 °C.¹⁶ In light of these results, it is likely that the formal 1,2-hydride shift responsible for the formation of **6** from **5** involves a similar MPV/O mechanism, assisted by catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ or the Et_3Si^+ silylium cation (Scheme 2). Importantly, in benzene, **5** and **6** are the end-products of the hydrosilylation of oxalic acid and **4**, ethoxysilane derivatives or ethane is not observed when oxalic acid is reacted with 10 equiv. Et_3SiH .



Compounds 1, 2, 4, 5 and 6 are functionalized C₂-chemicals and their de-silylation was explored in order to obtain 2-oxoacetic acid, glyoxal, glycolic acid and 2-hydroxyacetaldehyde. Nevertheless, classical methods involving acidic (HCl in THF) or basic (KOH in MeOH) conditions proved unsuccessful and complete degradation of the organic products was observed by NMR spectroscopy. Furthermore, 1, 2, 4, 5 and 6 are highly sensitive towards moisture and they readily degrade to unidentified products under reduced pressure. Current efforts are now devoted to exploiting the intrinsic reactivity of these molecules towards nitrogen- and carbon-based nucleophiles.

Conclusions

Generated by C–C coupling of two CO₂ molecules, oxalic acid affords a desirable platform to access functionalized C₂-products. In this context, we have investigated the partial reduction of oxalic acid with hydrosilanes. While B(C₆F₅)₃ was successfully utilized in the hydrosilylation of mono-functional carboxylic acids, it was shown to be also selective in the reduction of a geminal di-carboxylic acid. Inexpensive and air-stable PMHS and TMSD hydrosilanes are able to reduce oxalic acid to ethane at room temperature. In contrast, high chemoselectivity was achieved in the partial reduction of oxalic acid with Et₃SiH and dissymmetric C₂-compounds were successfully accessed. Depending on the nature of the solvent (CH₂Cl₂ vs. benzene), silylated derivatives of 2-oxoacetic acid, glyoxal, glycolic acid and glycolaldehyde were formed selectively.

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Notes and references

- (a) *Carbon dioxide as chemical feedstock*, ed. M. Aresta, Wiley-VCH Verlag GmbH, 2010; (b) K. Huang, C. L. Sun and Z. J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435–2452; (c) T. Sakakura, J. C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- (a) S. Wesselbaum, T. vom Stein, J. Klankermayer and W. Walter Leitner, *Angew. Chem., Int. Ed.*, 2012, **51**, 7499–7502; (b) C. D. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, **51**, 187–190; (c) O. Jacquet, X. Frogneux, C. D. Gomes and T. Cantat, *Chem. Sci.*, 2013, **4**, 2127–2131; (d) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, *J. Am. Chem. Soc.*, 2012, **134**, 2934–2937; (e) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, *ChemCatChem*, 2013, **5**, 117–122; (f) R. Tanaka, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2009, **131**, 14168; (g) A. Boddien, F. Gartner, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 6411–6414; (h) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurency and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 9777–9780; (i) Y. H. Li, X. J. Fang, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 9568–9571; (j) F. A. LeBlanc, W. E. Piers and M. Parvez, *Angew. Chem., Int. Ed.*, 2014, **53**, 789–792; (k) S. Bontemps and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2013, **52**, 10253–10255; (l) S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2012, **51**, 1671–1674; (m) S. Bontemps, L. Vendier and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2014, **136**, 4419–4425.
- (a) P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1995, **95**, 259–272; (b) P. G. Jessop, F. Joo and C. C. Tai, *Coord. Chem. Rev.*, 2004, **248**, 2425–2442; (c) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon and D. Milstein, *Nat. Chem.*, 2011, **3**, 609–614.
- (a) A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660–10661; (b) A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, *Chem. Sci.*, 2013, **4**, 2152–2162; (c) K. Motokura, D. Kashiwame, A. Miyaji and T. Baba, *Org. Lett.*, 2012, **14**, 2642–2645; (d) S. N. Riduan, Y. G. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322–3325; (e) S. Chakraborty, J. Zhang, J. A. Krause and H. R. Guan, *J. Am. Chem. Soc.*, 2010, **132**, 8872–8873; (f) M. J. Sgro and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2012, **51**, 11343–11345; (g) M. A. Courtemanche, M. A. Legare, L. Maron and F. G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326–9329.
- (a) K. Beydoun, T. vom Stein, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.*, 2013, **52**, 9554–9557; (b) Y. H. Li, I. Sorribes, T. Yan, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2013, **52**, 12156–12160; (c) A. Tlili, X. Frogneux, E. Blondiaux and T. Cantat, *Angew. Chem., Int. Ed.*, 2014, **53**, 2543–2545.
- (a) R. S. Kumar, S. S. Kumar and M. A. Kulandainathan, *Electrochem. Commun.*, 2012, **25**, 70–73; (b) Y. Tomita, S. Teruya, O. Koga and Y. Hori, *J. Electrochem. Soc.*, 2000, **147**, 4164–4167; (c) A. P. Abbott and C. A. Eardley, *J. Phys. Chem. B*, 2000, **104**, 775–779.
- W. Riemenschneider and M. Tanifuji, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- D. Andrzej, *Electrochemical Process for Manufacturing Concentrated Solution of Glyoxalic Acid*, *Pol. Pat.*, PL135855 (B1), 1984.
- V. Calkins, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**, 762–763.
- (a) D. Addis, S. Das, K. Junge and M. Beller, *Angew. Chem., Int. Ed.*, 2011, **50**, 6004–6011; (b) Y. Motoyama, K. Mitsui, T. Ishida and H. Nagashima, *J. Am. Chem. Soc.*, 2005, **127**, 13150–13151; (c) D. Bézier, G. T. Venkanna, L. C. Misal

- Castro, J. Zheng, T. Roisnel, J. B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2012, 354, 1879–1884; (d) J. Pouessel, O. Jacquet and T. Cantat, *ChemCatChem*, 2013, 5, 3552–3556; (e) D. Bézier, J. B. Sortais and C. Darcel, *Adv. Synth. Catal.*, 2013, 355, 19–33; (f) J. Zheng, S. Chevance, J.-B. Sortais and C. Darcel, *Chem. Commun.*, 2013, 49, 10010–10012.
- 11 (a) S. Das, Y. H. Li, K. Junge and M. Beller, *Chem. Commun.*, 2012, 48, 10742–10744; (b) S. Zhou, K. Junge, D. Addis, S. Das and M. Beller, *Angew. Chem., Int. Ed.*, 2009, 48, 9507–9510; (c) H. Li, L. C. Misal Castro, J. Zheng, T. Roisnel, V. Dorcet, J. B. Sortais and C. Darcel, *Angew. Chem., Int. Ed.*, 2013, 52, 8045–8049; (d) L. C. Misal Castro, H. Li, J. B. Sortais and C. Darcel, *Chem. Commun.*, 2012, 48, 10514–10516; (e) K. Miyamoto, Y. Motoyama and H. Nagashima, *Chem. Lett.*, 2012, 41, 229–231; (f) C. Cheng and M. Brookhart, *J. Am. Chem. Soc.*, 2012, 134, 11304–11307; (g) C. Cheng and M. Brookhart, *Angew. Chem., Int. Ed.*, 2012, 51, 9422–9424.
- 12 (a) R. D. Nimmagadda and C. McRae, *Tetrahedron Lett.*, 2006, 47, 5755–5758; (b) D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, 65, 3090–3098; (c) V. Gevorgyan, M. Rubin, S. Benson, J. X. Liu and Y. Yamamoto, *J. Org. Chem.*, 2000, 65, 6179–6186; (d) V. Gevorgyan, J. X. Liu, M. Rubin, S. Benson and Y. Yamamoto, *Tetrahedron Lett.*, 1999, 40, 8919–8922; (e) D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, 118, 9440–9441.
- 13 (a) E. Feghali and T. Cantat, *Chem. Commun.*, 2014, 50, 862–865; (b) L. L. Adduci, M. P. McLaughlin, T. A. Bender, J. J. Becker and M. R. Gagne, *Angew. Chem., Int. Ed.*, 2014, 53, 1646–1649.
- 14 N. J. Lawrence, M. D. Drew and S. M. Bushell, *J. Chem. Soc., Perkin Trans. 1*, 1999, 3381–3391.
- 15 D. Bézier, S. Park and M. Brookhart, *Org. Lett.*, 2013, 15, 496–499.
- 16 P. Y. Dapsens, C. Mondelli, B. T. Kusema, R. Verel and J. Perez-Ramirez, *Green Chem.*, 2014, 16, 1176–1186.