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Oxidation of primary and secondary benzylic alcohols with hydrogen peroxide and *tert*-butyl hydroperoxide catalyzed by a "helmet" phthalocyaninato iron complex in the absence of added organic solvent†

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The oxidation of four benzylic alcohols employing hydrogen peroxide and TBHP as oxidants, catalyzed by an iron(III) complex bearing a 14,28-[1,3-diiminoisoindolinato]phthalocyaninato (diiPc) ligand has been studied and found to proceed with good selectivity, high turnover numbers, and high turnover frequencies in the absence of organic solvents other than the substrates themselves.

The controlled oxidations of primary and secondary alcohols to produce aldehydes and ketones, respectively, together comprise two of the fundamental transformations in organic synthesis.^{1–3} These transformations are important across a broad range of applied industrial/commercial concerns, and among academic investigators with more basic research interests, largely because of the widespread utility of the carbonyl compounds that are produced as synthons for the ultimate preparation of fine chemicals, pharmaceuticals, fragrances, and many other products.^{4,5} Owing to these drivers and the fact that, historically, organic oxidations (especially on larger scales) have often employed stoichiometric amounts of environmentally harmful, dangerous, or expensive oxidants,^{6–10} the search for more environmentally benign "green" methods for alcohol oxidation has defined an active and growing area of interest in recent years, especially within the field of chemical catalysis.^{1,11} Indeed, catalyst-based alcohol oxidation methods likely hold the greatest promise for discovery of new, greener synthetic protocols that will hold advantages over many existing alcohol oxidation methods because of the general principle that an effective catalyst will promote a desired reaction to occur at a favorable rate in as efficient a manner as possible, with good selectivity for the desired product and minimum

waste. Thus, the search for green catalytic alcohol oxidation processes has rightly been pursued with vigor, and continues to define an extremely active area of study. Although many promising systems have been identified that can in an environmental sense be considered improvements over previously known and commonly utilized non-catalytic methods, significant challenges remain, especially in the (sometimes overlapping) areas of oxidations involving green, atom-efficient oxidants and oxidations that avoid the use of added organic solvents. Ideally, a green alcohol oxidation catalyst will show good performance as defined by metrics such as selectivity, yield, turnover number (TON) and turnover frequency (TOF), while avoiding the use of any added solvents or problematic oxidants. While many heterogeneous catalytic systems have been found that show potential in these regards^{1,12} the problem of finding green alcohol oxidation catalysts is of a sufficiently fundamental nature as to warrant a full exploration of the potential offered by both heterogeneous and homogeneous methods.

Our particular area of interest is in finding effective homogeneous catalytic processes for the oxidation of various hydrocarbons and derivatives thereof that simultaneously show good catalyst performance in terms of TON and TOF, and that also function in as environmentally benign a manner as possible. Thus, we seek catalytic methods that employ simple, easy to handle, non-polluting and atom-efficient oxidants. These methods should avoid the use of harmful or expensive metals, and ideally, should not require the use of added organic solvents. We prefer to develop reactions that occur either in aqueous solution or in the absence of added solvent altogether. Recent years have seen significant progress toward truly green homogeneous oxidation catalysis. To mention a few specific examples: catalytic oxidations of alcohols in aqueous solution have been described in which O₂ functions as the primary oxidant with water-soluble oxovanadium¹³ and palladium(II) complexes,^{14,15} and a simple zinc complex has been shown to catalyze the oxidation of benzyl alcohol to

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benzaldehyde with H_2O_2 in water.¹⁶ The past decade has also witnessed some exciting reports of homogeneous catalytic alcohol oxidations occurring in the absence of any added solvent other than the water in which the oxidant itself is dissolved. These include systems employing manganese Schiff base complexes,^{17,18} iron(III) bromide¹⁹ and iron(III) nitrate,²⁰ and a molybdenum acetylide oxo-peroxo complex.²¹ While all of these papers present results that demonstrate the promising nature of homogeneous green alcohol oxidation catalysis, the results communicated therein do not completely satisfy the ultimate need to find catalytic systems that are simultaneously environmentally benign and also show excellent performance, as most of the reported turnover numbers, turnover frequencies, and reaction times have been less than optimal. A very impressive report was made by Beller and co-workers in 2007 that detailed the performance of $\text{Ru}(\text{terpyridine})(2,6\text{-pyridinedicarboxylate})$ in the oxidation of a series of primary and secondary alcohols in the absence of organic solvents other than the substrate alcohols themselves, following their previous results employing similar catalysts for olefin epoxidation.¹¹ In the paper on alcohol oxidations, the authors describe reactions in which turnover numbers approaching 15 000 are seen for the oxidation of benzyl alcohol in only one hour, with lower but still impressive TON values and (in most cases) longer reaction times reported for other alcohols. With these results in mind, we have begun to explore the efficacy as a catalyst for oxidation of primary and secondary alcohols of a metallophthalocyanine-like iron complex discovered in our laboratory several years ago that is already known to function as a very effective homogeneous catalyst in both alkane oxidation and olefin epoxidation. Because we are working toward the discovery of truly green transformations, we have focused on systems that require no added organic solvents and that employ oxidants that are as environmentally benign as possible.

The reactions we will describe in the present communication are oxidations of two primary and two secondary benzylic alcohols, catalyzed by an iron(III) complex formulated as $\text{L}(14,28\text{-}[1,3\text{-diiminoisoindolinato}]\text{phthalocyaninato})\text{Fe}(\text{III})$ **1** where L is a labile axial ligand, either water or methanol as the complex is initially prepared *via* a very simple solvothermal technique that we reported in an earlier paper.²² The structure of **1** is shown in Fig. 1 as a line drawing, where ligand L has been omitted for the sake of clarity. We have previously demonstrated that this so-called “helmet” metallophthalocyanine **1**, after ligand L has been exchanged for acetonitrile, is a very effective catalyst for cyclohexane and cyclooctane oxidation using hydrogen peroxide as the primary oxidant to produce cyclohexanol and cyclooctanol, respectively, with good efficiency and TON, and excellent chemoselectivity.²³ Subsequent to our report on this reactivity, Sorokin and co-workers applied the same catalyst in the epoxidation of a series of olefins, producing the corresponding epoxides with very good selectivity and yields.²⁴ In general, phthalocyanine and phthalocyanine-like catalysts have been shown to catalyze a wide variety of important transformations, and thus have themselves been established as a versatile class of catalysts

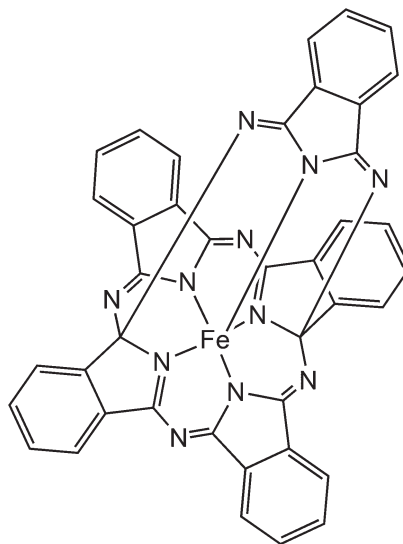


Fig. 1 Catalyst **1** with axial ligand L omitted for clarity.

that nonetheless remains underexplored, especially as applied to catalytic processes that do not rely on the use of added organic solvents.²⁵

In our alkane oxidation studies and also in the olefin epoxidation reactions reported by Sorokin, the use of hydrogen peroxide as the primary oxidant has identified an attractive feature for catalyst **1** in that for both reaction systems, water is the only oxidant-derived byproduct. It is also worthy of note that iron itself can very much be considered an environmentally benign and inexpensive metal. However, in previous reports on the use of **1** as an oxidation catalyst – in both alkane hydroxylation and olefin epoxidation – either acetonitrile²⁴ or mixed acetonitrile–dichloromethane solvent systems²³ are used, partially negating the environmental and cost advantages deriving from use of hydrogen peroxide oxidant and an iron based catalyst, especially if these processes were to be employed on a large scale. Issues relating to use and disposal of organic solvents are a centrally important factor in accounting for costs and environmental impact of industrial synthetic processes, including alcohol oxidations.^{4,26–28} Bearing this in mind, we have investigated the use of **1** as a catalyst for alcohol oxidation under conditions in which the alcohols themselves function as solvents. We have found that **1** is effective in oxidation reactions of primary and secondary benzylic alcohols to produce aldehydes and ketones, respectively, in neat solutions of the alcohol substrates themselves when either hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) is employed as the oxidant.

Specifically, we report here the catalytic oxidation with both hydrogen peroxide and TBHP of benzyl alcohol, 4-chlorobenzyl alcohol, 1-phenylethanol, and diphenylmethanol (benzhydrol) as indicated in Table 1. These substrates were chosen in part because they give sufficient catalyst solubility. From the results shown, it can be established that **1** is quite effective as a catalyst for oxidation of primary and secondary benzylic alcohols

Table 1 Summary of results from catalysis and control experiments

Entry	Substrate	Product	Oxidant	Reaction conditions ^a	TON ^b	TOF ^c (h ⁻¹)	Yield ^d percent
1	Benzyl alcohol	Benzaldehyde	H ₂ O ₂	Room temp, 15 min	84	340	1.6
2	Benzyl alcohol	Benzaldehyde	TBHP	Room temp, 0.5 h	370	730	21
3	Benzyl alcohol	Benzaldehyde	TBHP	Room temp, 2 h	420	210	29
4	Benzyl alcohol	Benzaldehyde	H ₂ O ₂	Room temp, 15 min no catalyst	—	—	0.030
5	Benzyl alcohol	Benzaldehyde	TBHP	Room temp, 2 h no catalyst	—	—	0.65
6	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	H ₂ O ₂	72 °C, 15 min	940	3800	40
7	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	TBHP	85 °C, 0.5 h	840	1700	82
8	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	TBHP	85 °C, 2 h	1300	660	90
9	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	H ₂ O ₂	Room temp, 15 min no catalyst	—	—	0.41
10	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	TBHP	Room temp, 2 h no catalyst	—	—	17
11	1-Phenylethanol	Acetophenone	H ₂ O ₂	Room temp, 6 min	230	2300	4.9
12	1-Phenylethanol	Acetophenone	TBHP	Room temp, 0.5 h	580	1200	62
13	1-Phenylethanol	Acetophenone	TBHP	Room temp, 2 h	720	360	53
14	1-Phenylethanol	Acetophenone	H ₂ O ₂	Room temp, 6 min no catalyst	—	—	0.085
15	1-Phenylethanol	Acetophenone	TBHP	Room temp, 2 h no catalyst	—	—	0.56
16	Benzhydrol	Benzophenone	H ₂ O ₂	70 °C, 10 min	210	1200	3.7
17	Benzhydrol	Benzophenone	TBHP	75 °C, 0.5 h	700	1400	56
18	Benzhydrol	Benzophenone	TBHP	68 °C, 2 h	770	390	71
19	Benzhydrol	Benzophenone	H ₂ O ₂	Room temp, 10 min no catalyst	—	—	0.77
20	Benzhydrol	Benzophenone	TBHP	Room temp, 2 h no catalyst	—	—	6.4

^a All reactions were run in magnetically stirred round-bottomed flasks open to the air. Catalyst **1** (1.0–2.8 mg, 1.2–3.5 μmol) was dissolved in the alcohol substrate before adding the oxidant as an aqueous solution. **Caution:** solutions containing significant concentrations of TBHP or hydrogen peroxide and metal-containing compounds are potentially dangerous, and reactions should be carried out behind adequate protection. Optimal reaction times for hydrogen peroxide oxidations were determined by quenching the reaction at various points with sodium thiosulfate.

^b TON = moles product/moles catalyst. Products were identified and quantified by HPLC vs. external standard. The catalyst **1** used in this study is prepared in crystalline form, where the composition of the crystals can vary slightly. In the crystallographically determined structure, ligand L is observed to be a mixture of methanol and water, with two co-crystallized methanol molecules also being present for every complex bearing a methanol ligand, whereas three co-crystallized methanol molecules are present for every complex bearing a water ligand. In a desire to report catalyst performance conservatively in light of this issue, we have calculated TON values based on an assumption that the catalyst has 100% methanol as the L ligand, which along with the two co-crystallized methanol molecules gives a formula weight of 806.65, less than that for the case where L = water and three co-crystallized methanol molecules are present, in which case the formula weight is 824.66. This results in slightly under-reported turnover numbers, assuming a mixture of the two species is actually present, because number of moles of catalyst actually present in the reaction mixtures will be very slightly less than the number used in TON calculations. ^c TOF = turnovers per hour, average over entire reaction period. ^d Oxidized product yields on the basis of total oxidant added.

without the need for highly problematic oxidants or added organic solvent. In fact, the reactions described in the present communication are, to the best of our knowledge, the first examples of alcohol oxidation catalysis employing a phthalocyanine or phthalocyanine-like homogeneous catalyst that do not require the use of relatively large amounts of added organic solvents, and simultaneously represent the first such transformations that utilize an iron-based catalyst other than simple iron containing salts. It is important to note that in the cases of primary alcohol (benzyl alcohol and 4-chlorobenzyl alcohol) oxidation, no significant amount of carboxylic acid (overoxidation) or other byproducts were evident in HPLC analyses of the product mixtures, indicating good selectivity. Oxidation reactions of secondary alcohols to produce ketones likewise proceeded with excellent selectivity for the desired products, again as evidenced by very clean chromatograms of the product solutions.

Perhaps most significantly, we observed very good performance in terms of TON and TOF in all of the oxidation reactions reported in Table 1. For the hydrogen peroxide oxidations, turnover numbers ranging from 84 for benzyl alcohol in fifteen minutes (entry 1 in Table 1) to 940 for 4-chlorobenzyl alcohol over an equivalent time period (entry 6) constitute performance that exceeds that of almost all of the similar homo-

geneous reaction systems that we are aware of.^{1,16–21} These reactions, and those involving the oxidation of 1-phenylethanol and benzhydrol to produce acetophenone and benzophenone, respectively, produce only water as an oxidant-derived byproduct and also show excellent turnover frequencies, with values (reported as averages over the entire reaction periods) ranging from 340 h⁻¹ for benzyl alcohol (entry 1) to 3800 h⁻¹ for 4-chlorobenzyl alcohol (entry 6). We did not observe the formation of significant additional product upon addition of a second aliquot of hydrogen peroxide after the completion of the reported reaction times in any of the hydrogen peroxide oxidations, nor did we observe significant additional product formation for longer reaction times than those indicated in Table 1 after one oxidant addition. The elevated temperatures necessary for solution formation in reactions involving the two substrates that are solids at room temperature (4-chlorobenzyl alcohol and benzhydrol) obviously account for some of the impressive performance of **1** in reactions involving these alcohols, but the reaction conditions employed in every case can nonetheless be considered relatively mild.

In most cases, blank reactions in which the substrate alcohols were combined with hydrogen peroxide or TBHP under conditions that were otherwise analogous to the reactions catalyzed by **1** produced very small amounts of the oxidized pro-

ducts – generally, two percent or less of the amounts observed as products in reactions catalyzed by **1**. More significant degrees of background oxidation were observed in the cases of 4-chlorobenzyl alcohol oxidation with TBHP alone (entry 10) and benzhydrol oxidation with hydrogen peroxide alone (entry 19) in which the amounts of oxidized product produced by reaction with hydrogen peroxide alone were about 20% of the amounts produced in the corresponding reactions catalyzed by **1**, and the oxidation of benzhydrol with TBHP alone (entry 20) where the background reaction amounted to 9% of that observed in the corresponding catalyzed reaction. It should be noted here that all three cases of significant background reactions occurred in reactions that were carried out at elevated temperatures.

The superior performance of the catalyst in reactions where TBHP served as the oxidant was unexpected, as this observation stands in stark contrast to our experience with the same oxidant and catalyst **1** in other attempted transformations. In the past we have endeavored to carry out hydroxylation of indan and epoxidation of styrene with the use of TBHP, but observed none of the desired products as the catalyst appeared to decompose rapidly. However, as shown in Table 1, TBHP functions as an excellent oxidant in all of the reactions reported in the present paper, with TON values ranging from 420 for benzyl alcohol oxidation in two hours (entry 3) to 1300 for 4-chlorobenzyl alcohol (entry 8) over an equivalent time period. While we recognize that TBHP is not as atom efficient as hydrogen peroxide (or molecular oxygen) and produces an organic byproduct (*tert*-butyl alcohol) we were nonetheless pleasantly surprised by the effectiveness of this oxidant working in conjunction with catalyst **1** in the reactions reported here.

We observed that the optimal reaction times for TBHP oxidations catalyzed by **1** were significantly longer than was the case for analogous reactions involving hydrogen peroxide. In Table 1 we have reported TON values for two different reaction times (thirty minutes and two hours) for each of the four alcohol substrates that were studied, in order to demonstrate the ability of these particular reaction systems to produce a large number of turnovers in thirty minutes, a relatively short reaction period compared to most of the related systems that we are aware of, and also to demonstrate the ability of **1** to catalyze reactions that produce significantly larger amounts of product upon extended (two hour) reaction times. Clearly, catalyst **1** remains in active form over a much longer period of time in the presence of TBHP in neat alcohol solutions than in the presence of hydrogen peroxide under otherwise similar conditions, for reasons that we do not yet fully understand. It is possible that the difference may be at least in part attributable to the fact that the reaction solutions containing 30% hydrogen peroxide were biphasic and contained more water, potentially resulting in catalyst precipitation that would be difficult to detect given the extremely small amounts of **1** that were employed, whereas reaction solutions in oxidations employing 70% aqueous TBHP were homogeneous. In fact, we have observed in the case of benzyl alcohol oxidation that the

catalyst remains active for many hours after the initial reaction has started in experiments where TBHP was used. This was shown by the observation that after the initial addition of TBHP oxidant had been made, the product mixture had been sampled and analyzed by HPLC and the remaining solution had been allowed to stand overnight, a second addition of TBHP resulted in a significant increase in the benzaldehyde to substrate ratio in solution. Therefore, in the cases of the two hour TBHP oxidations for which data are presented in Table 1 (entries 3, 8, 13, 18) we do not view the reported turnover numbers as absolute limits for the potential productivity of catalyst **1**, but rather as benchmark values for comparison with other systems that have been described elsewhere, and with the reactions reported in the present communication in which hydrogen peroxide was the primary oxidant.

While we were pleased with the results described above and in Table 1, it must be said that the catalytic systems described here have two drawbacks at the present time. First, product yields calculated on the basis of total oxidant are generally poor for hydrogen peroxide oxidations, below five percent with the exception of the oxidation of 4-chlorobenzyl alcohol (entry 6). The yields in TBHP oxidations were generally better, ranging (for two hour reactions) between 29% for the oxidation of benzyl alcohol (entry 3) to 90% for the oxidation of 4-chlorobenzyl alcohol (entry 8). Secondly, it must be stated that while the TON and TOF values – and in some cases the yields on the basis of total oxidant – are encouraging, the percent conversion values for the alcohols studied are quite low. Improvement on the latter of these two issues will require the development of derivatives of **1** that are significantly more soluble in the substrate alcohols that also serve as reaction solvents.

Conclusions

We have shown that a “helmet” metallophthalocyanine complex of iron functions as a very effective homogeneous alcohol oxidation catalyst in the absence of added organic solvents for primary and secondary benzylic alcohols. Oxidations proceed quickly with good TON and selectivity for the desired products. The reactivity reported here represents progress toward the goal of developing truly green alcohol oxidation methods, and suggests the potential that related systems could be efficacious in the ultimate realization of that goal. We believe that advantages deriving from conditions requiring no organic solvent other than the substrate alcohols themselves, the absence of harmful or expensive metals, as well as TON and TOF values that surpass many known catalytic systems of an otherwise similar nature portend a promising future for yet to be discovered complexes of iron that are related to **1** but differ in the presence of modifying substituents on the “helmet” ligand that could provide improved solubility characteristics and tune the catalytic properties of the iron center.

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Notes and references

- 1 R. A. Sheldon, I. W. C. E. Arends and A. Dijkstra, *Catal. Today*, 2000, **57**, 157, and references therein.
- 2 T. Naota, H. Takaya and S. I. Murahashi, *Chem. Rev.*, 1998, **98**, 2599.
- 3 R. C. Larock, *Comprehensive Organic Transformations*, VCH, New York, 1999.
- 4 M. Hudlicky, *Oxidations in Industrial Chemistry*, ACS, Washington, D.C., 1990.
- 5 S. Rochat, C. Minardi, J. Y. de saint-Laumer and A. Herrmann, *Helv. Chim. Acta*, 2000, **83**, 1645.
- 6 G. Cainelli and G. Cardillo, *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, 1984.
- 7 F. M. Menger and C. Lee, *Tetrahedron Lett.*, 1981, **22**, 1655.
- 8 C. K. Lee, B. S. Koo, Y. S. Lee, H. K. Cho and K. K.-J. Lee, *Bull. Korean Chem. Soc.*, 2002, **23**, 1667.
- 9 A. J. Mancuso and D. Swern, *Synthesis*, 1981, 165.
- 10 D. B. Dess and J. C. Martin, *J. Org. Chem.*, 1983, **48**, 4155.
- 11 F. Shi, M. K. Tse and M. Beller, *Chem. – Asian J.*, 2007, **2**, 411, and references therein.
- 12 For some examples see: F. Z. Su, Y. M. Liu, L. C. Wang, Y. Cao, H. Y. He and K. N. Fan, *Angew. Chem., Int. Ed.*, 2008, **47**, 334; Z. Guo, B. Liu, Q. Zhang, W. Deng, Y. Wang and Y. Yang, *Chem. Soc. Rev.*, 2014, **43**, 3480; S. Pathan and A. Patel, *Chem. Eng. J.*, 2014, **243**, 183; S. E. Davis, M. S. Ide and R. J. Davis, *Green Chem.*, 2013, **15**, 17; K. Kaneda, K. Ebitani, T. Mizugaki and K. Mori, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 981.
- 13 K. Marui, Y. Higashiura, S. Kodama, S. Hashidate, A. Nomoto, S. Yano, M. Ueshima and A. Ogawa, *Tetrahedron*, 2014, **70**, 2431.
- 14 G.-J. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636.
- 15 B. P. Buffin, N. L. Belitz and S. L. Verbeke, *J. Mol. Catal. A: Chem.*, 2008, **284**, 149.
- 16 X.-F. Wu, *Chem. – Eur. J.*, 2012, **18**, 8912.
- 17 H. Golchoubian and S. E. Babaei, *Chin. J. Catal.*, 2010, **31**, 615.
- 18 H. R. Mardani and H. Golchoubian, *Tetrahedron Lett.*, 2006, **47**, 2349.
- 19 S. E. Martin and A. Garrone, *Tetrahedron Lett.*, 2003, **44**, 549.
- 20 V. V. Namboodiri, V. Polshettiwar and R. S. Varma, *Tetrahedron Lett.*, 2007, **48**, 8839.
- 21 A. V. Biradar, M. K. Dongare and S. B. Umbarkar, *Tetrahedron Lett.*, 2009, **50**, 2885.
- 22 H. M. Kieler, M. J. Bierman, I. A. Guzei, P. J. Liska and R. W. McGaff, *Chem. Commun.*, 2006, 3326.
- 23 E. S. Brown, J. R. Robinson, A. M. McCoy and R. W. McGaff, *Dalton Trans.*, 2011, **40**, 5921.
- 24 I. Y. Skobelev, E. V. Kudrik, O. V. Zalomaeva, F. Albrieux, P. Afanasiev, O. A. Kholdeeva and A. B. Sorokin, *Chem. Commun.*, 2013, **49**, 5577.
- 25 A. B. Sorokin, *Chem. Rev.*, 2013, **113**, 8152.
- 26 H. A. Wittcoff, B. G. Reuben and J. S. Plotkin, *Industrial Organic Chemicals*, Wiley, Hoboken, N.J., 3rd edn, 2013.
- 27 A. Behr and P. Neubert, *Applied Homogeneous Catalysis*, Wiley-VCH Verlag and Co., Weinheim, 2012.
- 28 L. Lloyd, *Handbook of Industrial Catalysts*, Springer, New York, 2011.