Salalen vs. thiolen: in the ring(-opening of epoxide and cyclic carbonate formation)†

Oliver J. Driscoll, Jack A. Stewart, Paul McKeown† and Matthew D. Jones*

A range of Fe(III)-salalen and -thiolen–chloride complexes have been prepared and are shown to be active catalysts for the selective coupling of CO2 and cyclohexene oxide (CHO). The first Fe(III)-thiolen–acetate complex is also reported. The effect of the structure of the complex on activity is explored. An epoxide substrate scope is also provided, using the most active catalyst, as well as a study into the effect of co-catalyst equivalents on activity and selectivity.

Introduction

Two contemporary, rapidly growing areas of green chemistry involve the use of sustainable metal complexes, such as iron, for catalysis and catalytic transformations involving CO2, ideally utilising a waste stream as part of a ‘circular economy’ approach.1–12 The coupling of CO2, a renewable, abundant, cheap, non-toxic, ‘waste’ material, with reactive epoxides enables the formation of cyclic organic carbonates (COCs) and/or aliphatic polycarbonates (APCs).3,4,7–9,13–20 COCs are used in a range of applications including: high boiling, polar aprotic solvents; lithium-ion battery electrolytes; plasticisers; anti-foam additives; intermediates in both organic synthesis and industry and as monomers for copolymerisation with cyclic esters.7,8,14,15,21–23 This is a more sustainable method compared to the use of highly toxic phosgene employed in the traditional synthesis.8,14,16,17 Examples for the selective and effective Fe-mediated CO2/epoxide coupling reaction remain less prevalent than complexes containing metals such as Mg, Cr, Co, Zn and Al.15,22–33 This is despite the numerous benefits associated with iron such as high abundance, low toxicity and low commercial and industrial cost.1,2,5

Della Monica et al. recently reviewed a variety of ligand classes complexed to iron such as salalen {ONNO} and phenoxy-thioether {OSSO}.7 Lamberti and co-workers reported the first example of a Fe(III)-salalen–chloride complex, together with Fe-salen and -salan complexes, for CO2/epoxide coupling.28 More recently, we reported examples of air-stable Fe(III)-acetate complexes with salalen, salan and salen ligands for the selective coupling of CO2 with a series of epoxides, predominantly cyclohexene oxide (CHO).34 cis-Cyclohexene carbonate (cis-CHC) was formed as the exclusive product under mild, solvent-free conditions (80 °C, 10 bar CO2, 0.08 mol% metal loading). This is rare in the literature due to the bicyclic ring strain of CHC and the challenging nature of the internal CHO epoxide which imparts steric hindrance and regioselectivity issues associated with the possibility of four different products.

Della Monica, Capacchione and co-workers have reported a variety of mononuclear and dinuclear Fe(n)/ni–bis(thioether)-phenolate {OSSO} complexes with two hemilabile sulfur donor atoms.7,21,35,36 Indeed, the application of the mononuclear Fe(n)/ni–bis(thioether)-diphenolate complexes with an onium salt co-catalyst achieved very high TOFs and selectivity under mild conditions at 1 bar CO2 for a large range of internal and terminal epoxide substrates.21 For example, the conversion of propylene oxide (PO) to propylene carbonate (PC) achieved a TOF of 290 h−1 at 35 °C and 1 bar CO2. However, the cis-CHC product was not observed with CHO and a TBAC co-catalyst, instead polycyclohexene carbonate (PCHC) was selectively formed.21

We recently reported the synthesis of a range of Fe(ni)-salalen–chloride {ONNO} and Fe(ni)-thiolen–chloride {ONSO} complexes and their application to the isoselective ring-opening polymerisation (ROP) of rac-lactide.37,38 In particular, there are scarce examples of the ‘thiolen’, imine-thiobis(phenolate), family of ligands,39,40 and they have not been applied to CO2/epoxide coupling despite the similarities to Della Monica’s bis(thioether)–phenolate {OSSO} complexes.41 Herein, this work represents the application of previously synthesised Fe(ni)-salalen–chloride and Fe(ni)-thiolen–chloride complexes (Scheme 1) to the selective coupling of CO2 and epoxides. Furthermore, a new Fe(ni)-thiolen–acetate complex is reported, applied and fully characterised through High-Resolution Mass-Spectrometry (HR-MS) and single crystal XRD. The most effective catalyst was tested with a range of epoxide substrates and co-catalyst equivalents.
concentrations. Modification of the ligand structure allows for comparison between donor atoms (N/S) as well as sterics and electronics.

Results and discussion

The Fe(n) chloride complexes bearing salalen [Fe(A–G)] and thiolen [Fe(1–6)] ligands have been previously synthesised (Scheme 1), and were screened for CO₂/epoxide coupling with distilled CHO. Additionally, one Fe(n)-thiolen–acetate complex [Fe(6)] (Fig. 1) has been synthesised with the identity of the ML⁺ ion confirmed by ESI-MS. The solid-state structure of Fe(6) displays a distorted pseudo-trigonal bipyramidal geometry (τ₁ = 0.63) with an equatorial site occupied by an acetate auxiliary group (Fig. 1). Although this geometry leans closer to a square-based pyramid compared with Fe(2) (τ₂ = 0.78), bearing a chloride auxiliary group, it is similar to the salalen complex, Fe(C), and the acetate auxiliary group analogue {Fe(C), τ₂ = 0.66 and Fe(C)OAc}, τ₂ = 0.65. We have previously reported a carbonato-bridged dimer arising from the recrystallisation of Fe(2) in air and suggested that it could represent an intermediate in halide free CO₂/epoxide coupling as reported by Muller and co-workers.

The reactions were performed, using previously reported conditions, at a low catalyst loading of 0.08 mol% and 0.64 mol% tetrabutylammonium chloride (TBAC) co-catalyst loading in solvent-free conditions at 80 °C and 10 bar CO₂ for 24 h (Table 1). The reaction mixtures changed colour from purple to red over the course of the reaction; this has previously been attributed to the formation of μ-oxo-bridged Fe(n) species.

Aliquots of the crude product mixtures were taken and analysed using ¹H NMR spectroscopy to determine the conversion, product selectivity and TOF values through integration of the methine proton resonance signals for cis-cyclohexene carbonate (cis-CHC), trans-cyclohexene carbonate (trans-CHC), polycyclohexene carbonate (PCHC), and polycyclohexene oxide (PCHO) respectively relative to unreacted CHO. At 80 °C, the strained bicyclic cis-CHC product was formed exclusively for all complexes, with the exception of Fe(4), which is rare in the literature.

A range of techniques were applied to corroborate the findings from ¹H NMR spectroscopy. ESI-MS of the crude product mixtures was used to confirm the presence of cyclic CHC. Although ESI-MS is unable to differentiate between the cis- and trans-CHC, ¹H NMR spectroscopy identifies the methine resonance signals with cis-CHC appearing at δ 4.66 ppm and trans-CHC at δ 3.99 ppm, in agreement with previous reports. The characteristic methine resonance associated with PCHC is reported to appear at δ 4.65 ppm.

Table 1. CO₂/CHO reaction catalysed by Fe(A–G) and Fe(1–6) with TBAC.

| Entry | Catalyst | Conv./% | Selectivity cis-CHC:% | trans-CHC:% | PCHC: ratio/| TOF/H⁻¹ |
|-------|----------|---------|------------------------|------------|-----------|---------|
| 1     | FeCl₃    | 44      | 83                     | 83:10:16   | 23        |
| 2     | None     | 43      | 83                     | 83:0:0:17  | 22        |
| 3     | Fe(A)    | 53      | >99                    | >99:0:0:0  | 28        |
| 4     | Fe(B)    | 47      | >99                    | >99:0:0:0  | 28        |
| 5     | Fe(C)    | 41      | >99                    | >99:0:0:0  | 21        |
| 6     | Fe(D)    | 44      | >99                    | >99:0:0:0  | 23        |
| 7     | Fe(E)    | 46      | >99                    | >99:0:0:0  | 24        |
| 8     | Fe(F)    | 48      | >99                    | >99:0:0:0  | 25        |
| 9     | Fe(G)    | 51      | >99                    | >99:0:0:0  | 27        |
| 10    | Fe(1)    | 47      | >99                    | >99:0:0:0  | 24        |
| 11    | Fe(2)    | 43      | >99                    | >99:0:0:0  | 22        |
| 12    | Fe(3)    | 54      | >99                    | >99:0:0:0  | 28        |
| 13    | Fe(4)    | 51      | 90                     | 90:1:0:9   | 27        |
| 14    | Fe(5)    | 60      | >99                    | >99:0:0:0  | 31        |
| 15    | Fe(6)    | 75      | 94                     | 94:1:0:5   | 156       |
| 16    | Fe(6)    | 44      | >99                    | >99:0:0:0  | 23        |

Conditions: Fe(n) catalyst (0.08 mol%, 1 eq.), TBAC (0.64 mol%, 8 eq.), CHO (5.0 mL), 10 bar CO₂, 80 °C, 24 h. Determined via ¹H NMR spectroscopy using the methine resonances of cis-CHC (δ = 4.66 ppm), trans-CHC (δ = 3.99 ppm) and PCHO (δ = 3.35 ppm). TOF = [%Conv./%100 × (100/0.8 mol%)]/24 h = [%Conv./100 × 1250]/24. 4. 120 °C, 6 h.
which is very close to the desired cis-CHC product.\textsuperscript{23} To confirm the identity of the signal and that no polymer (PCHC) was formed, GPC analysis was carried out which showed no evidence of polymer formation. Therefore, \textsuperscript{1}H NMR spectroscopy, ESI-MS and GPC analysis confirmed that cis-CHC was formed as the exclusive product.

Control reactions were carried out and activity was observed using the FeCl3 synthetic metal precursor with TBAC co-catalyst (Table 1, entry 1). Although cis-CHC remained the major product, two additional products were present and identified as trans-CHC, the thermodynamic product, and PCHO, formed via polymerisation of the epoxide without CO\textsubscript{2} insertion. This PCHO side-product was also produced when TBAC co-catalyst was used without any [Fe] catalyst (Table 1, entry 2). No reaction was observed when [Fe] catalyst was used without co-catalyst; the TBAC being required to open the epoxide and initiate the catalytic cycle (Table 2, entry 1).

The increase of steric bulk at R\textsubscript{1}, for both salalen and thiolen complexes, decreased conversion \{Fe(A), R\textsuperscript{1} = H, 53\% vs. Fe(B), R\textsuperscript{1} = Me, 47\% vs. Fe(C), R\textsuperscript{1} = \text{-}Bu, 41\% and Fe(1), R\textsuperscript{1} = H, 47\% vs. Fe(2), R\textsuperscript{1} = Bu, 44\% respectively\} but maintained product selectivity at >99\% for the cis-CHC. Thiolen complexes were generally more active than their salalen counterparts with the exception of the unsubstituted analogues \{Fe(A), R\textsuperscript{1} = H, 53\% vs. Fe(1), R\textsuperscript{1} = H, 47\%\}. This was proposed to be due to the softer sulfur donor atom being more labile allowing for more space around the Fe(III) centre for the binding of epoxide, enhancing the reactivity. Similar observations were made for the comparisons of Fe(III)-salalen-salalen and -thiolene complexes when applied to the ROP of lactide.\textsuperscript{37,38} Thiolen complex Fe(6), bearing \text{-}Bu substituents and an acetate auxiliary ligand, displayed similar activity to the analogous chloride complex \{Fe(2), X = Cl, 43\% vs. Fe(6), X = OA\textsubscript{c}, 44\%\}. This is in contrast to the substituted Fe(III)-salalen–chloride/acetate complexes previously investigated, where the acetate complex was more active.\textsuperscript{34}

For the salalen complexes, modifying the ethylene backbone by installing a planar phenyl ring increased activity \{Fe(C), L = \text{-}CH\textsubscript{2}C\textsubscript{5}H\textsubscript{9}, 41\% vs. Fe(E), L = \text{-}C\textsubscript{6}H\textsubscript{4}, 46\%\} and this is further emphasised when using a more rigid aminopiperidine backbone \{Fe(F), R\textsuperscript{1} = \text{-}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2}, 48\%\}. Moving from the ethylene backbone to a sterically hindered cyclohexane ring had minimal effect on activity \{Fe(A), R\textsuperscript{1} = H, L = \text{-}CH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{2}, 53\% vs. Fe(G), R\textsuperscript{1} = \text{-}C\textsubscript{6}H\textsubscript{4}, 51\%\}. The trends observed with the modification of backbone structure are in agreement with the Fe(III)-acetate complexes previously reported.\textsuperscript{34}

As expected, installing chloro-functionality at R\textsuperscript{1} thus increasing the Lewis acidity of the Fe(III) centre, increased conversion; the thiolene complex was moderately more active than the salalen \{Fe(D), R\textsuperscript{1} = \text{-}Bu, 44\% vs. Fe(3), R\textsuperscript{1} = Cl, 54\%\}. The use of halide substitution was further explored using the Fe(III)-thiolene complexes. Modifying the R\textsuperscript{1} position from a chloride to a heavier bromide slightly decreased activity, presumably due to a decrease in Lewis acidity at the Fe(III) centre \{Fe(3), R\textsuperscript{1} = Cl, 54\% vs. Fe(4), R\textsuperscript{1} = Br, 51\%\}. Additionally, this was accompanied by a decrease in product selectivity to 90\%.

Transferring the bromide to the thio-phenolate moiety (R\textsuperscript{2}) increased activity while maintaining the cis-CHC as the exclusive product \{Fe(5), R\textsuperscript{1} = Cl, 60\%\}. Indeed, this complex was found to be the most active in this study with a TOF value of 31 h\textsuperscript{-1}; a TOF value similar to that reported by Lamberti using Fe(III)-salalen, -salen, -salan–chloride complexes at 100 °C, 20 bar CO\textsubscript{2} for 22 h using CHO.\textsuperscript{28} This value was increased to 156 h\textsuperscript{-1} by increasing the temperature to 120 °C and using a shorter reaction time of 6 hours (Table 1, entry 15). However, the formation of PCHO and trans-CHC decreased cis-CHC selectivity to 94\%.

The effect of using different equivalents of TBAC co-catalyst was explored using the most active catalyst, Fe(5) (Table 2). As mentioned previously, no reaction was observed with 0 eq. of TBAC (Table 2, entry 1). Increasing TBAC concentration improved the activity and also had a positive effect on selectivity; a mixture of products was observed using 2 and 4 eq. of TBAC (Table 2, entries 2 and 3). Increasing the TBAC loading to 8 eq. formed cis-CHC as the only product >99\% and gave the highest TOF value at 80 °C (31 h\textsuperscript{-1}) (Table 2, entry 4). This underlines the importance of employing an elevated concentration of co-catalyst when targeting CHCs with this reaction. The formation of cis-CHC selectively has previously been reported and discussed in literature; the presence of co-catalyst and particularly excess co-catalyst favours the formation of carbonate anions after CO\textsubscript{2} insertion. Therefore intramolecular ring-closing nucleophilic substitution, forming the cis-CHC product, is strongly favoured and potential competitive binding of further CHO and polymerisation is disfavoured (although PCHC is not observed in this study even when 0 eq. of TBAC was employed).\textsuperscript{23,47}

High functional group tolerance was observed when Fe(5) and TBAC co-catalyst were applied to a substrate scope of commercially available, terminal epoxides (Table 3). As with the CHO reactions, identification of the product and determination of selectivity was achieved through a combination of \textsuperscript{1}H NMR, GPC and ESI-MS. In all cases, the epoxide was selectively converted to the corresponding cyclic carbonate with moderate to high conversions. As expected, the least sterically hindered epoxide, propylene oxide (PO), was significantly more reactive than CHO (PO, TOF = 42 h\textsuperscript{-1}, CHO, TOF = 31 h\textsuperscript{-1}). Styrene oxide (SO), bearing a bulky phenyl group, was closer in reactivity to CHO, presumably as a result of similar steric profiles (TOF = 40 h\textsuperscript{-1}). The addition of electron withdrawing groups increased reactivity, with the
Table 3 CO₂ coupled with various epoxides catalysed by Fe(5) and TBAC

| Entry | Epoxide | Conv./% | Product selectivity/% | TOF/h⁻¹ |
|-------|---------|---------|-----------------------|---------|
| 1     |        | 81      | >99                   | 42      |
| 2     |        | 76      | >99                   | 40      |
| 3     |        | 73      | >99                   | 38      |
| 4′    |        | 92      | >99                   | 64      |
| 5     |        | 93      | >99                   | 48      |

Conditions: [Fe] catalyst (0.08 mol%, 1 eq.), TBAC (0.64 mol%, 8 eq.), CHO (5.0 mL), 10 bar CO₂, 80 °C, 24 h. * Determined via 1H NMR spectroscopy. † TOF = [(Conv.%/100) × (100/0.08 mol%)]/24 h = [(Conv./100) × 1250]/24. ‡ Reduced reaction time of 18 h.

exception of epichlorohydrin (ECH) (TOF = 38 h⁻¹). Allylglycidyl ether (AGE) gave the highest conversion in 24 h (93%); however, due to the solidification of phenoxymethyl ethylene carbonate, the reaction time with phenylglycidyl ether (PGE) was reduced to 18 h resulting in a higher TOF value (TOF = 64 h⁻¹).

Conclusions

Fe(n) chloride complexes bearing a range of salalen and thiolen ligands were prepared and applied to the coupling of CO₂ and CHO. Additionally, the first Fe(n)-thiolen–acetate was reported, fully characterised and also shown to be active for CO₂/epoxide coupling. With the exception of Fe(4), all catalysts gave cis-CHC as the exclusive product at 80 °C. Thiolen complexes tended to be more active than their direct salalen counterparts and structure–activity-relationships were explored within the ligand classes. The most active catalyst, Fe(5), gave a TOF of 31 h⁻¹ at mild conditions that could be increased to 156 h⁻¹ when the temperature was raised to 120 °C. A substrate scope of terminal epoxides demonstrated high functional group tolerance for Fe(5) and the importance of using 8 eq. of TBAC co-catalyst was highlighted.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank the University of Bath and the EPRSC (EP/L016443/1 and EP/P016405/1) for funding. We also thank Isabel Thomlinson for help with the graphical abstract. MC² are also acknowledged for the use of their analytical facilities.

References

1. Iron Catalysis, ed. B. Plietker, Springer, Berlin, 2011, vol. 33.
2. M. Albrect, R. Bedford and B. Plietker, Organometallics, 2014, 33, 5619–5621.
3. C. Martin, G. Fiorani and A. W. Kleij, ACS Catal., 2015, 5, 1353–1370.
4. M. North, B. Wang and C. Young, Energy Environ. Sci., 2011, 4, 4163–4170.
5. P. Chirik and R. Morris, Acc. Chem. Res., 2015, 48, 2495.
6. C. Darcel and J.-B. Sortais, Isr. J. Chem., 2017, 57, 1069.
7. F. Della Monica, A. Buonerba and C. Capacchione, Adv. Synth. Catal., 2019, 361, 265–282.
8. M. North, R. Pasquale and C. Young, Green Chem., 2010, 12, 1514–1539.
9. J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow and W. Leitner, Chem. Rev., 2018, 118, 434–504.
10. A. J. Hunt, E. H. K. Sin, R. Marriott and J. H. Clark, ChemSusChem, 2010, 3, 306–322.
11. J. A. Martens, A. Bogaerts, N. De Kimpe, P. A. Jacobs, G. B. Marin, K. Rabaey, M. Saey and S. Verhelst, ChemSusChem, 2010, 17, 1039–1055.
12. E. S. Sanz-Pérez, C. R. Murdock, S. A. Didas and C. W. Jones, Chem, 2016, 116, 11840–11876.
13. T. Sakakura and K. Kohn, Chem. Commun., 2009, 1312–1330.
14. B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, Chem. Rev., 2010, 110, 4554–4581.
15. A. Buonerba, A. De Nisi, A. Grassi, S. Milione, C. Capacchione and B. Rieger, Catal. Sci. Technol., 2015, 5, 118–123.
16. A-A. G. Shaikh and S. Sivaram, Chem. Rev., 1996, 96, 951–976.
17. H. Büttner, L. Longwitz, J. Steinbauer, C. Wulf and T. Werner, Top. Curr. Chem., 2017, 375, 1–56.
18. V. Besse, F. Camara, C. Voirin, R. Auvergne, S. Caillol and B. Boutevin, Polym. Chem., 2013, 4, 4545–4561.
19. H. Zhang, H. Liu and J. Yue, Chem. Rev., 2014, 114, 883–898.
20. J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, Green Chem., 2015, 17, 1966–1987.
21. F. Della Monica, B. Maiy, T. Pehl, A. Buonerba, A. De Nisi, M. Monari, A. Grassi, B. Rieger, L. Cavallo and C. Capacchione, ACS Catal., 2018, 8, 6882–6893.
22. K. A. Andrea, T. R. Brown, J. N. Murphy, D. Jagota, D. McKearney, C. M. Kozak and F. M. Kerton, Inorg. Chem., 2018, 57, 13494–13504.
23. A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, Chem. Commun., 2011, 47, 212–214.
24. M. A. Fuchs, T. A. Zevaco, E. Ember, O. Walter, I. Held and E. Dinjus, Dalton Trans., 2013, 42, 5322–5329.
25. E. Fazekas, G. S. Nichol, M. P. Shaver and J. A. Garden, Dalton Trans., 2018, 47, 13106–13112.
26. G. Bresciani, M. Bortoluzzi, F. Marchetti and G. Pampaloni, ChemSusChem, 2018, 11, 2737–2743.
27. D. Alhashmialameer, J. Collins, K. Hattenhauer and F. M. Kerton, Catal. Sci. Technol., 2016, 6, 5364–5373.
28. M. Cozzolino, V. Leo, C. Tedesco, M. Mazzeo and M. Lambert, Dalton Trans., 2018, 47, 13229–13238.
29 F. Chen, N. Liu and B. Dai, *ACS Sustainable Chem. Eng.*, 2017, 5, 9065–9075.
30 M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chem.*, 2013, 15, 3083–3090.
31 M. Taherimehr, J. P. C. Sertà, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, 8, 1034–1042.
32 C. J. Whiteoak, B. Gjoka, E. Martin, M. Mart, E. C. Escudero-ada, C. Zonta, G. Licini and A. W. Kleij, *Inorg. Chem.*, 2012, 51, 10639–10649.
33 X. Sheng, L. Qiao, Y. Qin, X. Wang and F. Wang, *Polyhedron*, 2014, 74, 129–133.
34 O. J. Driscoll, C. H. Hafford-Tear, P. Mckeown, J. A. Stewart, G. Kociok-Köhn, M. F. Mahon and M. D. Jones, *Dalton Trans.*, 2019, 48, 15049–15058.
35 F. Della Monica, M. Leone, A. Buonerba, A. Grassi, S. Milione and C. Capacchione, *Mol. Catal.*, 2018, 460, 46–52.
36 F. Della Monica, A. Buonerba, V. Paradiso, S. Milione, A. Grassi and C. Capacchione, *Adv. Synth. Catal.*, 2019, 361, 283–288.
37 O. J. Driscoll, C. K. C. Leung, M. F. Mahon, P. McKeown and M. D. Jones, *Eur. J. Inorg. Chem.*, 2018, 5129–5135.
38 J. A. Stewart, P. Mckeown, O. J. Driscoll, M. F. Mahon, B. D. Ward and M. D. Jones, *Macromolecules*, 2019, 52, 5977–5984.
39 A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, 45, 698–704.
40 A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, 53, 9140–9150.
41 E. L. Whitelaw, G. Loraine, M. F. Mahon and M. D. Jones, *Dalton Trans.*, 2011, 40, 11469.
42 E. L. Whitelaw, M. G. Davidson and M. D. Jones, *Chem. Commun.*, 2011, 47, 10004–10006.
43 S. M. Kirk, G. Kociok-Köhn and M. D. Jones, *Organometallics*, 2016, 35, 3837–3843.
44 P. McKeown, M. G. Davidson, J. P. Lowe, M. F. Mahon, L. H. Thomas, T. J. Woodman and M. D. Jones, *Dalton Trans.*, 2016, 45, 5374–5387.
45 A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349–1356.
46 J. A. Castro-Osma, M. North, W. K. Offermans, W. Leitner and T. E. Müller, *ChemSusChem*, 2016, 9, 791–794.
47 M. Cozzolino, T. Rosen, I. Goldberg, M. Mazzeo and M. Lamberti, *ChemSusChem*, 2017, 10, 1217–1223.