Chemical Science



PERSPECTIVE

View Article Online



Cite this: Chem. Sci., 2020, 11, 12604

Huaquan Fang and Martin Oestreich **

d All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 6th July 2020 Accepted 22nd July 2020

DOI: 10.1039/d0sc03712e

rsc.li/chemical-science

Selective defunctionalisation of organic molecules to valuable intermediates is a fundamentally important transformation in organic synthesis. Despite the advances made in efficient and selective defunctionalisation using transition-metal catalysis, the cost, toxicity, and non-renewable properties limit its application in industrial manufacturing processes. In this regard, boron Lewis acid catalysis has emerged as a powerful tool for the cleavage of carbon-heteroatom bonds. The ground-breaking finding is that the strong boron Lewis acid $B(C_6F_5)_3$ can activate Si–H bonds through η^1 coordination, and this Lewis adduct is a key intermediate that enables various reduction processes. This system can be tuned by variation of the electronic and structural properties of the borane catalyst, and together with different hydride sources high chemoselectivity can be achieved. This Perspective provides a comprehensive summary of various defunctionalisation reactions such as deoxygenation, decarbonylation, desulfurisation, deamination, and dehalogenation, all of which catalysed by boron Lewis acids.

Defunctionalisation catalysed by boron Lewis acids

Introduction

The conversion of organic functional groups into hydrogen atoms, namely defunctionalisation, is an important transformation in synthetic chemistry. Although it turns more functionalised raw materials into less functionalised products, the latter are considered to be more valuable than their precursors

Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 115, 10623 Berlin, Germany. E-mail: martin.oestreich@tu-berlin.de

for diverse aspects such as high-value feedstocks produced by degradation of biomass sources1 and environmentally friendly fuels prepared by desulfurisation and deamination of crude liquid fuels.² In addition, this process has also found application in environmental remediation, for example, dechlorination of toxic persistent polychlorinated biphenyls (PCBs).3

Numerous methods have been developed for the defunctionalisation of a variety of functional groups. Traditional approaches generally utilise stoichiometric amounts of pyrophoric metallic hydrides as reductant. Although widely used in laboratories, this



Huaquan Fang (born in 1992 in Jiangxi/China) studied chemistry at Beijing Normal University (2009-2013), completing his final year research project with Professor Guohua Hou. He then pursued his doctoral studies with Professor Zheng Huang at Shanghai Institute of Organic Chemistry, CAS (2013-2018), where he received his Ph.D. degree developing new pincer ruthenium complexes for

catalytic activation and conversion of inert chemical bonds. He is currently funded by the Humboldt Foundation to support postdoctoral studies with Professor Martin Oestreich at the Technische Universität Berlin, where he is developing new applications of the $B(C_6F_5)_3/hydrosilane$ combinations.



Martin Oestreich (born in 1971 Pforzheim/Germany) Professor of Organic Chemistry at the Technische Universität Berlin. He received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe (Münster, 1999). After a twoyear postdoctoral stint with Larry E. Overman (Irvine, 1999-2001), he completed his habilitation with Reinhard Brückner

(Freiburg, 2001-2005) and was appointed as Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster (2006-2011). He also held visiting positions at Cardiff University in Wales (2005), at The Australian National University in Canberra (2010), and at Kyoto University in Japan (2018). Martin recently edited a monograph entitled Organosilicon Chemistry: Novel Approaches and Reactions together with Tamejiro Hiyama.

Perspective

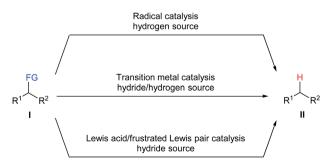
approach is only applicable to certain leaving groups and suffers from the formation of inorganic salts as stoichiometric waste as

from the formation of inorganic salts as stoichiometric waste as well as poor selectivity and functional-group tolerance. Catalytic approaches are highly demanded and can serve as convenient, efficient, and economic alternatives for established methods. Three common catalytic strategies for the defunctionalisation of a variety of functional groups, including radical catalysis, transition-metal catalysis, and Lewis acid/frustrated Lewis pair catalysis, have been developed (Scheme 1). Reductive radical chain defunctionalisation of I with tin hydrides as the hydrogen source in the presence of a radical starter had been developed over the last 60 years.4 However, this method suffers from the use of toxic organotin compounds and the difficulty to completely remove the corresponding tin by-products. Several improvements including the use of a catalytic amount of tin hydrides and the use of other hydrogen sources have also been developed. Transition metal-catalysed defunctionalisation of I with a hydrogen source has provided an efficient and selective protocol for the cleavage of carbon-heteroatom bonds.5 However, the use of rare, expensive, and toxic transition metal catalysts limit their applications in industrial manufacturing processes. Recently, Lewis acid/frustrated Lewis pair-catalysed defunctionalisation of I with various hydride sources has emerged as a promising tool to this end.6

Among various Lewis acids investigated, boron Lewis acids are particularly attractive due to their high Lewis acid strength, low cost, and benign environmental impact and have been developed rapidly in the last two decades. What's more, the Lewis acidity and reactivity of boron Lewis acid can be easily tuned by changing or modifying substituents attached to the boron atom. A variety of defunctionalisation reactions catalysed by boron Lewis acids, such as deoxygenation, decarbonylation, desulfurisation, deamination, and dehalogenation, have been reported (Scheme 2). This review provides a comprehensive summary of defunctionalisation catalysed by boron Lewis acids. The condensation of alkoxysilanes and hydrosilanes to synthesize structurally complex functional silicones and an alkane as a by-product catalysed by a $B(C_6F_5)_3$ catalyst, known as the Piers–Rubinsztajn reaction, is not covered.

Boron Lewis acids-catalysed deoxygenation

Deoxygenation of organic molecules to hydrocarbons is a step frequently encountered in organic synthesis. In fact, boron



Scheme 1 Ways of catalytic defunctionalisation. FG = functional group.

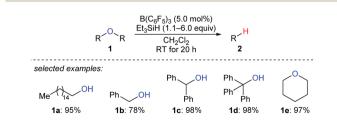
OR deoxygenation
$$R^1$$
 R^2 R^2 R^1 R^2 R^2 R^1 R^2 R^2 R^2 R^3 R^4 R^2 R^4 R^2 R^4 R^2 R^4 R^2 R^4 R^4

Scheme 2 Scope of boron Lewis acids-catalysed defunctionalisation.

Lewis acid-mediated deoxygenation of alcohols and their derivatives with a hydrosilane as the reductant is known since the 1970s.9 However, the application of boron Lewis acid in catalysis remained undeveloped until 1999. Inspired by the pioneering work of Piers *et al.* on $B(C_6F_5)_3$ -catalysed hydrosilylation of carbonyl functions, ¹⁰ Gevorgyan, Yamamoto, and co-workers found that alcohols and ethers were effectively reduced by excess Et_3SiH in the presence of catalytic amounts of $B(C_6F_5)_3$ to give the corresponding hydrocarbons at room temperature (Scheme 3). ¹¹ This catalytic system is efficient for the deoxygenation of primary alcohols, however, the deoxygenation of secondary and tertiary alcohols, except for those alcohols possessing strong carbocation-stabilising groups, was failed. Hence, the relative reactivity order of different types of alcohols was found to be $1^\circ\gg 2^\circ>3^\circ$.

A proposed mechanism for $B(C_6F_5)_3$ -catalysed deoxygenation of alcohols and ethers is depicted in Scheme 4.^{11b,12} The association of $B(C_6F_5)_3$ with hydrosilane generates an η^1 -adduct IV, either represented as Si-H···B $(C_6F_5)_3$ or Si···H-B $(C_6F_5)_3$. The adduct is subsequently attacked by the substrate to form ion pairs V or VI; hydride transfer from the borohydride to the electrophilic carbon atom of the oxonium ion produces the silyl ether and hydrocarbon, respectively, with regeneration of III. It is worth noting that Lewis adduct IV is usually spectroscopically undetectable when mixing $B(C_6F_5)_3$ and a hydrosilane. However, an isolable borane-hydrosilane adduct formed by mixing 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene and Et_3SiH was reported by Piers, Tuononen, and co-workers.¹³

By using that catalytic system, Gevorgyan, Yamamoto, and co-workers described the exhaustive deoxygenation of a variety of carbonyl functions such as carboxylic acids, aldehydes, acyl



Scheme 3 Deoxygenation of alcohols and ethers catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

Chemical Science Perspective

$$R-OSi + R'-H$$
 $B(C_6F_5)_3$
 III
 Si
 Si
 Si
 $F-B(C_6F_5)_3$
 V
 $Si-H-B(C_6F_5)_3$
 Si
 $F-B(C_6F_5)_3$
 Si
 $F-B(C_6F_5)_3$
 Si
 $F-B(C_6F_5)_3$
 Si
 $F-B(C_6F_5)_3$
 $F-B(C_6F_5)_3$

Scheme 4 Proposed mechanism for $B(C_6F_5)_3$ -catalysed deoxygenation of alcohols and ethers.

chlorides, and esters to give the corresponding hydrocarbons at room temperature (Scheme 5).¹⁴

To produce long-chain hydrocarbons (carbon number > 10), Fu and co-workers developed a $B(C_6F_5)_3$ -catalysed deoxygenation of biomass-derived fatty acids and derivatives thereof with the silicone industry byproduct polymethylhydrosiloxane (PMHS) as the reductant (Scheme 6).¹⁵ The successful conversion of commercially available plant oils to hydrocarbons demonstrated the value of this method and also provided a useful strategy for the production of liquid hydrocarbon fuels by upgrading of biodiesel. Later, $B(C_6F_5)_3$ -catalysed deoxygenation of triglycerides to give a mixture of alkanes and alkenes with hydrosiloxanes as reductants was further explored by Gale and Brook (not shown).¹⁶

A mild and rapid $B(C_6F_5)_3$ -catalysed deoxygenation of a variety of ketones $5\mathbf{a}$ - \mathbf{c} to afford the corresponding hydrocarbons with PMHS as the reductant was disclosed by Chandrasekhar and co-workers (Scheme 7). This system exhibits good efficiency and selectivity and is compatible with various functional groups such as chloride, silyl ether, ester, and alkenyl groups. Later, these authors employed this catalytic

Scheme 5 Deoxygenation of carbonyl and carboxy compounds catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

Scheme 6 Deoxygenation of biomass-derived fatty acid esters catalysed by $B(C_6F_5)_3$ with PMHS as the reductant.

Scheme 7 Deoxygenation of ketones catalysed by $B(C_6F_5)_3$ with PMHS as the reductant.

system for the deoxygenation of Baylis–Hillman adducts to form (Z)- or (E)-trisubstituted alkenes (not shown);¹⁸ the process involves the elimination of the hydroxy group followed by double bond migration. In addition, Cantat and co-workers developed B(C_6F_5)₃-catalysed deoxygenation of oxalic acid with tetramethyldisiloxane (TMDS) or PMHS as reductants (not shown).¹⁹ Nimmagadda and McRae found the combined use of B(C_6F_5)₃ with the less sterically hindered Et₂SiH₂ or nBuSiH₃ proved to be a more reactive catalytic system for the deoxygenation of polycarboxylic acids, aldehydes, ketones, and alcohols (not shown).²⁰ The B(C_6F_5)₃/Ph₂SiH₂ catalytic system demonstrated by Tan and Zhang was shown to be efficient for the reduction of an alcohol, a ketone, an α , β -unsaturated carboxylic acid, and an enol ether to their corresponding hydrocarbons (not shown).²¹

The use of H_2 as a reductant in boron Lewis acid-catalysed deoxygenation is challenging yet highly attractive, and only water is formed as a by-product. Repo and co-workers found that Lewis pair of $B(C_6F_5)_3$ and aromatic carbonyl compounds can heterolytically activate H_2 at elevated temperature (110 °C).²² By this, the stoichiometric reduction of benzophenone with H_2 as the reductant became feasible. However, the catalytic deoxygenation of ketones with H_2 by $B(C_6F_5)_3$ still is a difficult task due to the hydrolysis of $B(C_6F_5)_3$ with the by-product H_2O . By employing molecular sieves as a heterogeneous Lewis base and a desiccant to adsorb water, Mahdi and Stephan developed a $B(C_6F_5)_3$ -catalysed deoxygenation of diaryl ketones $5\mathbf{d}-\mathbf{g}$ with H_2 as the reductant at 70 °C (Scheme 8).²³

The degradation of readily available carbohydrates to valueadded feedstocks and fuels is an attractive yet challenging endeavour which requires the activation of several nonactivated C-O bonds. In 2014, Gagné and co-workers reported the

Scheme 8 Deoxygenation of ketones catalysed by $B(C_6F_5)_3$ with H_2 as the reductant.

Perspective

Average $M_n \approx 40000$

Scheme 9 Deoxygenation of carbohydrates catalysed by $B(C_6F_5)_3$ with Et_2SiH_2 as the reductant.

 $B(C_6F_5)_3$ -catalysed deoxygenation of carbohydrates **6** to afford mixtures of hexanes and hexenes with Et_2SiH_2 as the reductant (Scheme 9).²⁴ The degree of deoxygenation was influenced by the choice of hydrosilane. Secondary hydrosilanes as reductants led to exhaustive reduction while tertiary hydrosilanes generated partially deoxygenated products. Later, $B(C_6F_5)_3$ -catalysed deoxygenation of lignin²⁵ and various polymeric materials based on polyethers, polyesters, polycarbonates,²⁶ and poly(methyl acrylate)²⁷ with hydrosilanes as reductants were demonstrated by the groups of Cantat, Chang, and Seo (not shown).

The chemoselective partial deoxygenation of a variety of biologically sourced polyols to produce various oxygenfunctionalised chiral synthons using a combination of B(C₆F₅)₃ and tertiary hydrosilanes was described by Gagné and co-workers (Scheme 10).28 For example, the deoxygenation of galactitol 7 with Me₂EtSiH (7.0 equiv.) in the presence of B(C₆F₅)₃ (10 mol%) generated a C2-reduced triol 9 with inversion at C5. The deoxygenation of 7 with 2.5 equivalents of Me₂EtSiH gave 1,6-deoxygenated tetraol 8, which underwent intramolecular nucleophilic attack from the C2-OSi group to the activated C5-OSi₂⁺ in **VII** to generate the cyclic oxonium ion intermediate VIII. Subsequent hydride transfer from borohydride to the C2 position of VIII formed the observed triol 9 with inversion at C5. The formation of cyclic intermediates caused by neighbouring group participation is crucial for achieving high site- and chemoselectivity. Later, these authors reported B(C₆F₅)₃-catalysed chemoselective deoxygenation of unsaturated polyols to produce highly enriched (Z)-triols and partial deoxygenation of disaccharides to yield 1,6-deoxygenated tetraols and 1-deoxyglucose with a tertiary hydrosilane as the reductant (not shown).29 Moreover, site- and chemoselective deoxygenations of carbohydrates and its derivatives by

Scheme 10 Selective deoxygenation of biologically sourced polyols catalysed by $B(C_6F_5)_3$ with Me_2EtSiH as the reductant.

a combination of $B(C_6F_5)_3$ /catecholborane (HBcat) and $B(3,5-(CF_3)_2C_6H_3)_3$ /tertiary hydrosilane combinations were also developed (not shown). More recently, the Gagné group found the polarity of solvent to exert a profound influence on reactivity and regioselectivity of the deoxygenation of sugars using the $B(C_6F_5)_3$ /hydrosilane catalytic system (not shown). Mechanistic investigations indicated low-dielectric solvents can shorten inter-ion bond lengths of the key ion-pair intermediates due to electrostatic compressive forces.

By tuning the electronic properties of fluoroaryl borane catalysts and utilising different reductants, chemo- and siteselective modifications of various complex natural products to yield divergent products were achieved by Gagné and coworkers (Scheme 11).32 For example, the reaction of gibberellic acid (10a) with excess Et₃SiH in the presence of a catalytic amount of $B(C_6F_5)_3$ generated the known diacid 11a in 93% yield. This process involves a sequence of dehydrosilylation and ring-opening of the lactone group accompanied by an allylic transposition. In addition, 11a can also be obtained in excellent vields by the deoxygenation of pre-silvlated gibberellic acid 10b with a combination of B(C₆F₅)₃/HBcat or B(2,4,6-F₃C₆H₂)₃/ Me₂EtSiH (not shown). By employing a combination of $B(C_6F_5)_3$ HBcat, full isomerisation of 10a to 11b was observed after deprotection. The deoxygenation of 10b with excess Et₃SiH catalysed by B(3,5-(CF₃)₂C₆H₃)₃ provided a conjugated diene derivative of 11c in 51% yield after deprotection.

The beautiful work of Gagné prompted chemists to develop new approaches to selective deoxygenation. In 2015, Drosos and Morandi introduced a highly selective $B(C_6F_5)_3$ -catalysed monodeoxygenation of terminal 1,2- and 1,3-diols **12a-d** to give 2-alkanols by using a combination of Ph_2SiH_2 and Et_3SiH (Scheme 12).³³ The overall reaction is a sequence of protection to form cyclic siloxane intermediates and selective reduction at their primary position to afford 2-alkanols. Computational

$$\begin{array}{c} B(C_6F_5)_3 \ (10 \ \text{mol}\%) \\ Et_3SiH \ (4.5 \ \text{equiv}) \\ CH_2Cl_2 \\ RT \ \text{for } 3 \ \text{h} \\ (R = H) \\ \end{array}$$

$$\begin{array}{c} SiO_2C^{\text{LV}} \\ \text{Me} \\ CO_2Si \\ \text{Me} \\ \text{CO}_2Si \\ \text{Me} \\ \text{Me} \\ \text{CO}_2Si \\ \text{Me} \\ \text{CO}_2Si \\ \text{Me} \\ \text{CO}_2Si \\ \text{Me} \\ \text{Me} \\ \text{Me} \\ \text{CO}_2Si \\ \text{Me} \\ \text{Me} \\ \text{Me} \\ \text{CO}_2Si \\ \text{Me} \\ \text{$$

Scheme 11 Chemoselective deoxygenation of gibberellic acids catalysed by $B(C_6F_5)_3$ or $B(3,5-(CF_3)_2C_6H_3)_3$ with Et_3SiH or HBcat as reductants.

Chemical Science Perspective

Scheme 12 Selective deoxygenation of terminal 1,2- and 1,3-diols catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

studies reveals that the formation of cyclic siloxane intermediates, which facilitates the deoxygenation by minimizing the steric repulsions between cyclic siloxane and borane-hydrosilane complex and hinders the further deoxygenation due to the bulky disiloxane moiety, plays a significant role.³⁴

A two-step strategy for the $B(C_6F_5)_3$ -catalysed chemoselective deoxygenation of 1,n-diols and the hydroxymethyl group of an orthogonally protected carbohydrate with Et_3SiH as the reductant was disclosed by Oestreich and co-workers (Scheme 13). 35 The cleavage of C–O bonds of primary tosylates **14a–c** proceeds preferentially over that of bromide, silyl ethers, and aryl ethers at room temperature. Later, Song and co-workers used (HMe₂-SiCH₂)₂ as a new reductant for the chemoselective deoxygenation of ether-substituted alcohols and carbonyl compounds (not shown), and the authors proposed that (HMe₂SiCH₂)₂ promotes an intramolecular Si–O activation pathway. 36

Selective deoxygenation of enol ethers **15a–e** with Et₃SiH as the reductant catalysed by B(C₆F₅)₃ was achieved by Chulsky and Dobrovetsky (Scheme 14).³⁷ This process involves the selective "indirect" cleavage of alkenyl–oxygen bonds in the presence of alkyl–oxygen bonds; the mechanism is believed to be a sequence of hydrosilylation followed by silicon-assisted β -elimination.

The reduction of amides to the corresponding amines, which is another synthetically useful transformation in organic synthesis, with hydrosilanes as reductants catalysed by a boron Lewis acid was first described by Tan and Zhang (Scheme 15). Various *N*-phenylamides **17a–c** were successfully reduced to the corresponding amines at 75 °C. However, the reduction of the parent benzamide using this catalytic system was unsuccessful, even at 120 °C. Later, McGrath and coworkers found that various functional groups such as ether, ketone, and ester groups were tolerated in the $B(C_6F_5)_3$ -catalysed reduction of acetanilides to secondary amines with Et_3SiH

$$FG \xrightarrow{\begin{subarray}{c} FG \\ \end{subarray}} OTS & \frac{E(_{6}F_{6})_{3} \ (10 \ mol\%)}{E(_{3}SiH \ (1.1-1.2 \ equiv)} & FG \xrightarrow{\begin{subarray}{c} FG \\ \end{subarray}} H$$

$$CH_{2}Cl_{2} & \\ RT \ for \ 12 \ h & 2 \\ \hline \end{subarray}} Selected \ examples: \\ Br \xrightarrow{\begin{subarray}{c} FG \\ \end{subarray}} TBDMSO \xrightarrow{\begin{subarray}{c} GH_{2}Cl_{2} \\ \end{subarray}} OTS & MeO_{2}C & MeC_{2}Cl_{2} \\ \hline \end{subarray}} OTS$$

Scheme 13 Selective deoxygenation of primary alkyl tosylates catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

Scheme 14 Selective deoxygenation of enol ethers catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

Scheme 15 Deoxygenation of amides and isocyanate catalysed by $B(C_6F_5)_3$ with Ph_2SiH_2 as the reductant.

as the reductant (not shown).³⁹ The reactivity of hydrosilanes with different steric demand in this reaction was also examined.

By utilising TMDS or PMHS as reductants, reduction of various secondary and tertiary amides 17e-h to the corresponding amines catalysed by $B(C_6F_5)_3$ were independently described by the groups of Cantat⁴⁰ and Adronov⁴¹ (Scheme 16). The reduction of benzamide with TMDS (2.0 equiv.) in the presence of $B(C_6F_5)_3$ (10 mol%) gave mixtures of dibenzylamine, *N*-benzylbenzamide, and (*E*)-*N*-benzyl-1-phenylmethanimine at $100\,^{\circ}$ C after 18 h. To prevent the formation of benzonitrile, which was formed by slow dehydrogenative silylation of the N–H bonds of benzamide and subsequent elimination of a siloxane, the protection of benzamide using Me_3SiCl prior to the reduction was performed. Using this strategy, primary amides were successfully converted into the corresponding primary amines in excellent yields.

By merging Tf₂O/2-F-pyridine activation and B(C₆F₅)₃/TMDS reduction, Huang and co-workers found that various *N*-alkyl

Scheme 16 Deoxygenation of amides catalysed by $B(C_6F_5)_3$ with TMDS or PMHS as reductants.

Perspective **Chemical Science**

Scheme 17 Hydroxy-directed deoxygenation of amides catalysed by B(C₆F₅)₃ with MePhSiH₂ as the reductant.

secondary amides, which had been difficult to reduce previously, were efficiently reduced to secondary amines at room temperature (not shown).42 A variety of functional groups such as methoxy, trifluoromethyl, bromo, nitro, ester, cyano, alkenyl, alkynyl, cyclopropyl, and silyl ether was compatible.

In 2018, Sohma, Kanai, and co-workers described a B(C₆F₅)₃catalysed chemo- and regioselective reduction of various hydroxy amides 17i-k with MePhSiH2 as the reductant to synthesize 1,n-aminoalcohols under mild conditions with high functional group tolerance (Scheme 17).43 This process undergoes a sequence of B(C₆F₅)₃-catalysed dehydrogenative silylation of the hydroxy group and selective deoxygenation through intramolecular Lewis acid/base type interaction between the silicon atom and oxygen atom of the amide carbonyl group. The application of this catalytic system to chemo- and site-selective reduction of a specific amide bond in cyclosporin A, which contains four secondary and seven tertiary amide bonds, demonstrated the power of this catalytic system when applied to complex molecules.

As described above, the strong boron Lewis acid B(C₆F₅)₃ proved to be a potent catalyst in the reduction of amides. In 2013, Beller and co-workers introduced benzothiophene-functionalised boronic acids 19 for the reduction of tertiary, secondary, and primary amides with PhSiH₃ as the reductant. At 110-130 °C, the corresponding amines were obtained and the functional-group tolerance was good (Scheme 18).44 Later, Blanchet and coworkers reported bis(2-chlorophenyl)borinic acid as an efficient catalyst for the reduction of tertiary amides with PhSiH3 under mild reaction conditions (not shown).45 Mechanistic investigations indicated that this process involves the formation of borane and an amine-borane complex.

Scheme 18 Deoxygenation of amides catalysed by boronic acids 19 with PhSiH₃ as the reductant.

Scheme 19 Deoxygenation of amides catalysed by BPh3 with MePhSiH₂ as the reductant

In 2016, Okuda and co-workers described the reduction of tertiary amides 170-q with MePhSiH2 as the reductant catalysed by moderately Lewis acidic BPh3 to give amines under mild conditions with high chemoselectivity in the presence of halide, nitro, ether, ketone, ester, imine, and isocyanate functions (Scheme 19).46 The authors proposed a carbonyl activation pathway for this catalytic system instead of the known Piers-Oestreich-type hydrosilane activation mechanism.

Based on the successful application of three boron catalysts with modified steric and electronic profiles for the selective modifications of natamycin, Gagné and co-workers developed the mixed alkyl(fluoroaryl)borane catalyst B(C₆F₅)₂(hex-3-yl) (20), which is generated in situ by the hydroboration of hex-3-ene with Piers' borane HB(C₆F₅)₂, for the chemoselective reduction of mycosamine acetamides (Scheme 20).32a The reaction of acetamide derivatives of natamycin 17r and 17s with Et2SiH2 (4.5 equiv.) in the presence of 20 (10 mol%) led to the selective reduction of the N-acetamide to the N-ethyl mycosamine derivatives of natamycin 18r and 18s in useful yields without the competing reduction of other sites. Later, these authors developed a heteroleptic borane catalyst B(C₆F₅)₂(CH₂CH₂CH₂Bpin) for the mild reduction of tertiary alkyl amides, N-acetyl proline dipeptides, and even cyclosporine A with Me₂EtSiH or Et₂SiH₂ as reductants with good functional-group tolerance (not shown).47

The reduction of tertiary amides with H2 as the reductant with the aid of oxalyl chloride as an activating agent catalysed by B(2,6-F₂C₆H₃)₃ was disclosed by Paradies, Grimme, and coworkers (Scheme 21).48 The process involves the in situ formation of a chloroiminium chloride intermediate by the reaction of the amide with oxalyl chloride and exhibits high functional-

Me OSi ON X
$$C_6F_5$$
 C_6F_5 C_6F_5

Scheme 20 Selective deoxygenation of mycosamine acetamides catalysed by $B(C_6F_5)_2(hex-3-yl)$ (20) with Et_2SiH_2 as the reductant.

Chemical Science Perspective

Scheme 21 Deoxygenation of tertiary amides catalysed by B(2,6- $F_2C_6H_3$)₃ with H_2 as the reductant.

group tolerance towards ester, ether, nitro, cyano, or thiophenyl groups. The corresponding amines were isolated as their HCl salts. The reduction of acetylamide 17v resulted in a low yield, and the authors attributed this to the polymerisation of the corresponding chloroiminium chloride intermediate. Mechanistic investigations indicated the key role of chloride as an active Lewis base in borane-mediated H2 activation.

Ammonia borane is an ideal H2 storage material49 owing to its high storage capacity (19.6 weight% H), low molecular weight (30.87 g mol⁻¹), good stability against air and moisture, easy availability, and simple handling. It has been intensively investigated as a reductant for the reduction of unsaturated C-C and carbon-heteroatom bonds. 50 Xu, Fan, Xiao, and co-workers reported the reduction of various amides with ammonia borane as the reductant in the presence of catalytic amounts of B(C₆F₅)₃ and BF₃·OEt₂ to provide a wide range of structurally diverse amines in good to excellent yields under mild reaction conditions with high functional-group tolerance (Scheme 22).51 The role of the BF₃·OEt₂ co-catalyst is to activate the carbonyl group of amide by Lewis adduct formation.

Some deoxygenation reactions accompanied by ring closure and rearrangement processes have been explored. This further highlights the synthetic applicability of defunctionalisation with B(C₆F₅)₃/hydrosilane combinations. In 2016, Gagné and coworkers disclosed a B(C₆F₅)₃-catalysed reductive carbocyclisation of unsaturated carbohydrates with hydrosilanes to give cyclopropanes and cyclopentanes with high efficiency and excellent diastereoselectivity (Scheme 23).52 The reaction of glucoderived 21a with Ph₃SiH (1.1 equiv.) in the presence of B(C₆F₅)₃ (10 mol%) generated a single diastereomer of cyclopropane 22a

B(C₆F₅)₃ (2.0 mol% OEt₂ (30 mol%) 1,2-dichloroethane 60 °C for 24 h 17 selected examples. Мe 17m: 90% 17h: 90% 17n: 29% 17w: 29%

Scheme 22 Deoxygenation of amides catalysed by $B(C_6F_5)_3$ with NH₃·BH₃ as the reductant.

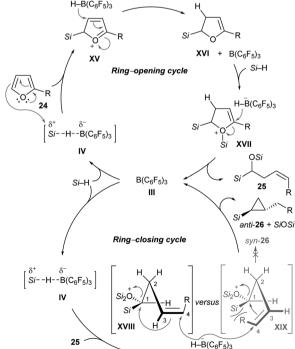
in 95% yield (Scheme 23, top). This process involves B(C₆F₅)₃catalysed intramolecular nucleophilic substitution of the activated primary C7 position by C4-OSi of 21a to form 23a, which captures a "silylium ion" by the more basic cyclic oxygen atom to generate silyloxonium IX. Borohydride reduction of alkene moiety in IX induces a cyclisation event to yield cyclopropane 22a after deprotection. Conversely, the allylic polyol derivative 21b provided a single cyclopentane diastereomer 22b in 82% yield under similar conditions (Scheme 23, bottom). After the formation of silyloxonium X, a 1,2-migration of the styryl group with inversion at C4 produces an silyloxycarbenium/silylcarboxonium ion intermediate XI, which is reduced by borohydride to the observed intermediate XII. Subsequent silylation of the primary silyl ether group of XII is followed by cyclisation through nucleophilic attack of the alkene to the activated C7 carbon atom. This generates a benzylic cation which is further reduced by borohydride to give cyclopentane 22b after deprotection.

Chang and co-workers reported the stereocontrolled conversion of furans into Z-configured homoallylic silanes 25 and antisubstituted cyclopropyl silanes 26 through selective ring-opening and subsequent ring-closing processes (Scheme 24).53 The $B(C_6F_5)_3$ -catalysed double hydrosilylation of furans with Me₂-PhSiH (2.05 equiv.) afforded 25 in excellent yields and with high

Scheme 23 Carbocyclisation of unsaturated carbohydrates catalysed by B(C₆F₅)₃ with Ph₃SiH or Me₂EtSiH as the reductant.

stereoselectivity (Scheme 24, top). The subsequent cyclopropanation can be simply achieved by the addition of further equivalents of the hydrosilane to furnish 26 with exclusive transselectivity. Isolation of ring-opened intermediates is not required. The authors proposed a cascade of B(C₆F₅)₃-catalysed ringopening (by two-fold hydrosilylation) and ring-closing reactions (by intramolecular cyclopropanation) (Scheme 24, bottom). The selective borohydride attack at the α-carbon of intermediate XVII and at the C4 of silyloxonium species XVIII leads to trans-(2-alkyl) cyclopropyl silanes exclusively. Later, these authors further reported the B(C₆F₅)₃-catalysed reductive carbocyclisation of homoallylic alcohols and dihydro-2H-pyrans with Me2EtSiH or PhSiH₃ as reductants to construct a range of 1,2-disubstituted (hetero)arylcyclobutanes under mild reaction conditions with high efficiency and excellent cis-selectivity.54 Mechanistic studies suggested a stepwise, dual ring-closing pathway (not shown).

During their investigation of chemoselective deoxygenation of protected 1,*n*-diols, Oestreich and co-workers found that diols **14d–f** were partially or fully transformed into the rearranged products (Scheme 25).³⁵ The authors proposed that



Scheme 24 Ring-opening and -closing cascades of furans catalysed by $B(C_6F_5)_3$ with Me_2PhSiH as the reductant.

Scheme 25 Rearrangement of primary alkyl tosylates catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

Scheme 26 Pinacol-type rearrangement of 1,2-diols catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

these processes involve phenonium ion intermediates **XX** for substrates **14d** and **14e** with anchimeric assistance by an adjacent aryl group or a three-membered silyloxonium ion intermediate **XXI** for aliphatic **14f**. A similar rearrangement was also observed by Song and co-workers (not shown).³⁶

A reductive pinacol-type rearrangement of internal 1,2-diols was described by Morandi and co-workers (Scheme 26). By employing a combination of $B(C_6F_5)_3$ and two hydrosilanes, a broad range of structurally diverse 1,2-diols 12e-h underwent reductive rearrangement with inversion to give primary and secondary alcohols. This process involves the formation of a cyclic siloxane, and mechanistic investigations indicated that alkyl migration occurs prior to deoxygenation in internal diols due to the hyperconjugative and steric effects of the alkyl substituent.

Boron Lewis acids-catalysed decarbonylation

A formal decarbonylation of aliphatic aldehydes **29a–d** *via* a sequence of Baeyer–Villiger oxidation and $B(C_6F_5)_3$ - or BF_3 - OEt_2 -catalysed deoxygenation of the resulting formate with Et_3SiH as the reductant was developed by Richter and Oestreich (Scheme 27). ⁵⁶ Mechanistic investigations suggested that an S_N1 mechanism is involved for the deoxygenation process.

Scheme 27 Formal decarbonylation of α -branched aliphatic aldehydes catalysed by B(C₆F₅)₃ with Et₃SiH as the reductant.

Boron Lewis acids-catalysed desulfurisation

The combination of a Lewis acid catalyst and a hydrosilane has been widely used for the activation of C–O bonds in the above deoxygenation processes. However, application of this catalytic system to the cleavage of other carbon–heteroatom bonds is far less explored. During their investigation of $B(C_6F_5)_3$ -catalysed chemoselective postpolymerisation modification of poly(phenylsilane), Rosenberg and co-workers observed the formation of diphenylmethane as a result of overreduction of thiobenzophenone (31a).⁵⁷ The authors demonstrated that the desulfurisation of 31a with PhSiH₃ or Ph₂SiH₂ as reductants occurred rapidly to furnish diphenylmethane (2c) in quantitative yield (Scheme 28).

A detailed investigation of $B(C_6F_5)_3$ -catalysed desulfurisation of various sulfides 32a–d was disclosed by Akiyama and coworkers (Scheme 29).⁵⁸ The desulfurisation of various benzyl and alkyl sulfides and dithianes with Et_3SiH as the reductant in the presence of a catalytic amount of $B(C_6F_5)_3$ generated the corresponding hydrocarbons in good yields under mild reaction conditions with high chemoselectivity. This process could be applied to the deprotection of dithioacetals.

Boron Lewis acids-catalysed deamination

More recently, the utility of boron Lewis acid/hydrosilane combinations in the cleavage of C–N bonds to effect catalytic deamination was described by Fang and Oestreich (Scheme 30). 59 With B(C₆F₅)₃ as the catalyst and PhSiH₃ as the reductant, a broad range of 1°, 2°, and 3° amines 33a–d as well as heterocumulenes (not shown) was converted into the corresponding hydrocarbons at 120 °C. Yields were moderate to good. The relative reactivity of 1°, 2°, and 3° benzylic amines under catalytic conditions was investigated and was opposite to

Scheme 28 Desulfurisation of thiobenzophenone catalysed by $B(C_6F_5)_3$ with PhSiH $_3$ or Ph $_2$ SiH $_2$ as reductants.

Scheme 29 Desulfurisation of sulfides catalysed by $B(C_6F_5)_3$ with $Et_{\tau}SiH$ as the reductant. $Ar = p-ClC_6H_4$.

Scheme 30 Deamination of amines catalysed by $B(C_6F_5)_3$ with PhSiH₃ as the reductant.

the order of reactivity seen in the deoxygenation of C–O bonds. This process involves the formation of bissilylammonium borohydride intermediates. These dissociate into the corresponding benzylic carbocations which could be further captured by the borohydride to generate the defunctionalised products.

Boron Lewis acids-catalysed dehalogenation

The combined use of boron Lewis acid and hydrosilanes can also be employed to the cleavage of carbon–halogen bonds. In 2012, Caputo and Stephan reported a mild $B(C_6F_5)_3$ -catalysed hydrodefluorination of 1°, 2°, and 3° alkyl fluorides with Et_3SiH as the reductant to afford the corresponding hydrocarbons in good to excellent yields (Scheme 31).⁶⁰ The hydrodefluorination of 1,1,1,3,3,3-hexafluoro-2-(fluoromethoxy)propane (34d) was more sluggish, and a temperature of 60 °C was required at which the trifluoromethyl groups remained intact. The authors

$$R = \frac{B(C_6F_5)_3 (5.0 \text{ mol}\%)}{Et_3SiH (1.0 \text{ equiv})} R = \frac{H}{34a: >95\%}$$

$$34b: >95\%$$

$$34b: >95\%$$

$$34c: >95\%$$

$$34c: >95\%$$

$$34c: >95\%$$

$$34c: >95\%$$

$$34d: 72\%$$

$$(60 \% \text{ for } 18 \text{ h})$$

Scheme 31 Hydrodefluorination of alkyl fluorides catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

Perspective Chemical Science

Scheme 32 Hydrodefluorination of trifluorotoluenes catalysed by the combination of $B(C_6F_5)_3$ and $Cp_2^*TiF_2$ with Et_3SiH as the reductant.

Scheme 33 Hydrodebromination of alkyl bromides catalysed by $B(C_6F_5)_3$ with Et_3SiH as the reductant.

attributed the slower reaction to the presence of the ethereal oxygen rendering the C-F bond less polar, thus leading to a weak donor-acceptor interaction between the substrate and the boron Lewis acid. Later, the selective hydrodefluorination of a C1-fluorinated glucose derivative with TMDS as the reductant catalysed by Piers' borane, $(C_6F_5)_2BH$, generated *in situ* from $(C_6F_5)_2BOH$ was described by Zhang, Park, and Chang (not shown).⁶¹

The hydrodefluorination of trifluorotoluenes with Et_3SiH as the reductant catalysed by $B(C_6F_5)_3$ alone was unsuccessful. By adding an extra group 4 metal complex as a co-catalyst, Lamač and co-workers realised this transformation. Among the metallocene co-catalysts screened, $Cp_2^*TiF_2$ was the most active co-catalyst and also promoted the hydrodechlorination of the aliphatic halogenated solvent, CHCl3. A quantitative yield of toluene was obtained for the hydrodefluorination of trifluorotoluene (35a) with Et_3SiH catalysed by the combination of $B(C_6F_5)_3$ and $Cp_2^*TiF_2$ in PhCl (Scheme 32). Et_3SiF was formed as a by-product, and a higher selectivity was achieved compared to previously reported catalytic systems by suppressing Friedel–Crafts side products generated by the alkylation of toluene with substrate.

Oestreich and co-workers also demonstrated $B(C_6F_5)_3$ -catalysed hydrodebromination of primary and secondary alkyl bromides **36a** and **36b** with Et_3SiH as the reductant at room temperature (Scheme 33).³⁵ However, hydrodechlorination of the corresponding alkyl chloride using this catalytic system was unsuccessful.

Summary and outlook

During the past two decades, significant achievements have been made in the field of defunctionalisation on the basis of boron Lewis acid catalysis, which exhibits comparable or even superior catalytic activity and selectivity to transition metal catalysis. Starting from Piers's seminal discovery of $B(C_6F_5)_3$ -catalysed hydrosilylation and Gevorgyan's early works on $B(C_6F_5)_3$ -catalysed deoxygenation, numerous reductive alcohol

deoxygenations by combinations of boron Lewis acids and hydride sources have been developed. Especially Gagné show-cased the impressive chemo-, regio-, and stereoselectivity that can be achieved with this tool. In addition, this boron Lewis acid catalysis has been successfully extended to the cleavage of C–S, C–N, and carbon–halogen bonds. However, the efficiency and selectivity of boron Lewis acid catalysis still needs to be further improved. Functional-group tolerance remains an issue. Thus, the development of air- and moisture-stable and easy-to-prepare and -handle catalysts with high activity and selectivity is desirable. Next to the significant advances made in the area of deoxygenation, selective decarbonylation, desulfurisation, deamination, and dehalogenation have just begun to flourish.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

H. F. gratefully acknowledges the Humboldt Foundation for a postdoctoral fellowship (2018–2020). M. O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship.

References

- 1 For reviews, see: (*a*) A. M. Robinson, J. E. Hensley and J. W. Medlin, *ACS Catal.*, 2016, **6**, 5026–5043; (*b*) C. Chatterjee, F. Pong and A. Sen, *Green Chem.*, 2015, **17**, 40–71.
- 2 J. J. Eisch, L. E. Hallenbeck and M. A. Lucarelli, Fuel, 1985, 64, 440–442.
- 3 For selected examples, see: (a) R. DeVor, K. Carvalho-Knighton, B. Aitken, P. Maloney, E. Holland, L. Talalaj, S. Elsheimer, C. A. Clausen and C. L. Geiger, *Chemosphere*, 2009, 76, 761–766; (b) B.-Z. Wu, H.-Y. Chen, S. J. Wang, C. M. Wai, W. Liao and K. Chiu, *Chemosphere*, 2012, 88, 757–768; (c) A. Ido, S. Ishihara, A. Kume, T. Nakanishi, Y. Monguchi, H. Sajiki and H. Nagase, *Chemosphere*, 2013, 90, 57–64.
- 4 For a review, see: A. Studer and S. Amrein, *Synthesis*, 2002, 835–849.
- 5 For a review, see: A. Modak and D. Maiti, *Org. Biomol. Chem.*, 2016, **14**, 21–35.
- 6 For reviews of boron Lewis acids/frustrated Lewis pair-catalysed H-H and Si-H bond activation, see: (a) D. Weber and M. R. Gagné, in *Organosilicon Chemistry: Novel Approaches and Reactions*, ed. T. Hiyama and M. Oestreich, Wiley-VCH, Weinheim, 2019, pp. 33–85; (b) T. Hackel and N. A. McGrath, *Molecules*, 2019, 24, 432–461; (c) M. Oestreich, J. Hermeke and J. Mohr, *Chem. Soc. Rev.*, 2015, 44, 2202–2220; (d) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, 54, 6400–6441; (e) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, 49, 46–76.
- 7 For a review, see: J. L. Carden, A. Dasgupta and R. L. Melen, *Chem. Soc. Rev.*, 2020, **49**, 1706–1725.

Chemical Science

8 For reviews, see: (a) X. J. Chen, M. H. Yi, S. F. Wu, L. W. Tan, X. Ge, M. He and G. Q. Yin, *Materials*, 2019, 12, 304–316; (b) M. A. Brook, Chem.-Eur. J., 2018, 24, 8458-8469; (c) R. Wakabayashi and K. Kuroda, ChemPlusChem, 2013, 78, 764-774; for selected examples of Piers-Rubinsztajn reaction, see: (d) S. Rubinsztajn and J. A. Cella, Macromolecules, 2005, 38, 1061-1063; (e) J. Chojnowski, S. Rubinsztajn, J. A. Cella, W. Fortuniak, M. Cypryk, J. Kurjata and K. Kazmierski, Organometallics, 2005, 24, 6077-6084; (f) J. Cella and S. Rubinsztajn, Macromolecules, 2008, 41, 6965-6971; (g) J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, Macromolecules, 2008, 41, 7352-7358; (h) J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, Chem. Commun., 2010, 46, 4988-4990; (i) B. A. Kamino, J. B. Grande, M. A. Brook and T. P. Bender, Org. Lett., 2011, 13, 154-157; (j) M. J. Gretton, B. A. Kamino, M. A. Brook and T. P. Bender, *Macromolecules*, 2012, **45**, 723–728; (k) M. J. Gretton, B. A. Kamino and T. P. Bender, Macromol. Symp., 2013, 324, 82-94; (1) J. F. Zhang, Y. Chen and M. A. Brook, ACS Sustainable Chem. Eng., 2014, 2, 1983-1991; (m) J. F. Zhang, E. Fleury and M. A. Brook, Green Chem., 2015, 17, 4647-4656; (n) J. F. Zhang, S. Liang, L. Y. Yu, A. L. Skov, H. M. Etmimi, P. E. Mallon, A. Adronov and M. A. Brook, J. Polym. Sci., Part A: Polym. Chem., 2016, 54, 2379-2385; (o) M. C. Liao, A. F. Schneider, S. E. Laengert, C. B. Gale, Y. Chen and M. A. Brook, Eur. Polym. J., 2018, 107, 287-293.

- 9 For selected examples, see: (a) M. G. Adlington, M. Orfanopoulos and J. L. Fry, *Tetrahedron Lett.*, 1976, 17, 2955–2958; (b) J. L. Fry, M. Orfanopoulos, M. G. Adlington, W. P. Dittman and S. B. Silverman, *J. Org. Chem.*, 1978, 43, 374–375; (c) J. W. Larsen and L. W. Chang, *J. Org. Chem.*, 1979, 44, 1168–1170; (d) M. Orfanopoulos and I. Smonou, *Synth. Commun.*, 1988, 18, 833–839; (e) I. Smonou, *Synth. Commun.*, 1994, 24, 1999–2002.
- 10 D. J. Parks and W. E. Piers, J. Am. Chem. Soc., 1996, 118, 9440–9441.
- 11 (a) V. Gevorgyan, J.-X. Liu, M. Rubin, S. Benson and Y. Yamamoto, *Tetrahedron Lett.*, 1999, 40, 8919–8922; (b)
 V. Gevorgyan, M. Rubin, S. Benson, J.-X. Liu and Y. Yamamoto, *J. Org. Chem.*, 2000, 65, 6179–6186.
- 12 For some mechanistic investigations on B(C₆F₅)₃-catalysed hydrosilylation of ketones and imines, see: (a) D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, 65, 3090–3098; (b) J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, 2, 3921–3923; (c) S. Shinke, T. Tsuchimoto and Y. Kawakami, *Silicon Chem.*, 2007, 3, 243–249; (d) S. Rendler and M. Oestreich, *Angew. Chem., Int. Ed.*, 2008, 47, 5997–6000; (e) D. T. Hog and M. Oestreich, *Eur. J. Org. Chem.*, 2009, 5047–5056; (f) J. Hermeke, M. Mewald and M. Oestreich, *J. Am. Chem. Soc.*, 2013, 135, 17537–17546; (g) K. Sakata and H. Fujimoto, *J. Org. Chem.*, 2013, 78, 12505–12512; (h) T. Fallon and M. Oestreich, *Angew. Chem., Int. Ed.*, 2015, 54, 12488–12491.

- 13 A. Y. Houghton, J. Hurmalainen, A. Mansikkamaki, W. E. Piers and H. M. Tuononen, *Nat. Chem.*, 2014, 6, 983– 988.
- 14 (a) V. Gevorgyan, M. Rubin, J.-X. Liu and Y. Yamamoto, J. Org. Chem., 2001, 66, 1672–1675; (b) G. B. Bajracharya, T. Nogami, T. Jin, K. Matsuda, V. Gevorgyan and Y. Yamamoto, Synthesis, 2004, 308–311.
- 15 X. Y. Li, R. Shang, M. C. Fu and Y. Fu, *Green Chem.*, 2015, 17, 2790–2793.
- 16 C. B. Gale and M. A. Brook, *Green Chem.*, 2018, **20**, 3717-3721.
- 17 S. Chandrasekhar, C. R. Reddy and B. N. Babu, *J. Org. Chem.*, 2002, **67**, 9080–9082.
- 18 S. Chandrasekhar, G. Chandrashekar, K. Vijeender and M. S. Reddy, *Tetrahedron Lett.*, 2006, 47, 3475–3478.
- 19 E. Feghali, O. Jacquet, P. Thuery and T. Cantat, *Catal. Sci. Technol.*, 2014, 4, 2230–2234.
- 20 (a) R. D. Nimmagadda and C. McRae, *Tetrahedron Lett.*, 2006,
 47, 3505–3508; (b) R. D. Nimmagadda and C. McRae, *Tetrahedron Lett.*, 2006,
 47, 5755–5758; (c)
 R. D. Nimmagadda and C. McRae, *Org. Geochem.*, 2007, 38,
 1061–1072.
- 21 M. X. Tan and Y. G. Zhang, *Tetrahedron Lett.*, 2009, **50**, 4912–4915.
- 22 M. Lindqvist, N. Sarnela, V. Sumerin, K. Chernichenko, M. Leskela and T. Repo, *Dalton Trans.*, 2012, 41, 4310–4312.
- 23 T. Mahdi and D. W. Stephan, Angew. Chem., Int. Ed., 2015, 54, 8511–8514.
- 24 L. L. Adduci, M. P. McLaughlin, T. A. Bender, J. J. Becker and M. R. Gagné, *Angew. Chem., Int. Ed.*, 2014, 53, 1646–1649.
- 25 (a) E. Feghali and T. Cantat, Chem. Commun., 2014, 50, 862–865; (b) E. Feghali, G. Carrot, P. Thuery, C. Genre and T. Cantat, Energy Environ. Sci., 2015, 8, 2734–2743.
- 26 E. Feghali and T. Cantat, ChemSusChem, 2015, 8, 980-984.
- 27 C. Jeon, D. W. Kim, S. Chang, J. G. Kim and M. Seo, ACS Macro Lett., 2019, 8, 1172–1178.
- 28 L. L. Adduci, T. A. Bender, J. A. Dabrowski and M. R. Gagné, Nat. Chem., 2015, 7, 576–581.
- 29 T. A. Bender, J. A. Dabrowski and M. R. Gagné, *ACS Catal.*, 2016, **6**, 8399–8403.
- 30 (a) Y. Seo and M. R. Gagné, ACS Catal., 2018, 8, 81–85; (b) J. M. Lowe, Y. Seo and M. R. Gagné, ACS Catal., 2018, 8, 8192–8198; (c) Y. Seo, J. M. Lowe and M. R. Gagné, ACS Catal., 2019, 9, 6648–6652.
- 31 J. Lowe, B. Bowers, Y. Seo and M. R. Gagné, *Angew. Chem., Int. Ed.*, 2020, **59**, DOI: 10.1002/anie.202007415.
- 32 (a) T. A. Bender, P. R. Payne and M. R. Gagné, *Nat. Chem.*, 2018, **10**, 85–90; (b) Y. Seo, A. Gudz, J. M. Lowe and M. R. Gagné, *Tetrahedron*, 2019, 75, 130712.
- 33 N. Drosos and B. Morandi, Angew. Chem., Int. Ed., 2015, 54, 8814–8818.
- 34 G. J. Cheng, N. Drosos, B. Morandi and W. Thiel, *ACS Catal.*, 2018, **8**, 1697–1702.
- 35 I. Chatterjee, D. Porwal and M. Oestreich, *Angew. Chem., Int. Ed.*, 2017, **56**, 3389–3391.
- 36 W. Y. Yang, L. Gao, J. Lu and Z. L. Song, *Chem. Commun.*, 2018, **54**, 4834–4837.

- 37 K. Chulsky and R. Dobrovetsky, *Org. Lett.*, 2018, **20**, 6804–6807.
- 38 For reviews, see: (*a*) A. Volkov, F. Tinnis, T. Slagbrand, P. Trillo and H. Adolfsson, *Chem. Soc. Rev.*, 2016, 45, 6685–6697; (*b*) A. M. Smith and R. Whyman, *Chem. Rev.*, 2014, **114**, 5477–5510.
- 39 K. M. Lucas, A. F. Kleman, L. R. Sadergaski, C. L. Jolly, B. S. Bollinger, B. L. Mackesey and N. A. McGrath, *Org. Biomol. Chem.*, 2016, 14, 5774–5778.
- 40 E. Blondiaux and T. Cantat, *Chem. Commun.*, 2014, **50**, 9349–9352.
- 41 R. C. Chadwick, V. Kardelis, P. Lim and A. Adronov, *J. Org. Chem.*, 2014, **79**, 7728–7733.
- 42 P. Q. Huang, Q. W. Lang and Y. R. Wang, J. Org. Chem., 2016, 81, 4235-4243.
- 43 J. Z. Ni, T. Oguro, T. Sawazaki, Y. Sohma and M. Kanai, *Org. Lett.*, 2018, **20**, 7371–7374.
- 44 Y. H. Li, J. A. M. de la Torre, K. Grabow, U. Bentrup, K. Junge, S. L. Zhou, A. Brückner and M. Beller, *Angew. Chem., Int. Ed.*, 2013, 52, 11577–11580.
- 45 A. Chardon, T. M. El Dine, R. Legay, M. De Paolis, J. Rouden and J. Blanchet, *Chem.-Eur. J.*, 2017, 23, 2005–2009.
- 46 D. Mukherjee, S. Shirase, K. Mashima and J. Okuda, *Angew. Chem., Int. Ed.*, 2016, **55**, 13326–13329.
- 47 (a) M. T. Peruzzi, Q. Q. Mei, S. J. Lee and M. R. Gagné, *Chem. Commun.*, 2018, 54, 5855–5858; (b) M. T. Peruzzi, F. Gallon, S. J. Lee and M. R. Gagné, *Org. Lett.*, 2019, 21, 3451–3455.
- 48 N. A. Sitte, M. Bursch, S. Grimme and J. Paradies, *J. Am. Chem. Soc.*, 2019, **141**, 159–162.
- 49 For reviews, see: (a) A. Rossin and M. Peruzzini, *Chem. Rev.*, 2016, 116, 8848–8872; (b) Z. Huang and T. Autrey, *Energy Environ. Sci.*, 2012, 5, 9257–9268; (c) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, 110, 4079–4124; (d) C. W. Hamilton, R. T. Baker, A. Staubitz

- and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279–293; (*e*) T. B. Marder, *Angew. Chem., Int. Ed.*, 2007, **46**, 8116–8118.
- 50 For selected examples, see: (a) S. Li, G. Li, W. Meng and H. Du, J. Am. Chem. Soc., 2016, 138, 12956–12962; (b) Q. Zhou, L. Zhang, W. Meng, X. Feng, J. Yang and H. Du, Org. Lett., 2016, 18, 5189–5191; (c) S. Li, W. Meng and H. Du, Org. Lett., 2017, 19, 2604–2606; (d) F. Ding, Y. Zhang, R. Zhao, Y. Jiang, R. L.-Y. Bao, K. Lin and L. Shi, Chem. Commun., 2017, 53, 9262–9264.
- 51 Y. Pan, Z. Luo, J. Han, X. Xu, C. Chen, H. Zhao, L. Xu, Q. Fan and J. Xiao, *Adv. Synth. Catal.*, 2019, **361**, 2301–2308.
- 52 T. A. Bender, J. A. Dabrowski, H. Y. Zhong and M. R. Gagné, *Org. Lett.*, 2016, **18**, 4120–4123.
- 53 C. K. Hazra, N. Gandhamsetty, S. Park and S. Chang, *Nat. Commun.*, 2016, 7, 13431–13439.
- 54 C. K. Hazra, J. Jeong, H. Kim, M. H. Baik, S. Park and S. Chang, *Angew. Chem.*, *Int. Ed.*, 2018, 57, 2692–2696.
- 55 N. Drosos, G. J. Cheng, E. Ozkal, B. Cacherat, W. Thiel and B. Morandi, *Angew. Chem., Int. Ed.*, 2017, 56, 13377–13381.
- 56 S. C. Richter and M. Oestreich, *Chem.-Eur. J.*, 2019, 25, 8508–8512.
- 57 P. T. K. Lee, M. K. Skjel and L. Rosenberg, *Organometallics*, 2013, 32, 1575–1578.
- 58 K. Saito, K. Kondo and T. Akiyama, *Org. Lett.*, 2015, **17**, 3366–3369.
- 59 H. Fang and M. Oestreich, *Angew. Chem., Int. Ed.*, 2020, **59**, 11394–11398.
- 60 C. B. Caputo and D. W. Stephan, *Organometallics*, 2012, 31, 27–30.
- 61 J. Zhang, S. Park and S. Chang, *Angew. Chem., Int. Ed.*, 2017, **56**, 13757–13761.
- 62 D. Dunlop, J. Pinkas, M. Horáček, N. Žilková and M. Lamač, Dalton Trans., 2020, 49, 2771–2775.