Halogenated Triarylboranes: Synthesis, Properties and Applications in Catalysis

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Halogenated triarylboranes (BAr_3) have been known for decades, however it has only been since the surge of interest in main group catalysis that their applications as strong Lewis acid catalysts has been recognised. This review aims to look past the popular tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] to the other halogenated triarylboranes, to give a greater breadth of understanding as to how tuning the Lewis acidity of BAr_3 by modifications of the aryl rings can lead to improved reactivity. In this review, a discussion on Lewis acidity determination of boranes is given, the syntheses of these boranes is discussed, and examples of how they are being used for catalysis and frustrated Lewis pair (FLP) chemistry are explained.

1. Introduction

The archetypal halogenated triarylborane, tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] was first synthesised in the 1960s by Massey *et al.*,[1,2] however little interest was generated from it aside from its use as an initiator in polymerisation catalysis.[3–8] In 1996, Piers discovered that $B(C_6F_5)_3$ was able to catalyse the hydrosilylation of carbonyls, the first of many halogenated triarylborane catalysed processes.[9] A decade later, Stephan discovered reversible hydrogen activation by a phosphinoborane bearing halogenated aryl groups at boron and coined the term 'frustrated Lewis pairs' (FLPs) a year later.[10,11] The attention gathered from this work not only initiated the field of FLP chemistry,[12–21] but it also regenerated interest in $B(C_6F_5)_3$ and other halogenated triarylboranes for applications in catalysis and small molecule activation. This review aims to highlight the many recent studies that have focused on halogenated triarylboranes other than the archetypal $B(C_6F_5)_3$. Subtle changes to structure on the aryl rings influence the accessibility and energy of the empty *p*-orbital on the central boron atom compared to $B(C_6F_5)_3$, thereby allowing the Lewis acidity and reactivity to be tuned. Whilst there are many reviews into the applications of $B(C_6F_5)_3$,[22–26] the chemistry of its halogenated triarylborane siblings have not been summarised before. This review will focus on: the design of halogenated triarylboranes by the measurement of Lewis acidity; different synthetic strategies for the preparation of halogenated triarylboranes; the catalytic activity of halogenated triarylboranes; discussions on their use in FLP chemistry; and miscellaneous stoichiometric reactivity.

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2. Lewis Acidity

The key to understanding and predicting the behaviour of halogenated triarylboranes is Lewis acidity. The concept of Lewis acidity was first coined by Lewis in 1923 as a compound which '*can employ a lone pair from another molecule in completing the stable group of one of its own atoms*'.[27] Pearson later built upon this definition with discussion on 'hard' and 'soft' acids,[28] and Wayland and Drago refined these ideas with parameters for predicting the enthalpy for the combination of gas-phase acids and bases.[29,30] The current description of a Lewis acid is described by IUPAC as '*a molecular entity that is an electron pair acceptor and therefore able to react with a Lewis base to form a Lewis adduct by sharing the electron*

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pair furnished by the Lewis base'. Despite these definitions, a universal method of scaling Lewis acidity has yet to be established. This section will discuss the various methods of determining Lewis acidity, both experimental and computational, in order to assist the design of halogenated triarylboranes.

2.1 Experimental methods of determining Lewis acidity

A well-established technique of determining Lewis acidity is the Gutmann-Beckett method (Figure 1). Gutmann first devised the acceptor number (AN) protocol for scaling the acidity of a range of common solvents, and Beckett later applied the AN scale for calculating the Lewis acidity of boron containing complexes.[31,32] The Gutmann-Beckett method is advantageous for its simplicity, wherein a Lewis acid is mixed with an excess of triethylphosphine oxide (Et_3P=O) to form an adduct which can be detected by ^{31}P NMR spectroscopy. The degree of the ^{31}P NMR signal shift upon adduct formation is compared to free Et_3P=O, and this shift is directly related to the strength of the Lewis acid.

$$AN = 2.21 \times (\delta_{sample} - 41.0)$$

Equation 1: Calculation of acceptor number (AN) by the Gutmann-Beckett method.[31,32]

Equation 1 states the method in which the AN of a Lewis acid is determined from the shift of Et_3P=O in the ^{31}P NMR spectrum. Higher ANs correspond to compounds with higher Lewis acidity, with the non-acidic hexane possessing an AN of 0 (^{31}P NMR shift of 41.0, a difference of 0 ppm), and the highly Lewis acidic SbF_5 possessing an AN of 100 (^{31}P NMR shift of 86.4, a difference of 45.4 ppm).

Rebecca Melen studied for her undergraduate and PhD degrees at the University of Cambridge, completing her PhD in 2012 with Prof. Wright. Following postdoctoral studies with Prof. Stephan in Toronto and with Prof. Gade in Heidelberg, she took up a position at Cardiff University in 2014, where she is now a reader in inorganic chemistry. In 2018, she was awarded an EPSRC early career fellowship and she is the recipient of the 2019 RSC Harrison Meldola Memorial Prize. Her research interests lie in main group chemistry and the applications of main group Lewis acids in synthesis and catalysis.

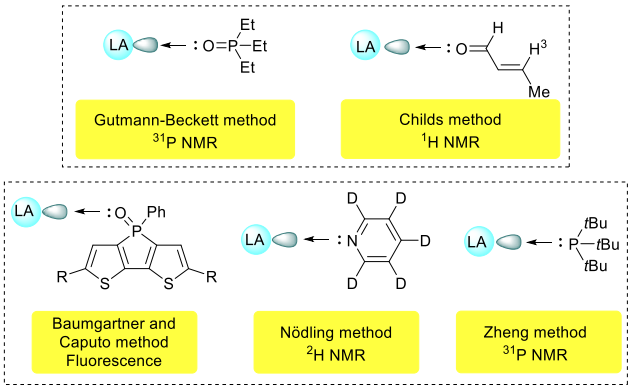


Figure 1: Experimental methods for determining Lewis acidity.[31–36]

The other popular method of experimentally determining Lewis acidity is the Childs method.[33] This method relies on the perturbation of the ^{1}H chemical shift of the H^3 proton in crotonaldehyde (Figure 1) upon complexation to a Lewis acid (LA). Lewis acids in this scale are measured in comparison to 0.3 M solutions of boron tribromide and hexane in dichloromethane at -20 °C. The relative acidity of the strong Lewis acid BBr_3 was assigned a value of 1.00 (^{1}H of H^3 = 8.47 ppm), meanwhile hexane was assigned a value of 0.00 (^{1}H of H^3 = 6.89 ppm).[33] The calculation of relative acidity is given in Equation 2.

$$\text{Relative acidity} = \frac{\Delta^1\text{H LA crotonaldehyde adduct}}{\Delta^1\text{H } BBr_3 \text{ crotonaldehyde adduct}}$$

Equation 2: Calculation of relative acidity by the Childs method.[33]

Recently, Baumgartner and Caputo have shown that fluorescent adducts containing dithienophospholes as the Lewis basic component can be used to scale the acidity of a range of compounds with distinct colouration using differences detectable by the naked eye (Figure 1).[34] Upon coordination of dithienophosphole to a Lewis acid, the polarity of the P=O bond is increased, thereby strengthening the σ*-π* interaction within the phosphole, lowering the LUMO, and red-shifting the emission of the adduct.[34]

Less established methods for the experimental determination of Lewis acidity of halogenated triarylboranes include Nödling's use of pyridine-d_5 for the change of the *para*-deuterium resonance in the ^{2}H NMR spectrum upon forming an adduct with a Lewis acid,[35] and Zheng's use of *tert*-butylphosphine (P^tBu_3) to rank the acidity of fluorinated triarylboranes.[36]

2.2 Computational methods of determining Lewis acidity

Whilst experimental methods for determining Lewis acidity are convenient and rapid to run, there is often inconsistency between them depending on the probe used. It has been suggested that the difference in values between the Gutmann-Beckett and Childs methods may be due to the difference in sterics or hardness between the bases.[37]

Furthermore, solvent effects have been shown to influence experimental Lewis acidity calculations, which causes inconsistency between experiments run in different solvents.[31] There is also the risk of experimental, machinery, and human errors in measurement of the NMR spectrum. Therefore, there is ongoing effort to determine the Lewis acidity of compounds *via* computational methods.

One of the most well-known computational methods to determine Lewis acidity is fluoride ion affinity (FIA), which calculates the reaction enthalpy of the complexation of a fluoride ion to a free gaseous Lewis acid. The concept of FIA for calculating Lewis acidity was first introduced by Bartlett in 1984.[38] However, the 'naked' fluoride ion that Bartlett used in his calculations was found to be difficult to calculate, and so the method was not popularised until Christe introduced the experimental ionisation of carbonyl fluoride (COF_2) as a reference in the calculation of FIA.[39] Christe found that the experimental calculation for the ionisation of COF_2 was -209 kJmol^{-1}. This value, along with the DFT calculation for the ionisation of a Lewis acid by COF_3^- forms the simple calculation for FIA (Equation 3).

$$COF_2 + F^- = COF_3^-$$

(experimentally found)

$$COF_3^- + (LA) = (LA)^- + COF_2$$

(DFT calculation)

$$(LA) + F^- = (LA)F^-$$

(overall FIA calculation)

Equation 3: Calculations required for FIA.[39]

The hydride ion affinity (HIA) has become another common method of computational Lewis acidity calculation.[40–42] DuBois demonstrated a calculation for HIA with the isodesmic reaction between $HBEt_3$ and a Lewis acid (Equation 4).[40] HIA has also been used to calculate why FLPs activate dihydrogen (see section 5.1).[43]

$$HBEt_3^- + BX_3 = BEt_3 + HBX_3^-$$

Equation 4: Calculation required for HIA.[40]

Many other ion affinities have also been tested for ranking Lewis acidity, including NH_3, PH_3, CH_3^-, and Cl^-, but are far less often used.[41,43–45]

The latest discussion of Lewis acidity is Stephan's global electrophilicity index (GEI).[46] The idea of an electrophilicity index was first discussed in the context of therapeutic targeting to HIV proteins,[47] but was refined by Parr who likened the index to electrophilic power and gave the calculation of ω: the measure of the ability of an acid to accept electrons (electrophilicity) (Equation 5).[48]

$$\omega = \mu^2/2\eta = \chi^2/2\eta$$

$$\eta = E_{LUMO} - E_{HOMO}$$

Equation 5: Calculations required for the GEI.[48]

In this equation ω is related to μ (chemical potential) and η (chemical hardness). ω can also be equated to the reciprocal of the Mulliken electronegativity χ.[49] All of these values are simple to calculate computationally, which reduces the time taken to deduce the Lewis acidity using the GEI compared to other methods. A further advantage to the GEI is that it does not rely on a base to calculate the Lewis acidity of a compound, simply its ability to accept a single electron, thereby reducing the time required to calculate. This simplifies calculations as the GEI can be derived from only the HOMO and LUMO energies (E_{HOMO} and E_{LUMO}) of the Lewis acid, whereas to calculate the FIA and HIA, fully optimised structures of the acid and adduct are required.[46]

2.3 Studies into Lewis acidity of halogenated triarylboranes

There have been multiple studies into ranking Lewis acids by their acidity. Sivaev and Bregadze recently compiled the Gutmann-Beckett and Childs Lewis acidity data for all literature known boron Lewis acids until 2014, including boranes, boroles and carboranes.[50]

By calculating the binding energies of a range of fluorinated triarylboranes [$B(F_{5-x}C_6H_x)_3$] to NMe_3 or PMe_3, the effects that the position of fluorine atoms around the borane's aryl rings had upon Lewis acidity were determined.[51] It was found that the Lewis acidity of triarylboranes increased when electron withdrawing substituents were positioned closer to the boron atom on the aryl ring, indicating that Lewis acidity is predominantly an electronic effect. It was further noted that steric influence towards Lewis acidity was only more important than the electronic influence when there was simultaneous fluorine substitution at both *ortho* positions, which had the effect of lowering the Lewis acidity of the borane instead of enhancing it.[51] These observations were subsequently used to synthesise the strong Lewis acids $B(2,3,4,5\text{-}F_4C_6H)_3$ and $B(2,3,5,6\text{-}F_4C_6H)_3$. However, $B(2,3,5,6\text{-}F_4C_6H)_3$ was found to

be more acidic by experimental methods than computational methods had predicted.[52]

The Gutmann-Beckett method was employed to assist the choice of borane as a catalyst for hydrosilylation reactions, with results suggesting that a borane with increased Lewis acidity had an increased Si–H bond activation potential.[53] The Gutmann-Beckett method has also been used to determine the best borane to augment the activation of dinitrogen at an iron centre.[54]

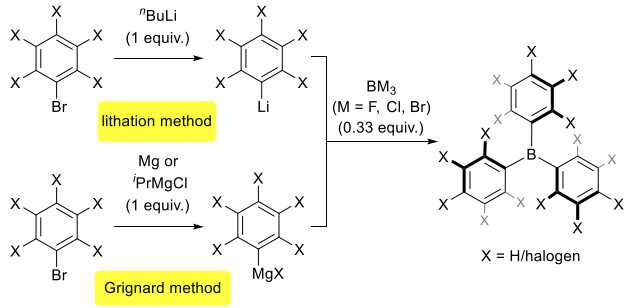
Similarly, the Childs method was used to rank the Lewis acidity of a range of perfluorinated boranes (including napthyl and biphenyl derivatives of $B(C_6F_5)_3$) and other Lewis acids in order to select an active polymerisation initiator.[55] Later, the Childs method was used to assess boranes for catalysis as part of an FLP with DABCO (1,4-diazabicyclo [2.2.2]octane) for the catalytic hydrogenation of alkylidene malonates.[56]

Computational studies have assisted in the discovery of a Lewis superacid. Upon calculation of the bond dissociation energy between the acid and base part of adducts, pyramidalisation of a boron centre was noted to increase Lewis acidity by 120–130 $kJmol^{-1}$, whilst fluorination of the acid enhanced Lewis acidity by 50–60 $kJmol^{-1}$.[57] When cumulative, these effects were equivalent to a 19–33 order of magnitude increase in Lewis acidity.[57] Theoretical calculations towards the binding energy of a range of fluorinated triarylboranes towards NH_3, H_2O, PH_3, H^-, CH_3^-, and F^- ions allowed for the acidity of boron to be compared to the later triels.[41]

Recently, the Lewis acidity of a wide library of homoleptic and heteroleptic halogenated triarylboranes have been calculated as part of discussion on the benefits of using the global electrophilicity index compared to other computational methods.[46]

3. Synthesis

Due to the air and moisture sensitivity of most halogenated triarylboranes, many procedures to synthesise them use Schlenk techniques and require air sensitive purification. This section will discuss the various methods to synthesise both homoleptic and heteroleptic halogenated triarylboranes.



Scheme 1: General synthesis of triarylboranes.

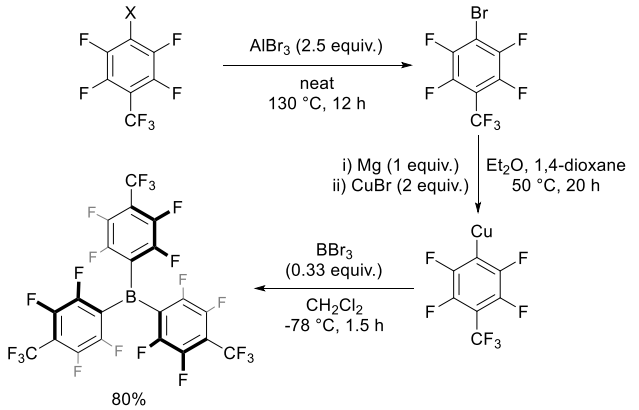
3.1 Synthesis of homoleptic halogenated triarylboranes

The synthesis of homoleptic halogenated triarylboranes is well documented, partially attributable to the recent popularity of $B(C_6F_5)_3$. Massey *et al.* first described the preparation of $B(C_6F_5)_3$ using a Grignard reagent with BCl_3 in 1963,[2] and a lithiation procedure was documented in the patent literature in 1994.[58] These synthetic procedures are ubiquitous to all homoleptic halogenated triarylboranes, with modifications to the bromobenzene reagent resulting in the formation of the corresponding borane. It is important to note that the Grignard method is safer, due to the instability of phenyl lithium intermediates above -40 °C from the lithiation procedure. The presence of *ortho*-fluorines in these compounds causes them to have a propensity to decompose into potentially explosive benzyne derivatives through the release of lithium fluoride.[59]

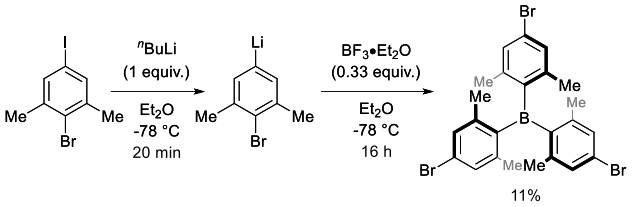
General procedures for both are shown in Scheme 1. Modern synthetic methods to prepare homoleptic halogenated triarylboranes follow the same general procedure, with gentle modifications and different purification methods for higher yields. $B(2\text{-}FC_6H_4)_3$, $B(4\text{-}FC_6H_4)_3$, $B(2,6\text{-}F_2C_6H_3)_3$, $B(2,4,6\text{-}F_3C_6H_2)_3$, $B(3,4,5\text{-}F_3C_6H_2)_3$, and $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ have all been synthesised using the Grignard method shown in Scheme 1 with subsequent purification using sublimation.[53,60–64] $B(2,3,5,6\text{-}F_4C_6H)_3$ was also prepared *via* the Grignard method, however Me_2SiHCl was used in a purification step prior to sublimation.[65]

Boranes with trifluoromethyl groups on the aryl ring, $B(2,4\text{-}(CF_3)_2C_6H_3)_3$, $B(2,5\text{-}(CF_3)_2C_6H_3)_3$, $B(3,5\text{-}(CF_3)_2C_6H_3)_3$, and the monosubstituted $B(2\text{-}(CF_3)C_6H_4)_3$ have been prepared by the lithiation method.[66–68] Bulkier analogues of $B(C_6F_5)_3$, tris(β-perfluoronapthyl)borane $[B(C_{10}F_7)_3]$ and tris(perfluorobiphenyl)borane $[B(2\text{-}(C_6F_5)C_6F_4)_3]$ have also been synthesised by the lithiation method.[69,70]

The synthesis of the tris(perfluorotolyl)borane $[B(4\text{-}(CF_3)_3C_6F_4)_3]$ was demonstrated using a Grignard reagent to prepare an arylcopper intermediate.[71] This copper species proceeded through a transmetallation reaction with BBr_3 to generate the desired borane (Scheme 2). Notably, the first



Scheme 2: Synthesis of tris(perfluorotolyl)borane.[71]



Scheme 3: Synthesis of B(4-Br-2,6-$Me_2C_6H_2$)$_3$.[72]

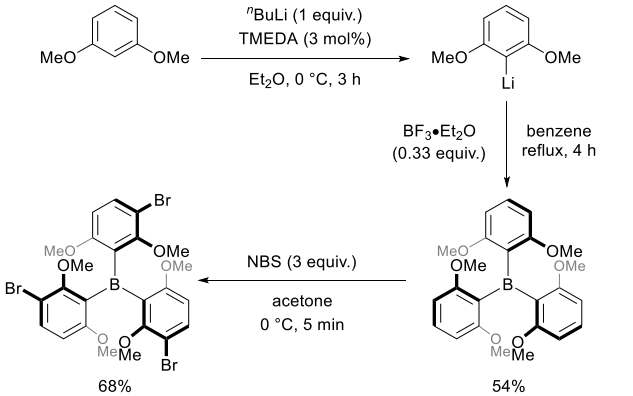
step of the reaction was a selective bromination of a commercially available perfluorotoluene in order to form the required bromobenzene for the preparation of the borane.[71]

Classically, the focus on producing novel halogenated triarylboranes was to investigate the electronic effects of fluorine at different positions on the aryl ring, which influenced the Lewis acidity of the borane. Recent investigations have probed the steric influence of larger halogen atoms on the acidity of the borane when positioned around an aryl ring.

B(4-ClC_6H_4)$_3$ was first prepared using the Grignard procedure in 1970.[73] In 2017, B(2-F-6-ClC_6H_3)$_3$ was prepared in a similar fashion and was used as the Lewis acidic component of an FLP for the reductive amination of carbonyls.[74]

We have prepared B(3,4-$Cl_2C_6H_3$)$_3$ using the lithiation method, and used the borane in part of the synthesis of the anti-depressant drug diclofensine.[75] B(C_6Cl_5)$_3$ has been synthesised using both Grignard and lithiation methods, and was observed to be remarkably air and moisture stable with purification consisting of a benchtop aqueous work-up.[76,77] Wet solvents have been shown to decompose the bench stable salt Na[B(3,5-$Cl_2C_6H_3$)$_4$] to afford B(3,5-$Cl_2C_6H_3$)$_3$, as the typical synthetic methods of using Grignard reagents or organolithium species were unsuccessful for its preparation.[78]

Triarylboranes with bromine or iodine atoms are observed to be air stable and are commonly used as linkers for the preparation of metal organic frameworks (MOFs),[79–87] in fluorescent materials,[72,88–103] or as catalysts.[104,105]



Scheme 4: Synthesis of B(2,6-$(OMe)_2C_6H_3$)$_3$ and subsequently B(3-Br-2,6-$(OMe)_2C_6H_2$)$_3$.[106]

B(4-Br-2,6-$Me_2C_6H_2$)$_3$ was synthesised using the lithiation procedure from a 1-I-4-Br-2,6-$Me_2C_6H_2$ (Scheme 3).[72] 1-bromo-4-iodo-2,3,5,6-tetramethylbenzene was also used as a reagent for the synthesis of B(4-Br-C_6Me_4)$_3$.[88] The three bromine atoms in B(4-Br-C_6Me_4)$_3$ were then replaced with iodine to generate B(4-I-C_6Me_4)$_3$ in the presence of ^{t}butyl lithium and I_2.[88]

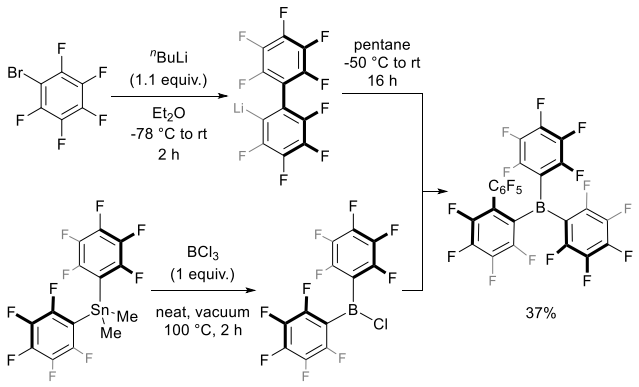
A similar synthesis has been demonstrated for the preparation of B(4-IC_6H_4)$_3$ from a diiodobenzene precursor.[92] Functionalisation of a non-halogenated triarylborane to B(3-Br-2,6-$(OMe)_2C_6H_2$)$_3$ has also been documented, where selective bromination of B(2,6-$(OMe)_2C_6H_3$)$_3$ at the *meta*-position of the aryl rings using *N*-bromosuccinimide (NBS) led to the formation of B(3-Br-2,6-$(OMe)_2C_6H_2$)$_3$ (Scheme 4).[106]

3.2 Synthesis of heteroleptic halogenated triarylboranes

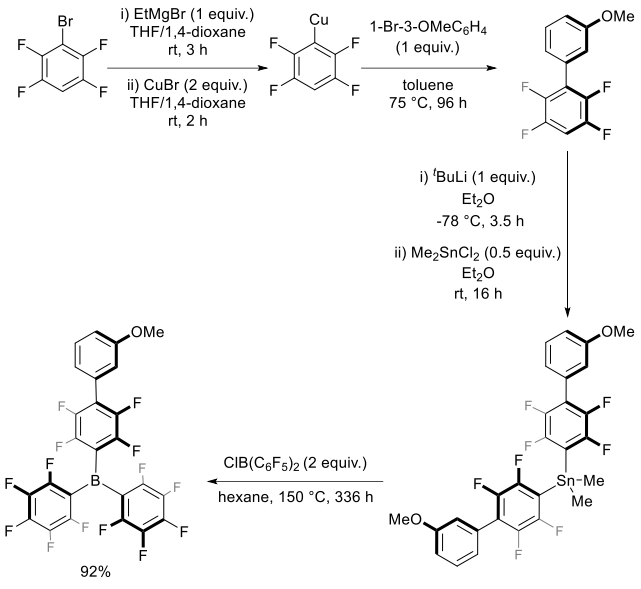
Whilst the Lewis acidity and catalytic activity of halogenated triarylboranes can be tuned by modifying the number of halogen atoms and their position on the aryl ring, further fine-tuning is possible through the synthesis of heteroleptic boranes. Whilst many heteroleptic triarylboranes have been analysed computationally,[46,107,108] far fewer have been synthesised.

In effort to expand the scope of B(C_6F_5)$_3$ as an initiator in polymerisation reactions, B(C_6F_5)$_2$(2-(C_6F_5)C_6F_4) was prepared by the replacement of one perfluorophenyl group with a perfluorobiphenyl moiety.[109] 2-Bromononofluoro-biphenyl was prepared from the reaction of (C_6F_5)Li and C_6F_5Br.[110] B(C_6F_5)$_2$Cl was also generated through the addition of BCl_3 to Sn(Me)$_2$(C_6F_5)$_2$.[111] The reaction between B(C_6F_5)$_2$Cl and 2-bromononofluoro-biphenyl afforded B(C_6F_5)$_2$(2-(C_6F_5)C_6F_4) (Scheme 5).[109] Further investigation into polymerisation optimisation founded the synthesis of B(3,5-$(CF_3)_2C_6H_3$)(C_6F_5)$_2$ from the addition of two equivalents of C_6F_5Li to BBr_2(3,5-$(CF_3)_2C_6H_3$).[112]

Two novel boranes in which a single fluorine atom of B(C_6F_5)$_3$ was replaced with a methoxy group, were prepared to produce dendrimers (Scheme 6).[113] For this, a five step



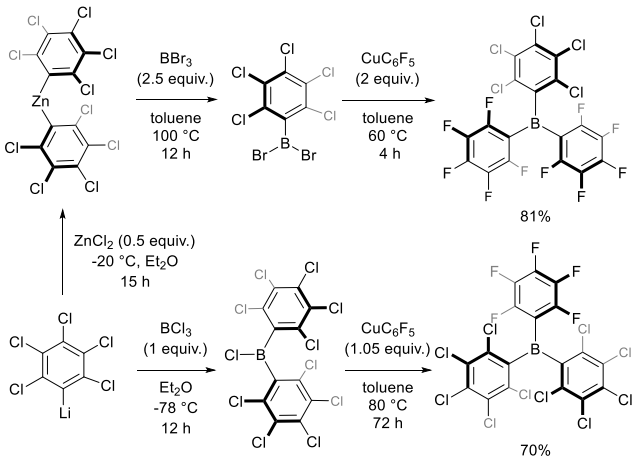
Scheme 5: Synthesis of B(C_6F_5)$_2$(2-(C_6F_4)C_6F_5).[109]



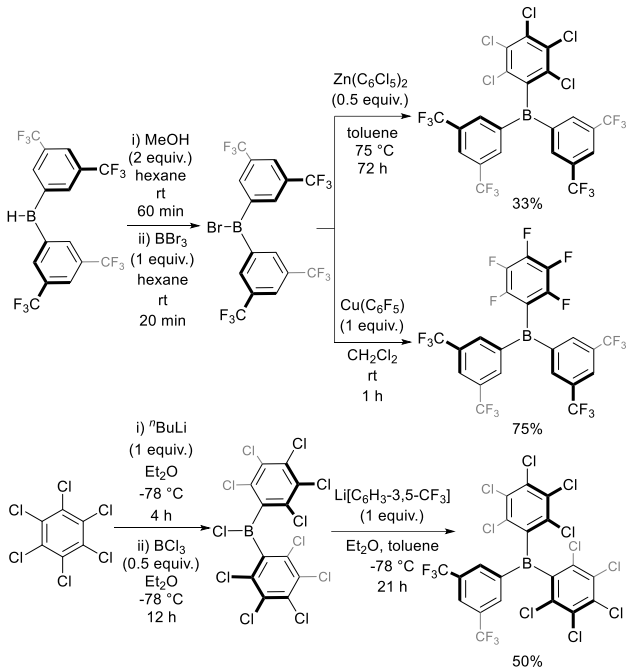
Scheme 6: Synthesis of $B(C_6F_5)_2((3\text{-}OMeC_6H_4)C_6F_4)$.[113]

synthesis was required, which began with the production of $Cu(4\text{-}BrC_6F_4)$ from BrC_6F_5. $Cu(4\text{-}BrC_6F_4)$ was able to promote a copper coupling reaction with $1\text{-}Br\text{-}3\text{-}OMeC_6H_4$ to afford the biphenyl species $2,3,5,6\text{-}F_4\text{-}4\text{-}(3\text{-}OMeC_6H_4)C_6H$. Further reaction of this biphenyl species with $SnMe_2Cl_2$ and subsequent transmetallation with $ClB(C_6F_5)_2$ allowed the borane to be used as the terminus of a dendrimer. The position of the methoxy group was found to be important, as when in the *para* position it was not basic enough to react with a silane for subsequent dendrimer synthesis.[113]

Heteroleptic boranes are notably more difficult to produce than homoleptic ones. Ashley and O'Hare found that the production of heteroleptic boranes through the use of organolithium or Grignard intermediates were unselective due to their high reactivity.[77] As a result, more selective copper-based aryl transfer reagents were used to



Scheme 7: Synthesis of heteroleptic boranes possessing a mix of C_6F_5 and C_6Cl_5 substituents.[77]



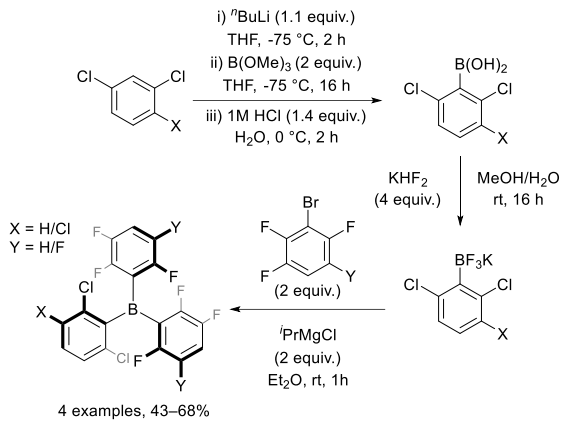
Scheme 8: Synthesis of heteroleptic boranes bearing $3,5\text{-}(CF_3)_2C_6H_3$ and C_6F_5 or C_6Cl_5 wingtip groups.[76]

synthesise heteroleptic boranes from mono- or di-chloroboranes, with a mix of perfluoro and perchloro aryl substituents (Scheme 7).[77]

In a similar way to the method described above, metal-based aryl transfer reagents were used to generate selectively a range of heteroleptic triarylboranes that contained the $3,5\text{-}(CF_3)_2C_6H_3$ aryl ring (Scheme 8).[76] Crystallographic data found that the steric and electronic contributions of CF_3 groups on the aryl ring caused the borane to twist into a paddlewheel structure, even when CF_3 groups were not present on all aryl moieties.[76] This paddlewheel conformation allowed the CF_3 moieties to donate electron density into the vacant *p*-orbital on the boron centre thereby reducing Lewis acidity in these boranes.[76]

Soós demonstrated the synthesis of four heteroleptic boranes bearing chlorinated and fluorinated aryl rings (Scheme 9).[114] Treatment of dihalobenzene derivatives with *n*butyl lithium and trimethyl borate afforded boronic acids. These boronic acids were then converted into the potassium trifluoroborate salt that could be reacted with Grignard reagents bearing different aryl frameworks to form the desired heteroleptic boranes. These boranes were notably moisture tolerant, attributable to the steric bulk of the chlorine atoms preventing water from binding to the boron centre.[114]

Subsequent investigations concerned the preparation of heteroleptic boranes with the additional variation of methyl substituents on one of the three aryl rings (Scheme 10).[115] Variation at the *meta* and *para* positions of the non-methylated aryl ring allowed for probes into the impact of the electronic effect on Lewis acidity, whilst variation of the

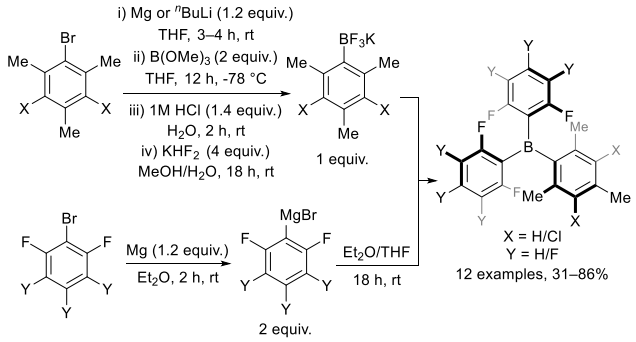


Scheme 9: Synthesis of heteroleptic boranes bearing fluorinated and chlorinated aryl wingtip groups.[114]

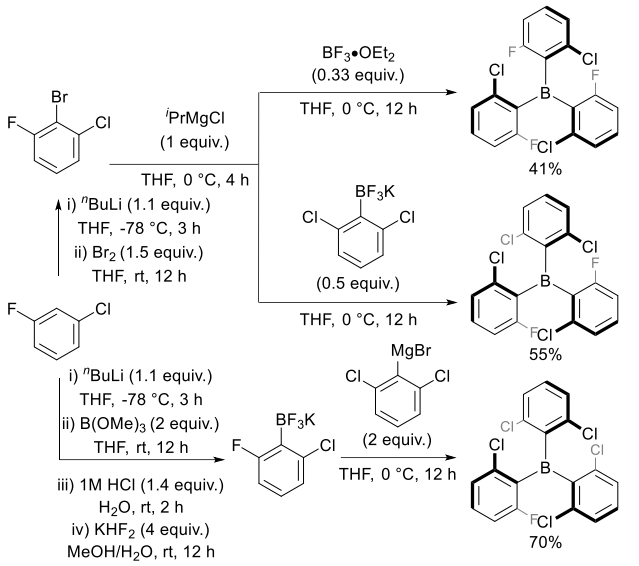
meta position on the methylated aryl ring allowed for investigation into steric effects.[115] By determining experimentally Lewis acidity *via* the Gutmann-Beckett method, it was found that replacing fluorine for hydrogen in the *meta* position enhanced the Lewis acidity of the borane, but introducing chlorine had negligible effects.[115]

A range of asymmetrically substituted boranes were prepared to evaluate the change in acidity when fluorine atoms were gradually replaced with chlorine atoms in B(2-F-6-ClC$_6$H$_3$)$_3$ (Scheme 11).[74] It was found that by increasing the number of chlorine atoms, the water tolerance of the borane increased. This was attributed to increased strain in the borane, making water binding more reversible when in the presence of a base.[74]

The first halogenated triarylborane with three different aryl rings, B(C$_6$F$_5$)(C$_6$Cl$_5$)(3,5-(CF$_3$)$_2$C$_6$H$_3$), was prepared from borane dimethylsulfide through a five-step synthesis Scheme 12).[116] First, a single equivalent of Li(C$_6$F$_5$) was generated at -78 °C and was reacted with borane diimethylsulfide to form [[H$_3$B(C$_6$F$_5$)]$^-$. The excess hydride was abstracted with TMSCl to afford H$_2$B(C$_6$F$_5$). In a similar manner, the trifluoromethyl bearing aryl ring was installed *via* the addition of Li(3,5-(CF$_3$)$_2$C$_6$H$_3$) and abstraction of the excess hydride by TMSCl. The resulting



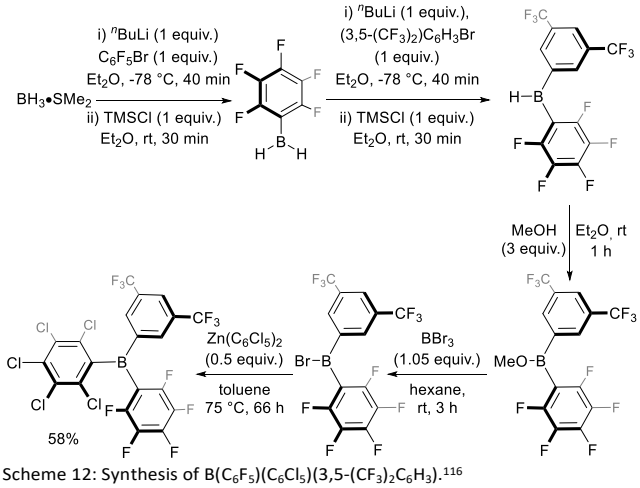
Scheme 10: Synthesis of heteroleptic boranes bearing fluorinated and chlorinated aryl wingtip groups.[115]



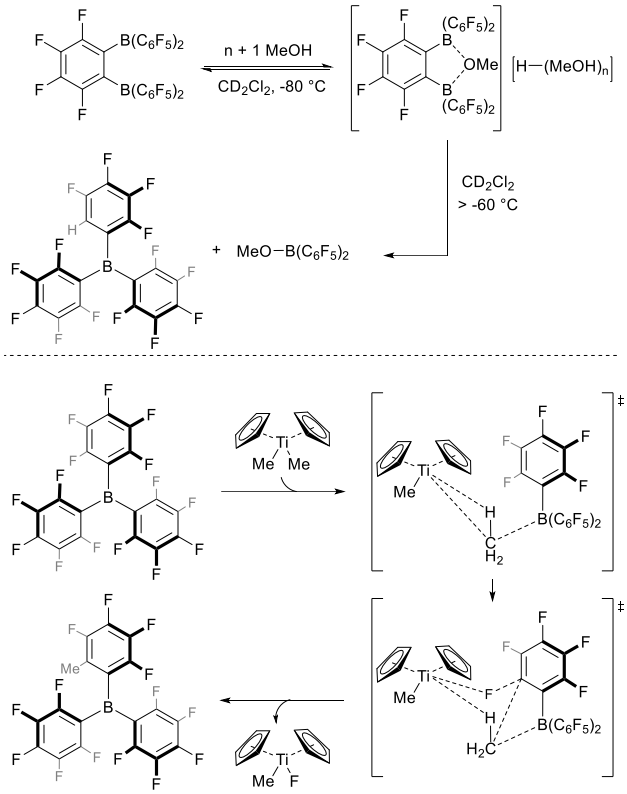
Scheme 11: Synthesis of heteroleptic boranes with aryl rings containing halogens at the 2 and 6 positions.[74]

HB(C$_6$F$_5$)(3,5-(CF$_3$)$_2$C$_6$H$_3$) was reacted with excess methanol and then BBr$_3$ to form BrB(C$_6$F$_5$)(3,5-(CF$_3$)C$_6$H$_3$). Finally, the bromoborane was reacted with half an equivalent of Zn(C$_6$Cl$_5$)$_2$ to install the final aryl ring.[116]

Heteroleptic boranes have also been formed as a result of decomposition in catalytic reactions. Whilst these may have been unwanted at the time, they may inspire novel methods of producing new complexes. During investigations into the mechanism of isobutene polymerisation catalysis with diborane initiators, a perfluorodiborane was observed to decompose in the presence of methanol to form a novel borane (Scheme 13 top).[117,118] Decomposition of B(C$_6$F$_5$)$_3$ has also been shown to form a methylated triarylborane *via* fluoride transfer (Scheme 13 bottom).[119]



Scheme 12: Synthesis of B(C$_6$F$_5$)(C$_6$Cl$_5$)(3,5-(CF$_3$)$_2$C$_6$H$_3$).[116]



Scheme 13: Decomposition routes to produce halogenated triarylboranes.[117–119]

4 Catalysis

Boranes are able to act as Lewis acid catalysts, as the empty *p*-orbital on the central boron atom can be readily accessed by nucleophiles. It is the attack and subsequent release of this empty *p*-orbital that forms the basis for Lewis acid catalysis by boranes. Whilst $B(C_6F_5)_3$ is still a popular catalyst, by attenuating the Lewis acidity or steric demand at the boron centre, the catalytic activity can be modulated and improved.

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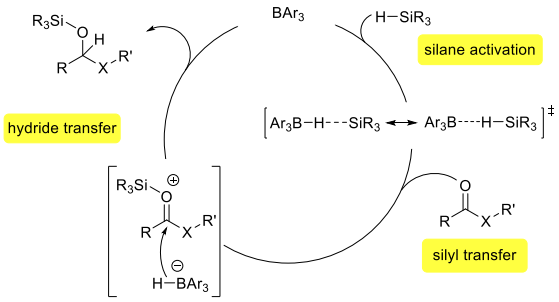


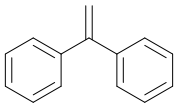
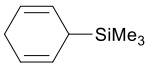
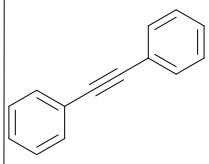
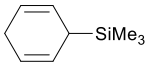
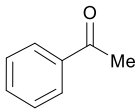
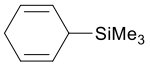
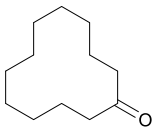
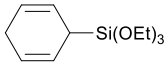
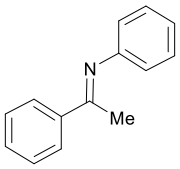
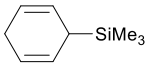
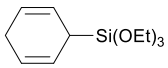
Figure 2: Catalytic cycle for triarylborane catalysed hydrosilylation reaction.[12,120]

4.1 Hydrosilylation reactions

In 1996, Piers first showed that $B(C_6F_5)_3$ could be used as catalyst towards the hydrosilylation of aldehydes, ketones, and esters.[9] Subsequent work determined the mechanism for this borane catalysed hydrosilylation reaction through computational and experimental studies (Figure 2).[12,120] It was found that silane activation by the borane was the rate determining step in the catalytic cycle. Once a borane-silane adduct had been formed, the silyl moiety could be transferred to the carbonyl substrate, and a subsequent hydride transfer could liberate the new silyl ether and regenerate the borane catalyst.[12,120]

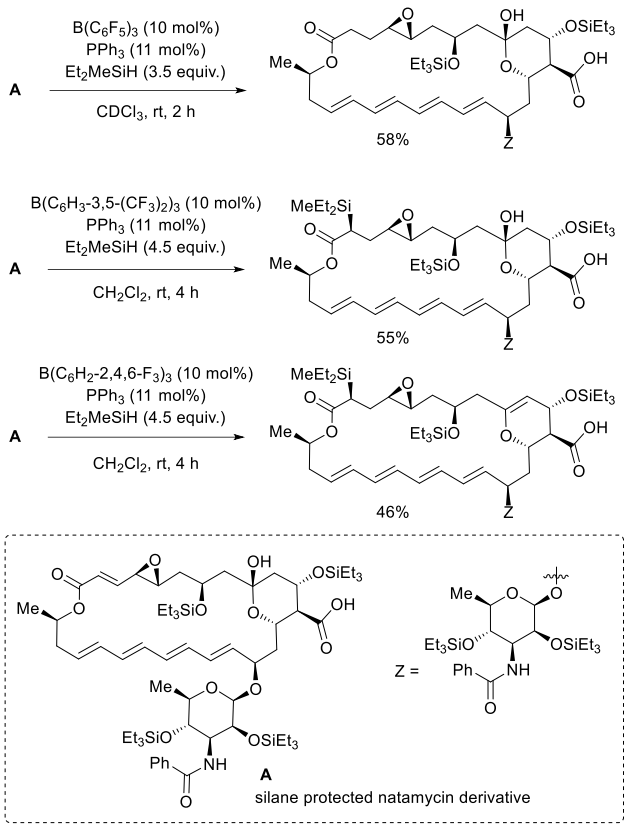
Oestreich demonstrated the use of a range of fluorinated triarylboranes in both direct and transfer hydrosilylation of typical σ and π Lewis basic substrates, as summarised in Table 1.[53] $B(2,3,5,6\text{-}F_4C_6H)_3$ was found to catalyse both direct and transfer hydrosilylation reactions, whilst $B(2,4,6\text{-}F_3C_6H_2)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$ were found to only be effective direct hydrosilylation catalysts. Computational analysis found transfer hydrosilylation was not possible with $B(2,4,6\text{-}F_3C_6H_2)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$ as catalysts, due to the *ortho*-fluorines assisting the release of the hydrosilane product, and not assisting the initial hydride abstraction.[53] The increased steric hinderance of $B(2\text{-}(C_6F_5)C_6F_4)_3$ prevented its *p*-orbital from being accessed, and resulted in poor reactivity.[53]

Table 1: Summary of direct and transfer hydrosilylation experiments with a range of borane catalysts.[53]
Catalyst loading of 5 mol% at a substrate concentration of 1.0 M, isolated yields given unless noted. [a] 2.5 mol% catalyst used. [b] 1.3 mol% catalyst used. [c] conversion determined by GLC analysis with an internal standard of mesitylene. [d] Conversion by ^{1}H NMR with an internal standard of mesitylene.

Substrate	Silane	$B(2\text{-}(C_6F_5)C_6F_4)_3$	$B(2,3,5,6\text{-}F_4C_6H)_3$	$B(2,4,6\text{-}F_3C_6H_2)_3$	$B(2,6\text{-}F_2C_6H_3)_3$
	$H-SiEt_3$	0% [a] (80 °C, 24 h)	22% [c] (80 °C, 72 h)	0% (80 °C, 12 h)	0% (80 °C, 12 h)
		0% [a] (rt, 24 h)	92% (rt, 6 h)	0% (rt, 46 h)	0% (rt, 46 h)
	$H-SiEt_3$	0% [a] (80 °C, 24 h)	13% [c] (80 °C, 48 h)	0% (110 °C, 48 h)	0% (110 °C, 48 h)
		0% [a] (rt, 24 h)	91% [c] (rt, 48 h)	0% (rt, 43 h)	0% (rt, 43 h)
	$H-SiEt_3$	92% [b] (rt, 2 h)	87% (rt, 3 h)	91% (rt, 3 h)	90% (rt, 3 h)
		Traces [b c] (80 °C, 24 h)	>95% [c] (80 °C, 4 h)	27% [c] (110 °C, 48 h)	0% (110 °C, 48 h)
	$H-Si(OEt)_3$	46% [b d] (rt, 96 h)	89% (rt, 1.5 h)	86% [c] (rt, 48 h)	70% [c] (80 °C, 96 h)
		0% [b] (80 °C, 48 h)	83% [c] (80 °C, 48 h)	Traces [c] (110 °C, 48 h)	0% (110 °C, 48 h)
	$H-SiEt_3$	56% [b c] (80 °C, 48 h)	96% (80 °C, 3 h)	71% [c] (80 °C, 48 h)	28% [c] (80 °C, 48 h)
		54% [b c] (80 °C, 48 h)	90% (80 °C, 2 h)	30% [c] (110 °C, 48 h)	3% [c] (110 °C, 48 h)
	$H-Si(OEt)_3$	77% [b c] (80 °C, 48 h)	31% [c] (rt, 1.5 h)	53% [c] (80 °C, 48 h)	25% [c] (80 °C, 48 h)
		49% [b c] (80 °C, 48 h)	87% [c] (80 °C, 48 h)	10% [c] (110 °C, 48 h)	Traces [c] (110 °C, 48 h)

Boranes have also been shown to catalyse chemo-selective hydrosilylation of complex bioactive compounds, including gibberellic acid, 10-deacetoxybaccatin III and natamycin derivatives.[121,122] $B(2,4,6\text{-}F_3C_6H_2)_3$ and $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ were tested in comparison with $B(C_6F_5)_3$, due to their similar Lewis acidities but different steric profiles. It was observed that by varying the catalyst, it was possible to functionalise selectively at different positions on a silane protected natamycin derivative (Scheme 14).[121] For example, whilst $B(C_6F_5)_3$ catalysed a conjugate reduction, $B(2,4,6\text{-}F_3C_6H_2)_3$ catalysed an enoate hydrosilylation with a lactol elimination to yield an α-silyl/enol ether, and $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ catalysed the hydrosilylation of the enoate to yield an α-silylester.[121]

The synthesis of allylic acetates from acetates or acrylates has been demonstrated through a combination of $B(2,3,5,6\text{-}F_4C_6H)_2(2,3,6\text{-}Cl_3C_6H_2)$ promoted hydrosilylation catalysis and Claisen-Ireland rearrangement (Scheme 15).[123] Whilst most reactions occurred through a two-step cascade, electron donating substituents on the aryl ring of the acetate were found to facilitate an allylic rearrangement which instead caused a three-step cascade reaction and a different allylic acetate product. The use of the air and moisture sensitive borane allowed the one-pot reaction to be completed on the bench, with 38 examples showing good yields (43–99%) and high diastereoselectivity (up to 30:1).[123] The solvent was found to play an important role in the

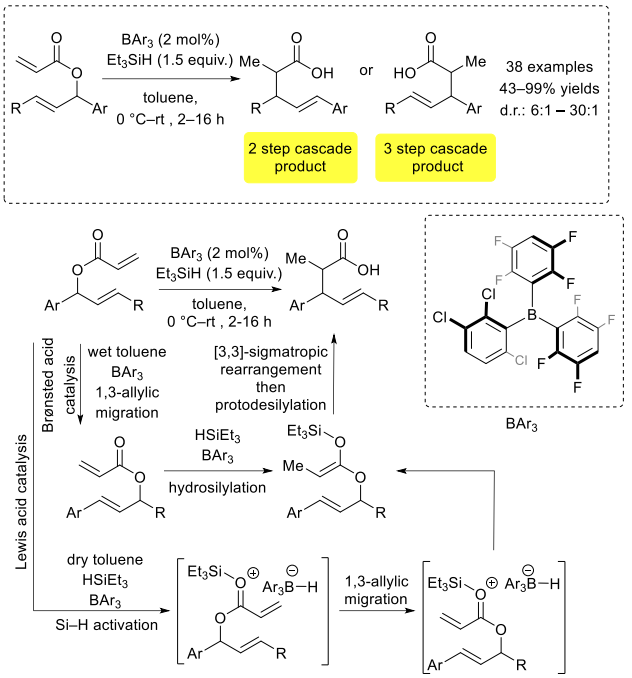


Scheme 14: Fluorinated triarylborane catalysed chemoselective hydrosilylation of bioactive compounds.[121]

mechanism of the tandem hydrosilylation and Claisen-Ireland rearrangement.[123] In anhydrous toluene, the reaction was Lewis acid catalysed, however when wet toluene was used, trace protonation of the borane caused the reaction to switch to Brønsted acid catalysis.[123]

There are examples where $B(C_6F_5)_3$ was found to be more efficient as a catalyst towards hydrosilylation reactions compared to other halogenated triarylboranes. For example, Oestreich explored the catalytic Si–H bond activation for the one pot hydrosilylation of C–C multiple bonds using $B(C_6F_5)_3$, $B(2,3,5,6\text{-}F_4C_6H)_3$, $B(C_6F_5)_2(2\text{-}(C_6F_5)C_6F_4)$, and $B(2\text{-}(C_6F_5)C_6F_4)_3$ as catalysts.[124] $B(2,3,5,6\text{-}F_4C_6H)_3$ and $B(C_6F_5)_2(2\text{-}(C_6F_5)C_6F_4)$ successfully catalysed the hydrosilylation, albeit with reduced reactivity attributed to the lower Lewis acidity of the boranes. The sterically encumbered $B(2\text{-}(C_6F_5)C_6F_4)_3$ was found to be non-catalytic despite its high Lewis acidity, resulting in $B(C_6F_5)_3$ being the focus of the study.[124]

A further example can be found in dendrimers with terminals based modelled on $B(C_6F_5)_3$ for the hydrosilylation of acetophenone by $HSiEt_3$.[113] These dendrimers were found to be inefficient catalysts towards the hydrosilylation reaction, with catalytic activity decreasing with increasing dendrimer size and $B(C_6F_5)_3$ outperforming all dendrimers in catalytic tests.[113]



Scheme 15: Mechanism for the production of allylic acetates by $B(2,3,5,6\text{-}F_4C_6H)_2(2,3,6\text{-}Cl_3C_6H_2)$ hydrosilylation catalysis and Claisen-Ireland rearrangements.[123]

4.2 Hydroboration reactions

As with hydrosilylation, hydroboration is another useful method of 1,2-functionalising unsaturated substrates. Studies into hydroboration reactions using boron based catalysts initially focused on borenium ions, wherein an external Lewis base was required to promote the reaction.[125–127] An example of hydroboration without an external base was shown by $B(3,5\text{-}(CF_3)_2C_6H_3)_3$, which could catalyse the hydroboration of 21 aliphatic and aromatic amines in up to 92% yield.[63]

Mechanistic studies revealed that $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ acted as a pre-catalyst, with redistribution of $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ and pinacol borane generating a mixture of active catalysts in solution: $[HBAr_2]_2$; $[H_2BAr]_2$; and $[(Ar)(H)B(\mu\text{-}H)_2BAr_2]$, as shown in Figure 3.[63] The B–H bonds of these three catalysts were all shown to immediately undergo a concerted 1,2-*syn* addition to alkenes, which could then undergo ligand exchange with HBPin to produce the desired hydroboration product and regenerate the active catalyst.[63] Further study found that $B(C_6F_5)_3$ did not readily exchange with HBPin, and thus failed to generate the catalytically active species required for hydroboration.[63]

Further investigation in the field of hydroboration catalysis found that $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ could also catalyse efficiently the hydroboration of 16 imines in up to 99% yield.[60] Mechanistic studies indicated that there was no ligand redistribution of the borane catalyst with pinacol borane in the hydroboration of imines (Figure 4). This was

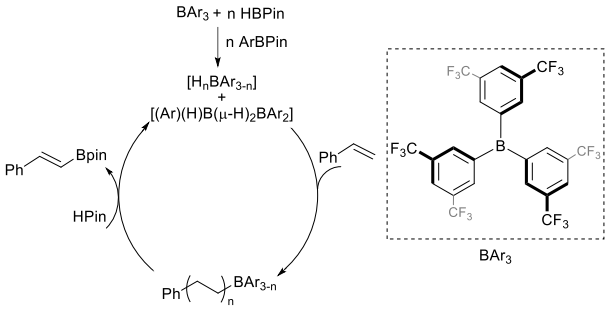


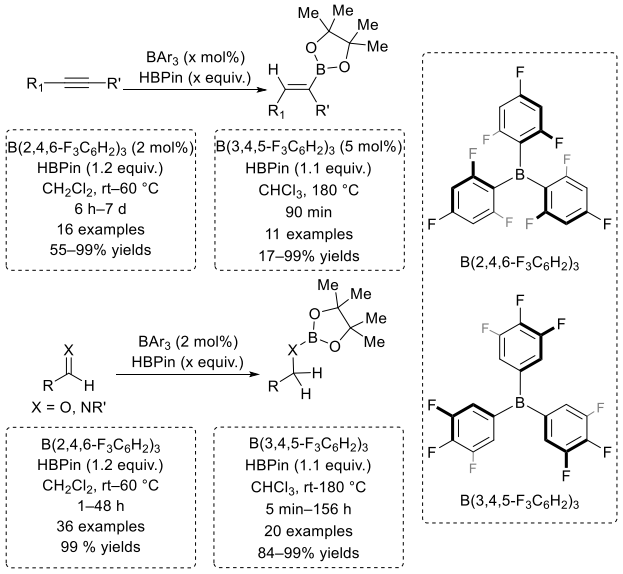
Figure 3: Mechanism for hydroboration of styrene, catalysed by $B(3,5\text{-}(CF_3)_2C_6H_3)_3$.[63]

attributed to the σ-basic imine preventing redistribution of the catalyst with HBPin, as was observed in the case of alkene hydroboration.[60] Upon co-ordination of the imine with $B(3,5\text{-}(CF_3)_2C_6H_3)_3$, the LUMO of the imine was lowered, allowing it to be reduced by HBPin.[60]

Our group has also investigated the use of fluorinated triarylboranes as efficient catalysts for hydroboration (Scheme 16). $B(2,4,6\text{-}F_3C_6H_2)_3$ was found to be an excellent hydroboration catalyst for a wide substrate scope, including alkynes, aldehydes, and imines.[128] It was also observed that $B(3,4,5\text{-}F_3C_6H_2)_3$ could catalyse the hydroboration of aldehydes, ketones, and imines.[61] Furthermore, it was shown that applying microwave irradiation to the $B(3,4,5\text{-}F_3C_6H_2)_3$ catalysed reaction allowed high temperatures and pressures to be safely attainable, enabling the facile hydroboration of alkenes and alkynes in 90 minutes, where there was no observed reactivity with conventional heating.[61]

4.3 Other catalytic reactions

Whilst 1,2-hydrofunctionalisation reactions catalysed by halogenated triarylboranes are well-documented, there are further avenues of Lewis acid catalysis that have been explored with the use of these boranes, such as



Scheme 16: Hydroboration of unsaturated substrates by $B(2,4,6\text{-}F_3C_6H_2)_3$ and $B(3,4,5\text{-}F_3C_6H_2)_3$.[61,128]

dehydrocoupling, Diels-Alder reactions, and transfer hydrogenation. For example, $B(2,3,5,6\text{-}F_4C_6H)_3$ has been explored as a Lewis acid catalyst for the dehydrocoupling of phosphines (Scheme 17).[129] Whilst forcing conditions (130 °C) and long reaction times (120 h) were required for efficient dehydrocoupling, it was found that the borane/phosphine combination could also catalyse transfer hydrogenation of *N*-benzylidene-*tert*-butylamine in 38 h and 1-phenyl-1-trimethylsiloxyethylene in 30 h.[129] A proposed mechanism for the catalytic phosphine dehydrocoupling by $B(2,3,5,6\text{-}F_4C_6H)_3$ is given in Figure 5.[129] This dehydrocoupling proceeded first by the formation of a boron-phosphine adduct. DFT calculations suggested that a second free phosphine was then able to undergo nucleophilic attack towards the electrophilic phosphorus centre in the adduct to produce a pentacoordinate phosphorus centre. This intermediate was then able to transfer a hydride to the boron atom to form the salt

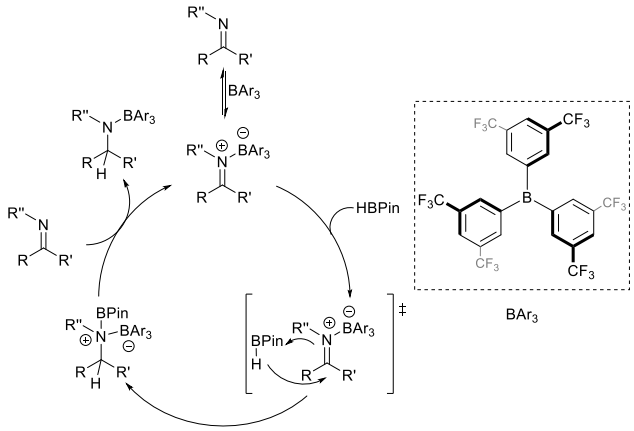
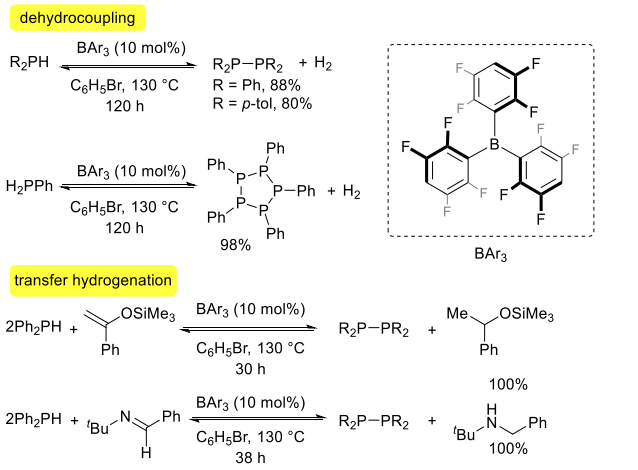


Figure 4: Mechanism for hydroboration of imines, catalysed by $B(3,5\text{-}(CF_3)_2C_6H_3)_3$.[60]



Scheme 17: Dehydrocoupling of phosphines with a $B(2,3,5,6\text{-}F_4C_6H)_3$ catalyst.[129]

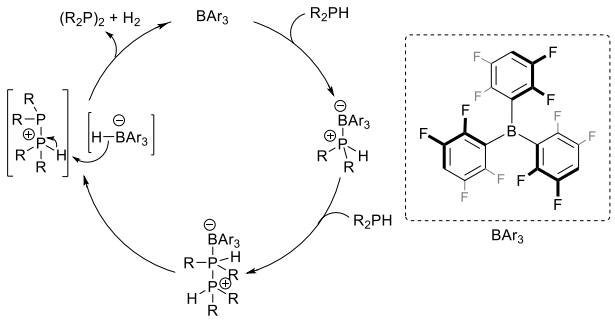
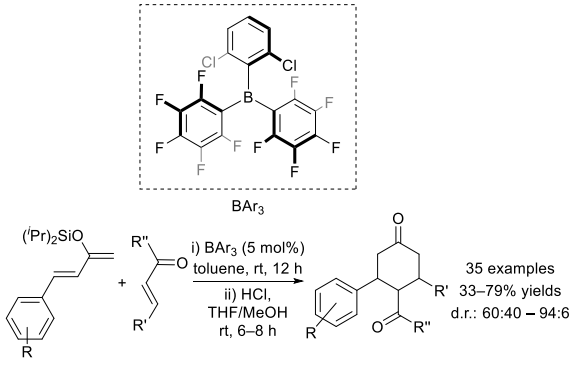


Figure 5: Mechanism for dehydrocoupling of phosphines with a $B(2,3,5,6\text{-}F_4C_6H)_3$ catalyst.[129]

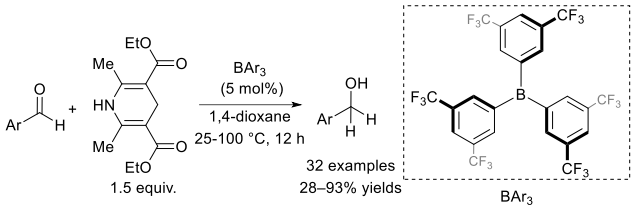
$[Ph_2(H)P\text{-}PPh_2][HB(2,3,5,6\text{-}F_4C_6H)_3]$. Liberation of H_2 from this salt was able to form the dehydrocoupled product.[129]

$B(C_6F_5)_2(2,6\text{-}Cl_2C_6H_3)$ was investigated as a catalyst in Diels-Alder reactions, as the steric repulsion of the $2,6\text{-}Cl_2C_6H_3$ aryl ring caused the Diels-Alder reaction to be *exo*-selective (Scheme 18). Thirty five examples were given, with yields up to 79%, and moderate to high diastereomeric ratios (60:40 to 94:6).[130] Theoretical calculations found that the selectivity of the Diels-Alder reaction was inflected by the steric bulk of the Lewis acids.[131] It was found that by producing an adduct with the enal in the Diels-Alder reaction, a bulky Lewis acid such as a fluorinated triarylborane could promote an *exo*-selective cycloaddition.[131] Further analysis with $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$ found that interaction between the *ortho* fluorine of the borane's aryl ring and the CH of the enal promoted the formation of the *exo*-product of the cycloaddition.[131]

Whilst FLPs are commonly used for H_2 reduction, boranes can be used in transfer hydrogenation catalysis to the same effect. $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ was employed as a Lewis acid catalyst for the hydrogenation of aldehydes with a Hantzsch ester as a hydrogen donor, in work inspired by the reduction of carbonyls by NADH, NADPH, and enzymes in biological systems (Scheme 19).[132] Thirty two examples of hydrogenations of aryl and alkyl aldehydes were given with up to quantitative conversions. Aromatic aldehydes were



Scheme 18: $B(C_6F_5)_2(2,6\text{-}ClC_6H_3)$ catalysed Diels-Alder reaction.[130]



Scheme 19: $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ catalysed reduction of aldehydes.[132]

found to be easier to hydrogenate and proceeded at lower temperatures.[132] $B(2,3,5,6\text{-}F_4C_6H)_3$ was used as part of the optimisation for transfer hydro-*tert*-butylation of 1,1-diphenylethylene, however $B(C_6F_5)_3$ was found to be slightly more active and selective due to its increased Lewis acidity.[133] A major side-product for the reactions with $B(2,3,5,6\text{-}F_4C_6H)_3$ was found to be the result of transfer hydrogenation.[133] The heteroleptic borane $B(2,3,5,6\text{-}F_4C_6H)_2(2,6\text{-}Cl_2C_6H_3)$ was considered as a catalyst for *ortho* alkylation of diols to 1,2-*cis*-glycosides, however ultimately tricyclic borinic acids were explored as catalysts.[134]

5 Frustrated Lewis pair chemistry

FLPs are systems in which a Lewis acid and a Lewis base combine, but due to the acidic and basic centres being segregated, often due to steric hinderance, are unable to form a classical Lewis adduct (Figure 6). This leads to both the Lewis acidic and basic centres possessing unquenched reactivity which can be used for small molecule activation or catalysis.[18–20] As halogenated triarylboranes possess an empty *p*-orbital on the central boron atom, protected by the steric encumbrance of aryl rings, they are well-suited to FLP chemistry.

5.1 H_2 activation by FLPs

A frequent test of FLP activity is the activation of molecular hydrogen. In the case of a borane and a phosphine FLP, the lone pair of electrons on the phosphorus atom is able to attack one of the hydrogen atoms to form a phosphonium cation, leaving behind a hydride which is able to fill the empty *p*-orbital on the boron, thereby forming a borohydride anion (Scheme 20). Examples include the

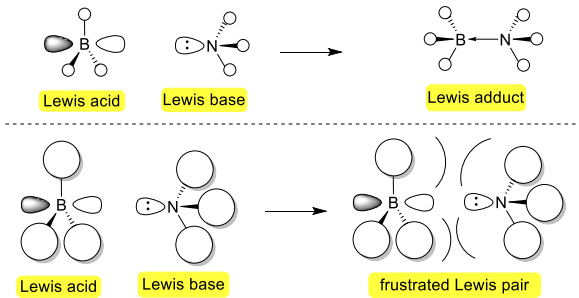
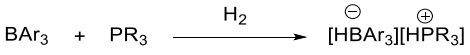


Figure 6: Comparison of classical Lewis adducts and frustrated Lewis pairs.



Scheme 20: Generic example of H_2 activation by an FLP.

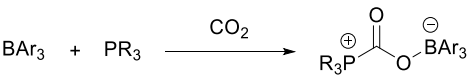
reversible activation of H_2 by FLP systems comprised of $B(2,3,5,6\text{-}F_4C_6H)_3$ with $PMes_3$, PCy_3, or P^tBu_3,[65,135] $B(2\text{-}(C_6F_5)_3C_6F_4)_3$ with P^tBu_3, DABCO, 2,6-lutidiene, or TMP (2,2,6,6-tetramethylpiperidine),[136,137] $B(C_6F_5)(C_6Cl_5)(3,5\text{-}(CF_3)_2C_6H_3)_3$ with P^tBu_3, TMP, or 2,6-lutidine,[116] $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ with TMP,[62] and $B(C_6F_5)_2(C_6Cl_5)$ with TMP.[138] The latter of which is notable as neutron diffraction studies found the first geometrically unconstrained dihydrogen bond within this FLP system.[138]

$B(2,4\text{-}(CF_3)_2C_6H_3)_3$ and $B(2,5\text{-}(CF_3)_2C_6H_3)$ were prepared to probe the effect of substituent position on boranes as the Lewis acidic component of FLPs in comparison with $B(3,5\text{-}(CF_3)_2C_6H_3)_3$.[67] It was found that triarylboranes which incorporated *ortho*-CF_3 groups were less active in H_2 activation, which was attributed to the steric bulk of the CF_3 group being positioned close to the Lewis acidic centre, and the resultant quenched electrophilicity of the borane from the induced B–F interaction.[67]

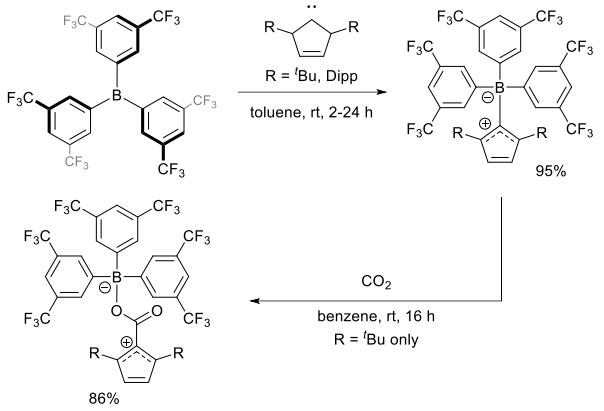
A range of triarylboranes incorporating C_6F_5, $3,5\text{-}(CF_3)_2C_6H_3$, and C_6Cl_5 groups were prepared to evaluate their ability to cleave dihydrogen.[76] It was found that $B(C_6Cl_5)_3$ was unable to cleave the dihydrogen when in an FLP with P^tBu_3 under mild conditions, as the chlorine atoms provided too much steric hindrance to the empty *p*-orbital on the boron atom. However, heteroleptic boranes with one or two C_6Cl_5 aryl group were able to cleave dihydrogen with P^tBu_3.[76] Later studies found that FLPs containing $B(C_6Cl_5)_3$ and PEt_3, PCy_3, P^nBu_3, P^tBu_3, or $P(p\text{-tol})_3$ were able to activate dihydrogen under harsher conditions (90 °C in THF-d_8 for up to 56 h).[136] Dihydrogen activation by FLPs has also been studied computationally and has shown that factors such as Lewis acid/base strength, steric bulk, and the ability to pre-organise into a position to accommodate the H_2 molecule all assist activation.[139]

5.2 CO_2 activation by FLPs

Carbon dioxide as a greenhouse gas is accredited as one of the primary causes of climate change. Since the first example of CO_2 activation by FLPs in 2009,[140] its capture and further utilisation has been an attractive target for chemists.[141] In the case of CO_2 activation, the basic phosphine attacks the electrophilic carbon atom, whilst one of the electron rich oxygen atoms donates into the empty *p*-orbital of the borane (Scheme 21).



Scheme 21: Generic example of CO_2 activation by an FLP



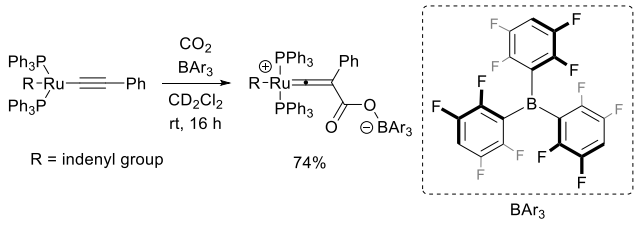
Scheme 22: CO_2 Activation by carbene-borane adducts.[142]

There have been examples of CO_2 activation and subsequent reduction to methanol by FLPs in the literature,[143] however there are few halogenated triarylboranes that have been used as the Lewis acidic component of FLPs to activate CO_2.

An FLP comprised of $B(2\text{-}(C_6F_5)_3C_6F_4)_3$ and P^tBu_3 was found to be efficient towards CO_2 activation,[136] whilst FLPs comprised of $B(2,3,5,6\text{-}F_4C_6H)_3$ and P^iPr_3 or P^tBu_3 have been shown to activate both CO_2 and formates.[144] A stoichiometric mixture of $B(2,3,5,6\text{-}F_4C_6H)_3$ and $P(TMS)_3$ was found to act as an FLP that allowed for sequential double CO_2 activation.[145]

DFT calculations and *ab initio* studies were conducted on a range of FLPs containing halogenated triarylboranes as the Lewis acidic component for the reduction of CO_2 to useful organic materials.[146] Stronger FLPs were found to have higher energy barriers for hydrogen transfer, but lower energy barriers for hydrogen activation, resulting in the optimum FLP systems having similar energy barriers for both. These calculations revealed that a $B(3,5\text{-}F_2C_6H_3)_3$/TMP FLP had the best parameters for CO_2 activation.[146]

CO_2 activation is not limited to FLPs where phosphines are the Lewis basic component. For example, a $B(3,5\text{-}F_2C_6H_3)_3/Cs_2CO_3$ FLP could catalyse the hydrogenation of CO_2 to formate, however this FLP was outperformed when $B(C_6F_5)_3$ was used as the Lewis acidic component.[147] Additionally, $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ has been combined with carbenes to form adducts that capable of FLP-type reactivity to activate CO_2, THF and phenyl acetylene (Scheme 22),[142] whilst $B(2,3,5,6\text{-}F_4C_6H)_3$ was combined with a metal complex, $(indenyl)Ru(PPh_3)_2(CCPh)$, to afford an FLP which was capable of activating CO_2, aldehydes, and alkynes (Scheme 23).[148]



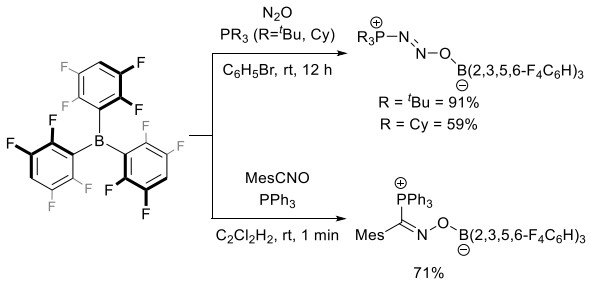
Scheme 23: CO_2 activation by a {$B(2,3,5,6\text{-}F_4C_6H)_3$ / (indenyl)$Ru(PPh_3)_2(CCPh)$} FLP.[148]

5.3 Further small molecule activation by FLPs

Subsequent to the discovery that FLP systems could activate H_2, numerous reports were made of further small molecule activation by FLPs. Examples have been summarised in recent reviews, and include the activation of olefins, nitrogen oxides, sulfur oxides, water, amongst many others.[20,21] Halogenated triarylboranes as Lewis acidic components in FLPs are just one section of the wide range of FLP chemistry, and thus examples of further small molecule activation by these systems are limited.

FLPs that consist of $B(2,3,5,6\text{-}F_4C_6H)_3$ or $B(4\text{-}FC_6H_4)_3$, combined with P^tBu_3 or PCy_3 have been shown to activate N_2O, in both computational and experimental studies (Scheme 24, top).[149–151] The binding mode of the activated N_2O was determined by infrared spectroscopy, which found a B-O-N=N-P type linkage formed by attack of the lone pair of the Lewis base toward the terminal nitrogen of N_2O and donation of the oxygen's lone pair of electrons into the empty *p*-orbital of the borane.[152]

Further investigation into the $B(2,3,5,6\text{-}F_4C_6H)_3/PPh_3$ FLP found it could trap out the 1,3-addition product upon addition of mesityl isocyanate (Scheme 24, bottom).[153] This gave evidence towards the Cummins proposition, which suggested that the oxidation of phosphines by mesitylisocyanate occurred through the initial interaction between the carbon atom of the isocyanate and the phosphine.[154]



Scheme 24: Activation of N_2O and mesityl isocyanate by FLP containing $B(2,3,5,6\text{-}F_4C_6H)_3$ as the Lewis acidic component.[150,153]

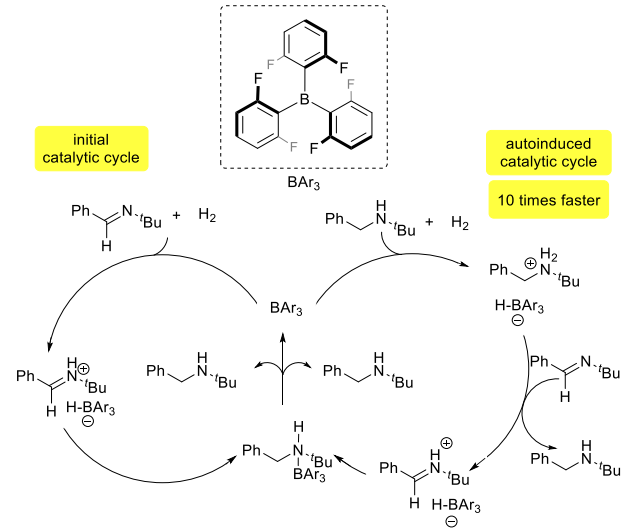
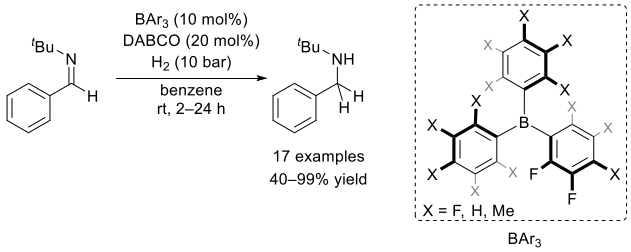


Figure 7: Proposed mechanism for autoinduced FLP hydrogenation of imines.[155]

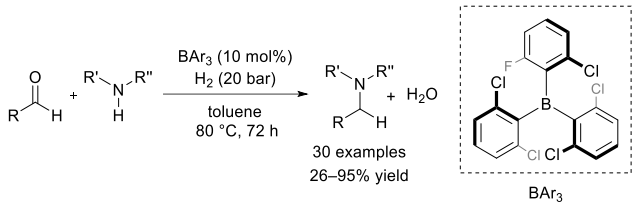
5.4 FLP catalysed hydrogenation reactions

Hydrogenation reactions which utilise FLPs as catalysts have been widely studied as an alternative to traditional transition metal-based hydrogenation catalysts. Whilst many FLPs reported in the literature contain $B(C_6F_5)_3$ as the Lewis acidic component, there are many other boranes that can also be used in hydrogenation reactions with typical substrates being imines, carbonyls and olefins.

Microwave assisted hydrogenation reactions have been reported using an FLP comprised of $B(2,4,6\text{-}F_3C_6H_2)_3$ and 2,6-dimethylpyridine to hydrogenate a nitroolefin, and an FLP comprised of $B(2,6\text{-}F_2C_6H_3)_3$ and collidine to hydrogenate a malonate.[156] $B(2,6\text{-}F_2C_6H_3)_3$ was also used to investigate kinetically the autoinduced FLP hydrogenation of 16 imines, and it was found that the autoinduced cycle was up to ten times faster than the initial cycle. A proposed mechanism for the autoinduced FLP hydrogenation is given in Figure 7, along with its initial catalytic cycle.[155] Computational studies provided inspiration for using $B(2,6\text{-}F_2C_6H_3)_3$ as the acidic component of an FLP catalyst, as the $\Delta G°$ for H_2 activation was determined to be 2 kcalmol^{-1} higher for weaker Lewis acids such as $B(2,6\text{-}F_2C_6H_3)_3$ compared to $B(C_6F_5)_3$.[157]



Scheme 25: Imine reduction by a range of heteroleptic triaryl boranes.[115]



Scheme 26: Water tolerant reductive amination by $B(2\text{-}F\text{-}6\text{-}ClC_6H_3)(2,6\text{-}Cl_2C_6H_3)_2$.[74]

The reduction of (*Z*)-*N*-*tert*-butyl-1-phenylmethanimine using FLPs consisting of DABCO and a range of heteroleptic triarylboranes was demonstrated to glean trends behind catalytic hydrogenation activity (Scheme 25).[115] Conversions were generally found to increase with the total number of fluorines on the aryl rings, whilst the number of chlorine atoms had a negligible effect on catalytic activity.[115]

The heteroleptic borane $B(2\text{-}F\text{-}6\text{-}ClC_6H_3)(2,6\text{-}Cl_2C_6H_3)_2$ was employed in FLP catalysed reductive aminations (30 examples, 26–95% yield) (Scheme 26). This borane was chosen as a catalyst due to large steric hinderance of chlorine atoms in the *ortho* positions of the aryl rings inducing water tolerance.[74]

When using $B(2,3,5,6\text{-}F_4C_6H)_2(2,6\text{-}Cl_2C_6H_3)$ as a catalyst, reductive alkylation of multiply substituted amines with H_2 was possible.[158] This was achieved through a combination of Lewis acid catalysis, and FLP mediated hydrogenation. A proposed mechanism for this catalytic system is shown in Figure 8.[158] The first step in the mechanism is the acid-catalysed cycle (Figure 8, left), wherein the borane catalyses the formation of an imine from an appropriate aldehyde. Here, the borane activates the aldehyde, allowing for subsequent attack by an amine to form the desired imine whilst regenerating the free borane catalyst. The second FLP catalysed cycle (Figure 8, right) could occur either with the imine acting as the Lewis base (path a), or THF (path b) as a partner for the borane Lewis acid. In either case, dihydrogen

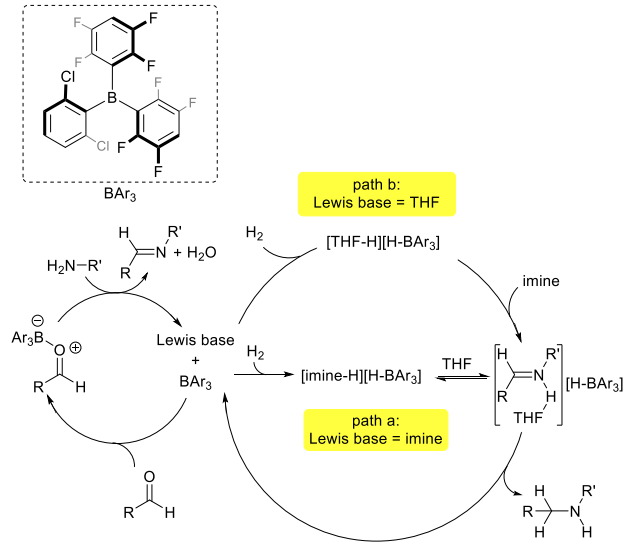


Figure 8: FLP catalysed reductive alkylation of amines.[158]

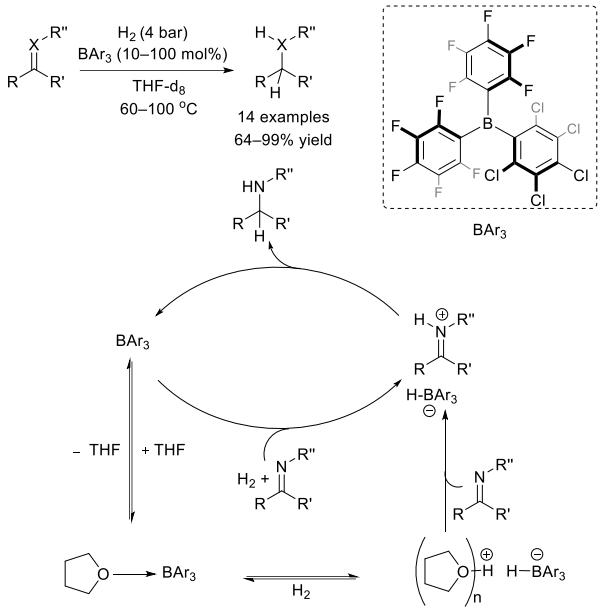
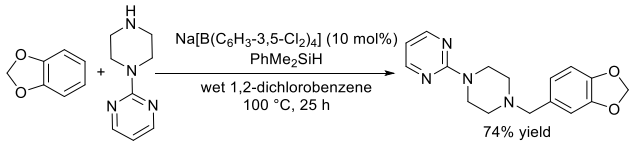


Figure 9: Solvent assisted imine reduction catalysed by $B(C_6F_5)_2(C_6Cl_5)$.[159]

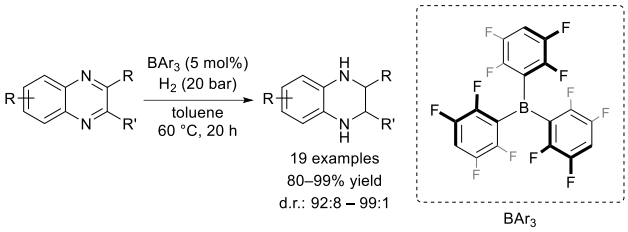
is activated by the FLP, and depending upon the path, THF was coordinated to the resultant complex or an imine was introduced to form the intermediate [imine-H-THF][H-borane]. Subsequent hydride transfer from the borane liberated the imine product and regenerated the FLP catalyst. Forty four examples of reductive alkylation were given, with yields ranging from 29 to 99% with high functional group tolerance including carboxylic acids, sulphonamides, and alcohols being observed.[158]

A solvent assisted FLP mediated imine reduction has been investigated, wherein $B(C_6F_5)_2(C_6Cl_5)$ was combined with THF (acting as the Lewis basic component) to form an FLP system capable of imine reduction (Figure 9).[159] Fourteen weakly basic substrates (including furans, pyrroles, and aromatic rings) were efficiently hydrogenated under relatively mild reaction conditions in up to 95% yield.[159]

Upon the decomposition of the air stable salt $Na[B(3,5\text{-}Cl_2C_6H_3)_4]$, catalytically active $B(3,5\text{-}Cl_2C_6H_3)_3$ was shown to form and promote the reductive amination of aldehydes in wet solvent (4 examples, 60–93% yield). A gram scale synthesis for Piridebil, a drug for the treatment of Parkinson's disease, using a $Na[B(3,5\text{-}Cl_2C_6H_3)_4]$ precatalyst is shown in Scheme 27, with a yield of 74%.[75]



Scheme 27: Synthesis of Piridebil by $B(C_6H_3\text{-}3,5\text{-}Cl_2)_3$ catalysed reductive amination.[75]

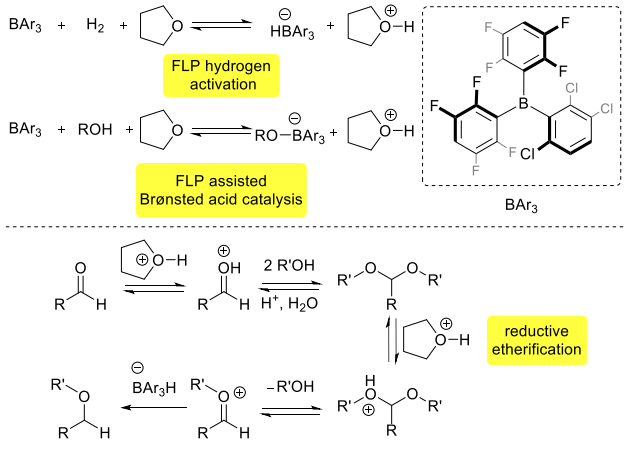


Scheme 28: FLP catalysed hydrogenation of quinoxalines.[160]

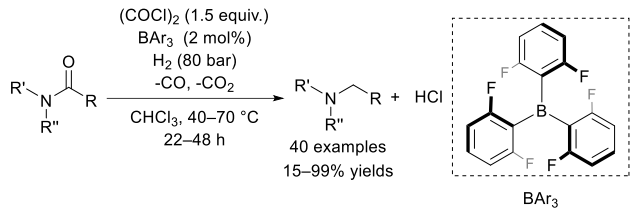
$B(2,3,5,6\text{-}F_4C_6H)_3$ was shown to be used as an FLP catalyst for the hydrogenation of 2,3-disubstituted quinoxalines, with the quinoxaline acting as the Lewis base in the reaction (Scheme 28). The FLP system was found to be highly *cis*-selective, with 2,3-disubstituted 1,2,3,4-tetrahydroquinoxalines formed (19 examples) in good yields (80–99%), with high diastereomeric ratios (92:8-99:1).[160]

The water tolerant $B(2,3,5,6\text{-}F_4C_6H)_2(2,6\text{-}Cl_2C_6H_3)$ was used in the FLP catalysed hydrogenation of carbonyl compounds with conversions up to 95% (10 examples).[114] Subsequently, an alternate water tolerant borane, $B(2,3,5,6\text{-}F_4C_6H)_2(2,3,6\text{-}Cl_3C_6H_2)$, was employed in the reduction of acetals to ethers (16 examples, up to 99% yield) and reductive etherification of carbonyls (20 examples, 28–32% yield), by using a mixture of FLP hydrogenation and Brønsted acid catalysis, wherein the THF solvent acted as a base.[161] A proposed mechanism of this auto-tandem catalysis is given in Scheme 29. Here, the Brønsted acid catalysis generated an oxonium cation out of the THF solvent, thereby also forming a borate anion from the borane. Also, FLP catalysed hydrogenation formed a secondary oxonium cation as well as a borohydride from the borane. These oxonium cations were used to protonate the aldehyde or acetal, whilst the borohydride was used to transfer a hydride to the final ether product.[161]

$B(2\text{-}6\text{-}F_2C_6H_3)_3$ was shown to catalyse the reduction of amides with the assistance of oxalyl chloride in the role of a deoxygenating agent (Scheme 30).[162] Whilst the use of halides as bases in FLP chemistry is uncommon (due to being



Scheme 29: Proposed autotandem catalysis mechanism for reductive etherification of carbonyls.[161]

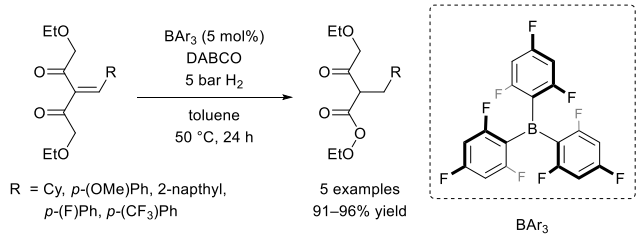


Scheme 30: $B(2,6\text{-}F_2C_6H_3)_3$ catalysed reduction of carboxylic amides.[162]

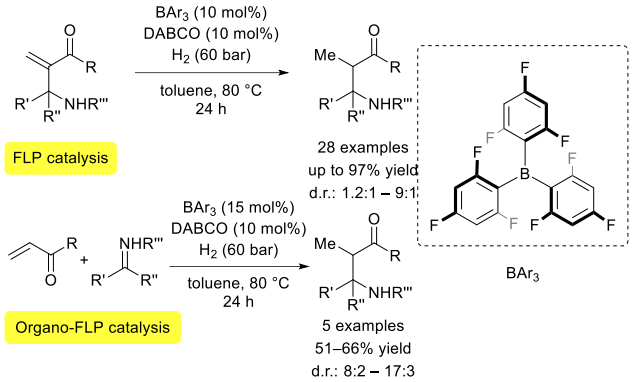
too basic), oxalyl chloride was found to be weak enough for FLP catalysis to occur instead of adduct formation. Catalytic reduction of amides showed conversions of up to 15–99%, with good yields (40 examples) and good functional group tolerance.[162] DFT calculations were employed to investigate the mechanism for the hydrogenation of tertiary amides after activation by oxalyl chloride.[163] It was identified that during a one-pot reaction, the borane was trapped by the amide substrate, thereby reducing the rate of hydrogenation. It was therefore suggested that stepwise amide activation and reduction could improve reactivity.[163] $B(2,6\text{-}F_2C_6H_3)_3$ has also been shown to promote the reduction of phosphine oxides when in combination with 2,6-lutidene, oxalyl chloride and dihydrogen.[164] However, whilst this reaction was near quantitative at 4 bar pressure, it was observed that the reduction did not require a catalyst if the hydrogen pressure was increased to 80 bar.[164] DFT calculations were used to investigate the mechanism of this reduction, which found that the presence of the FLP formed from the borane made for more efficient hydrogenation, allowing for low pressure reduction.

An FLP comprised of $B(2,4,6\text{-}F_3C_6H_2)_3$ and DABCO was found to promote the catalytic hydrogenation of alkenes (10 examples, 65–95% yield) and alkylidene malonates (5 examples, 91–96% yield) (Scheme 31).[56] The choice of borane was guided by determining the Lewis acidity and steric demand of a range of boranes using the Childs method described earlier, with $B(2,4,6\text{-}F_3C_6H_2)_3$ being chosen due to its higher steric hinderance and low Lewis acidity.[56]

We have also used this borane in an FLP system with DABCO for catalytic hydrogenation of aza-Morita-Baylis-Hillman adducts and in sequential organo-FLP catalysis for the synthesis of stereoselective β-amino acid derivatives (Scheme 32).[165] Diastereoselectivity (9:1) and good to excellent yields were achieved for the hydrogenation step (up to 97%, 28 examples), whilst the sequential organo-FLP



Scheme 31: $B(2,4,6\text{-}F_3C_6H_2)_3$ catalysed hydrogenation reaction of alkylidene malonates.[56]



Scheme 32: FLP catalysed hydrogenation of aza Morita–Baylis–Hillman adducts.[165]

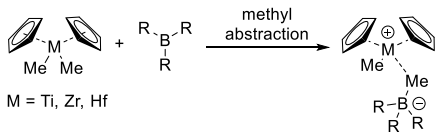
catalysis achieved up to 66% isolated yields and diastereomeric ratios up to 85:15 over five examples.[165]

A range of intermediates in many different FLP catalysed hydrogenation reactions (phosphonium and ammonium triarylborohydrides based on $B(C_6F_5)_3$, $B(2,6\text{-}F_2C_6H_3)_3$ or $B(2,4,6\text{-}F_3C_6H_2)_3$) were investigated to probe the mechanism and kinetics of C=C bond hydrogenation reactions.[166] It was found that the counterion had a negligible effect on the rate of hydrogenation, however the fluorine substitution pattern of the borane's aryl rings had a strong influence with *meta*-fluorine atoms on the aryl ring reducing hydride donating ability and thus the rate of hydrogenation.[166]

Hydrodesilylation of $Ph_2P(TMS)$ to $(Ph_2P)_2$ has been reported with catalytic $B(2,3,5,6\text{-}F_4C_6H)_3$ and sacrificial 4-heptanone.[167]

6 Polymerisation reactions

Before the resurgence of halogenated triarylboranes in FLP chemistry and as Lewis acidic catalysts, they were often used as initiators or co-initiators in polymerisation reactions. Traditionally, the combination of methylaluminoxane (MAO) and a group 4 metallocene was used for olefin polymerisation, but in 1994 Marks discovered that $B(C_6F_5)_3$ could be used to abstract a methyl group from dimethyl zirconocenes to form highly active polymerisation catalysts (Scheme 33).[168] This seminal study led to further investigation into the use of more sterically demanding analogues of $B(C_6F_5)_3$, tris(β-perfluoronapthyl)borane $[B(C_{10}F_7)_3]$ and tris(perfluorobiphenyl)borane



Scheme 33: Generic methyl abstraction of metallocenes by halogenated triarylboranes.

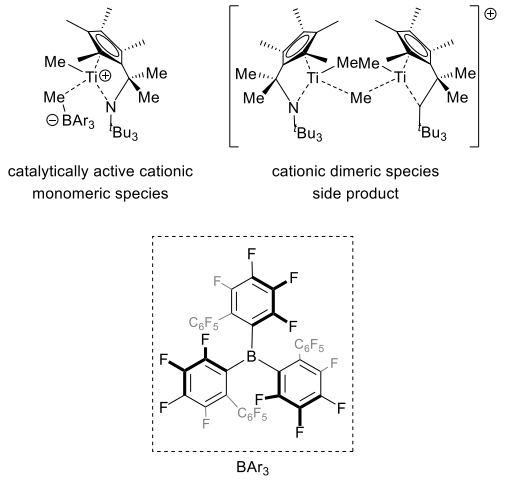


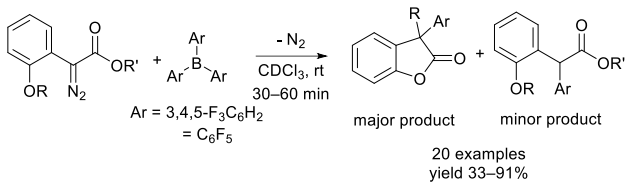
Figure 10: Cationic species species formed by $[B(2\text{-}(C_6F_5)C_6F_4)_3]$.[169]

$[B(2\text{-}(C_6F_5)C_6F_4)_3]$, as co-initiators to metallocene catalysts as it was found that the increased steric bulk assisted the abstraction of a metallocene's methyl group.

Meanwhile, it was shown that strong Lewis acidity was another key consideration for efficient methide abstraction, with less acidic boranes $B(3,5\text{-}(CF_3)_2C_6H_3)(C_6F_5)_2$ and $B(3,5\text{-}Me_2C_6H_3)(C_6F_5)_2$ shown to be less efficient at abstracting the methyl groups of group 4 metallocenes. This resulted in mediocre ethylene polymerisation activity compared to $B(C_6F_5)_3$.[112]

Examples of both bulky boranes showing increased reactivity in comparison to $B(C_6F_5)_3$ include the titanocene catalysed co-polymerisation of 1-octene and ethylene,[69,70] and the zirconocene catalysed polymerisation of propylene.[170] $B(2\text{-}(C_6F_5)C_6F_4)_3$ was shown to be more active than $B(C_6F_5)_3$ as an initiator for propylene catalysis with a zirconocene catalyst,[171,172] and also when acting as a co-initiator with half-sandwich titanocene catalysts towards the syndiospecific polymerisation of styrene or 4-(*N*,*N*-bis(trimethylsilyl)amino)styrene.[173,174] However, when the half-sandwich titanocene complexes contained a constrained geometry, $B(2\text{-}(C_6F_5)C_6F_4)_3$ was found to form cationic dinuclear complexes instead of a catalytically active mononuclear species due to the weak co-ordination of the borane to the methide ligand of titanium (Figure 10).[169]

$B(2\text{-}(C_6F_5)C_6F_4)_3$, $B(2,4,6\text{-}F_3C_6H_2)_3$, and $B(4\text{-}FC_6H_4)_3$ have all been used as co-initiators in the ring opening polymerisation of propylene oxide, when initiated by a range of hydroxylic aluminium complexes.[175] Aluminium aryloxides have also been used with triphenylmethyl fluoride and $B(C_6F_5)_2(2\text{-}(C_6F_5)C_6F_4)$ for *tert*-butyl vinyl ether polymerisation.[176] Further investigation into the catalytic properties of $B(C_6F_5)_2(2\text{-}(C_6F_5)C_6F_4)$ found that upon co-initiation by $AlMe_3$ or $GaMe_3$, it could polymerise isobutene.[177,178]



Scheme 34: Tandem rearrangement/lactonisation reaction with halogenated triarylboranes as substrates.[75]

7 Stoichiometric reactivity

Despite the many uses in catalysis and FLP chemistry, halogenated triarylboranes have been involved in some interesting chemistry through stoichiometric reactions. We have used a range of halogenated triarylboranes as stoichiometric reagents with diazo compounds in the preparation of 2-aryl propanoates through a 1,2-aryl transfer reaction.[75] It was found that when stronger acids such as $B(C_6F_5)_3$ and $B(3,4,5\text{-}F_3C_6H_2)_3$ were used as the aryl donor, sub-stoichiometric amounts were necessary, otherwise multiple aryl groups were transferred.[75] Further investigation revealed an unprecedented tandem rearrangement/lactonisation reaction between 2-benzyloxy-substituted diazo esters and $B(C_6F_5)_3$ or $B(3,4,5\text{-}F_3C_6H_2)_3$. Twenty examples of lactonisation were given with moderate to high conversions (33–91%) of the lactone product (Scheme 34).[75]

We have also shown that upon reaction with hydrazones or hydrazides, $B(2,4,6\text{-}F_3C_6H_2)_3$ and $B(3,4,5\text{-}F_3C_6H_2)_3$ are able to form adducts, heterocycles, or form products *via* the elimination of one of the borane's aryl groups.[179]

$B(4\text{-}FC_6H_4)_3$ has been employed as a component in a catalyst-free Mannich reaction, along with a diazo compound and an acyl imine, to produce highly diastereoselective beta-amino carbonyl compounds.[180] The majority of scope was investigated with BPh_3, however the Mannich reaction involving $B(4\text{-}FC_6H_4)_3$ was found to result in an 86% yield.[180]

8 Conclusions and outlook

In this review, the design of halogenated triarylboranes through careful consideration of their Lewis acidity has been discussed. From well-established NMR-based techniques such as the Gutmann-Beckett and Childs methods, to cutting-edge theoretical and visual procedures such as Stephan's global electrophilicity index and Baumgartner and Caputo's fluorescent adduct experiments, we have shown that there are a wide variety of ways to determine and tailor the Lewis acidity of a borane for a specific purpose.

The synthesis of these boranes has also been examined, with an in-depth analysis of how typical homoleptic boranes can be formed through the conventional Grignard and lithiation procedures, along with more complex methods to form heteroleptic boranes involving intermediates such as potassium trifluoroborate salts and copper-based aryl transfer reagents.

The catalytic properties of these boranes, both as a Lewis acid, and as the Lewis acidic component of FLPs was also reviewed, with many examples showing improved reactivity compared to $B(C_6F_5)_3$. Herein we have discussed the use of water tolerant boranes such as $B(2\text{-}F\text{-}6\text{-}ClC_6H_3)(2,6\text{-}Cl_2C_6H_3)_2$ and $B(3,5\text{-}Cl_2C_6H_3)_3$, which were shown to partake in FLP catalysed reductions conducted in wet solvents in which $B(C_6F_5)_3$ would simply be deactivated. We have shown that boranes with different Lewis acidity to $B(C_6F_5)_3$ can result in alternative reactivity, such as in the chemo-selective functionalisation of gibberellic acid and natamycin derivatives, or even outperform $B(C_6F_5)_3$ such as in base-free hydroboration by $B(3,5\text{-}(CF_3)_2C_6H_3)_3$ or $B(2\text{-}(C_6F_5)C_6F_4)_3$ initiated polymerisation catalysis.

To summarise, whilst $B(C_6F_5)_3$ may still be known as the archetypal halogenated triarylborane, we hope to have highlighted to the reader that there are many more triarylboranes that can offer superior reactivity or alternate chemoselectivity to the main group chemist and we look forward to seeing further additions to the field in the near future.

Conflicts of interest

There are no conflicts to declare.

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References

1 A. C. Massey, A. J. Park and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, **127**, 212–212.
2 A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245–250.
3 J. Klosin, P. P. Fontaine and R. Figueroa, *Acc. Chem. Res.*, 2015, **48**, 2004–2016.
4 C. Janiak, P. G. Lassahn and V. Lozan, *Macromol. Symp.*, 2006, **236**, 88–99.
5 F. Focante, P. Mercandelli, A. Sironi and L. Resconi, *Coord. Chem. Rev.*, 2006, **250**, 170–188.
6 G. Erker, G. Kehr and R. Fröhlich, *J. Organomet. Chem.*, 2005, **690**, 6254–6262.
7 W. E. Piers, Y. Sun and L. W. M. Lee, *Top. Catal.*, 1999, **7**, 133–143.
8 K. Ishihara and H. Yamamoto, *Eur. J. Org. Chem.*, 1999, **1999**, 527–538.
9 D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441.
10 G. C. Welch, R. R. San Juan, J. D. Masuda and D. W.

Stephan, *Science*, 2006, **314**, 1124–1126.
11 J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2007, **46**, 4968–4971.
12 W. E. Piers, A. J. V. Marwitz and L. G. Mercier, *Inorg. Chem.*, 2011, **50**, 12252–12262.
13 D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, **50**, 12338–12348.
14 J. Paradies, *Eur. J. Org. Chem.*, 2019, **2019**, 283–294.
15 D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400–6441.
16 D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032.
17 D. W. Stephan, *Science*, 2016, 354, aaf7229–aaf7229.
18 D. W. Stephan, *Org. Biomol. Chem.*, 2012, 10, 5740–5746.
19 J. Lam, K. M. Szkop, E. Mosaferi and D. W. Stephan, *Chem. Soc. Rev.*, 2019, **48**, 3592–3612.
20 D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625–2641.
21 D. W. Stephan, *J. Chem. Soc., Dalton Trans.*, 2009, 3129–3136.
22 J. R. Lawson and R. L. Melen, *Inorg. Chem.*, 2017, **56**, 8627–8643.
23 R. L. Melen, *Chem. Commun.*, 2014, **50**, 1161–1174.
24 M. Oestreich, J. Hermeke and J. Mohr, *Chem. Soc. Rev.*, 2015, **44**, 2202–2220.
25 K. Matsumoto, S. Shimada and K. Sato, *Chem. Eur. J.*, 2019, **25**, 920–928.
26 W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345–354.
27 G. N. Lewis, *J. Franklin Inst.*, 1938, **226**, 293–313.
28 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533–3539.
29 R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, 1965, **87**, 3571–3577.
30 A. P. Marks and R. S. Drago, *Inorg. Chem.*, 1976, **15**, 1800–1807.
31 U. Mayer, V. Gutmann and W. Gerger, *Monatshefte für Chemie*, 1975, **106**, 1235–1257.
32 M. A. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polymer* , 1996, **37**, 4629–4631.
33 R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 801–808.
34 J. R. Gaffen, J. N. Bentley, L. C. Torres, C. Chu, T. Baumgartner and C. B. Caputo, *Chem*, 2019, **5**, 1567–1583.
35 G. Hilt and A. Nödling, *Eur. J. Org. Chem.*, 2011, 7071–7075.
36 D. C. Bradley, I. S. Harding, A. D. Keefe, M. Motevalli and D. H. Zheng, *J. Chem. Soc., Dalton Trans.*, 1996, 3931–3936.
37 G. J. P. Britovsek, J. Ugolotti and A. J. P. White, *Organometallics*, 2005, **24**, 1685–1691.
38 T. E. Mallouk, G. L. Rosenthal, G. Muller, R. Brusasco and N. Bartlett, *Inorg. Chem.*, 1984, **23**, 3167–3173.
39 K. O. Christe, D. A. Dixon, D. McLemore, W. W. Wilson, J. A. Sheehy and J. A. Boatz, *J. Fluor. Chem.*, 2000, **101**, 151–153.
40 M. T. Mock, R. G. Potter, D. M. Camaioni, J. Li, W. G. Dougherty, W. S. Kassel, B. Twamley and D. L. DuBois, *J. Am. Chem. Soc.*, 2009, **131**, 14454–14465.
41 A. Y. Timoshkin and G. Frenking, *Organometallics*, 2008, **27**, 371–380.
42 E. R. Clark, A. Del Grosso and M. J. Ingleson, *Chem. Eur. J.*, 2013, **19**, 2462–2466.
43 T. A. Rokob, A. Hamza and I. Pápai, *J. Am. Chem. Soc.*, 2009, **131**, 10701–10710.
44 Z. M. Heiden and A. P. Lathem, *Organometallics*, 2015, **34**, 1818–1827.
45 H. Böhrer, N. Trapp, D. Himmel, M. Schleep and I. Krossing, *Dalton Trans.*, 2015, **44**, 7489–7499.
46 A. R. Jupp, T. C. Johnstone and D. W. Stephan, *Dalton Trans.*, 2018, **47**, 7029–7035.
47 A. T. Maynard, M. Huang, W. G. Rice and D. G. Covell, *Proc. Natl. Acad. Sci.*, 1998, **95**, 11578–11583.
48 R. G. Parr, L. V. Szentpály and S. Liu, *J. Am. Chem. Soc.*, 1999, **121**, 1922–1924.
49 R. S. Mulliken, *J. Chem. Phys.*, 1934, **2**, 782–793.
50 I. B. Sivaev and V. I. Bregadze, *Coord. Chem. Rev.*, 2014, 270–271, 75–88.
51 B. L. Durfey and T. M. Gilbert, *Inorg. Chem.*, 2011, **50**, 7871–7879.
52 M. M. Morgan, A. J. V Marwitz, W. E. Piers and M. Parvez, *Organometallics*, 2013, **32**, 317–322.
53 S. Keess, A. Simonneau and M. Oestreich, *Organometallics*, 2015, **34**, 790–799.
54 J. B. Geri, J. P. Shanahan and N. K. Szymczak, *J. Am. Chem. Soc.*, 2017, **139**, 5952–5956.
55 L. Luo and T. J. Marks, *Top. Catal.*, 1999, **7**, 97–106.
56 J. A. Nicasio, S. Steinberg, B. Inés and M. Alcarazo, *Chem. Eur. J.*, 2013, **19**, 11016–11020.
57 L. A. Mück, A. Y. Timoshkin and G. Frenking, *Inorg. Chem.*, 2012, **51**, 640–646.
58 Eur. Pat., EP0604962 (A1), 1994.
59 D. D. Callander, P. L. Coe and J. C. Tatlow, *Tetrahedron*, 1966, **22**, 419–432.
60 Q. Yin, Y. Soltani, R. L. Melen and M. Oestreich, *Organometallics*, 2017, **36**, 2381–2384.
61 J. L. Carden, L. J. Gierlichs, D. F. Wass, D. L. Browne and R. L. Melen, *Chem. Commun.*, 2019, **55**, 318–321.
62 T. J. Herrington, A. J. W. Thom, A. J. P. White and A. E. Ashley, *Dalton Trans.*, 2012, **41**, 9019–9022.
63 Q. Yin, S. Kemper, H. F. T. Klare and M. Oestreich, *Chem. Eur. J.*, 2016, **22**, 13840–13844.
64 D. Naumann, H. Butler and R. Gnann, *ZAAC - J. Inorg. Gen. Chem.*, 1992, **618**, 74–76.
65 M. Ullrich, A. J. Lough and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 52–53.
66 S. M. Cornet, K. B. Dillon, C. D. Entwistle, M. A. Fox, A. E. Goeta, H. P. Goodwin, T. B. Marder and A. L. Thompson, *Dalton Trans.*, 2003, **3**, 4395–4405.
67 R. J. Blagg, E. J. Lawrence, K. Resner, V. S. Oganesyan, T. J. Herrington, A. E. Ashley and G. G. Wildgoose, *Dalton Trans.*, 2016, **45**, 6023–6031.
68 S. Toyota, M. Asakura, M. Oki and F. Toda, *Bull. Chem.*

Soc. Jpn., 2000, **73**, 2357–2362.
69 L. Li and T. J. Marks, *Organometallics*, 1998, **17**, 3996–4003.
70 Y. X. Chen, M. V. Metz, L. Li, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 6287–6305.
71 L. A. Körte, J. Schwabedissen, M. Soffner, S. Blomeyer, C. G. Reuter, Y. V. Vishnevskiy, B. Neumann, H. G. Stammler and N. W. Mitzel, *Angew. Chem. Int. Ed.*, 2017, **56**, 8578–8582.
72 J. Li, G. Zhang, D. Zhang, R. Zheng, Q. Shi and D. Zhu, *J. Org. Chem.*, 2010, **75**, 5330–5333.
73 J. E. Leffler, G. B. Watts, T. Tanigaki, E. Dolan and D. S. Miller, *J. Am. Chem. Soc.*, 1970, **92**, 6825–6830.
74 É. Dorkó, M. Szabó, B. Kótai, I. Pápai, A. Domján and T. Soós, *Angew. Chem. Int. Ed.*, 2017, **56**, 9512–9516.
75 M. Santi, D. M. C. Ould, J. Wenz, Y. Soltani, R. L. Melen and T. Wirth, *Angew. Chem. Int. Ed.*, 2019, **58**, 7861–7865.
76 R. J. Blagg, T. R. Simmons, G. R. Hatton, J. M. Courtney, E. L. Bennett, E. J. Lawrence and G. G. Wildgoose, *Dalton Trans.*, 2016, **45**, 6032–6043.
77 A. E. Ashley, T. J. Herrington, G. G. Wildgoose, H. Zaher, A. L. Thompson, N. H. Rees, T. Krämer and D. O'Hare, *J. Am. Chem. Soc.*, 2011, **133**, 14727–14740.
78 V. Fasano and M. J. Ingleson, *Chem. Eur. J.*, 2017, **23**, 2217–2224.
79 J. Y. Ryu, J. M. Lee, N. Van Nghia, K. M. Lee, S. Lee, M. H. Lee, P. J. Stang and J. Lee, *Inorg. Chem.*, 2018, **57**, 11696–11703.
80 S. Helten, B. Sahoo, V. Bon, I. Senkovska, S. Kaskel and F. Glorius, *CrystEngComm*, 2015, **17**, 307–312.
81 L. Zhai, N. Huang, H. Xu, Q. Chen and D. Jiang, *Chem. Commun.*, 2017, **53**, 4242–4245.
82 X. Wang, J. Yang, L. Zhang, F. Liu, F. Dai and D. Sun, *Inorg. Chem.*, 2014, **53**, 11206–11212.
83 Y. Liu, K. Mo and Y. Cui, *Inorg. Chem.*, 2013, **52**, 10286–10291.
84 B. A. Blight, R. Guillet-Nicolas, F. Kleitz, R.-Y. Wang and S. Wang, *Inorg. Chem.*, 2013, **52**, 1673–1675.
85 Y. Liu, X. Xu, W. Xuan, C. Zhu and Y. Cui, *Sci. China Chem.*, 2011, **54**, 1430–1435.
86 Y. Liu, W. Xuan, H. Zhang and Y. Cui, *Inorg. Chem.*, 2009, **48**, 10018–10023.
87 F. M. Ebrahim, T. N. Nguyen, S. Shyshkanov, A. Gładysiak, P. Favre, A. Zacharia, G. Itskos, P. J. Dyson and K. C. Stylianou, *J. Am. Chem. Soc.*, 2019, **141**, 3052–3058.
88 S. Yamaguchi, T. Shirasaka and K. Tamao, *Org. Lett.*, 2000, **2**, 4129–4132.
89 J. Liu, S. Zhang, C. Zhang, J. Dong, C. Shen, J. Zhu, H. Xu, M. Fu, G. Yang and X. Zhang, *Chem. Commun.*, 2017, **53**, 11476–11479.
90 J. Liu, X. Guo, R. Hu, X. Liu, S. Wang, S. Li, Y. Li and G. Yang, *Anal. Chem.*, 2016, **88**, 1052–1057.
91 M. Kinoshita, H. Kita and Y. Shirota, *Adv. Funct. Mater.*, 2002, **12**, 780–786.
92 Y. Nagata and Y. Chujo, *Macromolecules*, 2008, **41**, 2809–2813.
93 X. Liu, Y. Zhang, H. Li, S. A, H. Xia and Y. Mu, *RSC Adv.*, 2013, **3**, 21267–21270.
94 W. L. Jia, M. J. Moran, Y. Y. Yuan, Z. H. Lu and S. Wang, *J. Mater. Chem.*, 2005, **15**, 3326–3333.
95 Y. Kubo, M. Yamamoto, M. Ikeda, M. Takeuchi, S. Shinkai, S. Yamaguchi and K. Tamao, *Angew. Chem. Int. Ed.*, 2003, **42**, 2036–2040.
96 J. Yoshino, Y. Nakamura, S. Kunitomo, N. Hayashi and H. Higuchi, *Tetrahedron Lett.*, 2013, **54**, 2817–2820.
97 Z. Li, H. Li, H. Xia, X. Ding, X. Luo, X. Liu and Y. Mu, *Chem. Eur. J.*, 2015, **21**, 17355–17362.
98 Y. Liu, G. Xie, K. Wu, Z. Luo, T. Zhou, X. Zeng, J. Yu, S. Gong and C. Yang, *J. Mater. Chem. C*, 2016, **4**, 4402–4407.
99 V. M. Suresh, A. Bandyopadhyay, S. Roy, S. K. Pati and T. K. Maji, *Chem. Eur. J.*, 2015, **21**, 10799–10804.
100 X. Liu, S. Li, J. Feng, Y. Li and G. Yang, *Chem. Commun.*, 2014, **50**, 2778–2780.
101 T. Zhang, R. Wang, L. Wang, Q. Wang and J. Li, *Dye. Pigment.*, 2013, **97**, 155–161.
102 M. Mao, M. G. Ren and Q. H. Song, *Chem. Eur. J.*, 2012, **18**, 15512–15522.
103 Y. Liu, X. Xu, F. Zheng and Y. Cui, *Angew. Chem. Int. Ed.*, 2008, **47**, 4538–4541.
104 K. Yuan, X. Wang, S. K. Mellerup, I. Wyman, G. Schatte, Z. Ding and S. Wang, *Organometallics*, 2016, **35**, 3051–3059.
105 W. Zhao, F. Zhang, L. Yang, S. Bi, D. Wu, Y. Yao, M. Wagner, R. Graf, M. R. Hansen, X. Zhuang and X. Feng, *J. Mater. Chem. A*, 2016, **4**, 15162–15168.
106 M. Wada, M. Kanzaki, H. Ogura, S. Hayase and T. Erabi, *J. Organomet. Chem.*, 1995, **485**, 127–133.
107 K. Vanka, M. S. W. Chan, C. C. Pye and T. Ziegler, *Organometallics*, 2000, **19**, 1841–1849.
108 M. Heshmat and T. Privalov, *Chem. Eur. J.*, 2017, **23**, 11489–11493.
109 L. Li, C. L. Stern and T. J. Marks, *Organometallics*, 2000, **19**, 3332–3337.
110 D. E. Fenton, A. J. Park, D. Shaw and A. G. Massey, *J. Organomet. Chem.*, 1964, **2**, 437–446.
111 R. D. Chambers and T. Chivers, *J. Chem. Soc.*, 1965, 3933–3939.
112 P. A. Deck, C. L. Beswick and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 1772–1784.
113 R. Roesler, B. J. N. Har and W. E. Piers, *Organometallics*, 2002, **21**, 4300–4302.
114 Á. Gyömöre, M. Bakos, T. Földes, I. Pápai, A. Domján and T. Soós, *ACS Catal.*, 2015, **5**, 5366–5372.
115 É. Dorkó, B. Kótai, T. Földes, Á. Gyömöre, I. Pápai and T. Soós, *J. Organomet. Chem.*, 2017, **847**, 258–262.
116 R. J. Blagg and G. G. Wildgoose, *RSC Adv.*, 2016, **6**, 42421–42427.
117 J. Chai, S. P. Lewis, S. Collins, T. J. J. Sciarone, L. D. Henderson, P. A. Chase, G. J. Irvine, W. E. Piers, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2007, **26**, 5667–5679.

118 S. P. Lewis, L. D. Henderson, B. D. Chandler, M. Parvez, W. E. Piers and S. Collins, *J. Am. Chem. Soc.*, 2005, **127**, 46–47.

119 T. Wondimagegn, Z. Xu, K. Vanka and T. Ziegler, *Organometallics*, 2005, **24**, 2076–2085.

120 S. Rendler and M. Oestreich, *Angew. Chem. Int. Ed.*, 2008, **47**, 5997–6000.

121 T. A. Bender, P. R. Payne and M. R. Gagné, *Nat. Chem.*, 2018, **10**, 85–90.

122 Y. Seo, A. Gudz, J. M. Lowe and M. R. Gagné, *Tetrahedron*, , DOI:10.1016/j.tet.2019.130712.

123 D. Fegyverneki, N. Kolozsvári, D. Molnár, O. Egyed, T. Holczbauer and T. Soós, *Chem. Eur. J.*, 2019, **25**, 2179–2183.

124 A. Simonneau and M. Oestreich, *Nat. Chem.*, 2015, **7**, 816–822.

125 P. Eisenberger, A. M. Bailey and C. M. Crudden, *J. Am. Chem. Soc.*, 2012, **134**, 17384–17387.

126 A. Prokofjevs, A. Boussonnière, L. Li, H. Bonin, E. Lacôte, D. P. Curran and E. Vedejs, *J. Am. Chem. Soc.*, 2012, **134**, 12281–12288.

127 J. S. McGough, S. M. Butler, I. A. Cade and M. J. Ingleson, *Chem. Sci.*, 2016, **7**, 3384–3389.

128 J. R. Lawson, L. C. Wilkins and R. L. Melen, *Chem. Eur. J.*, 2017, **23**, 10997–11000.

129 R. Dobrovetsky, K. Takeuchi and D. W. Stephan, *Chem. Commun.*, 2015, **51**, 2396–2398.

130 M. Bakos, Z. Dobi, D. Fegyverneki, Á. Gyömöre, I. Fernández and T. Soós, *ACS Sustain. Chem. Eng.*, 2018, **6**, 10869–10875.

131 D. Yepes, P. Pérez, P. Jaque and I. Fernández, *Org. Chem. Front.*, 2017, **4**, 1390–1399.

132 G. Hamasaka, H. Tsuji and Y. Uozumi, *Synlett*, 2015, **26**, 2037–2041.

133 S. Keess and M. Oestreich, *Chem. Eur. J.*, 2017, **23**, 5925–5928.

134 S. Izumi, Y. Kobayashi and Y. Takemoto, *Org. Lett.*, 2019, **21**, 665–670.

135 M. Ullrich, A. J. Lough and D. W. Stephan, *Organometallics*, 2010, **29**, 3647–3654.

136 A. L. Travis, S. C. Binding, H. Zaher, T. A. Q. Arnold, J. C. Buffet and D. O'Hare, *Dalton Trans.*, 2013, **42**, 2431–2437.

137 S. C. Binding, H. Zaher, F. Mark Chadwick and D. O'Hare, *Dalton Trans.*, 2012, **41**, 9061–9066.

138 H. Zaher, A. E. Ashley, M. Irwin, A. L. Thompson, M. J. Gutmann, T. Krämer and D. O'Hare, *Chem. Commun.*, 2013, **49**, 9755–9757.

139 L. L. Zeonjuk, N. Vankova, A. Mavrandonakis, T. Heine, G. V. Röschenthaler and J. Eicher, *Chem. Eur. J.*, 2013, **19**, 17413–17424.

140 C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2009, **48**, 6643–6646.

141 F.-G. Fontaine, M.-A. Courtemanche, M.-A. Légaré and É. Rochette, *Coord. Chem. Rev.*, 2017, **334**, 124–135.

142 E. L. Kolychev, T. Bannenberg, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Chem. Eur. J.*, 2012, **18**, 16938–16946.

143 F.-G. Fontaine and D. W. Stephan, *Curr. Opin. Green Sustain. Chem.*, 2017, **3**, 28–32.

144 I. Peuser, R. C. Neu, X. Zhao, M. Ulrich, B. Schirmer, J. A. Tannert, G. Kehr, R. Fröhlich, S. Grimme, G. Erker and D. W. Stephan, *Chem. Eur. J.*, 2011, **17**, 9640–9650.

145 K. Takeuchi and D. W. Stephan, *Chem. Commun.*, 2012, **48**, 11304–11306.

146 L. Liu, N. Vankova and T. Heine, *Phys. Chem. Chem. Phys.*, 2016, **18**, 3567–3574.

147 T. Zhao, X. Hu, Y. Wu and Z. Zhang, *Angew. Chem. Int. Ed.*, 2019, **58**, 722–726.

148 M. P. Boone and D. W. Stephan, *Organometallics*, 2014, **33**, 387–393.

149 T. M. Gilbert, *Dalton Trans.*, 2012, **41**, 9046–9055.

150 R. C. Neu, E. Otten, A. Lough and D. W. Stephan, *Chem. Sci.*, 2011, **2**, 170–176.

151 R. C. Neu, E. Otten and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2009, **48**, 9709–9712.

152 E. Otten, R. C. Neu and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 9918–9919.

153 K. M. Szkop, D. Zhu, L. E. Longobardi, J. Heck and D. W. Stephan, *Dalton Trans.*, 2018, **47**, 8933–8939.

154 D. Tofan, M. Temprado, S. Majumdar, C. D. Hoff and C. C. Cummins, *Inorg. Chem.*, 2013, **52**, 8851–8864.

155 S. Tussing, K. Kaupmees and J. Paradies, *Chem. Eur. J.*, 2016, **22**, 7422–7426.

156 S. Tussing and J. Paradies, *Dalton Trans.*, 2016, **45**, 6124–6128.

157 S. Tussing, L. Greb, S. Tamke, B. Schirmer, C. Muhle-Goll, B. Luy and J. Paradies, *Chem. Eur. J.*, 2015, **21**, 8056–8059.

158 Y. Hoshimoto, T. Kinoshita, S. Hazra, M. Ohashi and S. Ogoshi, *J. Am. Chem. Soc.*, 2018, **140**, 7292–7300.

159 D. J. Scott, M. J. Fuchter and A. E. Ashley, *Angew. Chem. Int. Ed.*, 2014, **53**, 10218–10222.

160 Z. Zhang and H. Du, *Angew. Chem. Int. Ed.*, 2015, **54**, 623–626.

161 M. Bakos, Á. Gyömöre, A. Domján and T. Soós, *Angew. Chem. Int. Ed.*, 2017, **56**, 5217–5221.

162 N. A. Sitte, M. Bursch, S. Grimme and J. Paradies, *J. Am. Chem. Soc.*, 2019, **141**, 159–162.

163 H. Zhu, Z.-W. Qu and S. Grimme, *Eur. J. Org. Chem.*, 2019, **2019**, 4609–4612.

164 A. J. Stepen, M. Bursch, S. Grimme, D. W. Stephan and J. Paradies, *Angew. Chem. Int. Ed.*, 2018, **57**, 15253–15256.

165 I. Khan, M. Manzotti, G. J. Tizzard, S. J. Coles, R. L. Melen and L. C. Morrill, *ACS Catal.*, 2017, **7**, 7748–7752.

166 V. Morozova, P. Mayer and G. Berionni, *Angew. Chem. Int. Ed.*, 2015, **54**, 14508–14512.

167 K. Takeuchi, L. J. Hounjet and D. W. Stephan, *Organometallics*, 2013, **32**, 4469–4472.

168 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015–10031.

169 Y. X. Chen and T. J. Marks, *Organometallics*, 1997, **16**, 3649–3657.

170 M. C. Chen, J. A. S. Roberts and T. J. Marks,

Organometallics, 2004, **23**, 932–935.
171 M. C. Chen and T. J. Marks, *J. Am. Chem. Soc.*, 2001, **123**, 11803–11804.
172 J. A. S. Roberts, M. C. Chen, A. M. Seyam, T. Li, C. Zuccaccia, N. G. Stahl and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 12713–12733.
173 G. Xu and T. C. Chung, *Macromolecules*, 2000, **33**, 5803–5809.
174 T. C. Chung, G. Xu, Y. Lu and Y. Hu, *Macromolecules*, 2001, **34**, 8040–8050.
175 D. Chakraborty, A. Rodriguez and E. Y. X. Chen, *Macromolecules*, 2003, **36**, 5470–5481.
176 M. Oishi and H. Yamamoto, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 1445–1454.
177 J. Klosin, G. R. Roof, E. Y. X. Chen and K. A. Abboud, *Organometallics*, 2000, **19**, 4684–4686.
178 N. Hand, R. T. Mathers, K. Damodaran and S. P. Lewis, *Ind. Eng. Chem. Res.*, 2014, **53**, 2718–2725.
179 T. A. Gazis, A. Dasgupta, M. S. Hill, J. M. Rawson, T. Wirth and R. L. Melen, *Dalton Trans.*, 2019, **48**, 12391–12395.
180 Y. Luan, J. Yu, X. Zhang, S. E. Schaus and G. Wang, *J. Org. Chem.*, 2014, **79**, 4694–4698.