# Transborylation-Enabled Boron Catalysis

**Citation for published version:**
Bage, AD, Nicholson, K, Hunt, TA, Langer, T & Thomas, SP 2022, 'Transborylation-Enabled Boron Catalysis', *Synthesis: Journal of Synthetic Organic Chemistry*. https://doi.org/10.1055/s-0040-1720046

**Digital Object Identifier (DOI):**
10.1055/s-0040-1720046

**Link:**
Link to publication record in Edinburgh Research Explorer

**Document Version:**
Peer reviewed version

**Published In:**
Synthesis: Journal of Synthetic Organic Chemistry

# Transborylation-enabled Boron Catalysis

Andrew D. Bage[a]
Kieran Nicholson[a]
Thomas A. Hunt[b]
Thomas Langer[c]
Stephen P. Thomas*[a]

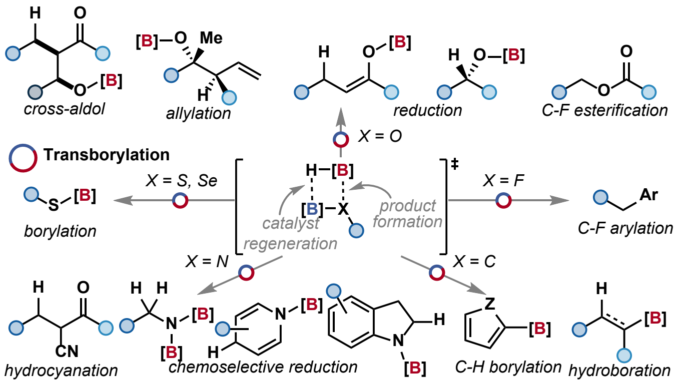
[a] EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ, United Kingdom

[b] Medicinal Chemistry, Early Oncology, AstraZeneca, Cambridge CB4 0WG, United Kingdom

[c] Pharmaceutical Technology & Development, Chemical Development U.K., AstraZeneca, Macclesfield SK10 2NA, United Kingdom

stephen.thomas@ed.ac.uk

Click here to insert a dedication.



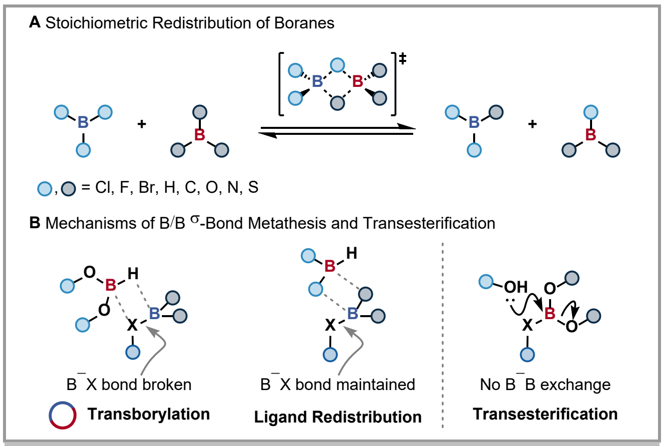
Received:
Accepted:
Published online:
DOI:

**Abstract** This review highlights transborylation (controlled boron-boron exchange) and its applications as a turnover strategy in boron-catalysed methodologies. Catalytic applications of *B*–C, *B*–O, *B*–N, *B*–F, *B*–S and *B*–Se transborylations are discussed in the context of transborylation-enabled catalysis, across a wide range of organic transformations including hydroboration, C–C bond formation, C–H borylation, chemoselective reduction, and asymmetric reduction.

**Key words** transborylation, boron, main-group, catalysis, metathesis

## 1 Introduction

Stoichiometric redistribution reactions (σ-bond metathesis) between two boron centres are well established, with halide,[1, 2-4] hydride,[1, 4-6, 7] alkyl,[4, 6, 8, 9, 10] alkoxide,[3-5, 9-11] amino,[3] aryl,[3] thiolate,[4] and alkenyl groups[11] shown to redistribute across two boron centres (Scheme 1a). Similarly, the stoichiometric reactivity of hydridoborane reagents is well known[12, 13] and has been applied broadly throughout organic synthesis.[14] However, stoichiometric organoborane chemistry has been largely superseded by transition metal catalysis.[15] A combination of stoichiometric borane reactivity and stoichiometric redistribution has provided a platform to develop borane-catalysed reactions that use transborylation (the controlled redistribution of substituents by σ-bond metathesis about two boron centres) as a turnover step in catalysis. This short review will provide an overview of the development of transborylation as a turnover strategy and the current state-of-the-art borane-catalysed transformations that exploit transborylation and is organised by the *B*–X bond undergoing transborylation.



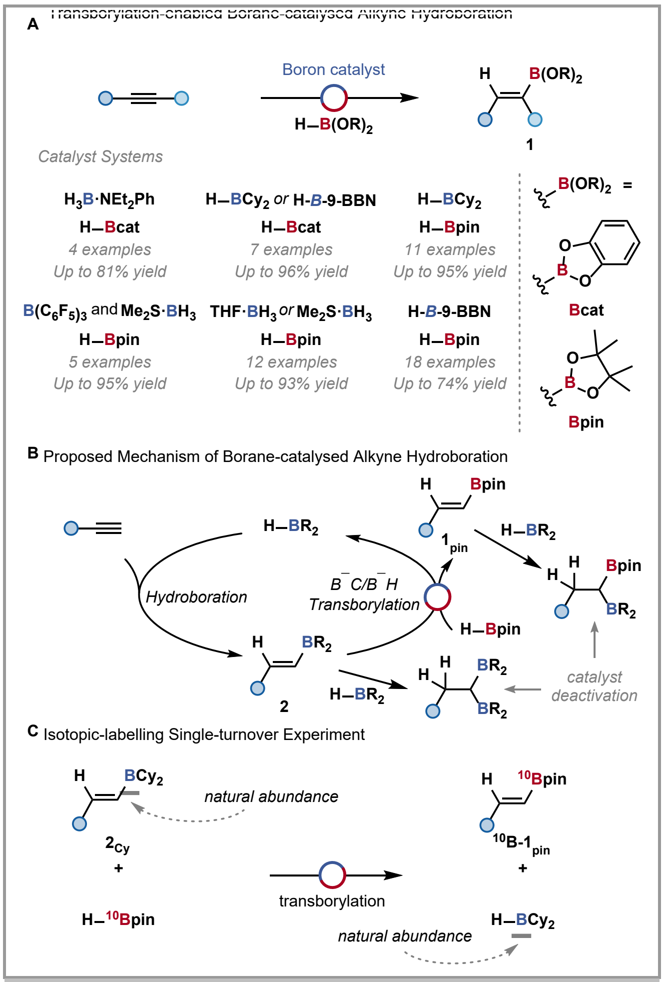
**Scheme 1** a) Stoichiometric borane redistribution b) Mechanisms of boron-boron σ-bond metathesis and transesterification

The use of σ-bond metathesis as a means for catalytic turnover has been applied to p-block catalysis using organoborane reagents [e.g. catecholborane (HBcat) and pinacolborane (HBpin)] as the stoichiometric turnover reagents. The gallium-catalysed asymmetric reduction of ketones used *Ga*–O/*B*–H σ-bond metathesis with catecholborane (HBcat).[16] Phosphorous-based catalysts have been developed for the hydroboration of pyridines,[17] ketones,[18] and imines,[19] and for the reductive coupling of α,β-unsaturated esters, all using *P*–X/*B*–H exchange.[20] Germanium- and tin hydride catalysts have been used in the catalytic reductions of carbonyl species[21] and carbon dioxide, and proceed through *M*–O/*B*–H σ-bond metathesis turnover steps.[22] *Al*–X/*B*–H σ-bond metathesis has enabled the development of several aluminium-catalysed reactions; the hydroboration of ketones,[23] alkynes,[24-26] alkenes,[27] aldehydes,[26] carbon dioxide,[28] nitriles,[29] and amides,[30] the borylation of alkynes,[31] and the dehydrocoupling of alcohols.[24]

The broadest application of σ-bond metathesis in the p-block is in the exchange between two boron atoms. Transborylation, akin to transmetallation, is mechanistically distinct from ligand exchange and transesterification (Scheme 1b). Transborylation is an isodesmic σ-bond metathesis between two boron-containing species, where the group of interest is exchanged from one boron to another boron. In ligand exchange, the bond between the group of interest and the boron atom in the intermediate remains intact during the σ-bond metathesis step. Instead, the backbone functionalities around each boron atom are exchanged from one boron atom to another. The substituent groups of a boron species can also be changed through transesterification with an alcohol, here no transfer of groups from boron to boron occurs, therefore, this is neither transborylation nor ligand exchange. Reactions that proceed through ligand exchange, including the diol-catalysed 1,4-addition to enones,[32] and the aminoborane-catalysed hydroboration of indoles,[33] will not be discussed further in this review, nor will reactions that use transesterification,[34, 35, 36] such as the tartaric acid-catalysed alkenylboration of enones[35] and the diol-catalysed allylboration of acyl imines.[36]

## 2 *B*–C Transborylation

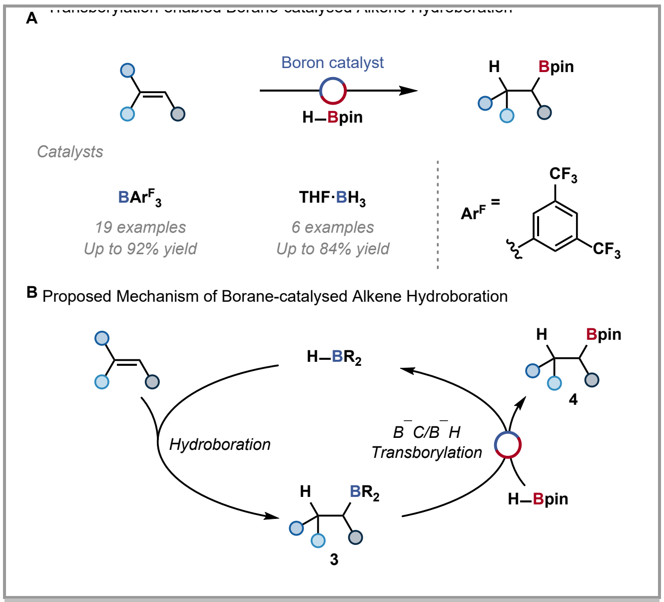
The first proposed *B*–C/*B*–H transborylation for catalysis was reported by Periasamy for the $PhEt_2N\cdot BH_3$-catalysed hydroboration of alkynes with HBcat to give alkenyl catechol boronic esters $\mathbf{1_{cat}}$ (Scheme 2a).[37] It was proposed that $PhEt_2N\cdot BH_3$ reacted with the alkyne to give an alkenylborane which underwent exchange with HBcat (*B*–C(sp$^2$)/*B*–H transborylation) to give the alkenyl catechol boronic ester and regenerate the catalyst. Subsequently, Arase and Hoshi used dicyclohexylborane ($HBCy_2$) or 9-borabicyclo[3.3.1]nonane (H-*B*-9-BBN) to catalyse the hydroboration of alkynes with HBcat.[38] The reaction was proposed to proceed by the same mechanism as that described by Periasamy. Hoshi expanded this reactivity using HBpin in place of HBcat to give alkenyl pinacol boronic esters $\mathbf{1_{pin}}$ and *B*–C(sp$^2$)/*B*–H transborylation was again proposed as the means for catalytic turnover.[39] Hoshi suggested that the turnover process was more challenging for more hindered, branched alkenylboranes, a similar steric argument to that postulated by Brown for stoichiometric redistribution reactions.[40] Subsequently, Hoshi developed an alternative system for alkyne hydroboration using $Me_2S\cdot BH_3$ and $B(C_6F_5)_3$ as pre-catalysts to generate $Me_2S\cdot BH(C_6F_5)_2$ *in situ* by *B*–C(sp$^2$)/*B*–H transborylation.[41] Catalysis was proposed to proceed by hydroboration of the alkyne by the *in situ*-generated $Me_2S\cdot BH(C_6F_5)_2$ to give an alkenyl$B(C_6F_5)_2$ which undergoes *B*–C(sp$^2$)/*B*–H transborylation with HBpin to regenerate the catalyst, $Me_2S\cdot BH(C_6F_5)_2$, and give an alkenyl pinacol boronic ester. An alkenyl$B(C_6F_5)_2$ was independently synthesised and used as a pre-catalyst to support the proposal of it being an on-cycle species. Stephan used Piers's borane, $HB(C_6F_5)_2$, as a catalyst for the hydroboration of alkynes with HBpin.[42] However, catalysis was proposed to proceed through a mechanism that did not involve transborylation. Vasko, Kamer and Aldridge reported an alkyne hydroboration system where $HB(C_6F_5)_2$ was generated *in situ* from *B*–C(sp$^2$)/*B*–H transborylation between HBpin and a FLP (Frustrated Lewis Pair) pre-catalyst.[43]



Scheme 2 a) Transborylation-enabled borane-catalysed hydroboration of alkynes b) Proposed mechanism of borane-catalysed alkyne hydroboration c) $^{10}$B-Labelling experiment

Thomas and Lloyd-Jones investigated the mechanism of the Arase-Hoshi dialkylborane-catalysed hydroboration of alkynes with HBpin (Scheme 2b),[44] using H-*B*-9-BBN and $HBCy_2$ as catalysts.[39] Kinetic analysis, isotopic-entrainment, and isotopic-labelling experiments ($H^{10}Bpin$ and $^2H$-$HBCy_2$) identified *B*–C(sp$^2$)/*B*–H transborylation as the mode of catalytic turnover. When $H^{10}Bpin$ was reacted with the alkenyldialkylborane $\mathbf{2_{Cy}}$ (Scheme 2c), $^{10}$B-alkenyl boronic ester $\mathbf{^{10}B\text{-}1_{pin}}$ was formed exclusively, supporting the proposal of a transborylation pathway (ligand exchange would have resulted in a mixture of $^{10}$B- and $^{11}$B-alkenyl boronic ester products). The metathesis step was computationally calculated ($\Delta G^\ddagger$ = 19.7 kcal mol$^{-1}$) and was measured experimentally ($\Delta G^\ddagger$ = 20.3 kcal mol$^{-1}$). Catalysis was shown to proceed by hydroboration of the alkyne by the dialkylborane catalyst to give an alkenyldialkylborane **2**. *B*–C(sp$^2$)/*B*–H transborylation with HBpin gives the alkenyl pinacol boronic ester $\mathbf{1_{pin}}$, concomitantly regenerating the dialkylborane catalyst. Hydroboration of both the alkenyldialkylborane **2** and the alkenyl boronic ester $\mathbf{1_{pin}}$ by the dialkylborane was shown to be irreversible under reaction conditions, leading to catalyst deactivation and a reduction in alkenyl boronic ester $\mathbf{1_{pin}}$ yield.

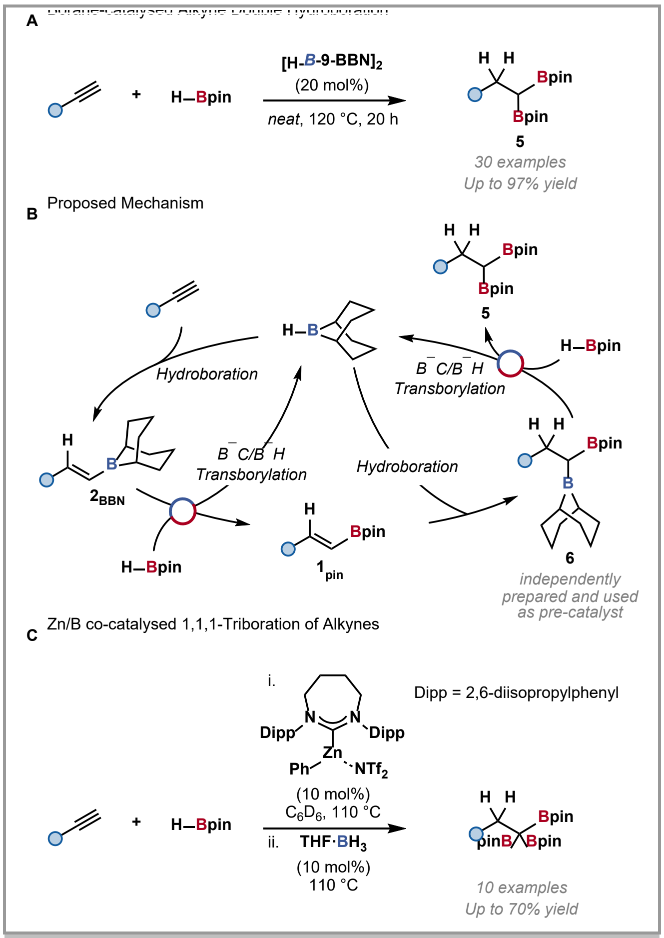
Oestreich developed the pre-catalyst tris[3,5-bis(trifluoromethyl)phenyl]borane ($BAr^F{}_3$) for the hydroboration of alkenes with HBpin (Scheme 3a).[45] The active catalysts, $HB(Ar^F)_2$ and $H_2BAr^F$, were generated *in situ* through *B*–C(sp$^2$)/*B*–H transborylation with HBpin. $HBAr^F_2$ (or $H_2BAr^F$) was proposed to undergo hydroboration of the alkene to give an alkylborane intermediate **3**, which reacted with HBpin through *B*–C(sp$^3$)/*B*–H transborylation to give the alkyl pinacol boronic ester **4** and regenerate the catalyst (Scheme 3b). Although Stephan reported $B(C_6F_5)_3$ as an active catalyst for alkyne hydroboration,[42] Oestreich observed only trace product when $B(C_6F_5)_3$ was used as a pre-catalyst for alkene hydroboration. Through stoichiometric studies, Oestreich showed that $HB(Ar^F)_2$ and $H_2BAr^F$ were generated by reaction of $BAr^F_3$ with HBpin, and that Piers's borane was not generated under the same conditions with $B(C_6F_5)_3$. Melen developed a similar system for hydroboration using Lewis acidic borane catalysts.[46] This widely applicable protocol was used for the hydroboration of alkynes, ketones, aldehydes and imines. A mechanism of catalysis was not proposed but may have proceeded through a transborylation mechanism akin to those proposed by Oestreich and Hoshi. However, in a separate report, Melen and Oestreich disclosed the use of boron Lewis acid catalysts for the hydroboration of imines and catalysis was proposed to proceed through Lewis acid catalysis and not transborylation.[47]



Scheme 3 a) Transborylation-enabled borane-catalysed hydroboration of alkenes c) Proposed mechanism of borane-catalysed alkene hydroboration

Thomas used THF·$BH_3$ or $Me_2S·BH_3$ as catalysts for the hydroboration of alkynes and alkenes with HBpin (Scheme 3a).[48] Interestingly HBpin could be reacted with substoichiometric KO$^t$Bu to generate the catalyst, $BH_3$, *in situ*. The nucleophile-promoted decomposition of boronic esters has been studied in detail for HBcat[49] and HBpin[50] and discussed elsewhere.[51] The hydroboration of alkenes and alkynes with HBpin, catalysed by $BH_3$, and $R_nBH_{3-n}$ species, was proposed to proceed through *B*–C/*B*–H transborylation (Scheme 3b).[50]

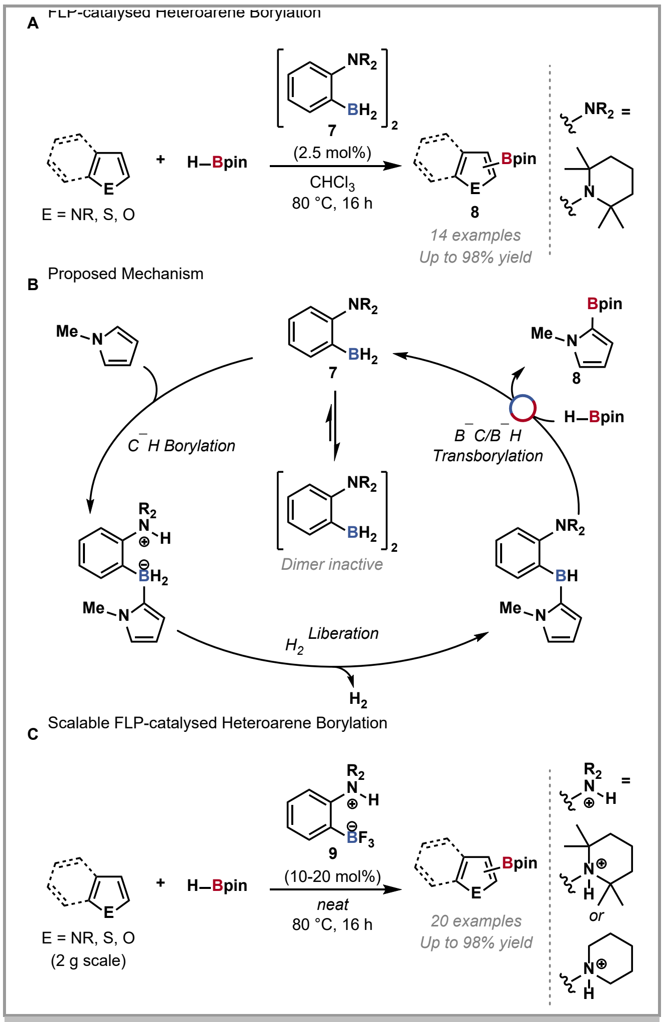
Thomas investigated the H-*B*-9-BBN-catalysed dihydroboration of alkynes with HBpin to give *gem*-diborylalkanes **5** (Scheme 4a).[52] The proposed catalytic pathway proceeded by hydroboration of the alkyne to give an alkenylborane **2**$_{\mathbf{BBN}}$, which underwent *B*–C(sp$^2$)/*B*–H transborylation with HBpin to give an alkenyl pinacol boronic ester **1**$_{\mathbf{pin}}$ (Scheme 4b). A second hydroboration of the alkenyl pinacol boronic ester **1**$_{\mathbf{pin}}$ with H-*B*-9-BBN gave the mixed *gem*-diborylalkane intermediate **6** which underwent *B*–C(sp$^3$)/*B*–H transborylation to give the *gem*-diborylalkane product **5**. The mixed *gem*-diborylalkane intermediate **6** was independently synthesised and successfully used as a pre-catalyst. Isotopic labelling experiments (H$^{10}$Bpin) and kinetic analysis ($\Delta S^\ddagger$ = 36 e.u.) supported the hypothesis of the second turnover step proceeding through *B*–C(sp$^3$)/*B*–H transborylation. The large value of $\Delta G^\ddagger$ (28 kcal mol$^{-1}$) is consistent with transborylation at a sterically congested centre[9, 38, 40] and the need for a high reaction temperature (120 °C). Ingleson reported a zinc/boron co-catalytic system for the synthesis of 1,1,1-triborylalkanes from alkynes (Scheme 4c).[53] The borylation of the alkyne and the hydroboration of the resulting alkynyl pinacol boronic ester were proposed to be catalysed by the zinc hydride, whereas the hydroboration of the 1,1-diborylalkene was catalysed by $BH_3$. High reaction temperatures (110 °C) were also required for *B*–C(sp$^3$)/*B*–H transborylation to proceed.



Scheme 4 a) Borane-catalysed double hydroboration of alkynes b) Proposed mechanism c) Zn/B co-catalysed preparation of 1,1,1-triborylalkanes

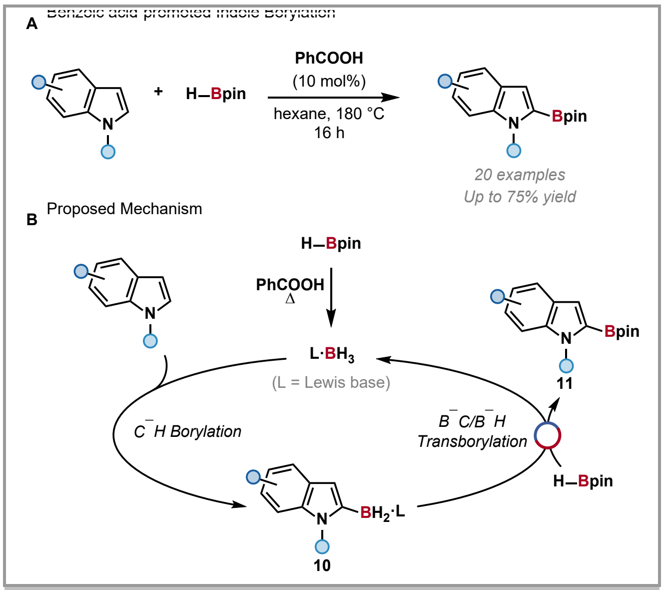
*B*–C(sp$^2$)/*B*–H transborylation has also found use as a means for catalytic turnover in C–H borylation chemistry. Fontaine reported the use of a boron-nitrogen FLP catalyst **7** for the metal-free borylation of pyrroles, indoles, thiophenes, and furans (Scheme 5a).[54] The mechanism was proposed to proceed by C–H insertion of the arene by the catalyst **7**, followed by $H_2$ liberation and *B*–C(sp$^2$)/*B*–H transborylation with HBpin to regenerate the catalyst **7** and give the aryl pinacol boronic ester

**8** (Scheme 5b). Kinetic isotope effect (KIE) studies suggested that the C–H insertion was the rate-limiting step, and a relatively low barrier was calculated by density functional theory (DFT) analysis for *B*–C(sp$^2$)/*B*–H transborylation ($\Delta G^{\ddagger}$ = 14.2 kcal mol$^{-1}$). Fontaine investigated the effect of steric bulk on catalyst activity through several FLP catalyst analogues by modification of the amine functionality. Catalysts with reduced steric bulk were found to undergo more facile C–H activation at the expense of slower dimer dissociation.[55] Fontaine developed air-stable trifluoroborate salt pre-catalysts **9** for the same transformation,[56] showed that the borylation system was effective on both 2 and 50 g scales (Scheme 5c)[57], and developed a heterogeneous polymeric version of this catalytic system.[58]



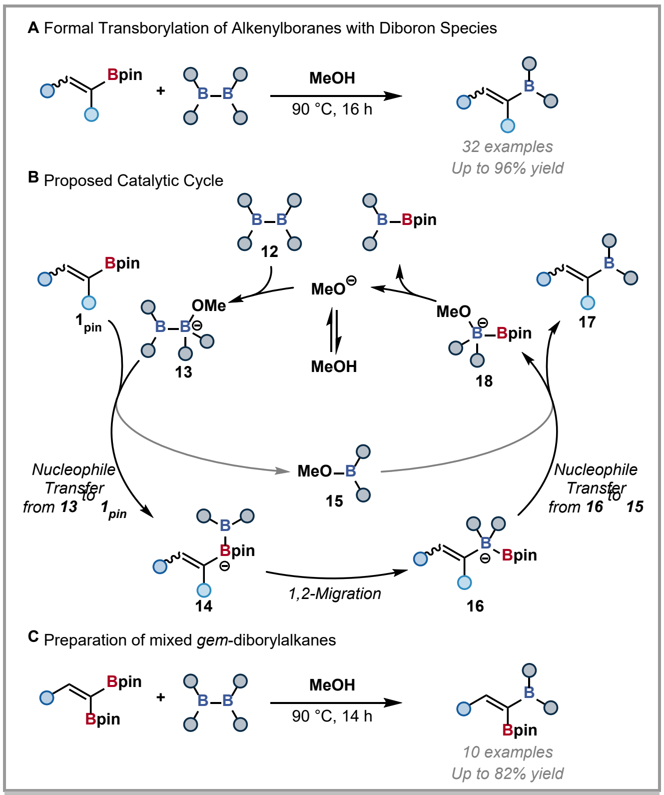
Scheme 5 a) FLP-catalysed borylation of heterocycles b) Proposed mechanism c) Scalable heteroarene borylation

Zhang developed the benzoic acid-promoted C-2 borylation of indoles (Scheme 6a), providing orthogonal regioselectivity to the C-3 borylation reported by Fontaine.[59] Benzoic acid was proposed to promote the decomposition of HBpin to give BH$_3$, which reacted with indole to give an arylborane **10** (Scheme 6b). Subsequent *B*–C(sp$^2$)/*B*–H transborylation gave the C-2 indolyl pinacol boronic ester **11** and regenerated the catalyst, BH$_3$.



Scheme 6 a) Benzoic acid-promoted borylation of indoles b) Proposed mechanism

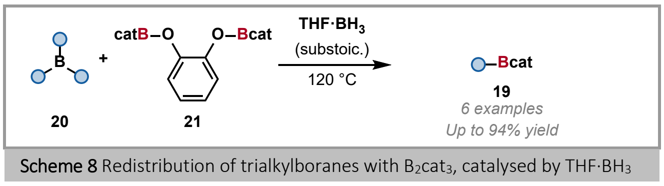
Fernández reported an (*E*)-alkenyl boronic ester exchange with diboron species in methanol (Scheme 7a).[60] Whilst previous transborylation-mediated reactions have been proposed to proceed by a concerted, redox neutral exchange of boron groups through a σ-bond metathesis pathway, here, the exchange was proposed to proceed by a coordination-migration pathway (Scheme 7b). Methoxide coordination to the diboron reagent **12** gave the diboron 'ate' complex **13**, which reacted with the alkenyl boronic ester **1**$_{\mathbf{pin}}$ to give a diboron 'ate' complex **14** and a boronate ester **15**. 1,2-Migration of the diboron 'ate' complex **14** exchanged the alkenyl group from boron to boron, and subsequent reaction of the new diboron 'ate' complex **16** with the boronate ester **15** gave the alkenyl boronic ester **17** and a mixed diboron 'ate' species **18**. Liberation of methoxide from the mixed diboron 'ate' **18** regenerated the catalyst, methoxide. In this instance, the reaction proceeded through a formal *B*–C(sp$^2$)/*B*–B transborylation where the groups are not exchanged in a concerted σ-bond metathesis pathway but by step-wise nucleophilic transfers. Several alkenyl boronic esters were prepared in good yields and with retention of stereochemistry. The reaction was shown to proceed chemoselectively with mixed diboron species, where the more Lewis acidic boron was exchanged, and to *gem*-diborylalkenes where the *trans*-boron was selectively exchanged. This method was subsequently used by Fernández to prepare diastereomerically-enriched *gem*-diborylalkenes for the palladium-catalysed stereoselective cyclopropanation of *gem*-diborylalkenes (Scheme 7c).[61]



Scheme 7 a) Formal transborylation of *E*-alkenylboranes with diboron species b) Proposed mechanism c) Preparation of mixed *gem*-diborylalkenes

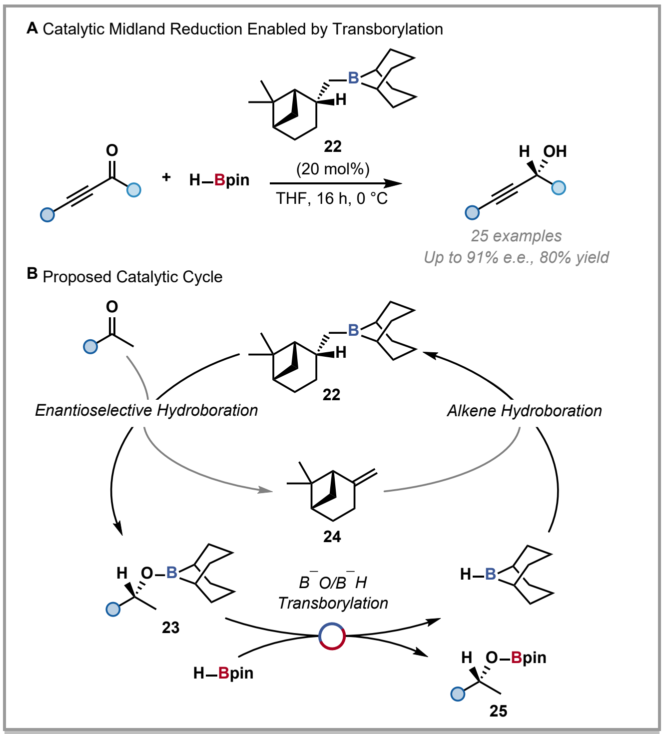
## 3 *B*–O Transborylation

*B*–O/*B*–H transborylation is possible for any species containing a B–O bond, including borinic ($R_2BOR$), boronic ($RB(OR)_2$), and boronate ($B(OR)_3$) esters. Investigations into stoichiometric redistribution involving B–O bonds have explored exchange with B–Cl,[3] B–H,[4, 5] and B–C bonds,[9-11] most notably by Brown in the preparation of alkyl catechol boronic esters **19** from trialkylboranes **20** and $B_2cat_3$ **21** (Scheme 8).[10] The redistribution was catalysed by the addition of THF·$BH_3$ and, whilst a mechanism was not proposed, it may proceed through *B*–O/*B*–H and *B*–C/*B*–H transborylation steps.



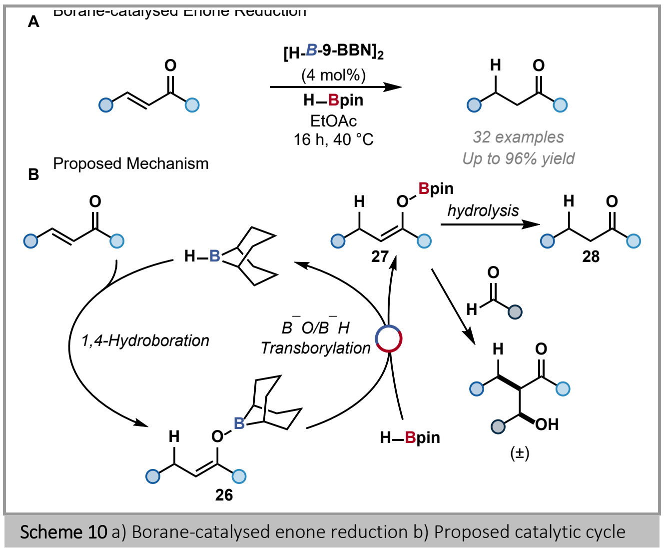
Scheme 8 Redistribution of trialkylboranes with $B_2cat_3$, catalysed by THF·$BH_3$

Thomas used *B*–O/*B*–H transborylation to transform the stoichiometric Midland reduction[62] into a catalytic reaction,[63] using HBpin as the turnover reagent to regenerate H-*B*-9-BBN through *B*–O/*B*–H transborylation, concurrently forming the product as a boronate ester (Scheme 9a). Myrtanyl-9-BBN **22** (derived from β-pinene) was used in place of Alpine-Borane®[62], aiding catalyst regeneration and suppressing direct ketone hydroboration.[64] The reaction was proposed to proceed by two interlinked catalytic cycles with *B*–O/*B*–H transborylation-enabled catalyst regeneration. This was supported by single-turnover experiments with H$^{10}$Bpin and Eyring analysis ($\Delta S^{\ddagger} = -21.5$ e.u.). Hydroboration of a ketone by myrtanyl-9-BBN **22** gave a borinic ester **23** and liberated β-pinene **24** (Scheme 9b). *B*–O/*B*–H transborylation of the borinic ester **23** with HBpin gave the boronate ester product **25** and generated H-*B*-9-BBN. Hydroboration of β-Pinene **24** by H-*B*-9-BBN regenerated the catalyst, myrtanyl-9-BBN **22**.



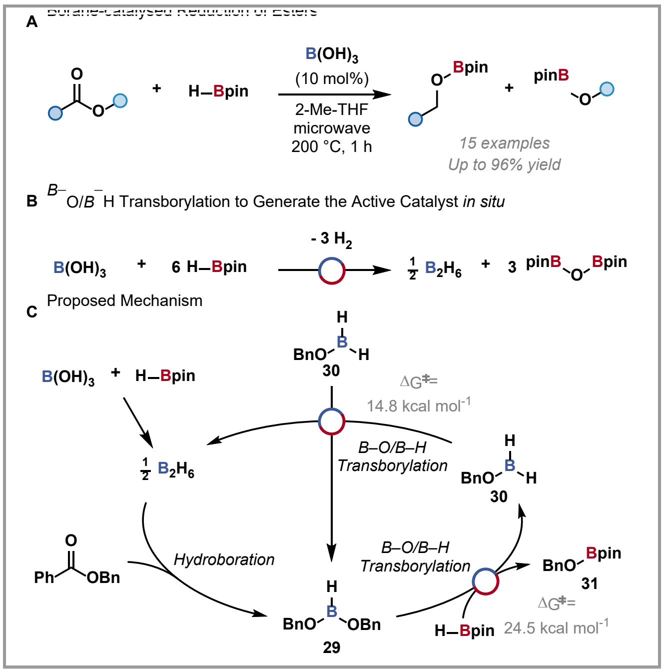
Scheme 9 a) A catalytic Midland reduction enabled by *B*–O/*B*–H transborylation b) Proposed catalytic cycle

Thomas expanded the applications of *B*–O/*B*–H transborylation to the chemoselective reduction of enones, catalysed by H-*B*-9-BBN using HBpin as the turnover reagent (Scheme 10a).[65] A dialkylborane, such as H-*B*-9-BBN, reacted with an enone to give the *O*-*B*-9-BBN-enolate **26** through 1,4-hydroboration, and subsequent *B*–O/*B*–H transborylation with HBpin regenerated the catalyst (Scheme 10b). The resulting *O*-Bpin-enolate **27** was hydrolysed on work-up to give saturated ketones **28** or reacted with electrophiles. The reaction was shown to proceed through *B*–O/*B*–H transborylation by the preparation of the *O*-*B*-9-BBN-enolate **26** and subsequent reaction with H$^{10}$Bpin.



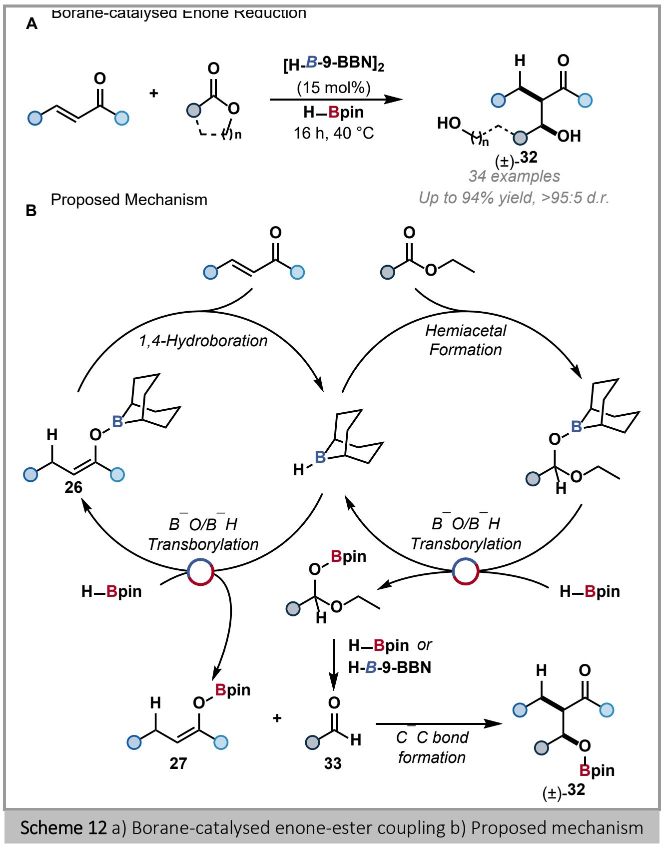
Scheme 10 a) Borane-catalysed enone reduction b) Proposed catalytic cycle

Fontaine used *B*–O/*B*–H transborylation for the borane-catalysed reduction of esters, lactones, and carbonates to alcohols (Scheme 11a).[66] *B*–O/*B*–H transborylation between HBpin and $B(OH)_3$ generated the catalyst, $BH_3$ (Scheme 11b). The reaction was proposed to proceed through hydroboration of the ester by $BH_3$,[67] giving a boronic ester **29**, and *B*–O/*B*–H transborylation of the boronic ester **29** with HBpin formed a borinic ester **30** and the boronate pinacol ester product **31**. *B*–O/*B*–H transborylation between two borinic ester molecules **30** regenerated the catalyst (Scheme 11c). The transition state energies were calculated for each *B*–O/*B*–H transborylation with the reaction of the boronic ester **29** with HBpin calculated to have a barrier of $\Delta G^{\ddagger}$ = 24.5 kcal mol$^{-1}$. *B*–O/*B*–H transborylation between two borinic ester molecules **30** to give $BH_3$ was calculated to be $\Delta G^{\ddagger}$ = 14.8 kcal mol$^{-1}$. The first *B*–O/*B*–H transborylation was shown to be the rate-limiting step, possibly due to the decreased Lewis acidity of the boron centre with increasing alkoxide substitution.



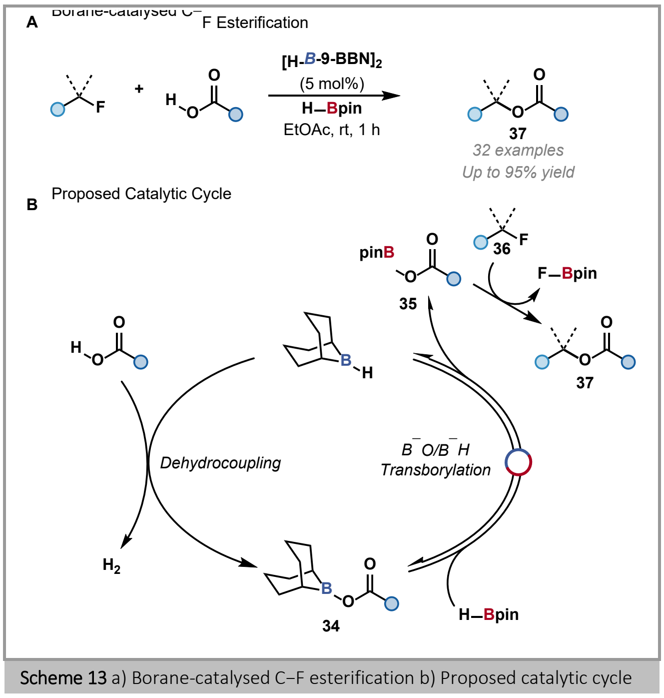
Scheme 11 a) Borane-catalysed reduction of esters to alcohols b) *in situ* Catalyst generation c) Proposed mechanism

*B*–O/*B*–H transborylation was applied by Nicholson and Thomas to generate cross-aldol products (±)-**32** by the borane-catalysed coupling of enones and esters (Scheme 12a).[68] This unique disconnection resulted from a two-fold catalytic process involving boron enolate generation from 1,4-hydroboration of the enone by H-*B*-9-BBN and an interrupted ester reduction to form an aldehyde *in situ* (Scheme 12b). *B*–O/*B*–H transborylation of the *O*-*B*-9-BBN-enolate **26** with HBpin generated the *O*-*B*-Bpin-enolate **27** and re-formed the catalyst, H-*B*-9-BBN. The ester was reduced by H-*B*-9-BBN to form an aldehyde **33**. The *O*-*B*-Bpin-enolate **27** reacted with the aldehyde **33** to generate the β-hydroxyketone product (±)-**32**. Lactones were also successfully used in place of the ester, demonstrating the utility of the reaction over the corresponding hydroxyaldehydes.



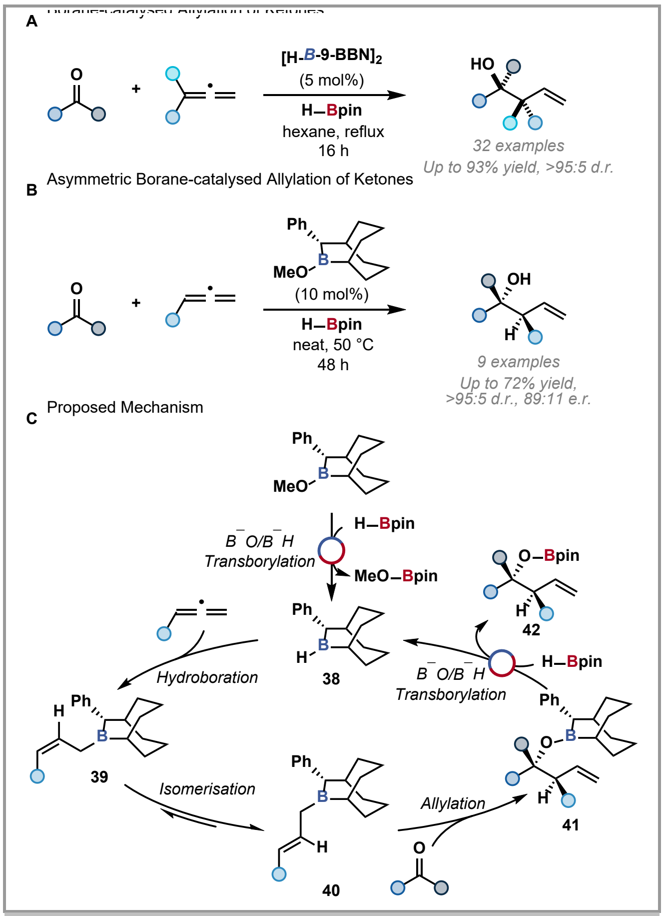
Scheme 12 a) Borane-catalysed enone-ester coupling b) Proposed mechanism

Willcox and Thomas used *B*–O/*B*–H transborylation in a borane-catalysed C–F esterification (Scheme 13a).[69] Dehydrocoupling of a carboxylic acid with H-*B*-9-BBN gave the acyloxy-*B*-9-BBN **34** which underwent *B*–O/*B*–H transborylation with HBpin to regenerate the catalyst and form the acyloxyboronic ester **35** (Scheme 13b). This reacted with an alkyl fluoride **36** to give the ester **37**, and FBpin as a by-product. The reaction was proposed to proceed through *B*–O/*B*–H transborylation. The reversibility of *B*–O/*B*–H transborylation was shown by the stoichiometric reactions of the acyloxy-*B*-9-BBN **34** with HBpin and the acyloxyboronic ester **35** with H-*B*-9-BBN. The reaction was applied to a broad substrate scope, showing extensive functional group tolerance, and used to generate ester derivatives of numerous biologically-active carboxylic acids.



Scheme 13 a) Borane-catalysed C–F esterification b) Proposed catalytic cycle

Nicholson and Thomas demonstrated that H-*B*-9-BBN catalysed the diastereoselective allylation of ketones with allenes and HBpin (Scheme 14a).[70] By using (*S*)-*B*-methoxy-phenyl-9-borabicyclo[3.3.2]decane [(*S*)-Ph-BBD-OMe][71] in place of H-*B*-9-BBN, an enantioselective variant of this transformation was also developed (Scheme 14b). Single turnover and isotopic-labelling experiments were used to postulate a mechanism (Scheme 14c). HBpin reacted with the pre-catalyst (*S*)-Ph-BBD-OMe through *B*–O/*B*–H transborylation to form the active catalyst, (*S*)-H-*B*-phenyl-9-borabicyclo[3.3.2]decane **38**. The allene underwent hydroboration by (*S*)-H-*B*-phenyl-9-borabicyclo[3.3.2]decane **38** to give the (*Z*)-allylic borane **39**. This underwent a series of 1,3-boratropic shifts, resulting in isomerisation to the (*E*)-allylic borane **40**. The ketone underwent allylation by the (*E*)-allylic borane **40** to give the *anti*-homoallylic borinic ester **41**. *B*–O/*B*–H transborylation between HBpin and *anti*-homoallylic borinic ester **41** generated the boronate pinacol ester product **42** with concomitant re-formation of the catalyst, (*S*)-H-*B*-phenyl-9-borabicyclo[3.3.2]decane **38**.

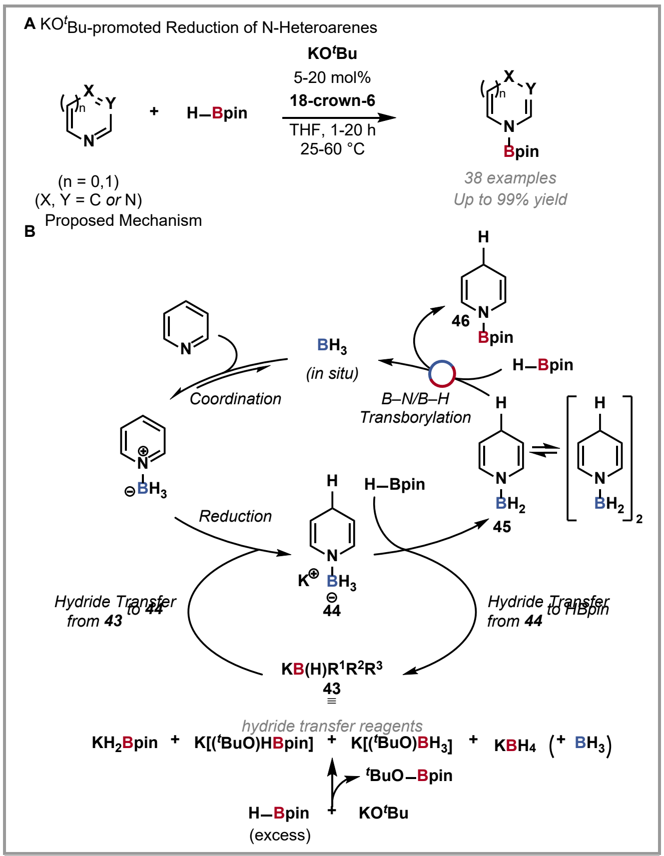


Scheme 14 a) Borane-catalysed diastereoselective allylation of ketones with allenes b) Asymmetric borane-catalysed allylation of ketones c) Proposed mechanism

## 4 *B*–N Transborylation

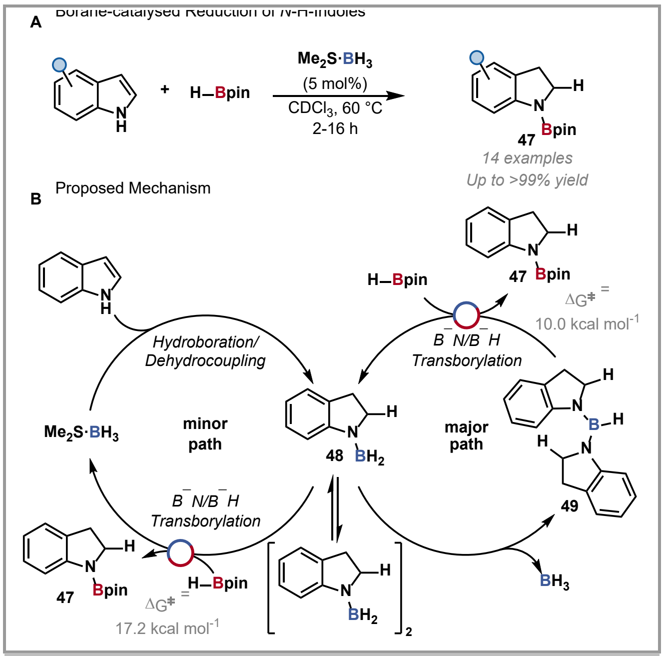
Unlike with B–O and B–C bonds, stoichiometric redistribution reactions of B–N containing species have not been widely explored.[3] However, numerous stoichiometric reactions of organoboranes result in the formation of a B–N bond, including the reduction of nitriles, amides,[12] imines,[72] and indoles,[73] and the reductive cyanation of enones.[74] Therefore, the development of catalytic methods using *B*–N/*B*–H transborylation is of synthetic interest.

The first notable example of *B*–N/*B*–H transborylation was reported by Chang as a means of catalytic turnover for the 1,4-reduction of pyridines (Scheme 15a).[75] Chang proposed that the nucleophile-promoted decomposition of HBpin by KO$^t$Bu gave borohydride species **43** and $BH_3$ in solution (Scheme 15b). N-coordination by $BH_3$ activated the pyridine to 1,4-reduction by the borohydride species **43** to give a dihydropyridyl borohydride **44**, identified as the resting-state by $^{11}$B NMR spectroscopy and mass spectrometry. Hydride transfer from the dihydropyridyl borohydride **44** to HBpin regenerated further borohydride species **43** and gave the 1,4-dipyridylborane **45**. *B*–N/*B*–H transborylation with HBpin gave the product, *N*-Bpin-1,4-dihydropyridine **46**, and regenerated $BH_3$. This catalytic reduction protocol was also applied to other N-heterocycles including quinolines, isoquinolines, pyrazines, quinoxalines, and imidazoles.



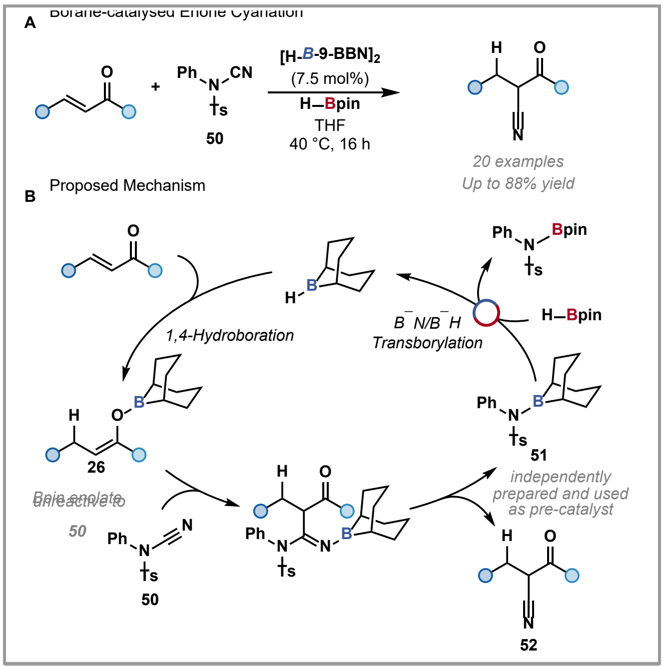
Scheme 15 a) B–N/B–H Transborylation-enabled 1,4-reduction of pyridines b) Proposed mechanism

Fontaine reported the use of $Me_2S·BH_3$ as a catalyst for the reduction of indoles with HBpin to N-Bpin-indolines **47**,[76] providing a catalytic alternative to the stoichiometric reaction (Scheme 16a).[73] The reactivity demonstrated impressive chemodivergence from their earlier report of the hydroboration of N-tosyl indoles to give indolin-3-yl boronic esters,[77] where the same catalyst and turnover reagent were used. Extensive computational studies indicated the reaction proceeded by hydroboration of the indole followed by dehydrocoupling to give an N-borylindoline species **48** (Scheme 16b). The N-borylindoline **48** existed in equilibrium with its dimer, which was proposed to be an off-cycle resting state, based on experimental and DFT analysis. The N-borylindoline **48** reacted with itself to give a bisindolineborane **49** which underwent B–N/B–H transborylation with HBpin to give the N-Bpin-indoline **47** and re-form the N-borylindoline **48**, completing the major pathway. In an alternative minor pathway, the N-borylindoline **48** reacted with HBpin through B–N/B–H transborylation to give the N-Bpin-indoline **47** and regenerate the catalyst. B–N/B–H transborylation of N-borylindoline **48** with HBpin was calculated to have a barrier of $\Delta G^‡ = 17.2$ kcal mol$^{-1}$. The analogous metathesis from the bisindolineborane **49** with HBpin was calculated to have a barrier of only $\Delta G^‡ = 10.0$ kcal mol$^{-1}$. Although both are reasonable at the reaction temperature of 60 °C, the bisindolineborane **49** pathway was proposed to be favoured.



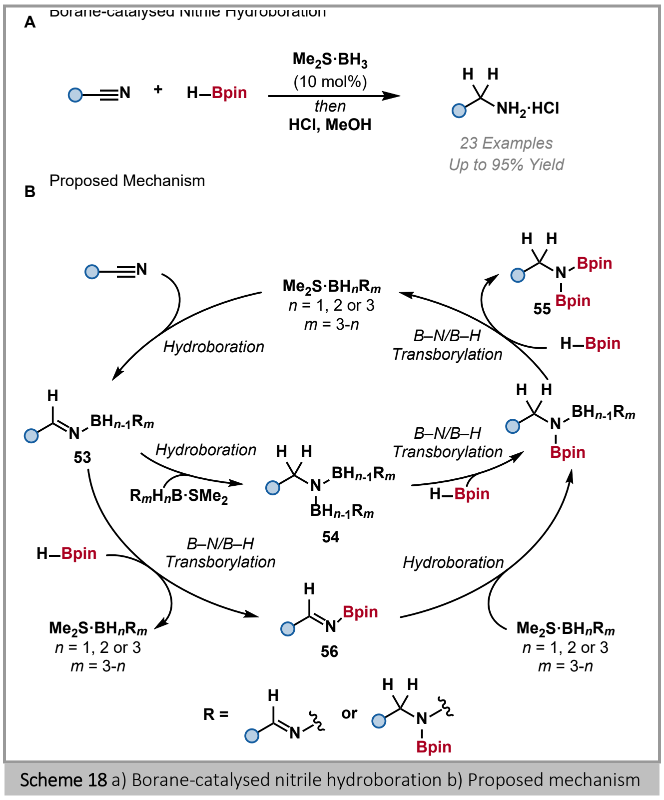
Scheme 16 a) Borane-catalysed reduction of indoles to indolines b) Proposed mechanism

Nicholson and Thomas used B–N/B–H transborylation for the borane-catalysed reductive cyanation of enones (Scheme 17a).[78] Catalysis was proposed to proceed by 1,4-hydroboration of the enone to give the O-B-9-BBN-enolate **26**, which reacted with the electrophilic cyanide source, N-cyano-N-phenyl p-toluenesulfonamide **50**, to give the amino-9-BBN **51** and form the α-cyanoketone product **52** (Scheme 17b). B–N/B–H transborylation between the amino-9-BBN **51** and HBpin regenerated the catalyst, H-B-9-BBN. The reversibility of the B–N/B–H transborylation was observed by $^{11}$B NMR spectroscopy. The amino-9-BBN **51** was independently prepared and successfully used as a pre-catalyst, supporting the proposal that this was an on-cycle species.



Scheme 17 a) Borane-catalysed formal hydrocyanation of enones enabled by B–N/B–H transborylation b) Proposed mechanism

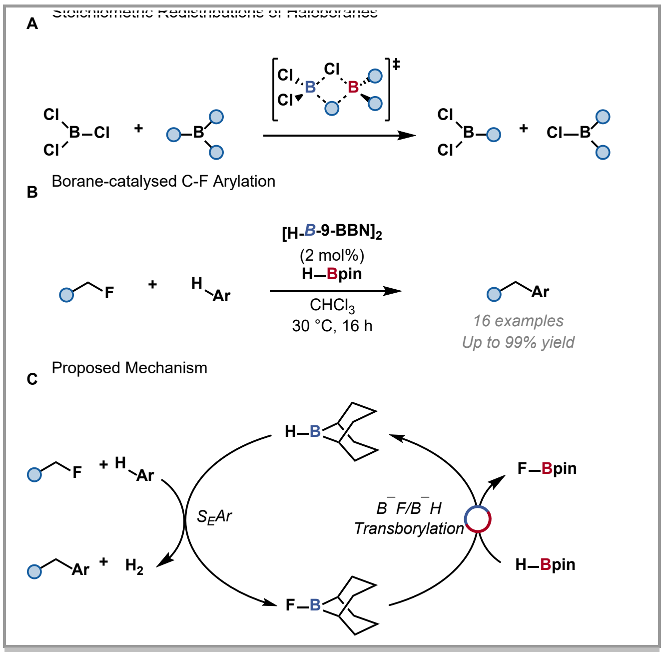
Me$_2$S·BH$_3$ was used by Thomas to catalyse the hydroboration of nitriles with HBpin (Scheme 18a). A mechanism was proposed based on DFT analysis whereby nitrile hydroboration by Me$_2$S·BH$_3$ gave the *N*-boryl imine **53**. This underwent a second hydroboration to form the *N*,*N*-*bis*-boryl amine **54**, followed by two sequential *B*–N/*B*–H transborylation reactions to give the *N*,*N*-*bis*-Bpin amine **55**, and re-form the borane catalyst (Scheme 18b). Alternatively, the *N*-boryl imine **53** underwent *B*–N/*B*–H transborylation to form the *N*-Bpin imine **56**, followed by a second hydroboration and *B*–N/*B*–H transborylation to form the *N*,*N*-*bis*-Bpin amine **55**. DFT analysis suggested that both mechanisms were likely operating.



Scheme 18 a) Borane-catalysed nitrile hydroboration b) Proposed mechanism

## 5 *B*–F Transborylation

The stoichiometric redistribution of boron-halogen bonds received much attention in the 1950s and 1960s, due the facile access to useful monohalo- and dihaloboranes (Scheme 19a).[1, 2-4] McCusker proposed that this redistribution proceeded by a σ-bond metathesis-type pathway.[2] These reactions have found limited application beyond stoichiometric redistribution.

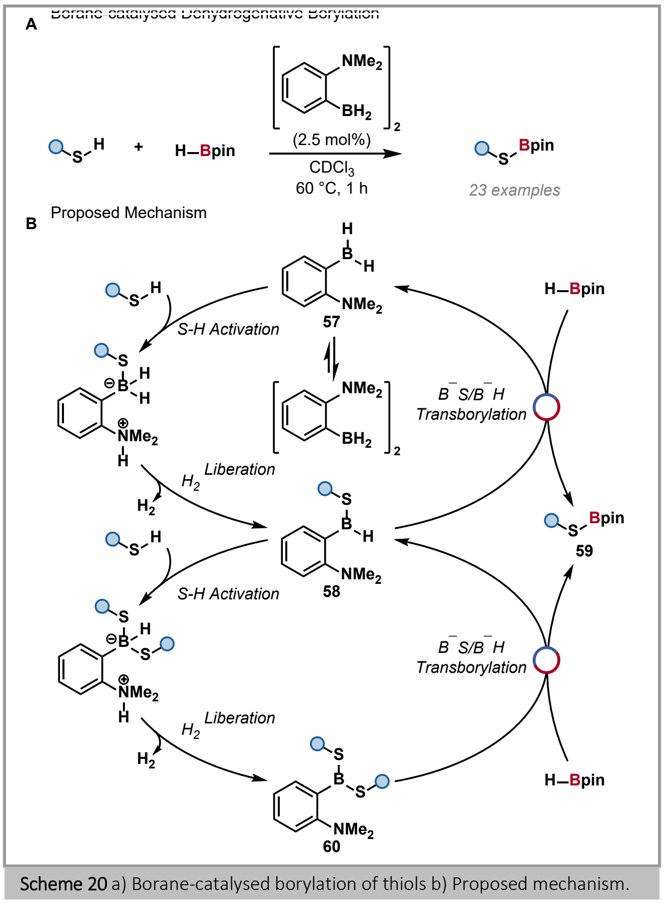


Scheme 19 a) Stoichiometric redistributions of haloboranes b) Borane-catalysed C–F arylation enabled by *B*–F/*B*–H transborylation c) Proposed mechanism

The first, and so far only, example of *B*-halogen transborylation in catalysis was the use of *B*–F/*B*–H transborylation by Willcox and Thomas in the borane-catalysed arylation of C–F bonds (Scheme 19b).[69] *B*–F/*B*–H transborylation with HBpin converted the stoichiometric C–F arylation reported by Stephan[79] into a borane-catalysed process. The reaction was proposed to proceed by a H-*B*-9-BBN-mediated S$_E$Ar of the benzylic fluoride with an arene. *B*–F/*B*–H transborylation of the resulting F-*B*-9-BBN with HBpin regenerated the catalyst (Scheme 19c). The proposed σ-bond metathesis type pathway for *B*–F/*B*–H transborylation was examined through DFT analysis and the activation barrier was calculated to be 25.8 kcal mol$^{-1}$.

## 6 *B*–S Transborylation

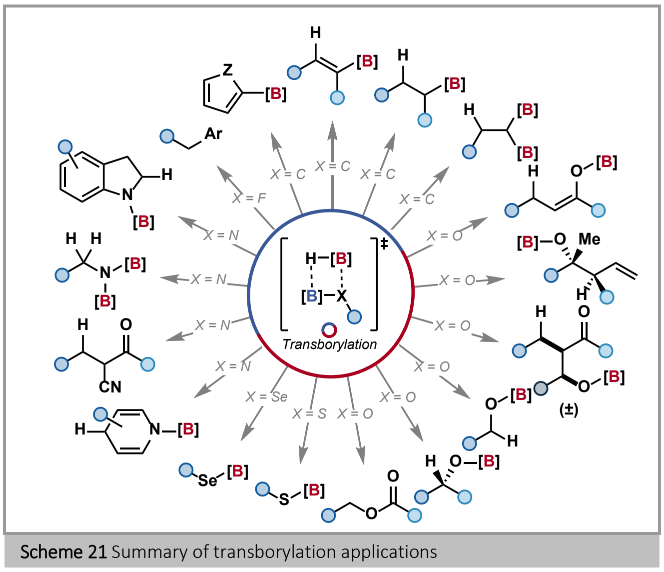
Pasto reported the stoichiometric redistribution of BH$_3$ with phenyl mercaptoborane to give borinic and boronic thioester products.[4] In catalysis, transborylation at *B*–S bonds has been used by Fontaine for the dehydrocoupling of thiols (Scheme 20a).[80] This protocol provided an advantage over stoichiometric dehydrocoupling which required high reaction temperatures and extended reaction times.[81] A mechanism was proposed based on DFT analysis (Scheme 20b) in which the catalyst **57** underwent dehydrocoupling with the thiol to give an alkylthiaborane **58** which reacted with HBpin by *B*–S/*B*–H transborylation to regenerate the catalyst **57** and form the thioboronate **59**. Alternatively, the alkylthiaborane intermediate **58** underwent a further dehydrocoupling with another equivalent of thiol to give an alkylboronic thioester **60**, which then underwent *B*–S/*B*–H transborylation with HBpin to give the thioboronate **59** and regenerate the alkylthiaborane intermediate **58**. *B*–S/*B*–H transborylation was found to be rate determining with a fairly large thermodynamic barrier (ΔG‡: EtSH = 30.5 kcal mol$^{-1}$, $^t$BuSH = 25.9 kcal mol$^{-1}$). This catalytic protocol could be further applied to the dehydrocoupling of selenols with HBpin and is currently the only example of *B*–Se/*B*–H transborylation.



Scheme 20 a) Borane-catalysed borylation of thiols b) Proposed mechanism.

## 7 Conclusion

This review outlines the developments in the application of transborylation as a turnover strategy for main-group catalysis. Transborylation has emerged as a powerful strategy for developing new boron catalysis by using this redox neutral catalytic turnover process, avoiding the traditional turnover pathways of oxidative addition and reductive elimination, which remain largely inaccessible to boron. Several reactions, which were previously limited to stoichiometric reactivity, are accessible to boron catalysts due to the development of transborylation. More significantly, new reactivity has been developed and enabled by transborylation. This turnover pathway has provided an efficient platform for catalysis across a diverse range of transformations including hydroboration, borylation, asymmetric reduction, and C–C bond forming reactions (Scheme 21). The highly generalisable nature of this catalytic turnover pathway allows it to be applied to turnover at many centres including carbon, oxygen, nitrogen, fluorine, sulfur, and selenium and to terminal reductants including HBpin and HBcat. The use of transborylation in catalysis has provided a highly versatile and simple method of catalytic turnover, allowing excellent yields, selectivity, and functional group tolerance. Several useful mechanistic experiments have been applied to probe transborylation, most notably isotopic entrainment experiments, single-turnover reactions with H$^{10}$Bpin, and Eyring analysis. Future borane-catalysed reactions enabled by transborylation should extend turnover to different heteroatoms, apply the method to further stereoselective transformations, and avoid the use of B–H bonds in transborylation.



Scheme 21 Summary of transborylation applications

## Funding Information

S.P.T. thanks the Royal Society for a University Research Fellowship (URF/R/191015). S.P.T., A.D.B., and K.N. thank AstraZeneca and the EPSRC for PhD studentships.

## Conflict of Interest

The authors declare no conflict of interest.

## References

1. Schlesinger, H. I.; Burg, A. B. *Journal of the American Chemical Society* **1931,** 53, (12), 4321-4332; Porter, R. F.; Wason, S. K. *The Journal of Physical Chemistry* **1965,** 69, (7), 2208-2212; Coyle, T. D.; Cooper, J.; Ritter, J. J. *Inorganic Chemistry* **1968,** 7, (5), 1014-1020.

2. McCusker, P. A.; Hennion, G. F.; Ashby, E. C. *Journal of the American Chemical Society* **1957,** 79, (19), 5192-5194.

3. Hofmeister, H. K.; Van Wazer, J. R. *Journal of Inorganic and Nuclear Chemistry* **1964,** 26, (7), 1209-1213.

4. Pasto, D. J.; Balasubramaniyan, V.; Wojtkowski, P. W. *Inorganic Chemistry* **1969,** 8, (3), 594-598.

5. Burg, A. B.; Schlesinger, H. I. *Journal of the American Chemical Society* **1933,** 55, (10), 4020-4025.

6. Schlesinger, H. I.; Walker, A. O. *Journal of the American Chemical Society* **1935,** 57, (4), 621-625; Schlesinger, H. I.; Horvitz, L.; Burg, A. B. *Journal of the American Chemical Society* **1936,** 58, (3), 407-409.

7. Contreras, R.; Wrackmeyer, B. *Spectrochimica Acta Part A: Molecular Spectroscopy* **1982,** 38, (8), 941-951.

8. Hennion, G. F.; McCusker, P. A.; Ashby, E. C.; Rutkowski, A. J. *Journal of the American Chemical Society* **1957,** 79, (19), 5194-5196; McCusker, P. A.; Bright, J. H. *The Journal of Organic Chemistry* **1964,** 29, (7), 2093-2094.

9. Brown, H. C.; Gupta, S. K. *Journal of the American Chemical Society* **1970,** 92, (23), 6983-6984.

10. Brown, H. C.; Gupta, S. K. *Journal of the American Chemical Society* **1971,** 93, (7), 1816-1818.

11. Hoshi, M.; Shirakawa, K.; Arase, A. *Chemical Communications* **1998**, (11), 1225-1226.

12. Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979,** 35, (5), 567-607.

13. Thomas, S. P.; Aggarwal, V. K. *Angewandte Chemie International Edition* **2009,** 48, (11), 1896-1898.

14. Pelter, A. *Chemical Society Reviews* **1982,** 11, (2), 191-225; Fyfe, J. W. B.; Watson, A. J. B. *Chem* **2017,** 3, (1), 31-55.

15. Dutta, S.; Bhattacharya, T.; Werz, D. B.; Maiti, D. *Chem* **2021,** 7, (3), 555-605; Carroll, A.-M.; O'Sullivan, T. P.; Guiry, P. J. *Advanced Synthesis & Catalysis* **2005,** 347, (5), 609-631; Chong, C. C.; Kinjo, R. *ACS Catalysis* **2015,** 5, (6), 3238-3259; Bisht, R.; Haldar, C.; Hassan, M. M. M.; Hoque, M. E.; Chaturvedi, J.; Chattopadhyay, B. *Chemical Society Reviews* **2022,** 51, (12), 5042-5100.

16. Blake, A. J.; Cunningham, A.; Ford, A.; Teat, S. J.; Woodward, S. *Chemistry – A European Journal* **2000,** 6, (19), 3586-3594.

17. Rao, B.; Chong, C. C.; Kinjo, R. *Journal of the American Chemical Society* **2018,** 140, (2), 652-656.

18. Chong, C. C.; Hirao, H.; Kinjo, R. *Angewandte Chemie International Edition* **2015,** 54, (1), 190-194.

19. Adams, M. R.; Tien, C.-H.; Huchenski, B. S. N.; Ferguson, M. J.; Speed, A. W. H. *Angewandte Chemie International Edition* **2017,** 56, (22), 6268-6271.

20. Chong, C. C.; Rao, B.; Kinjo, R. *ACS Catalysis* **2017,** 7, (9), 5814-5819.

21. Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *Journal of the American Chemical Society* **2014,** 136, (8), 3028-3031; Hermann, M.; Jones, C.; Frenking, G. *Inorganic Chemistry* **2014,** 53, (13), 6482-6490.

22. Hadlington, T. J.; Kefalidis, C. E.; Maron, L.; Jones, C. *ACS Catalysis* **2017,** 7, (3), 1853-1859.

23. Yang, Z.; Zhong, M.; Ma, X.; De, S.; Anusha, C.; Parameswaran, P.; Roesky, H. W. *Angewandte Chemie International Edition* **2015,** 54, (35), 10225-10229.

24. Yang, Z.; Zhong, M.; Ma, X.; Nijesh, K.; De, S.; Parameswaran, P.; Roesky, H. W. *Journal of the American Chemical Society* **2016,** 138, (8), 2548-2551.

25. Bismuto, A.; Thomas, S. P.; Cowley, M. J. *Angewandte Chemie International Edition* **2016,** 55, (49), 15356-15359.

26. Franz, D.; Sirtl, L.; Pöthig, A.; Inoue, S. *Zeitschrift für anorganische und allgemeine Chemie* **2016,** 642, (22), 1245-1250.

27. Bismuto, A.; Cowley, M. J.; Thomas, S. P. *ACS Catalysis* **2018,** 8, (3), 2001-2005; Li, F.; Bai, X.; Cai, Y.; Li, H.; Zhang, S.-Q.; Liu, F.-H.; Hong, X.; Xu, Y.; Shi, S.-L. *Organic Process Research & Development* **2019,** 23, (8), 1703-1708.

28. Courtemanche, M.-A.; Larouche, J.; Légaré, M.-A.; Bi, W.; Maron, L.; Fontaine, F.-G. *Organometallics* **2013,** 32, (22), 6804-6811.

29. Harinath, A.; Bhattacharjee, J.; Panda, T. K. *Advanced Synthesis & Catalysis* **2019,** 361, (4), 850-857.

30. Das, S.; Karmakar, H.; Bhattacharjee, J.; Panda, T. K. *Dalton Transactions* **2019,** 48, (31), 11978-11984.

31. Willcox, D. R.; De Rosa, D. M.; Howley, J.; Levy, A.; Steven, A.; Nichol, G. S.; Morrison, C. A.; Cowley, M. J.; Thomas, S. P. *Angewandte Chemie International Edition* **2021,** 60, (38), 20672-20677.

32. Wu, T. R.; Chong, J. M. *Journal of the American Chemical Society* **2005,** 127, (10), 3244-3245; Wu, T. R.; Chong, J. M. *Journal of the American Chemical Society* **2007,** 129, (16), 4908-4909; Turner, H. M.; Patel, J.; Niljianskul, N.; Chong, J. M. *Organic Letters* **2011,** 13, (21), 5796-5799.

33. Jayaraman, A.; Misal Castro, L. C.; Desrosiers, V.; Fontaine, F.-G. *Chemical Science* **2018,** 9, (22), 5057-5063.

34. Hoffmann, R. W.; Zeiss, H. J. *The Journal of Organic Chemistry* **1981,** 46, (7), 1309-1314; C. Chen, A.; Ren, L.; M. Crudden, C. *Chemical Communications* **1999**, (7), 611-612.

35. Grimblat, N.; Sugiura, M.; Pellegrinet, S. C. *The Journal of Organic Chemistry* **2014,** 79, (14), 6754-6758.

36. Lou, S.; Moquist, P. N.; Schaus, S. E. *Journal of the American Chemical Society* **2007,** 129, (49), 15398-15404.

37. Suseela, Y.; Prasad, A. S. B.; Periasamy, M. *Journal of the Chemical Society, Chemical Communications* **1990**, (6), 446-447; Suseela, Y.; Periasamy, M. *Journal of Organometallic Chemistry* **1993,** 450, (1), 47-52.

38. Arase, A.; Hoshi, M.; Mijin, A.; Nishi, K. *Synthetic Communications* **1995,** 25, (13), 1957-1962.

39. Shirakawa, K.; Arase, A.; Hoshi, M. *Synthesis* **2004,** 2004, (11), 1814-1820.

40. Brown, H. C.; Tsukamoto, A.; Bigley, D. B. *Journal of the American Chemical Society* **1960,** 82, (17), 4703-4707.

41. Hoshi, M.; Shirakawa, K.; Okimoto, M. *Tetrahedron Letters* **2007,** 48, (48), 8475-8478.

42. Fleige, M.; Mobus, J.; vom Stein, T.; Glorius, F.; Stephan, D. W. *Chemical Communications* **2016,** 52, (72), 10830-10833.

43. Vasko, P.; Zulkifly, I. A.; Fuentes, M. Á.; Mo, Z.; Hicks, J.; Kamer, P. C. J.; Aldridge, S. *Chemistry – A European Journal* **2018,** 24, (41), 10531-10540.

44. Nieto-Sepulveda, E.; Bage, A. D.; Evans, L. A.; Hunt, T. A.; Leach, A. G.; Thomas, S. P.; Lloyd-Jones, G. C. *Journal of the American Chemical Society* **2019,** 141, (46), 18600-18611.

45. Yin, Q.; Kemper, S.; Klare, H. F. T.; Oestreich, M. *Chemistry – A European Journal* **2016,** 22, (39), 13840-13844.

46. Lawson, J. R.; Wilkins, L. C.; Melen, R. L. *Chemistry – A European Journal* **2017,** 23, (46), 10997-11000; Carden, J. L.; Gierlichs, L. J.; Wass, D. F.; Browne, D. L.; Melen, R. L. *Chemical Communications* **2019,** 55, (3), 318-321.

47. Yin, Q.; Soltani, Y.; Melen, R. L.; Oestreich, M. *Organometallics* **2017,** 36, (13), 2381-2384.

48. Ang, N. W. J.; Buettner, C. S.; Docherty, S.; Bismuto, A.; Carney, J. R.; Docherty, J. H.; Cowley, M. J.; Thomas, S. P. *Synthesis* **2018,** 50, (04), 803-808.

49. Burgess, K.; Van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Journal of the American Chemical Society* **1992,** 114, (24), 9350-9359; Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorganic Chemistry* **1993,** 32, (10), 2175-2182.

50. Bage, A. D.; Hunt, T. A.; Thomas, S. P. *Organic Letters* **2020,** 22, (11), 4107-4112.

51. Bage, A. D.; Nicholson, K.; Hunt, T. A.; Langer, T.; Thomas, S. P. *ACS Catalysis* **2020,** 10, (22), 13479-13486.

52. Docherty, J. H.; Nicholson, K.; Dominey, A. P.; Thomas, S. P. *ACS Catalysis* **2020,** 10, (8), 4686-4691.

53. Uzelac, M.; Yuan, K.; Ingleson, M. J. *Organometallics* **2020,** 39, (8), 1332-1338.

54. Légaré, M.-A.; Courtemanche, M.-A.; Rochette, É.; Fontaine, F.-G. *Science* **2015,** 349, (6247), 513-516.

55. Légaré Lavergne, J.; Jayaraman, A.; Misal Castro, L. C.; Rochette, É.; Fontaine, F.-G. *Journal of the American Chemical Society* **2017,** 139, (41), 14714-14723.

56. Légaré, M.-A.; Rochette, É.; Légaré Lavergne, J.; Bouchard, N.; Fontaine, F.-G. *Chemical Communications* **2016,** 52, (31), 5387-5390.

57. Jayaraman, A.; Misal Castro, L. C.; Fontaine, F.-G. *Organic Process Research & Development* **2018,** 22, (11), 1489-1499.

58. Bouchard, N.; Fontaine, F.-G. *Dalton Transactions* **2019,** 48, (15), 4846-4856.

59. Zou, Y.; Zhang, B.; Wang, L.; Zhang, H. *Organic Letters* **2021,** 23, (7), 2821-2825.

60. Dominguez-Molano, P.; Bru, G.; Salvado, O.; Maza, R. J.; Carbó, J. J.; Fernández, E. *Chemical Communications* **2021**.

61. Salvado, O.; Dominguez-Molano, P.; Fernández, E. *Organic Letters* **2022,** 24, (27), 4949-4953.

62. Midland, M. M.; McLoughlin, J. I. *The Journal of Organic Chemistry* **1984,** 49, (21), 4101-4102.

63. Nicholson, K.; Dunne, J.; DaBell, P.; Garcia, A. B.; Bage, A. D.; Docherty, J. H.; Hunt, T. A.; Langer, T.; Thomas, S. P. *ACS Catalysis* **2021,** 11, (4), 2034-2040.

64. Brown, H. C.; Knights, E. F.; Scouten, C. G. *Journal of the American Chemical Society* **1974,** 96, (25), 7765-7770.

65. Nicholson, K.; Langer, T.; Thomas, S. P. *Organic Letters* **2021,** 23, (7), 2498-2504.

66. Légaré Lavergne, J.; To, H.-M.; Fontaine, F.-G. *RSC Advances* **2021,** 11, (51), 31941-31949.

67. Brown, H. C.; Heim, P.; Yoon, N. M. *Journal of the American Chemical Society* **1970,** 92, (6), 1637-1646.

68. Moreno González, A.; Nicholson, K.; Llopis, N.; Nichol, G. S.; Langer, T.; Baeza, A.; Thomas, S. P. *Angewandte Chemie International Edition* **2022**, e202209584.

69. Willcox, D. R.; Nichol, G. S.; Thomas, S. P. *ACS Catalysis* **2021,** 11, (6), 3190-3197.

70. Nicholson, K.; Peng, Y.; Llopis, N.; Willcox, D. R.; Nichol, G. S.; Langer, T.; Baeza, A.; Thomas, S. P. *ACS Catalysis* **2022,** 12, 10887-10893.

71. Gonzalez, A. Z.; Román, J. G.; Gonzalez, E.; Martinez, J.; Medina, J. R.; Matos, K.; Soderquist, J. A. *Journal of the American Chemical Society* **2008,** 130, (29), 9218-9219.

72. Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M. *The Journal of Organic Chemistry* **1998,** 63, (15), 5154-5163; Kamal, M. M.; Liu, Z.; Zhai, S.; Vidović, D. *Molecules* **2021,** 26, (18), 5443.

73. Monti, S. A.; Schmidt, R. R. *Tetrahedron* **1971,** 27, (15), 3331-3339.

74. Kiyokawa, K.; Nagata, T.; Minakata, S. *Angewandte Chemie International Edition* **2016,** 55, (35), 10458-10462; Nagata, T.; Tamaki, A.; Kiyokawa, K.; Tsutsumi, R.; Yamanaka, M.; Minakata, S. *Chemistry – A European Journal* **2018,** 24, (64), 17027-17032.

75. Jeong, E.; Heo, J.; Park, S.; Chang, S. *Chemistry – A European Journal* **2019,** 25, (25), 6320-6325.

76. Jayaraman, A.; Powell-Davies, H.; Fontaine, F.-G. *Tetrahedron* **2019,** 75, (14), 2118-2127.

77. Jayaraman, A.; Misal Castro, L. C.; Desrosiers, V.; Fontaine, F.-G. *Chemical Science* **2018,** 9, (22), 5057-5063.

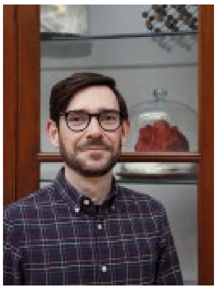
78. Benn, K.; Nicholson, K.; Langer, T.; Thomas, S. P. *Chemical Communications* **2021,** 57, (74), 9406-9409.

79. Guo, J.; Bamford, K. L.; Stephan, D. W. *Organic & Biomolecular Chemistry* **2019,** 17, (21), 5258-5261; Bamford, K. L.; Chitnis, S. S.; Qu, Z.-w.; Stephan, D. W. *Chemistry – A European Journal* **2018,** 24, (60), 16014-16018.

80. Rochette, É.; Boutin, H.; Fontaine, F.-G. *Organometallics* **2017,** 36, (15), 2870-2876.

81. Romero, E. A.; Peltier, J. L.; Jazzar, R.; Bertrand, G. *Chemical Communications* **2016,** 52, (69), 10563-10565.

## Biosketches



Stephen Thomas was born in Canada and moved to Somerset (UK) as a teenager. After obtaining his MChem from Cardiff University, working with Prof. Nick Tomkinson, he studied for his PhD at the University of Cambridge with Dr Stuart Warren. Postdoctoral work with Prof. Dr Andreas Pfaltz (University of Basel) was followed by a move to the University of Bristol as Research Officer in the group of Prof. Varinder Aggarwal FRS. Stephen began his independent research career at the University of Edinburgh in 2012 as a Chancellor's Research Fellow. He was awarded a Royal Society University Research Fellowship in 2014, promoted to Reader in 2016, and to a personal Chair in 2022. The Thomas group is interested in the development and understanding of sustainable catalysis with a focus on Earth-abundant element-based catalysts for organic transformations.