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The transition metal-catalysed hydroboration reaction†

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The use of transition metals to catalyse the addition of hydridoboranes to unsaturated organic molecules was initially realised several decades ago. Although this area of chemistry received considerable attention at the time, interest in this reaction and its use in organic synthesis waned for several years. Like a phoenix rising from the ashes, this amazing catalytic reaction has grown to include the use of earth-abundant metal catalysts and a much wider range of organic substrates. Indeed, it is now commonly utilised as a diagnostic tool to assess the reactivity and catalytic ability of newly generated transition metal and main group complexes. As this field is progressing so rapidly, this review highlights some important advances up to the end of 2021 and into early 2022. Excluded from this review are 'hydroboration' reactions using diboron sources.

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† Dedicated to the memory of Professor Stephen A. Westcott, a great mentor and friend.

1 Introduction

The hydroboration reaction is the addition of a boron–hydrogen bond to an unsaturated organic group and was first reported by H. C. Brown in 1956.¹ The pioneering work of Brown on organoborane chemistry resulted in his receipt of the Nobel Prize in 1979. The importance of the hydroboration reaction



Stephen J. Geier

Steve Geier is a native of Sackville, New Brunswick. He completed his BSc degree at Mount Allison University and went on to pursue his PhD degree at the University of Windsor under the supervision of Dr Douglas W. Stephan. His PhD work focused on "Frustrated Lewis Pair" chemistry. He accompanied Dr Stephan in his move to the University of Toronto, completing his PhD in 2010. He then spent 2 years as an NSERC Postdoctoral Fellow in the lab of Dr Jeffrey R.

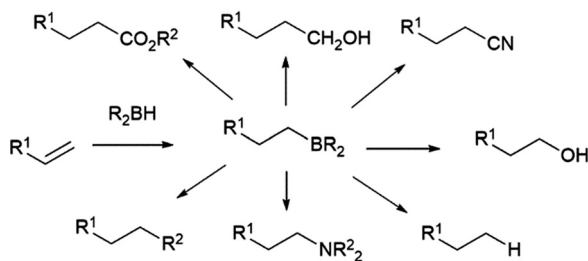
Long at the University of California, Berkeley where he helped develop and test new metal–organic frameworks for gas separations. In January 2013, he returned to Steve Westcott's group at Mount Allison University as a Research Associate and has been there ever since. During his time as a Research Associate, he completed a MLIS (Masters of Library and Information Studies) degree from the University of Alberta. His career interests include research dissemination and, of course, all things boron.



Christopher M. Vogels

Christopher M. Vogels received his BSc from Mount Allison University in 1993 and his MS from New Mexico State University in 1996 under the supervision of Michael Johnson. He has been working with the Wild Toads since 1997 and his current research interests include the synthesis and reactivity of E–B compounds (where E = S, Se, Ge and P).

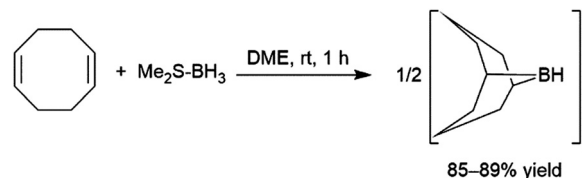




Scheme 1 Derivatization of organoboranes.

owes largely to the incredible synthetic versatility of organoboranes. Indeed, organoboranes can be readily transformed into several other functionalities with relative ease and in high yields (Scheme 1). While early efforts focused on converting the resulting organoboranes to the corresponding alcohol, the development of other transformations, in particular the carbon–carbon bond formation arising from the Suzuki–Miyaura cross-coupling reaction, has made the preparation of organoboranes even more important in organic synthesis.

Addition of boron hydride reagents to unsaturated organic functionalities usually occurs in a *cis*-fashion. Borane, BH_3 , which exists as a dimer or Lewis base adduct in solution, is found to react rapidly with unhindered alkenes, adding a B–H bond across the carbon–carbon double bonds of three alkenes, generating a trialkyl borane. Reactions with hindered substrates occur more slowly and, in the case of unsymmetrical

Scheme 2 Preparation of 9-borabicyclo[3.3.1]nonane dimer.^{2–7}

alkenes, the boryl group (BR_2) ends up on the less-substituted carbon atom. Though this regioselectivity is largely a steric effect, it is also electronically favoured, as the more electronegative hydrogen atom is added to the more substituted carbon of the alkene. One illustrative example of a hydroboration with a BH_3 –Lewis base adduct is the preparation of a very commonly used hydroborating agent, 9-borabicyclo[3.3.1]nonane (9-BBN, Scheme 2).^{2–7}

While borane and many dialkyl boranes often react rapidly with alkenes at temperatures as low as -80°C , other boranes, particularly bulky polyhedral boranes and more electron-rich boranes, react much more sluggishly. The reaction of polyhedral boranes with acetylene is believed to proceed *via* an initial hydroboration step, however the elevated reaction temperatures required for this addition resulted in several products arising from competing rearrangement reactions. The first reported transition metal-catalysed hydroboration investigated the addition of 2-butyne with B_5H_9 , using the bimetallic



Jennifer A. Melanson

focus is on the modification of natural products for medicinal and industrial use.

Jennifer completed her BSc degree at Mount Allison University as a Wild Toad in 2010 and her PhD degree in 2015 at Dalhousie University under the supervision of Dr Alison Thompson. She was then recruited by Dr Victor A. Snieckus to become a post-doctoral fellow at Queen's University and remained there until late 2018. Jennifer has since returned to work with the Wild Toads as a research associate. Her current research

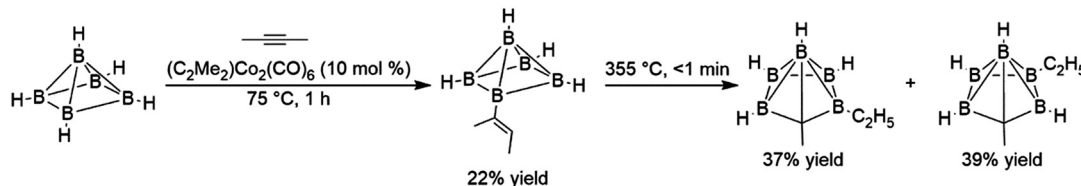


Stephen A. Westcott

Brookhart at the University of North Carolina at Chapel Hill, NC. He was at Mount Allison University from August 1995 through April 2022 and was a Canada Research Chair in Boron Chemistry in the later years of his employment there. He was also a Fellow of the Chemical Institute of Canada and the Royal Society of Chemistry (UK). His research interests included boron chemistry, catalysis, and the synthesis and development of biologically active small molecules. His research group was called the 'Wild Toads' (and it is best not to ask why). With his group, Westcott had published 172 papers with 172 different undergraduate authors as of November 2021 and helped send 125 students to graduate school in chemistry and biochemistry. Steve sadly passed away in April of 2022.

Steve Westcott was born in the sixties somewhere around Tecumseh and received his PhD from the University of Waterloo under the joint supervision of Drs Todd B. Marder (now at Universität Würzburg) and R. Tom Baker (now at the University of Ottawa) working on metal-catalyzed hydroborations. He was an NSERC PDF, where he spent one year at Emory University in Atlanta with Dr Lanny Liebeskind, and more than one year working with Dr Maurice





Scheme 3 Hydroboration of dimethylacetylene using a polyhedral borane (bridging hydrides between each equatorial boron atom are excluded for clarity).⁸

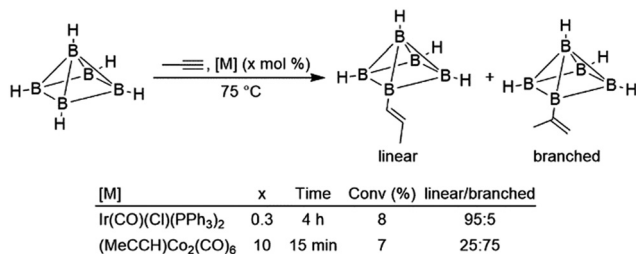
alkyne-bridged dimer dimethylacetylene dicobalthexacarbonyl. The catalytic reaction was desirable in this case because in the absence of catalyst, the elevated temperatures required for the reaction resulted in cage fragmentation and other undesired products. Although turnover numbers for the catalyst were quite low, the transition metal-catalysed hydroboration reaction takes place at 75 °C in the presence of 10 mol% catalyst and afforded the desired product in 22% yield.⁸ Subsequent thermolysis of this product gave higher yields of corresponding carborane products than reactions involving the direct thermolysis of B₅H₉ and dimethylacetylene (Scheme 3).

Intramolecular hydroboration of the alkenyl borane product was previously proposed as the first step of the thermolysis reaction, whereupon subsequent rearrangement gave predominantly two alkyl-substituted CB₅H₉ carborane products. The same reaction was subsequently examined using different alkynes and with Ir(CO)(Cl)(PPh₃)₂ as the catalyst precursor.⁹ While moderately successful, hydroborations using the iridium catalyst were ultimately limited by the complex's poor solubility and eventual deactivation. The authors concluded that while the iridium catalyst was more active for terminal alkynes, the cobalt catalyst was more active for internal alkynes and gave products with the opposite regioselectivity in reactions using propyne (Scheme 4), implying that the catalytic cycles for the two systems were significantly different. Alkyne insertions of related carboranes catalysed by analogous alkyne-bridged dinuclear cobalt carbonyl complexes were also reported.¹⁰ Olefin insertion into a rhodium-bound carborane has been observed, and catalytic turnover was noted in the presence of excess carborane.¹¹ Subsequent work improved activity for catalytic hydroborations of alkynes and alkenes involving polyhedral boranes and carboranes.^{12–25} Hydroborations of alkynes and alkenes with borazine and related compounds have been studied in detail.^{26–30} Due to prohibitive costs, reactions

involving these boranes are generally not synthetically useful and thus will not be comprehensively covered in this review.

Another borane that is much less reactive than most dialkyl borane reagents is catecholborane (HBcat; cat = 1,2-O₂C₆H₄), which is significantly more electron-rich than dialkyl boranes due to π -dative interactions between the neighbouring oxygen atoms and the boron center. First prepared in 1975 from the reaction of catechol with THF-BH₃, catecholborane requires elevated temperatures (70 °C and up) to react with alkynes and alkenes.³¹ This borane is known to decompose at elevated temperatures or in the presence of nucleophiles,³² to give a variety of boron-containing species, including a diboron species containing a bridging catecolato group (B₂cat₃), Lewis base adducts of BH₃, and salts of the tetracoordinate anion Bcat₂[–].

The first publication to describe the transition metal-catalysed hydroboration of alkenes and alkynes with catecholborane came from Männig and Nöth in 1985.³³ With low loadings of Wilkinson's catalyst, RhCl(PPh₃)₃, excellent yields and selectivities were observed in hydroborations at room temperature. Perhaps most interestingly, the authors found that the RhCl(PPh₃)₃-catalysed hydroboration of 5-hexen-2-one offered complementary chemoselectivity to the uncatalysed reaction, with the catalysed hydroboration occurring selectively at the less-reactive alkene moiety. The catalytic protocol offered high yields and selectivities using mild reaction conditions. Since then, many studies of catalysed hydroboration reactions employing catecholborane have been reported. Other boron reagents have also been developed for catalytic hydroborations, with the majority of them having heteroatom-substituted (N, O, S) ancillary groups.^{34–39} One example is pinacolborane (HBpin; pin = 1,2-O₂C₂Me₄),⁴⁰ which is a close relative of HBcat that yields more stable hydroboration products and, in some cases, offers complementary selectivity to catecholborane. Organoboron products derived from pinacolborane are of singular interest in organic synthesis as most are relatively stable to air, water, and chromatography, and therefore isolation of these valuable compounds is considerably easier than their reactive catecolato equivalents. Following the initial disclosure by Männig and Nöth, a number of reports emerged seeking to expand the substrate scope and elucidate the mechanism of these reactions. Particular attention has been paid to hydroborations yielding products with selectivities that are complementary to those observed in uncatalysed hydroborations. There have been many advances in transition metal-catalysed hydroborations in the nearly four decades that have



Scheme 4 Hydroboration of propyne using a polyhedral borane (bridging hydrides between each equatorial boron atom are excluded for clarity).⁹



passed since the Männig and Nöth publication, including the development of increasingly active and selective catalysts, enantioselective catalysts, and new hydroboration reagents. Recent efforts have also expanded the scope to immobilized (and reusable) catalysts as well as the use of more affordable earth-abundant transition metals.

This review will cover the development of the homogeneous transition metal-catalysed hydroboration reaction up to early 2022 using mono-boron hydrides, as well as the use of the resulting products in organic synthesis. A number of reviews have been published on catalytic hydroborations, however they are now dated, or only cover a subset of catalytic hydroborations.^{41–62} This field of chemistry has had a resurgence in recent years and we hope to represent some of the major advances in this area.

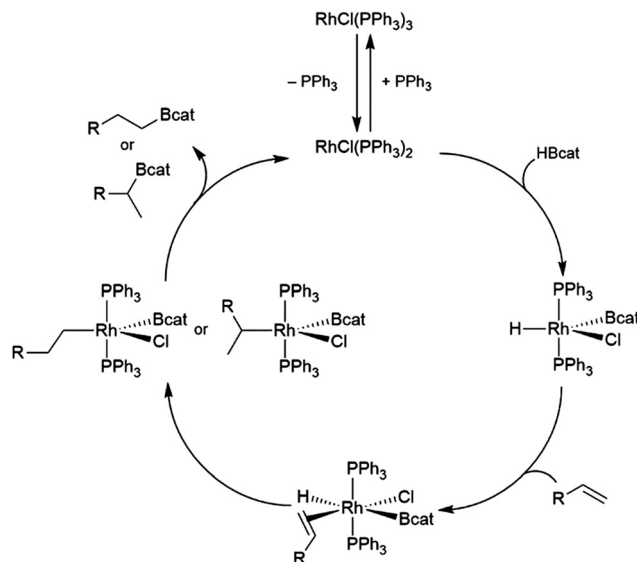
2 Mechanisms

2.1 General

As previously mentioned, uncatalysed hydroboration reactions proceed in a concerted *syn*-fashion with boron adding to the less substituted carbon, while the more electronegative hydrogen atom adds to the more substituted carbon atom, which can better stabilize a partial carbocation transition state. The reaction is believed to proceed *via* an initial coordination of the alkene unit to the Lewis-acidic empty p-type orbital of the boron atom, which is followed by a four-centered transition state (Scheme 5), resulting in *syn*-addition. The same selectivity trends are observed in additions of boranes to carbonyls and imines, with the more electropositive boron atom adding to the more electronegative heteroatom.

2.2 Oxidative addition

The generally accepted catalytic cycle for the rhodium-catalysed hydroboration varies only slightly from that proposed by Männig and Nöth in their landmark report, and a mechanism previously proposed for rhodium-catalysed hydroboration of olefins with polyhedral boranes (Scheme 6). The catalytic hydroboration reaction proceeds through the rhodium(III) compound $\text{RhCl}(\text{H})(\text{Bcat})(\text{PPh}_3)_2$, which was prepared independently,⁶³ generated from the stoichiometric reaction of catecholborane with $\text{RhCl}(\text{PPh}_3)_3$ (the tri-isopropylphosphine analog of this compound was later characterized crystallographically⁶⁴). Olefin coordination occurs next, followed by insertion of the alkene into the rhodium hydrogen bond. Finally, reductive elimination liberates the alkyl borane and regenerates the active catalyst. Interestingly, some reports have suggested that insertion of the alkene into the rhodium–boron bond may be favoured in certain circumstances. Among the clearest evidence for the feasibility of

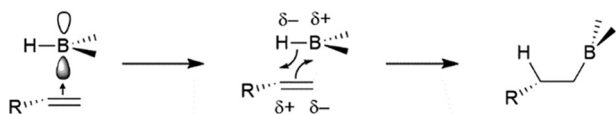


Scheme 6 Proposed catalytic cycle for the rhodium-catalysed hydroboration of alkenes.

this pathway is the fact that vinylboronate esters are often observed in hydroborations of monosubstituted aryl alkenes.⁶⁵ These products presumably arise from insertion of the alkene into the rhodium–boron bond, followed by β -hydride elimination. As hydrogen is a byproduct of this reaction, hydrogenation products are also frequently observed. Stoichiometric insertion reactions of ketones, imines, and alkenes into a rhodium–boron bond have been performed.⁶⁶

A computational study later suggested that insertion of the alkene into the rhodium–hydrogen bond is more facile, however this leads to a more difficult reductive elimination step; insertion into the rhodium–boron bond is more thermodynamically uphill, but leads to a more favourable reductive elimination step.⁶⁷ Several theoretical studies have examined the potential mechanism of the rhodium-catalysed hydroboration. Among the most notable is the aforementioned study, which found that the most stable conformation has the hydride and the boryl group *trans*-disposed to one another in the octahedral rhodium(III) intermediate, with both groups *cis* to the coordinated alkene (Scheme 6, bottom).⁶⁷ The study concluded that associative and dissociative mechanisms for olefin coordination, followed by hydride or boryl migration, are all viable. Earlier studies focused exclusively on either the associative⁶⁸ or dissociative⁶⁹ pathways. A study on related NHC-RhCl hydroboration catalysis suggested that with those catalysts the formation of the terminal hydroboration product proceeds through boryl migration as steric effects disfavour hydride migration.⁷⁰

While regioselectivity trends for simple alkyl-substituted alkenes are normally similar for catalysed and uncatalysed hydroboration reactions, differences have been observed in some cases with aryl alkenes. For uncatalysed hydroboration reactions of monosubstituted terminal aryl alkenes, the boryl group traditionally adds to the terminal carbon. Initial results



Scheme 5 Typical hydroboration of an alkene without a catalyst.

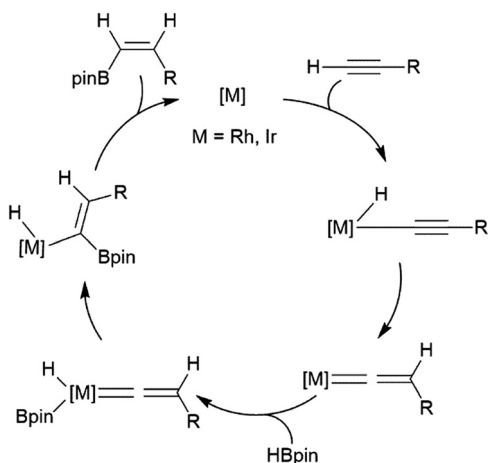


from the analogous catalytic hydroboration reactions were conflicting, as in many cases, the rhodium catalysed hydroboration of aryl alkenes using HBcat generally yielded the unexpected branched products, where the boryl group has added to the internal carbon. This selectivity is rationalized by insertion of the alkene into the rhodium–hydride bond to yield a relatively stabilized benzylic rhodium intermediate, whereupon a subsequent reductive elimination step would generate the branched product.

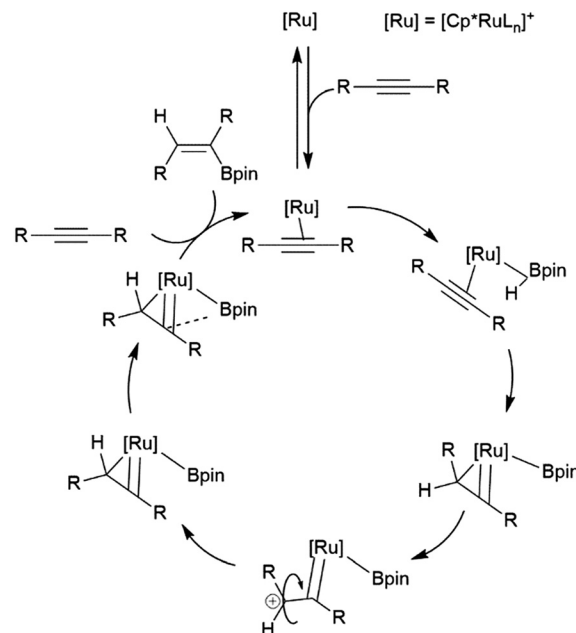
Studies were conducted utilizing DBcat in the catalysed hydroboration of 1-decene or styrene with Wilkinson's catalyst.⁷¹ The authors found that while the deuterium label appeared cleanly on the carbon α to the alcohol in the hydroboration and subsequent oxidation of styrene, the label was scrambled between the 1- and 2-positions of 1-decanol. This result implies that the reversibility of individual steps in the catalytic cycle can be substrate dependent. Likewise, a deuterium labelling study with a rhodium-catalysed hydroboration of styrene using DBpin demonstrated deuterium scrambling between the benzylic and terminal carbons, suggesting that reversibility within the catalytic cycle can also be borane- and/or catalyst-dependent.⁷²

2.3 *trans*-Hydroboration of alkynes

Alkynes have been reported to undergo *trans*-hydroboration using rhodium or iridium catalysts to give (*Z*)-alkenyl boronates. In the initial report of this reactivity, it was suggested that the reaction proceeds through initial oxidative addition of the terminal C–H bond.⁷³ Hydride migration from the metal then leads to a vinylidene complex, which oxidatively adds the B–H bond of the borane (Scheme 7). A stereospecific 1,2-migration of the boryl group leads to the metal-alkyl-hydride complex, which can then reductively eliminate the *trans*-hydroborated product. The key to promoting the *trans*-hydroboration product is the presence of triethylamine, which hinders the competitive oxidative addition of a B–H bond (instead of the alkynyl C–H bond).



Scheme 7 Proposed mechanism for the rhodium-catalysed *trans*-hydroboration of terminal alkynes.⁷³



Scheme 8 Proposed mechanism for the ruthenium-catalysed *trans*-hydroboration of internal alkynes.^{73,74}

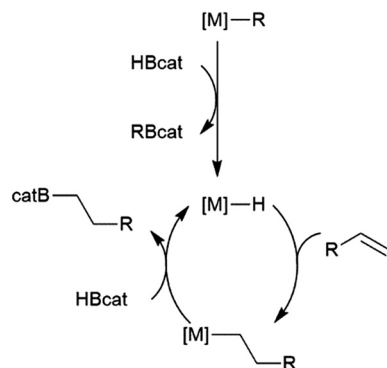
Similarly, a ruthenium complex has been shown to be capable of *trans*-hydroboration of internal alkynes. This is proposed to proceed through a metallacyclopentene intermediate (Scheme 8).^{74,75} Steric bulk is thought to play a key role in promoting the rotation about the carbon–carbon bond, as the same reactions using RuCp (Cp = cyclopentadienyl) catalyst precursors showed greatly reduced stereoselectivity.

2.4 σ -Bond metathesis

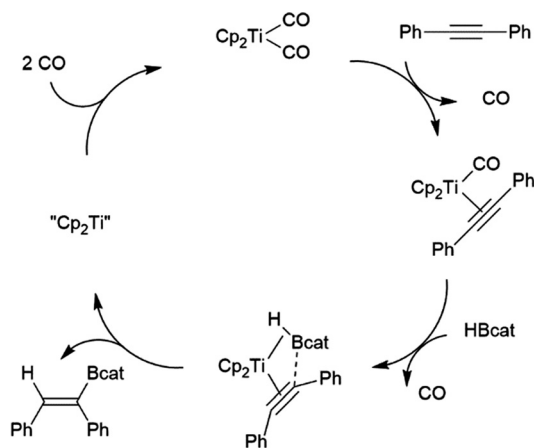
While many transition metal-catalysed hydroboration reactions utilize late transition metals, there are also hydroboration reactions using early transition metal catalysts. Noteworthy reports of catalysis by trivalent lanthanides,^{76–78} niobium,⁷⁹ titanium,^{78,80–82} zirconium^{78,83–87} and, more recently, scandium⁸⁸ have been reported. Although some reactions are found to be plagued by the metal-catalysed formation of BH_3 ,^{79,80,89} which can then act as a catalyst for the hydroboration of the substrate with the original borane, or add to the substrate itself, two other mechanisms are implicated in these reactions. Most suggested mechanisms involved the initial formation of a transition metal hydride by reaction of HBcat with the catalyst precursor. Subsequent insertion of an alkene or alkyne results in a transition metal-alkyl or transition metal-alkenyl species, respectively. Metathesis with HBcat yields the organoborane product and regenerates the transition metal hydride (Scheme 9).

Hartwig and co-workers found that reactions catalysed by Ti(II) precursors proceed through alternate pathways that differ slightly for alkenes and alkynes.⁸² $\text{Cp}_2\text{Ti}(\text{CO})_2$ was found to be an active catalyst for the hydroboration of alkynes. The cycle begins with displacement of one CO ligand for the alkyne substrate, followed by displacement of the second CO by HBcat (Scheme 10). Elimination of the product from the titanium





Scheme 9 Proposed general mechanism for hydroboration via σ -bond metathesis.

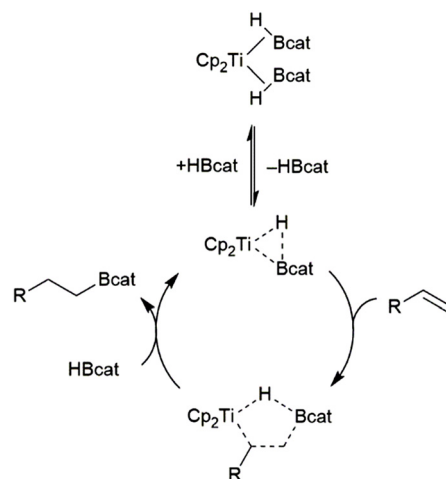


Scheme 10 Proposed mechanism for Ti(II)-catalysed hydroboration of alkynes.⁸²

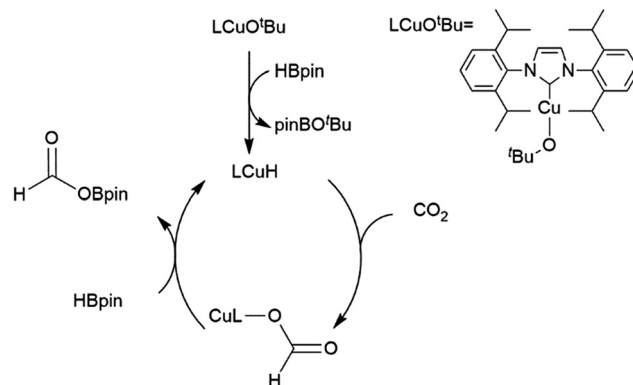
alkyne-borane/ β -borylvinyl-hydride resonance hybrid and coordination of CO restarts the catalytic cycle.

Hydroboration of alkenes catalysed by dimethyltitanocene was found to proceed through the titanium(II) bis(catecholborane) complex (Scheme 11).⁸² The reaction proceeds through the substitution of one equivalent of HBcat for the alkene substrate. Elimination of the product from the resulting titanium alkene-borane/ β -borylalkyl-hydride resonance hybrid and coordination of HBcat regenerates the active catalyst.

A computational study of nickel-catalysed hydroboration of CO₂ revealed that the transformation can be broken down into three separate hydride transfer steps (Scheme 12).⁹⁰ The first involves insertion of CO₂ into the metal-hydride bond in the catalyst precursor. Metathesis with HBcat results in the formation of HCO₂Bcat and regeneration of the nickel hydride. Insertion of HCO₂Bcat into the nickel hydride bond generates Ni(O₂CH₂Bcat). Reaction with another equivalent of catecholborane produces CH₂O, catBOBcat, and the nickel hydride catalyst precursor. Insertion of formaldehyde into the nickel-hydride bond yields a nickel methoxide complex, which reacts with a third equivalent of catecholborane, releasing CH₃OBcat and the nickel hydride catalyst precursor. The reaction mixture



Scheme 11 Proposed mechanism for Ti(II)-catalysed hydroboration of alkenes.⁸²



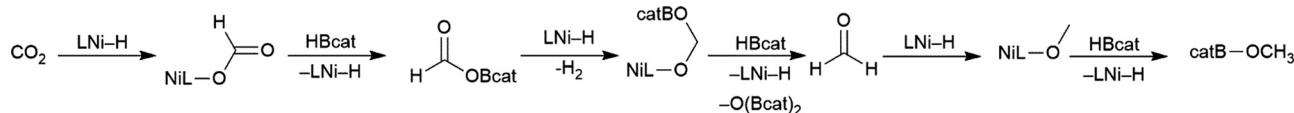
Scheme 12 Proposed mechanism for the copper-catalysed hydroboration of CO₂.⁹³

can be quenched with water to complete the transformation of CO₂ to methanol. Further experimental study of the system revealed that bulky groups on the phosphorus atom of the pincer ligand results in faster reactions. The use of 9-BBN as the boron source results in a similar reaction, but at a slower rate, while using HBpin resulted in the formation of HCO₂Bpin which did not react further. The use of BH₃ (from H₃B-SMe₂) results in the formation of a catalytically inactive nickel(II) borohydride complex.^{91,92} The catalytic cycle proposed for the copper-catalysed reduction of CO₂ with pinacolborane closely resembles the first hydride transfer in the nickel-catalysed reaction. As is the case with the nickel catalysed reduction with HBpin, the pinacolato borylformate in this case does not react further (Scheme 13).⁹³

3 Stereochemistry

The potential for hydroborations to create chiral centers was seen from the seminal paper by Männig and Nöth.³³ In the following years, chiral boranes and catalysts have been examined for their potential use in enantioselective hydroboration



Scheme 13 Hydroboration of CO₂ catalysed by a nickel hydride species.⁹⁰

reactions. Appropriate ligand choice has the potential to provide asymmetric induction with only a catalytic amount of the chiral reagent needed.

3.1 Chiral boranes

Hydroboration reactions using chiral boranes have been performed with rhodium catalysts and aryl alkenes as substrates. The hydroboration of aryl alkenes using these boranes were examined, catalysed by chiral and achiral catalysts.⁹⁴ The most promising result is a 88 : 12 enantiomeric ratio obtained using a rhodium/dppf catalyst system and a pseudoephedrine-derived borane. However, the reaction only showed 82% selectivity for the α -alcohol upon oxidation (Scheme 14). The relatively poor selectivity, along with the cost of using a stoichiometric amount of chiral reagent limits the utility of this approach. The use of some chiral catalysts with these chiral boranes showed no improvement in enantioselectivity.

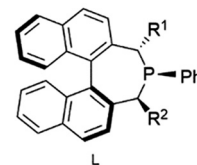
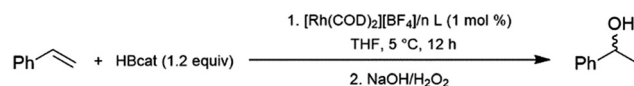
3.2 Catecholborane-monodentate ligands

Monodentate ligands have not been studied to the same extent as their bidentate counterparts in the catalytic hydroboration reaction. In 2005, a series of α -chiral monophosphine ligands were prepared and used with a cationic rhodium(i) precursor for the catalytic hydroboration of styrene with HBcat.⁹⁵ Conversions and yields were generally good, however, only relatively modest enantioselectivity was achieved (Scheme 15).

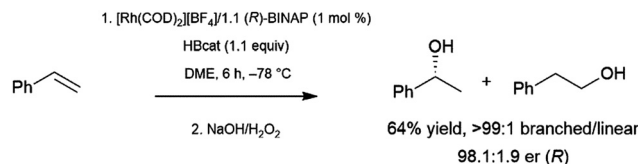
3.3 Catecholborane-bidentate ligands

Bidentate ligands have been quite popular in catalytic hydroboration reactions. The stronger binding and greater tunability when compared to monodentate ligands make them the ligands of choice in the enantioselective hydroboration of many substrates. Several transition metal starting materials contain labile ligands that can be readily substituted by a bidentate ligand. Thus, the catalyst precursor is often prepared *in situ*, prior to addition of the substrate and borane.

The branched product of styrene hydroboration, which can be transformed into a secondary alcohol upon oxidation, is chiral, offering the opportunity for asymmetric induction. This potential was realized quite early, as initial reports of styrene



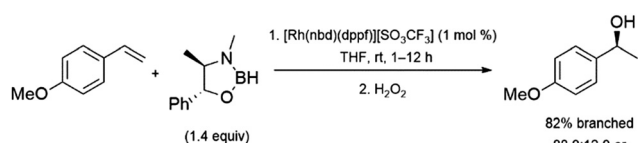
R ¹	R ²	n	Conv (%)	Yield (%)	er	Config
H	H	2	98	74	55.0:45.0	(R)
Me	H	1	98	56	53.5:46.5	(S)
Me	H	2	96	62	55.0:45.0	(S)
Et	H	2	98	80	65.5:34.5	(S)
Bn	H	2	98	57	53.0:47.0	(S)
Me	Me	2	98	73	71.0:29.0	(S)
Et	Et	2	98	52	56.5:43.5	(S)
Bn	Bn	2	98	80	53.5:46.5	(R)

Scheme 15 Rhodium-catalysed asymmetric hydroboration of styrene using a chiral phosphine ligand.⁹⁵Scheme 16 Asymmetric hydroboration of styrene catalysed by a cationic rhodium(i)/BINAP catalyst.⁹⁶

hydroboration^{96–99} included a cationic rhodium/binap catalyst system that was found to offer enantiomeric ratios of up to 98 : 2 at -78°C (Scheme 16).⁹⁶

Other ligands found to offer highly enantioselective catalyst systems in combination with a rhodium(i) catalyst precursor include QUINAP derivatives,^{100–102} ferrocene-based diphosphine,¹⁰³ and P,N ligands (Fig. 1).^{104,105} A dendrimer version of JOSIPHOS also gave an active catalyst on combination with [Rh(COD)₂][BF₄], with similar enantioselectivity to the heterogeneous analog, but poorer regioselectivity.¹⁰⁶ Heterogeneous analogs of BINAP^{107,108} and QUINAP^{107,109} have been successfully prepared and achieved good selectivities in rhodium-catalysed hydroboration reactions. As with their homogeneous analogs, QUINAP outperformed BINAP significantly in asymmetric induction. Both systems could be reused 4 times without appreciable loss in catalytic activity or selectivity. In terms of enantioselectivity, this methodology outperformed previously reported systems derived from zeolite-supported *N,N*- and *P,N*-ligands.^{110,111}

A variety of substituted aryl alkenes were explored in the initial study of the cationic Rh-BINAP catalyst system, finding

Scheme 14 Rhodium-catalysed hydroboration of 4-methoxystyrene with a chiral borane.⁹⁴

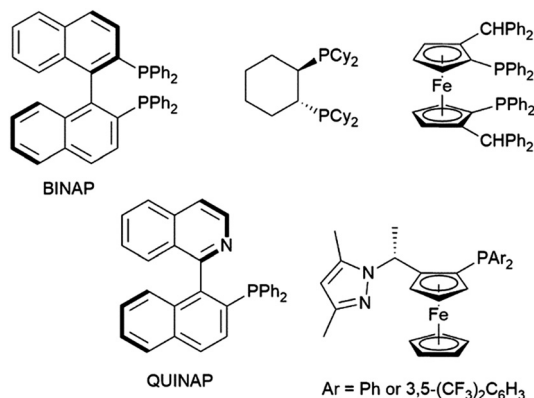


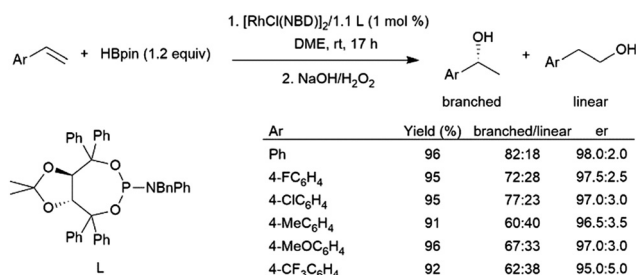
Fig. 1 Commonly used chiral ligands in asymmetric hydroboration reactions.

that electron-rich aryl alkenes underwent hydroboration with greater enantioselectivities than their electron-poor counterparts. The same study also found that asymmetric induction was poorer for α - and β -substituted aryl alkenes, which is likely at least partly due to the sluggish nature of these reactions which necessitates higher reaction temperatures than mono-substituted aryl alkenes.⁹⁹

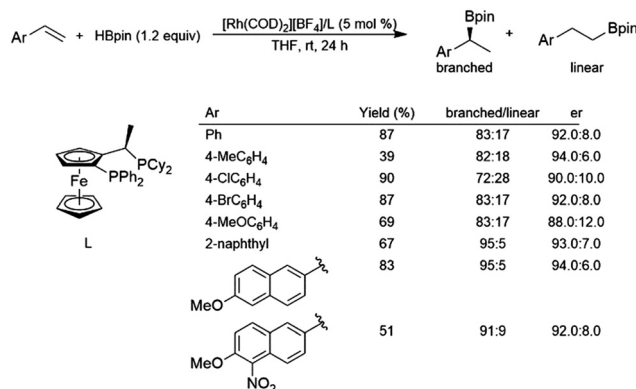
3.4 Pinacolborane-monodentate ligands

Pinacolborane was introduced as a hydroboration reagent in 1992.⁴⁰ While some alkenes and alkynes can undergo hydroboration with pinacolborane in the absence of a catalyst, it tends to be less reactive than HBcat and thus could offer some advantages in terms of selectivity. However, hydroboration reactions of aryl alkenes with HBpin tend to proceed with lower selectivity for the branched isomer than their catecholborane counterparts⁸⁶ and can give significant amounts of vinylboronate esters from dehydrogenative borylation.¹¹²

TADDOL-derived phosphite and phosphoramidite ligands have been successfully utilized with rhodium catalysts in the asymmetric hydroboration of aryl alkenes with HBpin.^{113,114} Up to 98:2 er's are achieved along with high yields, however the ligands providing the highest enantioselectivities of the branched product offer only modest regioselectivity, with significant amount of the linear product also being generated (Scheme 17). Conversion and selectivity for the branched isomer was good in the hydroboration of *ortho*-substituted aryl alkenes, however enantioselectivity was poor.¹¹⁵



Scheme 17 Rhodium-catalysed asymmetric hydroboration using a chiral TADDOL-derived phosphoramidite ligand.¹¹³



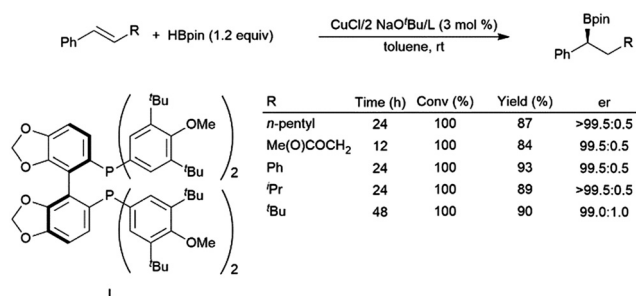
Scheme 18 Asymmetric hydroboration of styrene derivatives using a rhodium(i)/JOSIPHOS catalyst system.¹¹⁶

3.5 Pinacolborane-bidentate ligands

While hydroboration reactions using an iridium complex derived from $[\text{IrCl}(\text{COD})]_2$ and dppb gave >99% selectivity for the linear isomer, the branched isomer was obtained with 96% selectivity using a cationic complex derived from $[\text{Rh}(\text{COD})_2][\text{BF}_4]$ and dppb.¹¹⁶ The same study found that asymmetric hydroboration reactions of aryl alkenes using a cationic rhodium/JOSIPHOS system gave er's from 88:12 to 94:6 and selectivity for the branched isomer of 72–95% (Scheme 18).

A study using a Rh-(R)-QUINAP system found that while catalysed hydroboration reactions of aryl alkenes provided similar good yields, regioselectivities, and enantioselectivity, the use of a Rh-(R)-BINAP system showed poorer and inverse enantioselectivity, along with lower yields and regioselectivities.¹¹⁷ A supramolecular catalyst comprised of a zinc complex bearing pendant TADDOL-derived phosphites and $[\text{Rh}(\text{nbd})_2][\text{BF}_4]$ provided excellent regioselectivities and yields in the hydroboration of *meta*-substituted aryl alkenes.¹¹⁹

In recently developed chemistry, copper(i) diphosphine catalysts have been reported that give highly regio- and enantioselective hydroboration of aryl alkenes with HBpin.¹²⁰ A computational study found that bidentate phosphines accelerate the reaction by destabilizing intermediates involving aryl alkene coordination to a copper(i)-hydride complex and the ensuing copper(i) alkyl complex.¹²¹ A later publication detailed a more reactive catalyst system, capable of the asymmetric hydroboration of electron-rich and β -substituted aryl alkenes (Scheme 19).¹¹⁸



Scheme 19 Asymmetric hydroboration of *trans*-substituted aryl alkenes using a chiral bidentate phosphine ligand.¹¹⁸



4 Scope

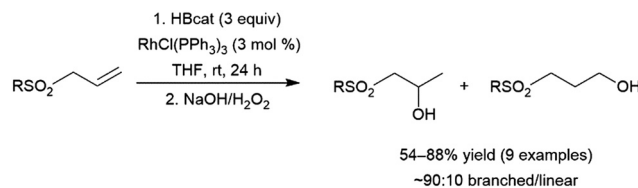
4.1 Aliphatic alkenes

Catalytic hydroboration reactions of simple alkyl-substituted alkenes have traditionally received relatively little attention, mainly because these reactions generally result in the same achiral linear products accessible through uncatalysed hydroboration reactions. Several systems have shown the capability of carrying out the hydroboration reaction to mono-substituted aliphatic alkenes, with selectivities favouring the terminal hydroboration product. Given the utility of pinacol boronate esters, reactions using HBpin have received considerable recent attention, particularly focusing on the use of first row transition metals for this transformation.^{122,123} Where catalytic hydroboration reactions of mono-substituted alkenes initially drew attention, many focused on alkenes bearing other reducible or directing functionalities. For example, the addition of HBcat to terminal alkenes using $\text{RhCl}(\text{PPh}_3)_3$ can be carried out in the presence of ketone and nitrile groups (Scheme 20).³³ In a similar fashion, the chemoselective addition of HBcat to the terminal alkene in 3-vinyl cyclohexene proceeded with excellent conversion at room temperature.³³

Catalytic hydroboration reactions of ethylene are not common in the literature but have been investigated, using ruthenium catalysts and HBpin or HBcat,^{125,126} and the rhodium catalysed hydroboration using *N*-alkylborazines.³⁰ In the case of the ruthenium catalysed hydroboration reactions, the vinylboronate ester product is also observed depending on the solvent used. Bromoethylene undergoes hydroboration with HBcat at room temperature in the presence of Wilkinson's catalyst, whereupon the branched product was isolated exclusively.¹²⁷

A number of allylic sulfones have been subjected to catalytic hydroboration with HBcat using Wilkinson's catalyst.¹²⁴ The authors noted selectivity that strongly favoured the branched isomer (~90:10), regardless of the sulfone substituent. Although the product distribution in the uncatalysed reaction with $\text{BH}_3\cdot\text{THF}$ also favoured the branched product, selectivity was greatly improved in the catalytic reaction suggesting complexation of the sulfone group to the rhodium center may serve to direct the hydroboration reaction (Scheme 21).

The synthesis of diborylalkanes from terminal aliphatic alkenes has been reported using a zirconium(IV) alkoxide catalyst.¹²⁸ The reaction proceeds through initial dehydrogenative borylation, followed by hydroboration of the boryl alkene. Catalytic hydroboration of allyl benzene with HBcat has been



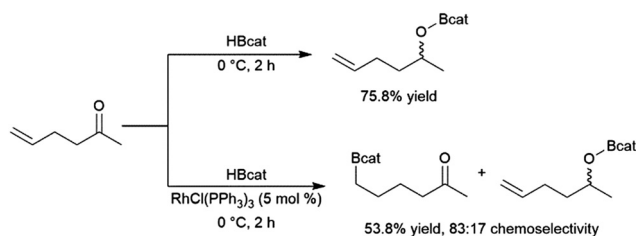
Scheme 21 Rhodium-catalysed hydroboration of allylic sulfones.¹²⁴

investigated using several rhodium catalysts.¹²⁹ While the linear hydroboration product is predominant with the three catalyst precursors utilized, significant amounts of benzylic and branched products were also observed (Scheme 22). The benzylic (1-boryl-1-aryl) product is formed as a result of alkene isomerization at the metal center towards the thermodynamically favourable aryl alkene, which subsequently undergoes hydroboration favouring the branched isomer (Scheme 22, α). A more recent publication highlights a cobalt catalyst capable for this transformation, showing isomerization of chains up to 12 carbon atoms long to selectively form the α -arylboronate ester.¹³⁰ A nickel(II) catalyst has been found to provide excellent selectivity for the terminal hydroboration product with pinacolborane.¹³¹

Teskey and co-workers have reported a photoswitchable cobalt(I)-hydride system which effects the hydroboration of terminal alkenes under visible light irradiation, while selectively effecting isomerization in the dark (only in the presence of pinacolborane and without subsequent hydroboration).¹³² Iridium-catalysed hydroboration of alkenes bearing pendant amides have been studied. It was found that $[\text{Ir}(\text{COD})(\text{PCy}_3)(\text{py})][\text{PF}_6]$ catalysed the hydroboration of monosubstituted β,γ -unsaturated amides with a regioselectivity slightly favouring the branched isomer.¹³³ Under identical conditions, 1-hexene gave almost exclusively the linear product suggesting that the amide group was directing the addition of the borane in these reactions.

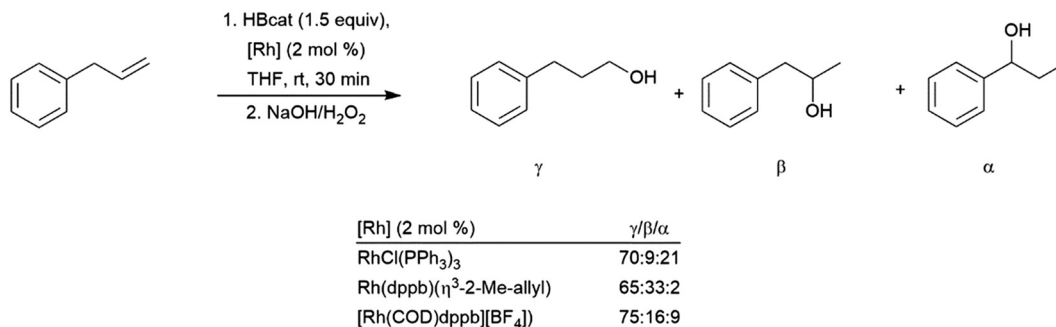
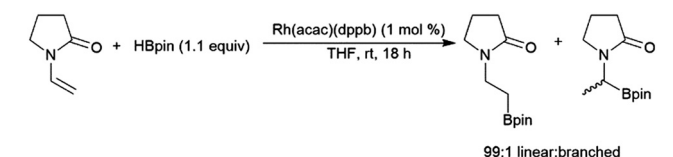
Enamines can undergo highly selective hydroboration reactions that are catalyst and borane dependent. For instance, 9-vinylcarbazole was efficiently hydroborated by HBcat using $\text{Rh}(\text{acac})(\text{dppb})$ to selectively generate the branched product, whereas using the same catalyst with HBpin selectively gave the terminal borylated product.¹³⁴ The hydroboration of 1-vinyl-2-pyrrolidinone catalysed by $\text{Rh}(\text{acac})(\text{dppb})$ proceeded efficiently with high selectivity for the linear hydroboration product (Scheme 23). Uncatalysed reactions with HBcat were complicated by partial reduction of the carbonyl group, and catalysed reactions gave significant amounts of dehydrogenative borylation.

A recent study has shown that judicious selection of rhodium catalyst and reaction conditions can provide the linear or branched isomers resulting from the hydroboration of vinylphosphine. This builds on previous work showing relatively low activity and selectivity for rhodium-catalysed hydroborations of the same substrate. Silyl enols can also undergo rhodium-catalysed asymmetric hydroboration in good yield and enantioselectivity.¹³⁶ Terminal alkenes can also be selectively hydroborated under appropriate conditions in the presence of internal



Scheme 20 Hydroboration of 5-hexen-2-one by HBcat in the absence of a catalyst (top) and using Wilkinson's catalyst (bottom).³³



Scheme 22 Catalytic hydroboration of allyl benzene.¹²⁹Scheme 23 Rhodium-catalysed hydroboration of 1-vinyl-2-pyrrolidinone.¹³⁴

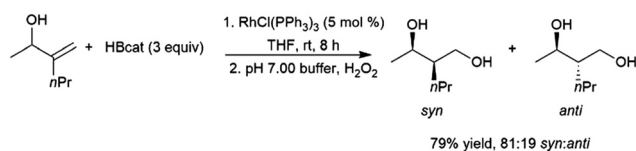
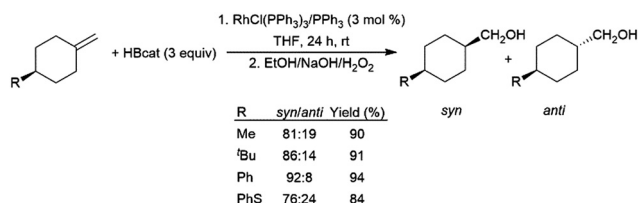
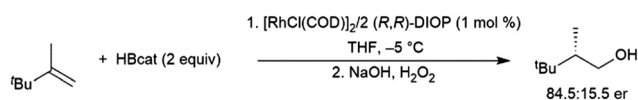
alkenes,^{33,137,138} 1,1-disubstituted alkenes,¹³⁸ ketone,^{33,138} and cyano^{33,139} groups. Pendant alkene groups have been hydroborated to functionalize a polymer.¹⁴⁰

4.2 1,1-Disubstituted aliphatic alkenes

As is the case with most monosubstituted aliphatic alkenes, the terminal alkylboronate ester tends to be preferentially generated in catalytic hydroboration reactions of 1,1-disubstituted aliphatic alkenes. This regioselectivity is often even higher than with the monosubstituted aliphatic alkenes due to increased steric crowding, which also results in more sluggish reactions. Although the terminal carbon atom bearing the boron group in the product is not chiral, in the case of unsymmetrical 1,1-disubstituted alkenes a chiral center is created at the internal carbon. As such, a number of studies have looked at asymmetric hydroboration of 1,1-disubstituted alkenes.

In the early days of transition metal-catalysed hydroboration reactions, allylic alcohol,^{77,129,135,141–149} and amine^{144,150,151} derivatives drew extensive attention as substrates as it was noted that these reactions produced predominantly *syn* isomers while uncatalysed variants gave the *anti* diol products on oxidation (Scheme 24).

In a similar fashion, 1-methylidene-4-cyclohexane derivatives undergo hydroboration/oxidation giving good diastereoselectivity in favour of the *syn* isomers, using RhCl(PPh₃)₃ or [RhCl(COD)]₂/4 PPh₃ as catalyst precursors (Scheme 25).^{152,153}

Scheme 24 Rhodium-catalysed hydroboration of an allylic alcohol.¹³⁵Scheme 25 Rhodium-catalysed hydroboration of 1-methylidene-4-cyclohexane derivatives.¹⁵²Scheme 26 Asymmetric hydroboration of 2,3,3-trimethylbut-1-ene using a rhodium(I) phosphine catalyst.¹⁵⁴

Chiral catalysts have been employed to induce chirality in hydroborations of 2,3,3-trimethylbut-1-ene, albeit with relatively modest enantioselectivity. Optimal conditions employed 2 equivalents of (*R,R*)-DIOP as a ligand with 1 mol% [RhCl(COD)]₂ at -5°C in THF, achieving 84.5 : 15.5 er favouring the *R*-isomer (Scheme 26).¹⁵⁴

1,1-Disubstituted aliphatic alkenes have been selectively reduced using hydridoboronate esters in the presence of a trisubstituted alkene,^{135,137,155–157} even in cases containing ester and amide functionalities.^{147,158} Interestingly, RhCl(PPh₃)₃-catalysed hydroboration of 2,2-disubstituted-1-methylidene cyclopropanes gave ring-opened borylated products bearing a terminal monosubstituted alkene.¹⁵⁹ Similarly, vinylcyclopropanes underwent ring-opening upon iron-catalysed hydroboration to give homoallylic organoboronic esters. As with other substrates, much recent attention has focused on the use of iron and cobalt as catalysts for the hydroboration of 1,1-disubstituted aliphatic alkenes.^{137,157,160,161} A recent report highlights the ability of a polystyrene-supported copper catalyst is effective for the efficient hydroboration of a 1,1-disubstituted alkene.¹⁶²

4.3 1,2-Disubstituted aliphatic alkenes

Regioselectivity is frequently problematic in the catalysed hydroboration of 1,2-disubstituted aliphatic alkenes. In addition to normal regioselectivity issues present in other substrates, competitive isomerization can lead to the formation of linear

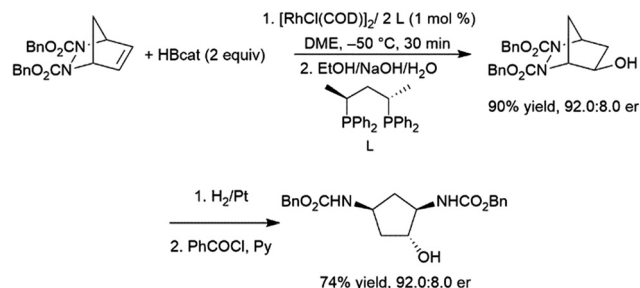


products.^{77,86,122,135,141,160,163–169} Some recent work has shown that these linear products of isomerization and subsequent hydroboration can be produced quite selectively.^{130,166,168–175} A zirconium(IV) catalyst has been shown to enable the isomerization, dehydrogenative borylation, and hydroboration of internal alkynes, generating 1,1-diborylalkanes from internal alkenes.¹²⁸ Frequently, to avoid isomerization, cyclic substrates were used. In particular, norbornene and derivatives have been investigated extensively as substrates in catalytic hydroborations.^{33,35,76,77,86,97–100,125,146,154–157,163,176–189} Transition metal-catalysed hydroborations are selective for giving the *exo*-hydroboration products. Several chiral ligands have also been used for the asymmetric hydroboration of these substrates, however many chiral rhodium complexes offered only modest levels of enantioselectivity.^{97–100,154,155,163,179} Systems containing copper,¹⁸⁰ cobalt,¹⁵⁷ or rhodium^{154,179} catalyst precursors have all shown promise in asymmetric hydroborations of these substrates (Scheme 27).¹⁸⁰

Norbornene has been a frequently examined substrate in catalytic asymmetric hydroboration reactions. In an initial study, BINAP was found to provide the best enantioselectivity for this reaction (Scheme 28).⁹⁸ It was subsequently discovered that bis-aminophosphine ligands could also provide reasonable yields and enantioselectivities for the hydroboration of norbornene.¹⁸⁴

Closely related *meso*-bicyclic hydrazines can also undergo asymmetric hydroboration, with *er*'s up to 93:7. The resulting alcohols are of great interest and can be reduced to diamino-cyclopentane species (Scheme 29).¹⁷⁶ Interestingly, enantioselectivity for the iridium catalysed reaction is opposite to that observed with the rhodium analogs.¹⁹⁰

Allylic alcohol derivatives have been substrates of interest due to the reversed regioselectivity observed in catalytic hydroborations *versus* uncatalysed hydroborations. Electronic effects cause hydroboration selective for the boron atom adding to the carbon α to the alcohol in uncatalysed hydroborations while steric effects dominate the catalytic process resulting



Scheme 29 Asymmetric hydroboration of *meso*-bicyclic hydrazines.¹⁷⁶

in selectivity favouring the *trans*-1,3-disubstituted product (Scheme 30).^{142,155,191,192} An extra carbon atom between the alkoxide group and the alkene double bond results in generally poorer selectivity,^{191,193} frequently favouring the *cis*-1,3-disubstituted product.

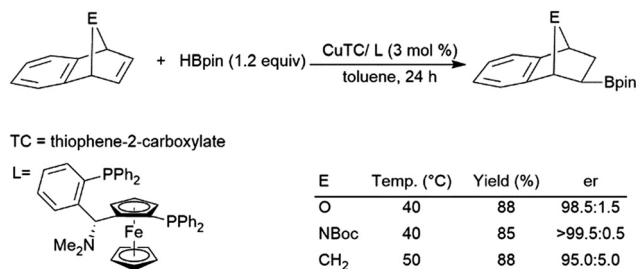
1,2-Disubstituted¹⁹⁴ alkenes bearing pendant amide groups have also been examined extensively as substrates in metal-catalysed hydroboration reactions.^{133,135,195,196} β,γ -Alkenyl amides generally show strong regioselectivity favouring the boryl group in the β -position, though Zhang, Zu, and co-workers have reported an iridium-catalysed protocol which strongly favours the γ -boryl hydroboration product.¹⁹⁷ Judicious ligand selection also allows for excellent enantioselectivity in these reactions.^{195,196} Similarly, γ,δ -alkenyl amides underwent highly selective asymmetric hydroboration incorporating the boryl group in the γ -position.¹⁹⁸ Cyclic alkenes bearing exocyclic amide groups have similarly shown potential for highly regio- and enantioselective metal-catalysed hydroborations.^{133,135,199} Similarly, 2,4,6-trichlorobenzoate substituents have been utilized as directing groups in the asymmetric copper-catalysed hydroboration of internal alkenes.²⁰⁰

Z-Alkenes bearing a halogen substituent undergo hydroboration with catecholborane catalysed by $\text{RhCl}(\text{PPh}_3)_3$, with the boryl moiety being regioselectively added to the carbon bearing the halogen atom.¹²⁷ Cyclopropenes undergo catalytic hydroboration reactions with selectivities favouring addition of the boryl group *trans* to the larger group. Methyl esters serve as directing groups, with the boryl group adding on the same face as the methyl ester (Scheme 31).^{194,201}

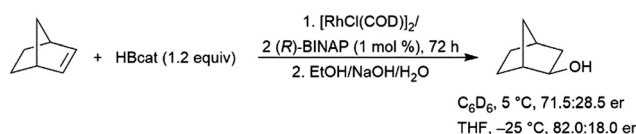
A platinum-coordinated 4-(3-cyclohexen-1-yl)pyridine was submitted to $\text{RhCl}(\text{PPh}_3)_3$ -catalysed hydroboration using catecholborane.²⁰² Regioselectivity was, perhaps not surprisingly, quite poor as there is little steric or electronic differentiation between the two carbon atoms.

4.4 Trisubstituted alkenes

Among the most challenging substrates for catalytic hydroborations are trisubstituted alkenes. Many attempts at catalytic hydroboration reactions are plagued by low conversions¹⁸⁵ and competitive substrate isomerization.^{77,129,160,166,167} Isomerization can be highly selective, resulting in the formation of a terminal alkene, which subsequently undergoes hydroboration, forming alternative hydroboration products (Scheme 32).¹⁷³ A zirconium(IV) system was used to generate the corresponding

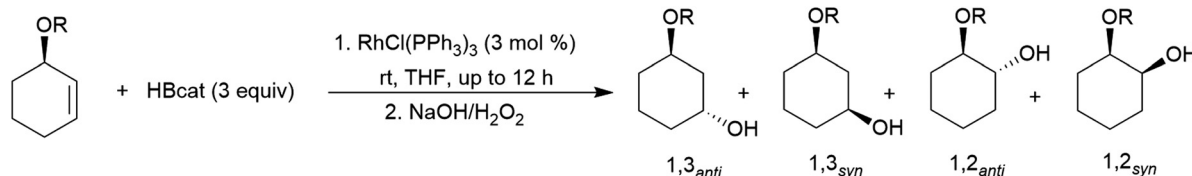


Scheme 27 Copper-catalysed hydroboration of norbornene derivatives.¹⁸⁰

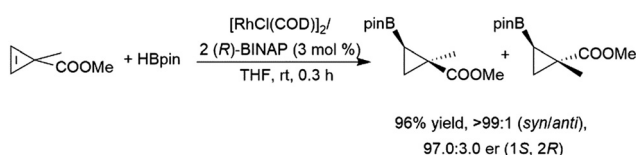
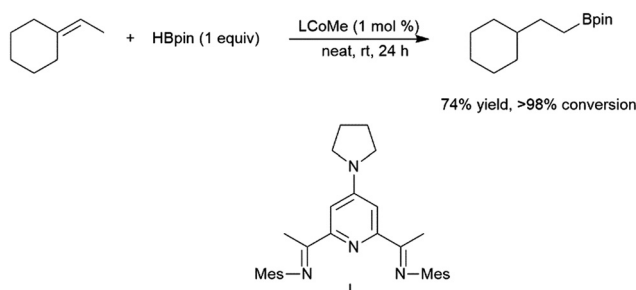


Scheme 28 Asymmetric hydroboration of norbornene.⁹⁸





R	Yield (%)	1,3 _{anti} /1,3 _{syn} /1,2 _{anti} /1,2 _{syn}
H	84	72:9:18:1
Bn	87	72:13:7:8
Si(^t Bu)Me ₂	79	86:11:2:1

Scheme 30 Rhodium-catalysed hydroborations of cyclic allylic alcohol derivatives.¹⁴²Scheme 31 Rhodium-catalysed asymmetric hydroboration of a cyclopropene derivative.^{194,201}Scheme 32 Cobalt-catalysed hydroboration of a trisubstituted alkene.¹⁷³

1,1-diborylalkane product through isomerization and subsequent dehydrogenative borylation.¹²⁸

Trisubstituted allylic amides undergo catalytic hydroborations using a variety of rhodium-based catalysts and pinacolborane.^{195,203,204} The amide directing group, combined with

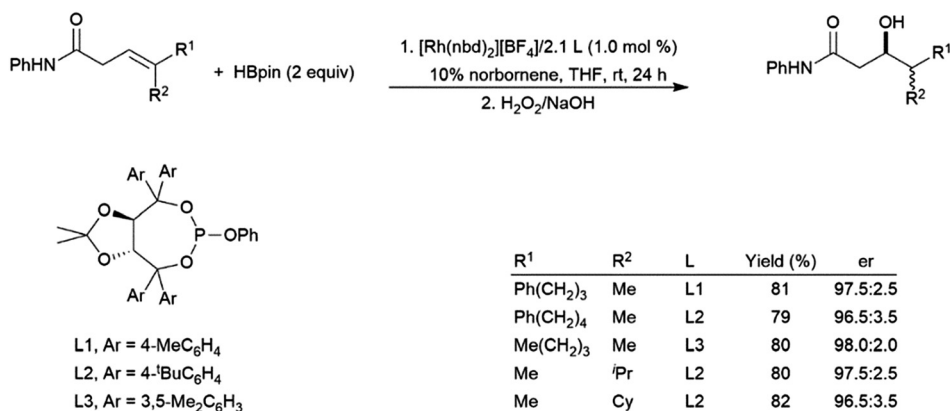
steric effects, results in hydroboration selective for the boryl group β to the amide (Scheme 33).²⁰³

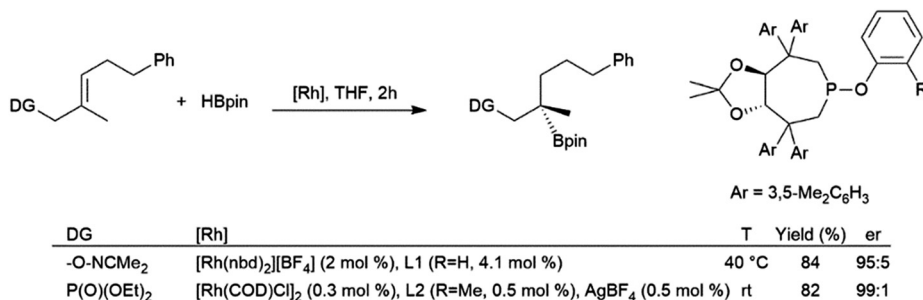
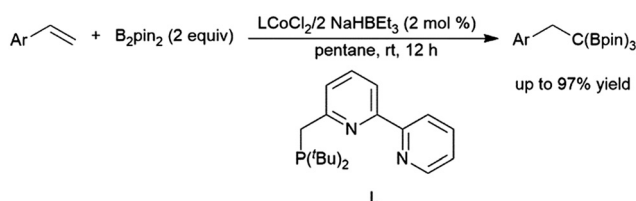
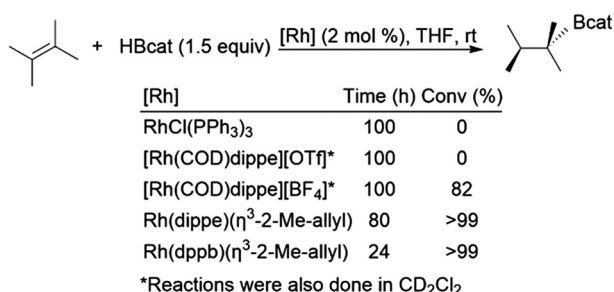
The utilization of oxime²⁰⁵ and phosphonate^{206,207} directing groups has allowed for the asymmetric hydroboration of trisubstituted alkenes with the boryl group selectively adding to the disubstituted carbon, resulting in the formation of chiral tertiary boronic esters (Scheme 34). Substrates with an aryl group²⁰⁶ instead of an alkyl group²⁰⁷ *gem*- to the directing group provided complimentary enantioselectivity.

A recent publication cites the *in situ* formation of HBpin and a cobalt-catalysed hydroboration of a 1,2,2-trisubstituted aryl alkene as a key step in the synthesis of 1,1,1-tris(boronates) from the reaction of monosubstituted aryl alkenes with B₂pin₂ (Scheme 35).²⁰⁸ Cobalt(II) hydrides appended to bipy-type functionalities in metal-organic frameworks (MOFs) proved to be effective in the hydroboration of 2-methyl-2-butene, in addition to other mono- and di-substituted alkenes, as well as ketones and aldehydes, albeit with relatively long reaction times in all cases.²⁰⁹

4.5 Tetrasubstituted alkenes

There are several examples of hydroboration reactions of 2,3-dimethylbut-2-ene. To the best of our knowledge, the most selective hydroboration of this substrate was the first one reported in 1992 by Baker, Marder, and co-workers (Scheme 36).¹²⁹ While several of the catalysts examined were inactive for the reaction,

Scheme 33 Asymmetric amide-directed hydroboration of trisubstituted alkenes.²⁰³

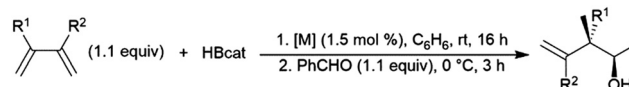
Scheme 34 Oxime-²⁰⁵ and phosphonate-^{206,207} directed asymmetric hydroboration of trisubstituted alkenes.Scheme 35 Cobalt-catalysed synthesis of tris(boronates).²⁰⁸Scheme 36 Rhodium-catalysed hydroboration of 2,3-dimethylbut-2-ene.¹²⁹

two rhodium bisphosphine η³-2-methylallyl catalyst precursors provided nearly quantitative yield of the hydroboration product at room temperature, albeit with extended reaction times. More recent attempts to hydroborate the same substrate have been plagued by alkene isomerization.^{160,166,173}

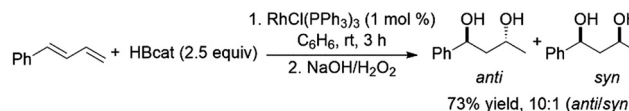
4.6 Dienes

Dienes have also been found to present problems in terms of selectivity. Hydroboration of the terminal alkene occurs in hydroborations using dialkylboranes, leaving the other π-bond unaltered. Good selectivity for 1,2-hydroboration is observed using Pd(0), Pd(II), and Rh(I) catalyst precursors (Scheme 37).²¹⁰ In a similar fashion, an Ir(I) system was found to catalyse the 3,4-hydroboration of 2-substituted 1,3-dienes, giving the terminal hydroboration product.²¹¹

Another report has also highlighted the 1,2-hydroboration of the terminal double bond of dienes using a CuCl/diphosphine catalyst system.¹¹⁸ Using 2.5 equivalents of catecholborane and a variety of Rh(I) catalyst precursors the bis-hydroboration of 1-phenylbutadiene was achieved in moderate yields and with facial selectivity (Scheme 38).²¹²



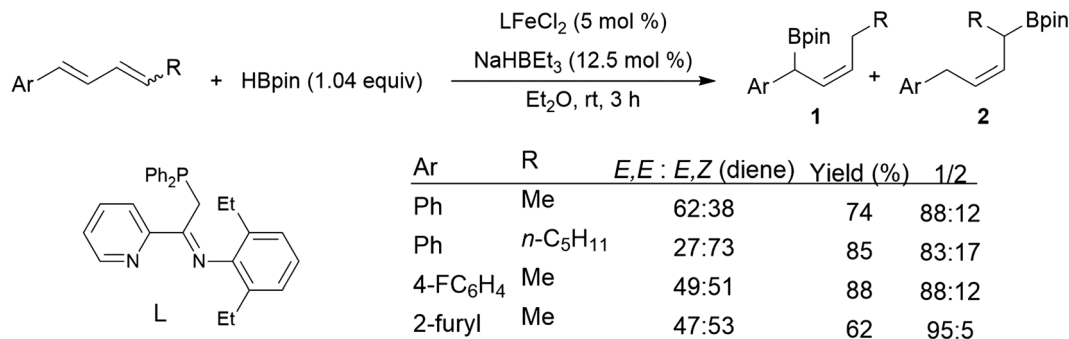
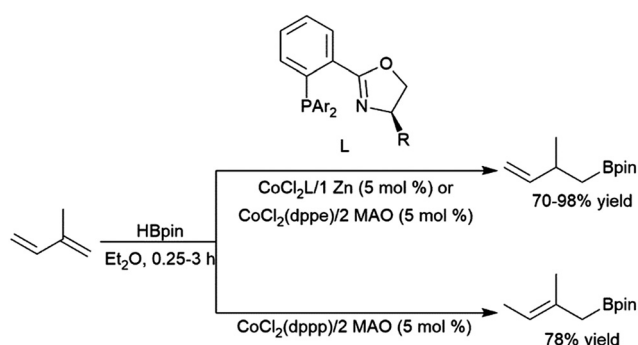
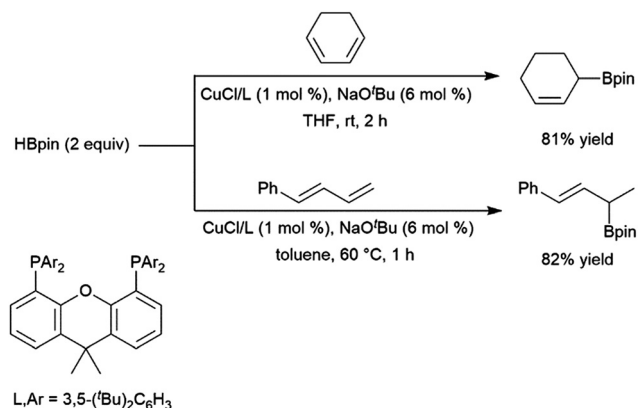
R ¹	R ²	[M]	Yield (%)
H	H	Pd(PPh ₃) ₄	81
H	Me	Pd(PPh ₃) ₄	89
H	Me	PdCl ₂ (PPh ₃) ₂	81
H	Me	Pd(OAc) ₂	24
H	Me	RhCl(PPh ₃) ₃	2
H	Me	RhCl(CO)(PPh ₃) ₂	19
H	-(CH ₂) ₂ CH=CH=CH ₂	Pd(PPh ₃) ₄	77
Me	Me	Pd(PPh ₃) ₄	81

Scheme 37 Catalytic hydroboration of dienes.²¹⁰Scheme 38 Rhodium-catalysed bis-hydroboration of dienes.²¹²

Chemo- and regioselectivity are often issues in Ni(II) and Co(II) diphosphine-catalysed hydroborations using catecholborane, giving significant amounts of products resulting from differing regioselectivity in 1,2-hydroborations and also products of 1,4-hydroboration.^{214–216} Improved selectivity for 1,4-hydroboration is observed using Ni(0)^{217–221} and Fe(II)^{213,222} catalyst precursors (Scheme 39).²¹³

Rajanbabu and co-workers reported divergent selectivity depending on ligand choice in cobalt(I) catalytic hydroboration of dienes (Scheme 40).²²³ The best achiral system for 1,4-hydroboration of 2-substituted 1,3-dienes came from the *in situ* generation of a cobalt(I) dppp complex. Chiral systems derived from bulky 2-oxazolyl-phenyldi(aryl)phosphine ligands (with chirality built into the oxazolyl fragment) were found to provide good regio- and enantioselectivities (up to 94:6 er) in this transformation. A computational study from Liu, Jiang, and Chen found that the dppp ligand donates strongly and provides steric bulk, while the narrower bite angle of dppe alongside the reduced bulk and electron donating ability of (2-oxazolyl)-phenyldiphenylphosphine alter the reaction pathway to favour 1,4-addition.²²⁴ A CuCl/diphosphine-based catalyst system was found to be quite selective for the 1,4-hydroboration of

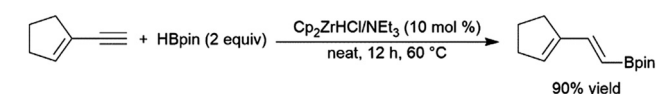
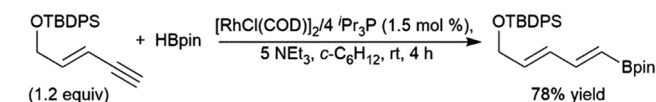


Scheme 39 Iron-catalysed hydroboration of 1,4-di-substituted 1,3-dienes.²¹³Scheme 40 Cobalt-catalysed hydroboration of dienes.²²³Scheme 41 Copper-catalysed hydroboration of dienes.²²⁵

1,3-cyclohexadiene and the 1,2-hydroboration of 1-phenylbuta-1,3-diene (Scheme 41).²²⁵

4.7 Enynes

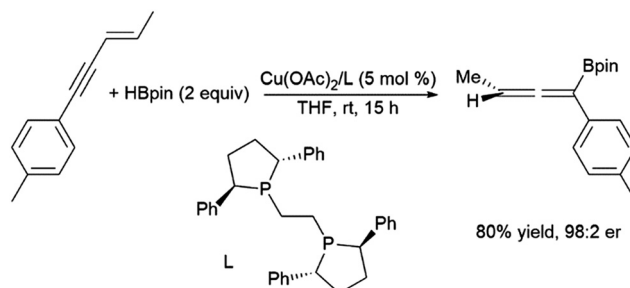
Enynes have been shown to exhibit a wide variety of reactivity in catalytic hydroboration reactions. In many cases, hydroboration occurs selectively at the more reactive terminal alkyne functionality. Regioselectivity for the *cis*-hydroboration of the terminal alkyne in conjugated enynes has been found to be excellent with a catalyst system based on Schwartz's reagent, triethylamine, and pinacolborane (Scheme 42).^{226,227} Selectivity

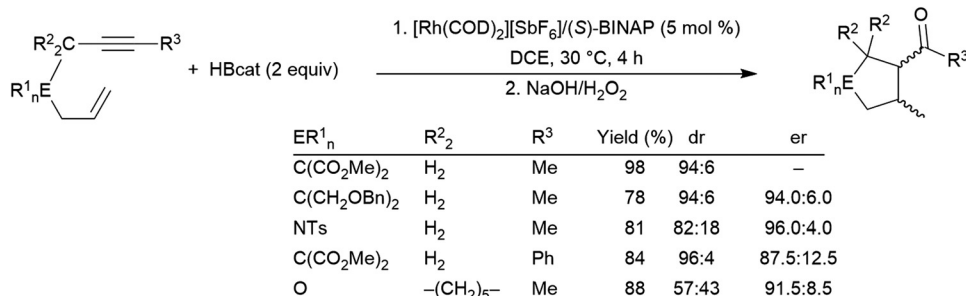
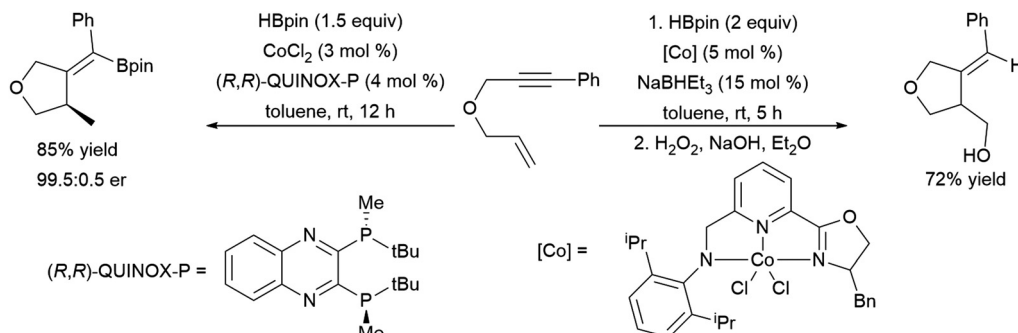
Scheme 42 Zirconium-catalysed hydroboration of terminal alkynes.^{236,237}Scheme 43 Selective *trans*-hydroboration of the alkyne functionality of an enyne.²³¹

for the linear borylated product is reduced somewhat using a NiCl₂/dppe catalyst system.²²⁸

trans-Hydroboration reactions have also been demonstrated using catecholborane and a palladium(0)/1,4-azaborine-based phosphine ligand system.^{229,230} As previously discussed for simple terminal alkynes, *trans*-hydroboration of a terminal alkyne functionality of an enyne is also possible using a rhodium(i) tri-isopropyl phosphine/triethylamine catalyst system with pinacolborane.⁷³ This reaction has seen some practical applications with enynes in synthetic chemistry (Scheme 43).^{231,232}

In reactivity analogous to that observed with conjugated dienes, 1,4-hydroborations of enynes generating allenes with the boryl group tending to add to the end of what was the alkynyl moiety.²³³ This can be achieved using Pd(0)^{210,234–236} and, more recently, enantioselective reactions using Cu(II) catalyst precursors (Scheme 44).^{237,238}

Scheme 44 Copper-catalysed hydroboration of enynes.²⁴⁶

Scheme 45 Rhodium-catalysed cyclization of 1,6-enynes via hydroboration.²³⁹Scheme 46 Cobalt-catalysed cyclization of enyne derivatives via hydroboration.^{241,243}

1,6-Enynes can undergo hydroboration resulting in ring-closing carbon–carbon bond formation, first reported in 2006, using a rhodium(i) catalyst precursor (Scheme 45).²³⁹ The authors propose that the reaction must proceed *via* η^4 -coordination of the enyne to the cationic rhodium(III) intermediate after the initial B–H oxidative addition, followed by either insertion of the alkyne into the Rh–B bond or insertion of the alkene into the Rh–H bond followed by insertion of the other unsaturated functionality into the resulting Rh–C bond forming the 5-membered ring. Reductive elimination yields the cyclic product.

More recent work has shown the ability of the simple cobalt(II) catalyst precursor Co(acac)₂ in combination with chiral phosphine ligands to promote the reductive cyclization of 1,6-^{240,241} and 1,7-enynes.²⁴² Depending on the nature of the substrate, vinyl boronate ester or alkyl boronate esters can be generated. A similar cyclization of 1,6-enynes was also reported, using a bulky cobalt(II) catalyst precursor in combination with NaHBET₃.²⁴³ This protocol offered complementary regioselectivity to that found with the Co(acac)₂/(R,R)-Quinox-P combination with some substrates (Scheme 46). Similar reactivity has since been observed with Ni(II)²⁴⁴ and Fe(II)²⁴⁵ catalysts. 1,5-Ynones have been cyclized with Cu(I) catalysts and trimethylamine-borane as the boron source.²⁴⁶

4.8 Allenes

While less extensively studied than many other substrates, allenes have proven to be interesting substrates in transition metal-catalysed hydroborations as the utilization of different

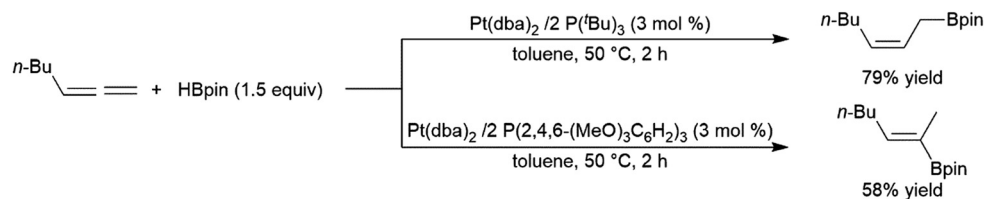
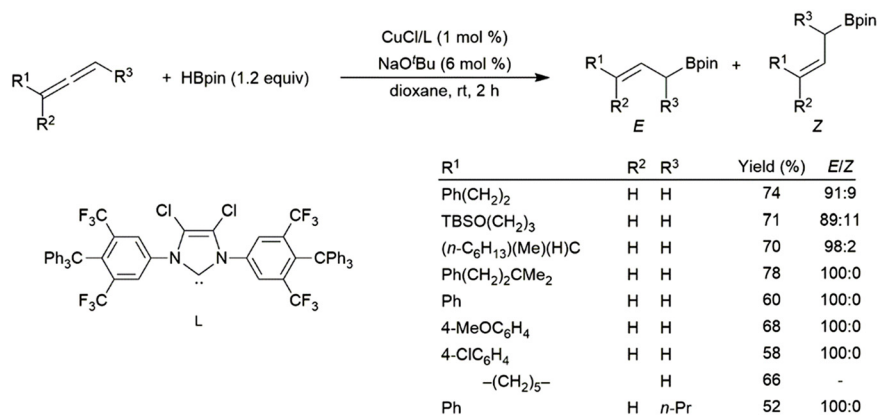
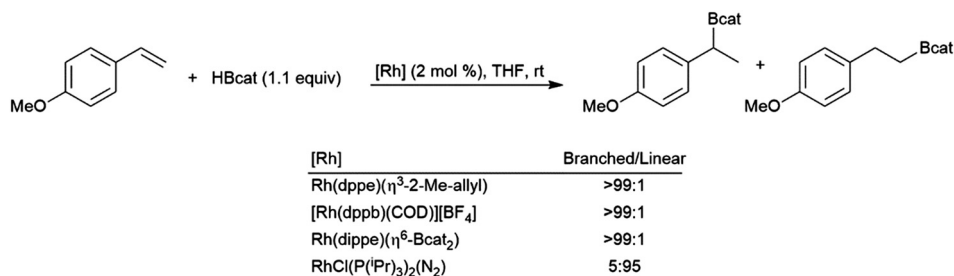
ligands under identical conditions can offer products with different regioselectivities.^{202,203} This is particularly true of Pt(0) catalyst precursors (Scheme 47).²⁴⁷

Rhodium(i)-based catalysts were found to be less effective in the reaction, providing low yields and little regioselectivity.²⁴⁷ Recently, copper(i) catalysts have proven to be effective in the hydroboration of allenes, with strong selectivity for the linear hydroboration product. The remaining double bond exists as a mixture of *E*- and *Z*-isomers, generally favouring the *E*-isomer (Scheme 48).²²⁵ More recent work has unearthed a cobalt-based protocol which yields primarily the *Z*-isomer on the terminal end of the allene,²⁴⁸ a metal-dependant regio-divergent protocol that selectively installs the boron moiety on the central carbon of the allene using either a nickel- or cobalt-catalyst,²⁴⁹ and a chromium-based protocol which yields boronated (*E,Z*)-skipped dienes through tandem dimerization and hydroboration.²⁵⁰

4.9 Monosubstituted aryl alkenes

From the very early days of transition metal-catalysed hydroborations, styrene and derivatives have been of great interest. In the absence of a catalyst, the reaction is highly selective for the linear hydroboration product. In 1989, it was reported that some cationic rhodium(i) phosphine complexes were able to catalyse hydroborations using catecholborane that are highly selective for the branched borylated product.⁹⁶ Over the next few years contradicting reports of the selectivity of hydroborations using Wilkinson's catalyst (RhCl(PPh₃)₃) and catecholborane were published.^{96,99,251} Soon thereafter, these contrasting results were



Scheme 47 Platinum-catalysed hydroboration of allenes.²⁴⁷Scheme 48 Copper(I)-catalysed hydroboration of allenes.²²⁵Scheme 49 Rhodium-catalysed hydroboration of 4-methoxystyrene.¹²⁹

explained by the partial oxidation of the rhodium(I) catalyst in some cases.^{129,141} Selectivity for either the branched or linear products is achievable, depending on catalyst selection (Scheme 49).¹²⁹

The frequently observed selectivity for the branched isomer is rationalized by the preferential formation of a benzylic intermediate following insertion of the alkene into the rhodium–hydrogen bond. Further evidence for this assertion comes from the results of the hydroborations of *ortho*-substituted aryl alkenes. While regioselectivity in the rhodium-catalysed hydroboration of 2,4-dimethylstyrene is quite high at 95–97%, this number drops significantly in the hydroboration of 2,4,6-trimethylstyrene to 63% due to the steric constraint that destabilizes the planar benzylic intermediate in this substrate.²⁵² Rhodium-BABAR-phos complexes were found to be remarkably stable, however regioselectivity in the catalysed hydroboration of aryl alkenes was relatively poor.^{253,254}

Iridium-catalysed reactions tend to produce the linear isomer.^{35,116,117,156,185,255–258} It has been suggested that this

may be due to olefin insertion first into the M–B bond, as opposed to initial insertion into the M–H bond, as is the case with many rhodium catalysts. The readily available ruthenium-based catalyst [Ru(*p*-cymene)Cl₂]₂ was also found to provide terminal-selective hydroboration of vinyl arenes.²⁵⁹

In recent years, first row transition metals have been utilized in this reaction. Many of these initially provided poor selectivity or selectivity for the linear isomer. Metals utilized included cobalt,^{123,260–264} iron,^{265–267} and manganese.^{268,269} More recently, earth-abundant catalysts providing branched selectivity in the hydroboration of vinyl arenes have been developed, including nickel,^{270,271} cobalt,^{131,272} and iron.^{273,274} These developments are covered in a 2019 review.²⁷⁵ This has been extended to heterogeneous catalysis using a cobalt(II) coordination polymer.²⁷⁶

Catecholborane could be added to a platinum complex of 2-vinylpyridine using RhCl(PPh₃)₃ as a catalyst, but the regioselectivity observed under these reaction conditions was poor.²⁰²



Each hydroboration isomer accounted for 45% of the product mixture, while dehydrogenative borylation and hydrogenation products were also observed.

Heterogeneous catalyst systems based on rhodium(i) catalyst precursors in combination with silica bearing diphenylphosphine groups showed good regioselectivity for the branched isomer in the hydroboration of aryl alkenes with catecholborane, particularly when $\text{Rh}(\text{acac})(\text{COE})_2$ was used as the rhodium(i) source.²⁷⁷ Only a slight decrease in activity was observed over 3 runs. The synthesis of diborylalkanes from terminal aryl alkenes has been effected in a zirconium(iv)-catalysed dehydrogenative borylation-hydroboration sequence.¹²⁸

4.10 1,1-Disubstituted aryl alkenes

Like their aliphatic counterparts, hydroborations of 1,1-disubstituted aryl alkenes are more sluggish than their mono-substituted analogs. An early study discovered that selectivity in the rhodium-catalysed hydroboration of 2-phenylpropene with catecholborane could be altered by the choice of catalyst.⁶⁵ The combination of $[\text{MCl}(\text{COE})_2]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) with one equivalent of PPh_3 per M was found to give >98% selectivity for the linear product while using $\text{Rh}(\text{acac})(\text{dppb})$ as the catalyst results in 95% selectivity for the tertiary product (Scheme 50).

Selective formation of the tertiary product is relatively rare and unique to some rhodium-based systems.^{99,129,154,258,278,279} Most hydroboration catalysts based on rhodium,^{65,97–100,129,154,156,163,167,280,281} iridium,^{281–283} cobalt,^{157,160–162} lanthanum,²⁸⁴ samarium,⁷⁷ nickel,¹⁸¹ iron,^{137,168,285} and copper²⁸⁶ selectively provide the linear product. Chiral cobalt^{161,287,288} and iron catalyst²⁸⁵ precursors gave good activity and enantioselectivity in this transformation. Asymmetric cobalt-catalysed hydroborations of 1-aryl-1-silyl alkenes have drawn interest as the second part of a hydrosilylation/hydroboration sequence, starting with the hydrosilylation of a terminal alkyne.^{289–292} Substrates that are bulkier⁹⁹ or more electron-poor²⁷⁸ than 2-phenylpropene also showed increased selectivity for the linear hydroboration product in rhodium-catalysed reactions. The copper catalysed

hydroboration of a 1-phenyl-1-borylalkene gave the tertiary diborylated product (Scheme 51).²⁹³

Recent work has demonstrated the ability of amide and oxime ether groups to direct asymmetric hydroborations using HBpin and chiral Rh catalysts. Interestingly, while a phosphonate group provided regioselectivity for the quaternary isomer when the substrate's aromatic group is unsubstituted or had *meta*- or *para*-substituents, the use of *ortho*-substituted aryl groups led to an inversion in regioselectivity and a significant loss of asymmetric induction (Scheme 52).²⁰⁶ Oxime ether directing groups were found to promote differing regioselectivity in catalytic asymmetric hydroborations of the same substrate, depending on the ligand utilized.²⁹⁴

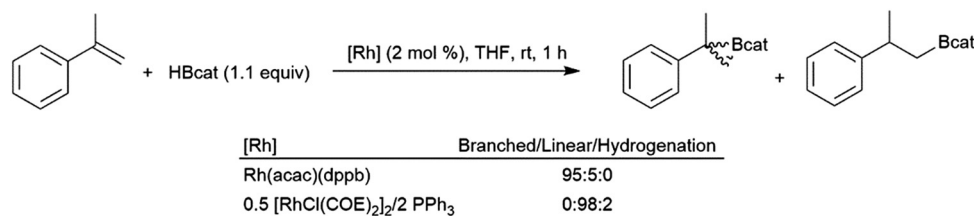
4.11 1,2-Disubstituted aryl alkenes

Rhodium-catalysed hydroborations of *trans*-3-phenyl-2-propene, *cis*-3-phenyl-2-propene, indene, and other 1-aryl-2-alkyl alkenes generally proceed with the boryl group adding α to the aromatic ring. As with monosubstituted aromatic alkenes, this selectivity is rationalized through the formation of a rhodium-benzyl intermediate.

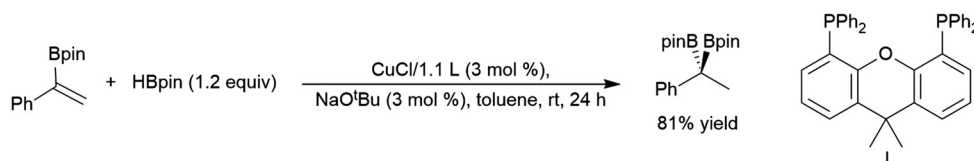
Some 1,2-disubstituted aryl alkenes, including indene and dihydronaphthalene and their derivatives are commonly used substrates in asymmetric hydroboration reactions. Rhodium catalysts with QUINAP-type ligands are among the most effective ligands for these transformations, achieving excellent *ee*'s at room temperature (Scheme 53).^{100,101,108,252,295–301}

Recent work has demonstrated the potential of cobalt catalysts with amide ligands in the asymmetric hydroboration of 1,2-disubstituted aryl alkenes, with enantiomeric ratios up to >99:1 (Scheme 54).²⁶⁴ The reaction is thought to proceed through a benzylic intermediate similar to that found in the case of many rhodium catalysts.

Later work by Takacs showed that the use of amide,³⁰² or phosphonate³⁰³ directing groups in the substrate, in rhodium-catalysed hydroborations with bulky chiral TADDOL-based ligands led to highly regio- and enantioselective hydroborations

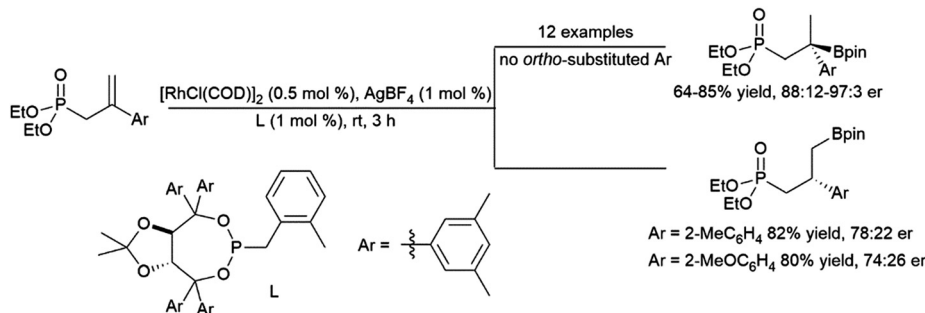
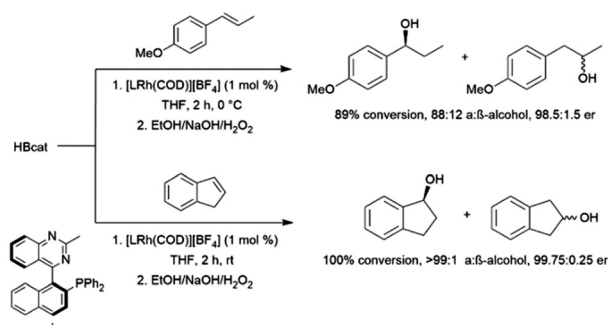
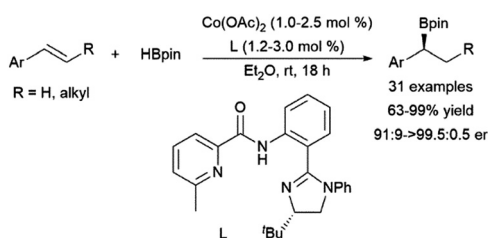


Scheme 50 Rhodium-catalysed hydroboration of 2-phenylpropene.⁶⁵



Scheme 51 Catalytic hydroboration of a 1-phenyl-1-borylalkene.²⁹³

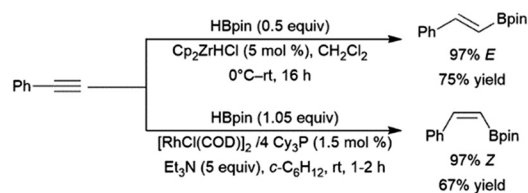


Scheme 52 Phosphonate-directed rhodium-catalysed hydroborations of 1,1-disubstituted aryl alkenes.²⁰⁶Scheme 53 Rhodium-catalysed hydroboration of *trans*-1-methoxy-(1-propenyl)benzene (top) and indene (bottom).²⁹⁵Scheme 54 Cobalt-catalysed α -selective hydroborations of *trans*-1,2-disubstituted aryl alkenes.²⁶⁴

of 1,2-disubstituted aryl alkenes. A zirconium(IV) catalyst has demonstrated the isomerization, dehydrogenative borylation, and hydroboration of *trans*- β -methylstyrene, generating the 1,1-diborylalkane.¹²⁸

4.12 Terminal alkynes

A variety of catalysts have found use in the *cis*-hydroboration of terminal alkynes³⁰⁴ including nickel,^{181,214,305} palladium,³⁰⁶⁻³⁰⁸ rhodium,^{182,183,309-313} ruthenium,³¹⁴ iron,^{267,315-317} copper,³¹⁸⁻³²⁰ titanium,^{81,82,321} scandium,³²² silver,³²³ gold,³²⁴ iridium,^{38,39} and molybdenum.^{325,326} However, the most popular catalyst system for this transformation has been the combination of pinacolborane with a catalytic amount of Schwartz's reagent (Scheme 55, top⁸⁵).^{83-85,327-336} While rates and selectivities are frequently acceptable in the absence of triethylamine, the additive was found to improve the results in some cases.^{226,337-346} As discussed in the enyne section, the system provides generally good

Scheme 55 *cis*- and *trans*-hydroborations of phenylacetylene by zirconium⁸⁵ and rhodium⁷³ catalysts.

yields and excellent selectivity for *cis*-hydroboration of the terminal alkyne functionality, with the boryl group being added to the terminal carbon. In competition experiments, using a gold(I) catalyst, terminal alkynes were hydroborated preferentially over alkenes.³²⁴

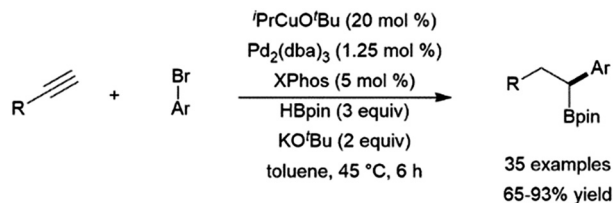
In many cases, the hydroboration of terminal alkynes catalysed by rhodium(I) complexes was found to produce a mixture of products containing the *trans*-hydroboration product.^{33,129,304,309,314,347} Building on these results, a protocol was developed for *trans*-selective hydroboration using rhodium³⁴⁸ or iridium catalysts (Scheme 55, bottom).⁷³ Since its development, this protocol has seen some use in synthetic chemistry.^{73,349-354} Ruthenium,^{268,309,355,356} copper,³⁵⁷ cobalt,^{358,359} and iron^{360,361} catalysts have since also been shown to be capable of the same transformation. It should be noted that in many cases, the reaction proceeds through initial migration of the alkynyl proton (see Section 2.3 *trans*-Hydroboration of alkynes).^{314,362}

Dehydrogenative borylation (replacing the terminal hydrogen atom with a boryl group) is another possible outcome for transition metal-catalysed reactions of boranes with terminal alkynes, this has been achieved in high selectivity with a copper(I) catalyst system.³⁶³ See Section 4.13 Internal alkynes for reactions involving the dehydrogenative borylation of terminal alkynes followed by hydroboration.

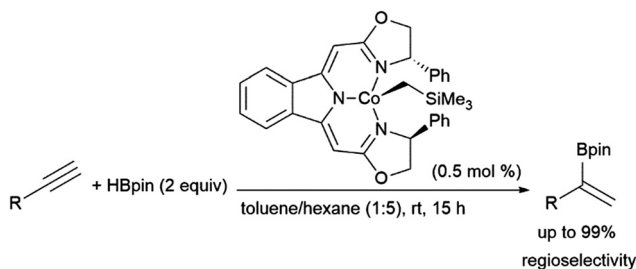
Copper(I)-based hydroboration catalyst systems have found use in multi-step catalytic reactions, including a sequential hydroboration-hydrocupration-palladium catalysed cross-coupling reaction, resulting in the dihydrofunctionalization of terminal alkynes (Scheme 56).³⁶⁴

Gade and co-workers found that cobalt(II) complexes could catalyse α -selective hydroborations of terminal alkynes (Scheme 57).³⁶⁵ The use of similar *N,N,N*-pincer cobalt(II) complexes and HBpin to achieve this Markovnikov-type selectivity

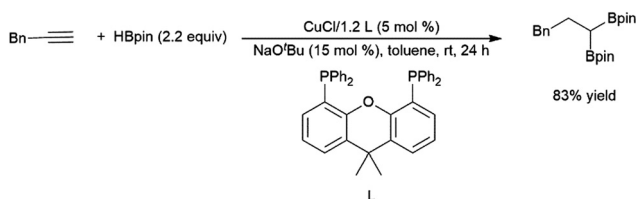




Scheme 56 One pot hydroboration-hydrocupration-cross-coupling reaction.³⁶⁴



Scheme 57 Cobalt-catalysed α -selective hydroboration of terminal alkynes.³⁶⁵



Scheme 58 Copper-catalysed bis-hydroboration of a terminal alkyne.²⁹³

was later mechanistically explored by Chen and co-workers, whereby they suggest that the reaction proceeds by alkyne coordination with a cobalt hydride intermediate, followed by alkyne insertion and σ -bond metathesis with HBpin to provide the α -selective product.³⁶⁶

As hydroborations of 1,2-disubstituted alkenes are well established, in some cases terminal alkynes can be hydroborated twice to achieve geminal substitution on the terminal carbon. Copper,²⁹³ cobalt,³⁶⁷ platinum,³⁶⁸ and rhodium^{313,369} catalysts have been shown to demonstrate this reactivity (Scheme 58).^{293,370}

Recently, onium salt-stabilized nanocatalysts of Ru, Ir, Rh, and Pt were effective in the hydroboration of phenylacetylene in supercritical carbon dioxide. These reactions were quite selective for *cis*-hydroboration, though conversions were often not quantitative and reusing the catalyst led to a decrease in activity.³⁷¹ Separate studies have looked specifically at ruthenium catalysts in ionic liquids (with or without supercritical CO₂),³⁷² in supercritical CO₂,³⁷³ or in polyethylene glycol,³⁷⁴ finding good selectivity through multiple catalytic cycles.

4.13 Internal alkynes

A variety of catalysts have been used for the hydroboration of internal alkynes. In addition to rhodium catalysts,^{305,322,375} this

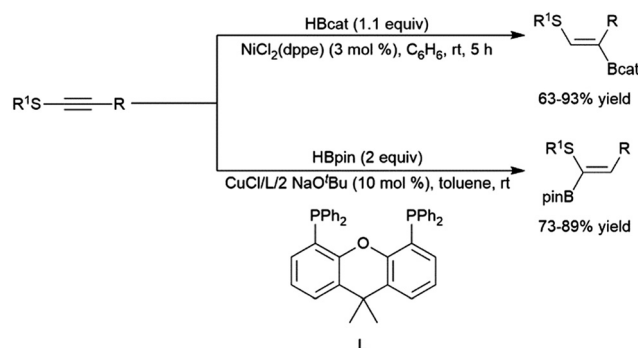
reactivity has also been demonstrated using titanium,^{81,82} zirconium,⁸⁵ nickel,^{214,305} palladium,^{305,376} copper,^{320,341,377–381} ruthenium,^{382,383} manganese,³⁸⁴ molybdenum,³²⁵ cobalt,^{385,386} iron,^{137,315,316,387,388} platinum,³⁶⁸ and iridium^{39,322} catalysts. A recent report has highlighted the ability of cobalt centers appended to a MOF to effect the transformation (albeit quite slowly).³⁸⁹

Alkynes with alkyl and α -ester substituents undergo copper(i)-catalysed hydroborations with pinacolborane adding in a *cis*-fashion with the boryl group preferentially adding to the carbon bearing the ester group.^{377,378} Catalytic hydroborations of thioalkynes generally proceed with the boryl group adding to the carbon bearing the alkyl group.^{305,376} Conversely, a more recent report has shown the inverse regioselectivity can be strongly favoured using a copper(i) catalyst and pinacolborane (Scheme 59).³²⁰

A ruthenium system was found to catalyse the preferential *trans*-hydroboration of internal alkynes, including macrocyclic examples (Scheme 60).⁷⁴ While providing some functional group tolerance, problems with the ruthenium-catalysed *trans*-hydroboration protocol were encountered with conjugated enynes, terminal alkynes and small cyclic substrates, which were either non-reactive, showed poor selectivity, or underwent polymerization. A recent report has demonstrated the *trans*-selective hydroboration of ynamides using a carbene-BH₃ adduct and ZnEt₂ as a catalyst.³⁹⁰

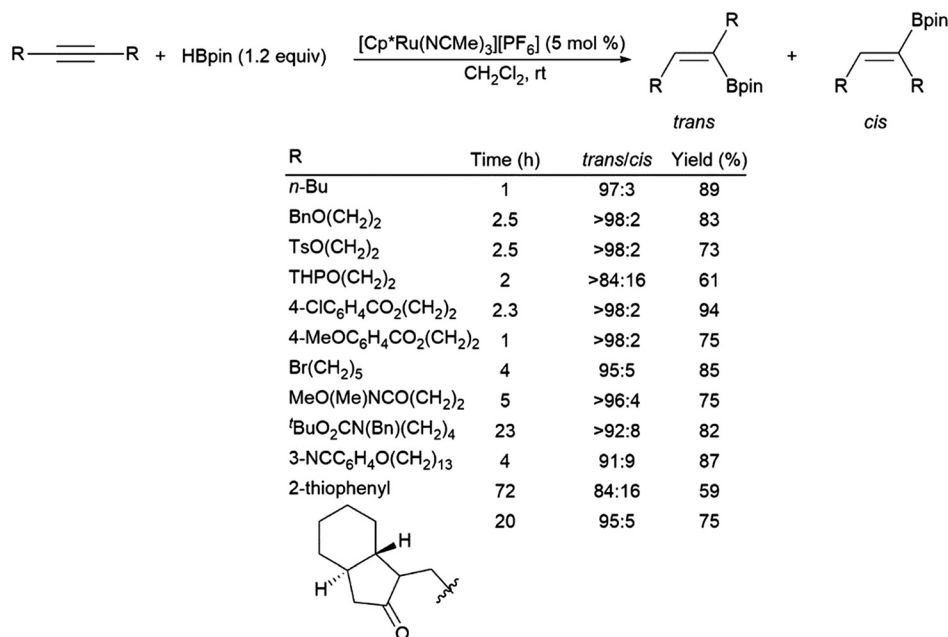
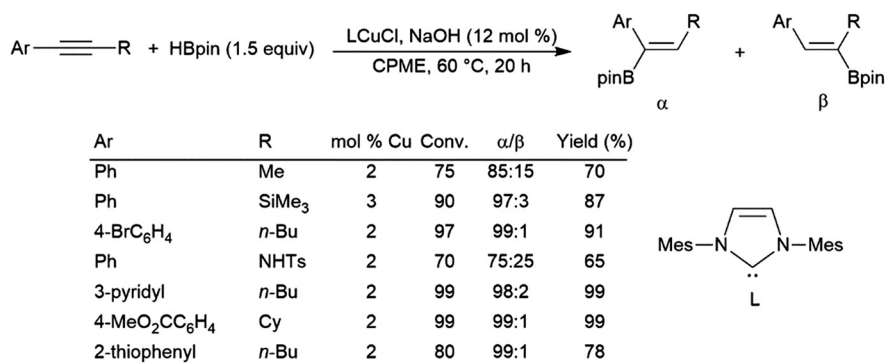
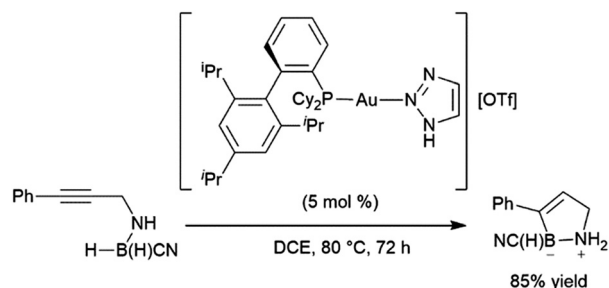
Simple unsymmetrical internal alkynes undergo hydroboration with the boryl group being preferentially added to the carbon bearing the smaller substituent, but selectivities are often relatively poor. Alkynes with aryl and alkyl substituents are catalytically hydroborated with the boryl group typically adding preferentially to the carbon bearing the aryl group. The most regioselective and general protocols for unsymmetrical alkynes use pinacolborane and copper(i) catalysts.^{378,379} Additionally, one of these systems even functions in the presence of air (Scheme 61).³⁷⁹

Bis-hydroboration of diphenylacetylene with catecholborane and rhodium catalysts has also been examined, although selectivity is relatively low, with a maximum of 68% selectivity for the diol following oxidative workup.³⁷⁵ Shi and co-workers have reported an elegant intramolecular hydroboration



Scheme 59 Catalytic hydroborations of thioalkynes using nickel^{304,372} (top) and copper³²⁰ (bottom) catalyst systems.

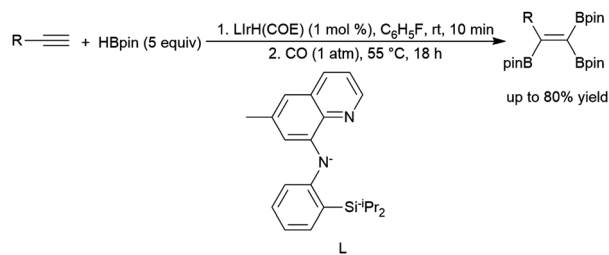
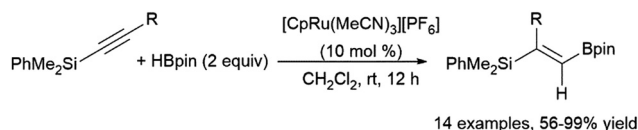


Scheme 60 Ruthenium-catalysed *trans*-hydroborations of internal alkynes.⁷⁴Scheme 61 Copper-catalysed α -selective hydroboration of internal aryl alkynes.³⁷⁹Scheme 62 Intramolecular gold-catalysed hydroboration of internal alkynes.³⁹¹

catalysed by gold(i) complexes in the synthesis of cyclic amine boranes (Scheme 62).³⁹¹ This methodology would later be modified to incorporate the catalyst in a porous organic polymer³⁹² and to include the analogous intramolecular reactions with terminal alkynes.³⁹³

Engle and co-workers demonstrated a stepwise reaction involving dehydrogenative hydroboration of terminal alkynes with HBdan (HBdan = 1,8-diaminonaphthylborane), followed by hydroboration with pinacolborane to generate the 1,1-bis-boryl alkene product.³⁹⁴ 1,2-Bis-boryl alkene products are also accessible: Weber and co-workers reacted a bench-stable manganese(i) alkyl complex and HBpin with terminal alkynes to provide *trans*-1,2-bis-boryl alkene products,²⁶⁹ and Lai and Ozerov produced the *cis*-1,2-bis-boryl products using a Ir/CO/*t*BuNC system.³⁹⁷ A protocol by Ingleson and co-workers employing pinacolborane and a zinc-hydride catalyst was shown to perform dehydrogenative borylation and subsequent bis-hydroboration of terminal alkynes, generating 1,1,1-triborylalkanes.³⁹⁸ Notably, the final step of the reaction demonstrates that the hydroboration of the bis-borylalkene requires the addition of catalytic THF-BH₃ to proceed. Iridium-catalysed hydroboration of a 2-borylalkyne serves as part of the preparation of triboryl alkenes from terminal alkynes (Scheme 63).³⁹⁵



Scheme 63 Iridium-catalysed preparation of triborylalkenes.³⁹⁵Scheme 64 Ruthenium-catalysed *gem*-hydroboration of a silylalkyne.³⁹⁶

Initial dehydrogenative borylation of terminal alkyl or aryl alkynes generates the boryl alkyne, which undergoes hydroboration and subsequent dehydrogenative borylation to give the triboryl alkene. The synthesis of multiboronate esters by catalytic hydroboration has been recently included in a review.³⁷⁰

Another multi-step, one-pot reaction proceeds *via* alkyne hydroboration followed by asymmetric hydrogenation, generating chiral alkylboronate esters.³⁹⁹ One-pot hydrosilylation and asymmetric hydroboration has also been achieved, producing chiral *gem*-(borylsilyl)alkanes.⁴⁰⁰ A ruthenium-catalysed geminal hydroboration of silyl alkynes was reported by Chung, Wu, Sun, and co-workers (Scheme 64).³⁹⁶ Silyl migration *via* a ruthenium carbene intermediate is proposed to allow this transformation. Hydrosilylation of alkynylboranes was found to provide the same products, supporting the proposed migration from a α -boryl- α -silyl intermediate.

4.14 Aldehydes

In the early days of catalytic hydroborations, reactions employing simple aldehydes did not spark much interest. This is likely because the regioselectivity is fixed, with the boryl group adding to the oxygen atom, and the transformation is readily achieved using conventional reagents in the absence of catalysts. Despite this, there is a recent increase of reports on the reaction. A number of catalysts promote the addition of pinacolborane to simple aryl or alkyl aldehydes, including a titanocene(II) catalyst,⁴⁰¹ titanium(IV),⁴⁰² hafnium,⁴⁰³ ruthenium,^{404,405} silver,⁴⁰⁶ rhodium,⁴⁰⁷ manganese,⁴⁰⁸ nickel,^{409–411} zinc,^{412,413} palladium,⁴¹⁴ iron,^{415–420} and copper.^{421,422} Using [Ru(*p*-cymene)Cl₂]₂, aldehydes could undergo hydroboration selectively in the presence of ketone or ester functionalities.⁴⁰⁵ A titanium(IV) amide was also found to be highly selective for hydroboration of aldehydes over their corresponding methyl ketones.⁴⁰² Notably, while both copper(I) and copper(II) catalysts have been reported, the copper(II) catalyst exhibits greater chemoselectivity for aldehydes over ketones.⁴²² A report has highlighted the potential of zirconium amide

compounds as homogeneous and heterogeneous catalysts appended to mesoporous silica nanoparticles.⁴²³ Catalytic reactions involving catecholborane addition to aldehydes are relatively rare, likely due to the relatively rapid uncatalysed reaction, noted in a publication examining rhodium-catalysed addition of catecholborane to carbonyls.⁴²⁴

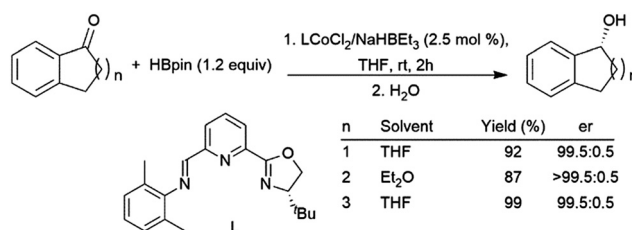
Reusable options for heterogeneous catalysis include iron(II)⁴²⁵ and cobalt(II)⁴²⁶ coordination polymers, Fe₂O₃ nanoparticles,⁴²⁷ along with Co(II)⁴²⁸ or Ti(IV)⁴²⁹ sites in MOFs.

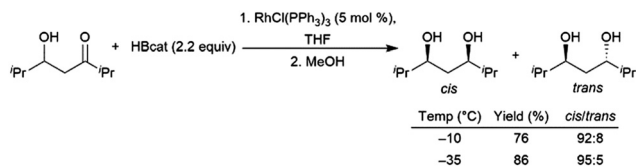
4.15 Ketones

As ketones are a more challenging substrate in the absence of a catalyst, the potential for catalysis and asymmetric catalysis with catechol- or pinacolborane is attractive. In many cases for the hydroboration of carbonyls, the catalyst functions mainly as a Lewis acid, activating the carbonyl carbon for nucleophilic attack by the hydride of the borane reagent. A number of different transition metals have been used to catalyse this reaction,⁴³⁰ including rhodium,^{424,431} titanium,^{401,402,432–438} hafnium,⁴⁰³ molybdenum,³²⁵ silver,⁴⁰⁶ cobalt,^{169,439–442} ruthenium,⁴⁰⁴ palladium,^{414,443} zinc,^{412,413,444–450} iron,^{415,418–420,439,440,451,452} nickel,^{409,410} manganese,^{408,440,453} copper,^{421,422} and yttrium.^{454,455} Chiral diols combined with titanium(IV) complexes provide up to 99:1 enantiomeric ratios in the hydroboration of simple ketones with catecholborane.^{432,434,435,438} The most effective zinc-catalysed hydroboration with catecholborane involves the use of bulky iminoxazoline, which provided *er*'s of at least 92.5:7.5 for most ketones examined.⁴⁴⁷ Hydroborations with pinacolborane can be catalysed by chiral iron and cobalt catalysts, providing excellent enantioselectivity (Scheme 65).^{439,456} Heterogeneous and homogeneous zirconium amide catalysts were also effective for the catalytic hydroboration of ketones.⁴²³ Other heterogeneous systems are also capable of catalysing the hydroboration of ketones including Co(II) sites in MOFs⁴²⁸ and coordination polymers,⁴²⁶ iron(II) sites in MOFs^{457,458} and coordination polymers,^{425,459} Fe₂O₃ nanoparticles,⁴²⁷ a manganese coordination polymer,⁴⁶³ and Ti(IV) sites in a MOF.⁴²⁹

Using an excess of catecholborane, to protect the alcohol, β -hydroxyketones can be hydroborated in a diastereoselective fashion using Wilkinson's catalyst RhCl(PPh₃)₃, producing *cis*-1,3-diols (Scheme 66).⁴³¹

Chen and co-workers have reported reduction of the α -ketone functionality in α -ketoamides, catalysed by chiral oxido-vanadium(V) complexes.⁴⁶⁴ Fascinatingly, enantioselectivity was found to be nearly reversed depending on the use

Scheme 65 Cobalt-catalysed asymmetric hydroboration of cyclic ketones.⁴³⁰



Scheme 66 Diastereoselective rhodium-catalysed hydroboration of a β -hydroxyketone.⁴³¹

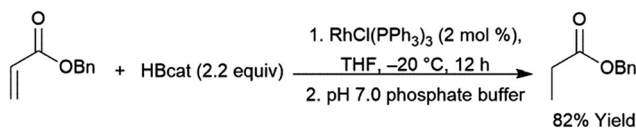
of pinacolborane or catecholborane. The same systems were also used in the hydroboration of β -ketoamides with pinacolborane to achieve moderate to high enantioselectivity.⁴⁶⁵

4.16 α,β -Unsaturated carbonyls

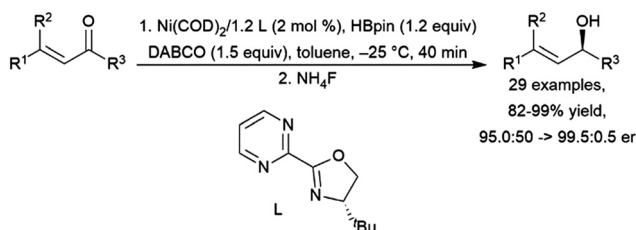
Catalytic hydroborations of α,β -unsaturated ketones, esters, and amides can occur in a 1,4-fashion.⁴⁶⁰ Quenching with an aqueous buffer solution gives the reduced ketone (Scheme 67).

Addition of pinacolborane to cyclohexen-2-one catalysed by a titanocene(II) complex occurs selectively at the ketone, leaving the carbon-carbon double bond intact.⁴⁰¹ Several other catalyst systems have been shown to hydroborate the carbonyl groups while maintaining the carbon-carbon double bond.⁴¹⁷ Protocols for asymmetric hydroboration of the ketone groups of α,β -unsaturated ketones have been developed using a copper(I)/(R)-DBTM-SEGPHOS system,⁴⁶⁶ a manganese(II) pincer catalyst precursor,⁴⁶⁷ a cobalt(II)/chiral 8-oxazoline iminoquinoline system,⁴⁶⁸ and a nickel(0)/chiral bidentate oxazoline-based ligand system (Scheme 68).⁴⁶¹

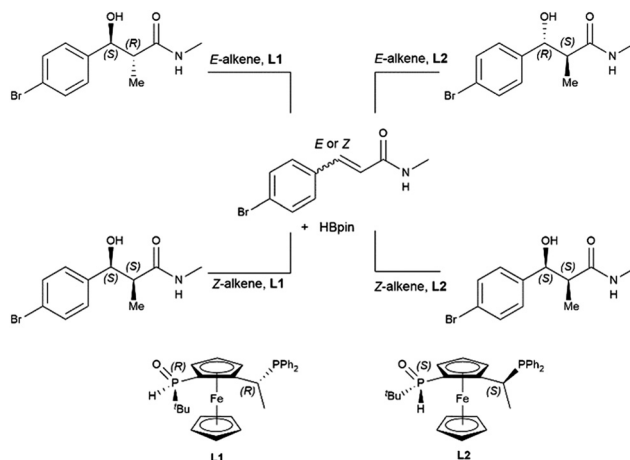
Hydroboration of substituted cyclohexenone substrates by catecholborane, catalysed by a chiral rhodium complex, has been shown to produce moderate yields of the product of alkene hydroboration with low enantioselectivity.¹⁸⁴ Optimization of a cationic rhodium phosphine catalyst precursor gave good yields and high enantioselectivity for the alkene reduction product of α,β -unsaturated amides.⁴⁶² Selection of *Z*- or *E*-alkene and the appropriate chiral ligand allowed for the synthesis of all diastereomers of a product with two vicinal chiral centers created by the hydroboration reaction (Scheme 69).



Scheme 67 Rhodium-catalysed 1,4-hydroboration of an α,β -unsaturated ester.⁴⁶⁰



Scheme 68 Nickel-catalysed hydroboration of the ketone group of an α,β -unsaturated ketone.⁴⁶¹



Reactions done with $[\text{Rh}(\text{COD})_2][\text{OTf}] 1.2 \text{ L}$ (3–5 mol %), 2.0 equivalents HBpin, 12 h, rt, CHCl_3
70–84% yield, dr >20:1 in all cases, 96.0:4.0 \rightarrow 98.0:2.0 er

Scheme 69 Rhodium-catalysed asymmetric hydroboration of *E*- and *Z*-alkene isomers of α,β -unsaturated amides.⁴⁶²

Teskey and co-workers recently reported the photo-controlled hydroboration of unsaturated carbonyls, providing differing regioselectivity depending on whether the reaction was conducted in presence or absence of light (Scheme 70).⁴⁶⁹

Copper(I) catalysts have been employed in the hydroboration of unsaturated carbonyls. For example, the addition of diethylborane to an α,β -unsaturated ketone was carried out as part of a one pot hydroboration/aldol cascade reaction (Scheme 71).⁴⁷⁰ The use of borane instead of silane resulted in improved selectivity for the *syn*-product when acyclic enones are used and for *anti*-products in cyclic enones. A similar procedure has been employed involving the 1,4-hydroboration of unsaturated esters and addition to ketimines.⁴⁷³ Achiral systems were able to provide good diastereoselectivity, and excellent enantioselectivity was obtained with a chiral ligand.

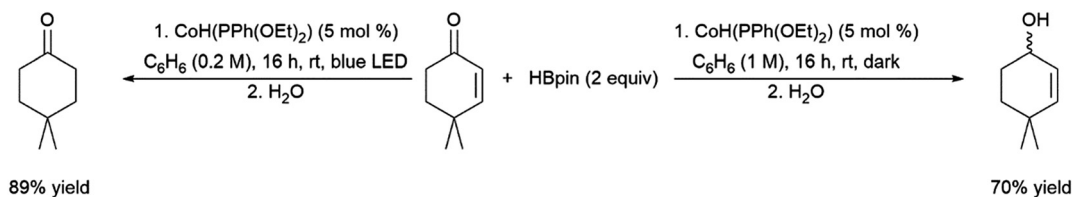
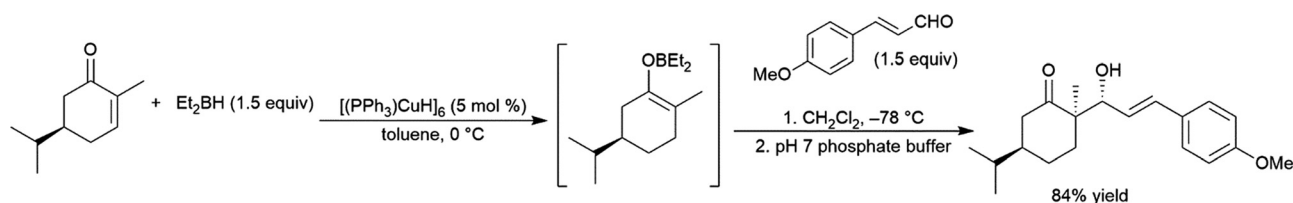
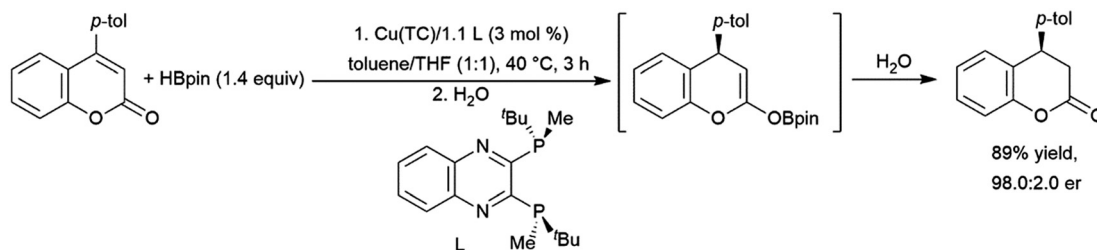
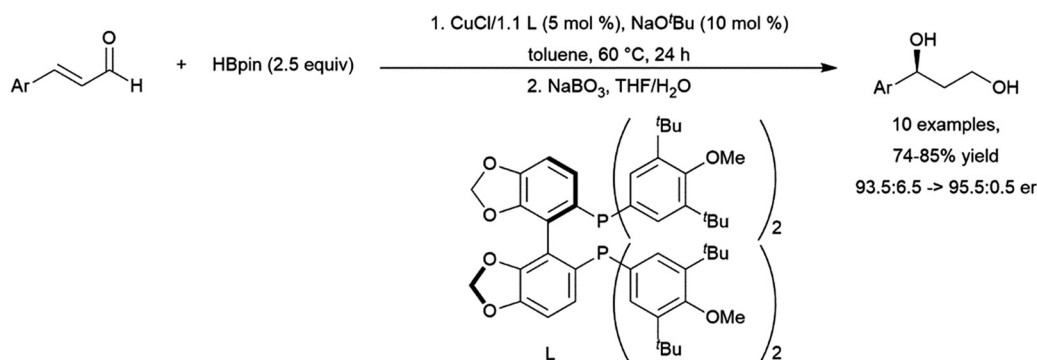
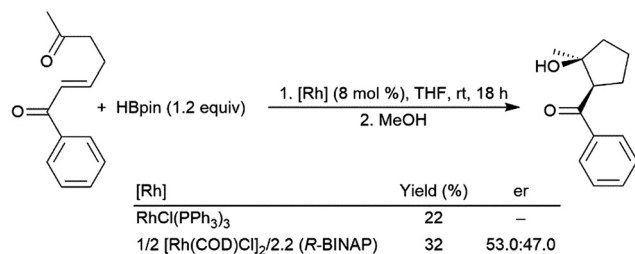
A similar protocol was developed for the asymmetric hydroboration of coumarin derivatives using chiral copper(I) catalysts (Scheme 72).⁴⁷¹ Upon quenching with water, the reduced ketones are obtained in high er's (over 95:5).

The aldol cycloreduction of certain enone-ketone substrates with pinacolborane catalysed by a rhodium(I) complex results in carbon-carbon bond formation, closing a 5- or 6-membered ring (Scheme 73).⁴⁷⁴ While with some substrates the same reaction can be accomplished with catecholborane without the need for a catalyst, the use of pinacolborane and a rhodium catalyst increased the yield in the case of a phenyl-substituted substrate. The near-racemic mixture implies the ring closing step occurs *via* a boron-enolate intermediate as opposed to a rhodium-enolate.

Yun and co-workers have reported the synthesis of chiral β -hydroxy pinacolboronates by asymmetric hydroboration of α,β -unsaturated aldehydes.⁴⁷² The reaction proceeds through initial 1,2-reduction of the aldehyde, followed by the asymmetric hydroboration of the aryl alkene product (Scheme 74).

Gade and co-workers have developed asymmetric hydroboration of *N,N*-disubstituted α -amino ketones and chloroalkyl



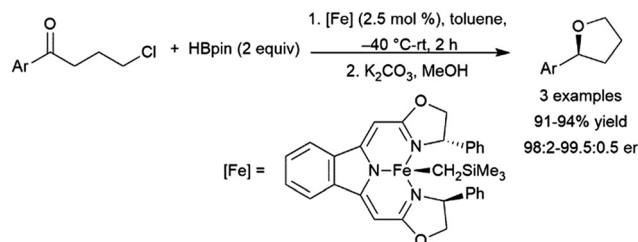
Scheme 70 Photoswitchable cobalt-catalysed hydroboration of α,β -unsaturated ketones.⁴⁶⁹Scheme 71 One-pot hydroboration-aldol cascade reaction.⁴⁷⁰Scheme 72 Asymmetric hydroboration of coumarin derivatives.⁴⁷¹Scheme 73 Bis-hydroboration of an α,β -unsaturated aldehyde.⁴⁷²Scheme 74 Rhodium-catalysed aldol cycloaddition of an enone-ketone.⁴⁷⁴

ketones. Use of basic conditions with α -, β -, γ -chloroketones, and chloro keto ethers caused the hydroboration products to cyclize and produce chiral heterocyclic compounds in good yields (Scheme 75).⁴⁷⁵ A manganese analogue of this iron catalyst precursor was also found to be effective for the asymmetric hydroboration of ketones.^{467,477}

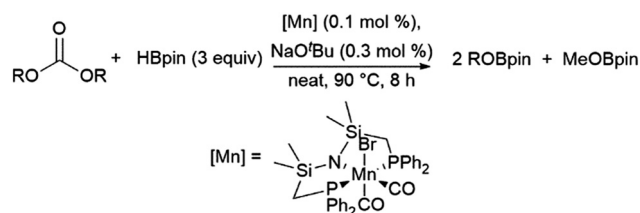
4.17 Esters, amides, acyl silanes, carboxylic acids, and carbonates

Ethyl acetate has been shown to undergo catalytic hydroboration with 2 equivalents of catecholborane using molybdenum





Scheme 75 Generation of chiral heterocyclic compounds via hydroboration.⁴⁷⁵



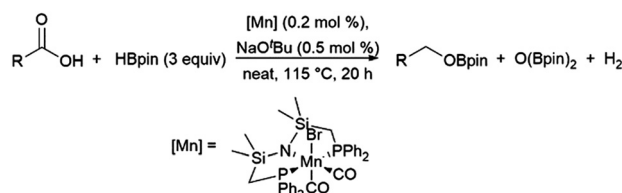
Scheme 76 Manganese-catalysed hydroboration of carbonates.⁴⁷⁶

catalysts, resulting in the formation of EtOBcat and presumably, the loss of MeOBcat.^{325,326} In a similar fashion, manganese^{476,478,479} and ruthenium^{480,481} catalysts were able to reduce carboxylic acids to generate the equivalent alkylboronate and O(Bpin)₂. One of the manganese systems was also found to reduce carbonates, resulting in the loss of MeOBpin and the formation of alkylboronic acid esters (Scheme 76).⁴⁷⁶

The same catalyst system was also found to be effective for the reduction of carboxylic acids, generating the corresponding boron-protected alcohol, O(Bpin)₂, and hydrogen (Scheme 77).⁴⁷⁶ Similarly, a vanadium(III) catalyst was able to promote the deoxygenation of esters and carboxamides.⁴⁸² The deoxygenation of amides can be achieved using yttrium,⁴⁸³ zirconium,⁴⁸⁴ and manganese⁴⁸⁵ catalysts, and a zinc catalyst was also found to selectively reduce an isocyanate group to a *N*-boryl formamide, a *N*,*O*-bis(boryl)hemiaminal, or a *N*-borylmethylamine using 1, 2, or 3 equivalents of HBpin respectively.⁴⁸⁶ Deoxygenative reduction of amides through use of hydroboration, as well as other methods, has been recently reviewed.⁴⁸⁷

Riant, Leyssens, and co-workers have demonstrated the asymmetric reduction of acylsilanes to generate the corresponding chiral α -hydroxysilanes using a copper(II)-phosphine catalyst and pinacolborane.⁴⁸⁸

A nickel(II) iminophosphinite pincer complex has been utilized in the catalytic reduction of primary and secondary



Scheme 77 Manganese-catalysed hydroboration of carboxylic acids.⁴⁷⁶

amides to their corresponding boryl amines.⁴¹⁰ Hydroboration of esters was complicated by intramolecular boryl group transfer from the initially reduced carbonyl group to the alkoxy group, generating aldehydes in addition to boryl ethers. The hydroboration of *N*-methylsuccinimide proceeded cleanly with the addition of pinacolborane to just one carbonyl group.

4.18 Thioketones

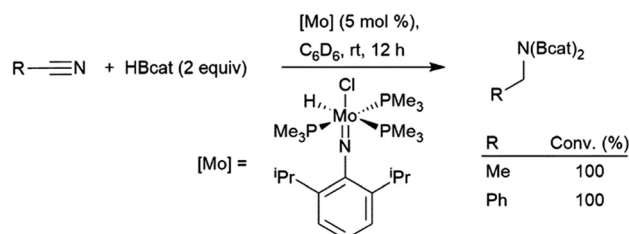
There is one paper describing the rhodium-catalysed hydroboration of thiocarbonyls, forming the expected thioboronate esters and generating trace amounts of borane degradation products and thiols.⁴⁸⁹ Nonetheless, yields were improved when compared to the uncatalysed hydroboration of the same substrate with 9-BBN.

4.19 Nitriles

Uncatalysed addition of HBpin to nitriles proceeds slowly, adding one equivalent of borane.⁴⁹⁰ The monohydroboration can also be effected more efficiently using 9-BBN and a ruthenium catalyst.⁴⁹¹ It has been demonstrated that several molybdenum imido complexes could catalyse the addition of two equivalents of catecholborane to a variety of nitriles (Scheme 78)^{325,326} and that a molybdenum nitride could even convert N₂ to ammonia.⁴⁹² Titanium(IV) amidophosphine-borane complexes were found to add two equivalents of pinacolborane to nitriles.³²¹ Under their reaction conditions, ketones, alkenes, and alkynes underwent hydroboration selectively over nitriles. More recent publications highlight the ability of ruthenium,^{493,494} osmium,⁴⁹⁵ manganese,^{479,485,496} nickel,⁴⁹⁷ cobalt,^{123,498,499} silver,⁵⁰⁰ a MOF-based cobalt system,³⁸⁹ iron,⁵⁰¹ and an iron-indium⁵⁰² catalyst system to catalyse nitrile bis-hydroboration. In one case the diborylamines were shown to subsequently react with aldehydes *in situ*, providing an elegant route from nitriles to aldimines.⁴⁹⁸ The iron-indium system was also found to catalyse the addition of one equivalent each of HBpin and of silane to acetonitrile, forming a borylsilylamine.⁵⁰² This chemistry has been recently reviewed.⁵⁰⁶

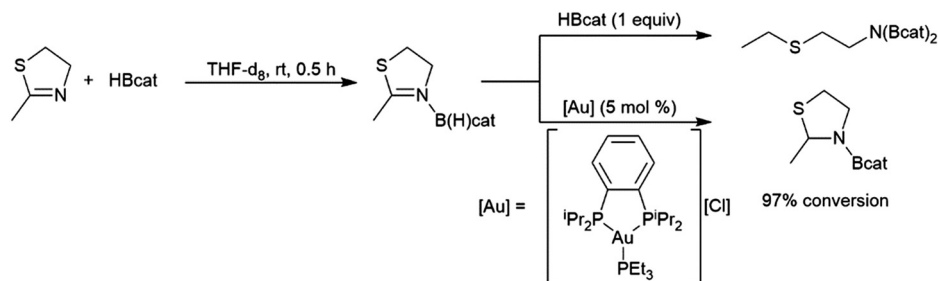
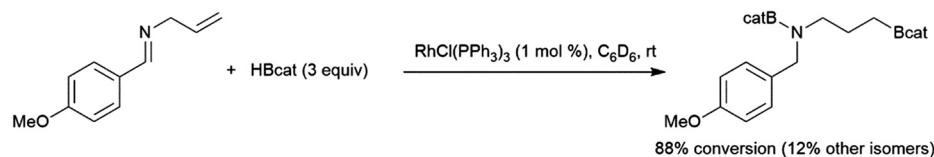
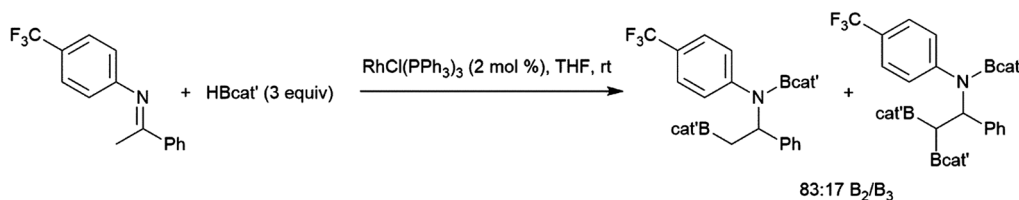
4.20 Imines

The catalytic hydroboration of aldimines and 2-methyl-2-thiazoline using gold(I) precursors has been reported.⁵⁰³ In the hydroboration of aldimines, gold species were found to be more active than RhCl(PPh₃)₃. For 2-methyl-2-thiazoline, selectivity for the *N*-borylamine hydroboration product was much higher with gold than with rhodium and was complementary to



Scheme 78 Molybdenum-catalysed bis-hydroboration of nitriles.^{325,326}



Scheme 79 Hydroboration of 2-methyl-2-thiazoline.⁵⁰³Scheme 80 Rhodium-catalysed hydroboration of an allyl imine.⁵⁰⁴Scheme 81 Rhodium-catalysed hydroboration/borylation of an imine.⁵⁰⁵

the uncatalysed hydroboration, which generates only the adduct in a stoichiometric reaction or the ring-opened product with excess catecholborane (Scheme 79).

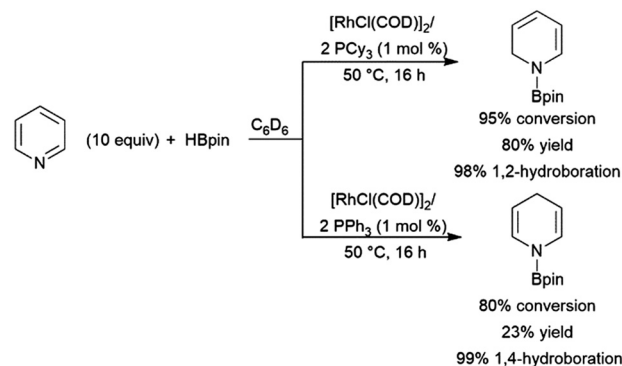
A series of allyl imines react with two equivalents of HBcat in the presence of various rhodium catalysts forming a mixture of products that favour the terminal hydroboration of the alkene and the imine (Scheme 80).⁵⁰⁴ The same study also reported the hydroboration of an aldimine derived from 2-thiophene-carboxaldehyde. A ruthenium(II) dimer was found to catalyse the hydroboration of aldimines.⁴⁰⁴

Rhodium-catalysed addition of 4-*tert*-butylcatecholborane (HBcat') to ketimines gives substrate-dependent mixtures of products arising from multiple hydroborations and β -hydride eliminations (Scheme 81).⁵⁰⁵

Many more reports have since emerged, often accompanying studies of hydroborations of carbonyl groups. These include catalysis using nickel,^{409,411} rhenium,⁴⁰⁷ a cobalt coordination polymer,⁴²⁶ rhodium,⁴²⁴ ruthenium,^{494,507} iron,⁵⁰¹ and zinc.⁴⁴⁹ Most tend to focus on benzylic aldimines, with only isolated examples of the catalysed hydroboration of imines derived from acetophenone⁴²⁴ and benzophenone.⁴⁰⁹ More recently, Gade and co-workers presented a broadly applicable method for the asymmetric hydroboration of *N*-alkyl imines using an iron catalyst (See Scheme 102 for an example).⁵⁰⁸ Eisen, Tamm, and co-workers have demonstrated the mono-hydroboration of carbodiimides using a hafnium(IV) catalyst.⁴⁰³

4.21 Pyridines

Pyridines can undergo hydroboration with pinacolborane catalysed by rhodium(I) complexes.⁵⁰⁹ Careful selection of the phosphine ligand provides the 1,2- or 1,4-addition product in good conversion, although the generation of 1,4-addition product was plagued by the formation of unidentified byproducts (Scheme 82). Since this initial report several publications have emerged detailing pyridine hydroboration. Selective 1,2-hydroborations of pyridines and related compounds have been catalysed by zinc,^{511,512} iron,⁵¹³ and nickel,⁵¹⁴ though selectivity and activity can suffer with *ortho*-substituted pyridines.

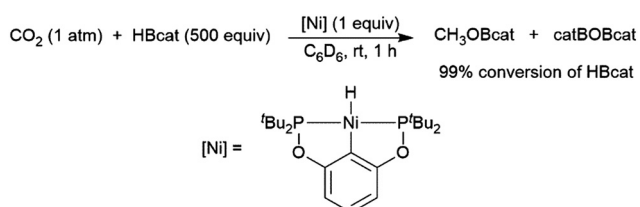
Scheme 82 Rhodium-catalysed hydroboration of pyridine.⁵⁰⁹

A report has also emerged detailing organolanthanide-catalysed 1,2-hydroborations of pyridine derivatives.⁵¹⁵ Selective 1,4-hydroborations of pyridines have also been catalysed by ruthenium,⁵¹⁶ nickel,⁵¹⁷ zinc,⁴⁴⁹ and trivalent zirconium or hafnium-based MOFs.⁵¹⁸ A heterobimetallic iron–copper protocol was found to have enhanced activity and selectivity for the 1,4-hydroboration product when compared to the analogous copper-only reactions.^{519,520}

4.22 Carbon dioxide

Recent interest in chemistry involving the reduction of carbon dioxide has led researchers to look into the hydroboration reaction.⁵²¹ The first transition metal-catalysed catalytic hydroboration of carbon dioxide was reported in 2010. A nickel(II) pincer complex catalyses the reaction of CO₂ with 3 equivalents of catecholborane (Scheme 83).⁵¹⁰ The reaction is performed under 1 atm of CO₂ and in the presence of 500 equivalents of catecholborane, relative to the catalyst. An exceptional turnover frequency of 495 per hour was observed. Since then, several closely related Ni-POCOP systems were also found to be effective in this transformation.^{522–526} A related nickel system containing a P–Si–P pincer ligand catalysed the reduction of CO₂ with HBpin, although it yielded only 13% of the desired MeOBpin product.⁵²⁷ Another P–Si–P pincer ligand system was used with nickel to produce H₂C(OBpin)₂ in good selectivity.¹⁷⁴ Hazari and co-workers found that selectivity could be altered through the choice of nickel or palladium-based catalyst, ligand, borane, and reaction conditions.⁵²⁸ Guan and co-workers also reported a palladium-POCOP catalyst system capable of the efficient and selective reduction of CO₂ to MeOBcat and O(Bcat)₂.⁵²⁹

A copper(I) catalyst system capable of reducing carbon dioxide with HBpin to generate HCO₂Bpin, which could be protonated or used *in situ* as a formylation reagent for primary amines and some secondary amines (Scheme 84) was reported.⁹³



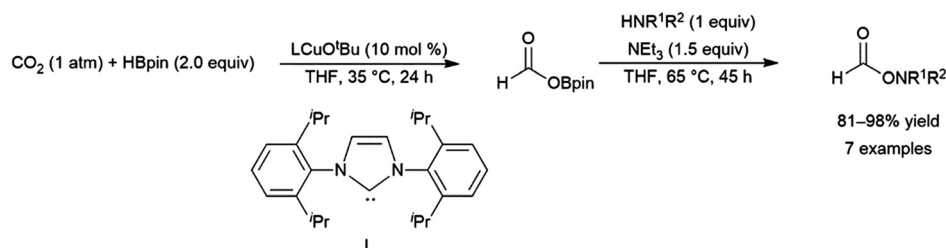
Scheme 83 Nickel-catalysed hydroboration of CO₂.⁵¹⁰

A heterogeneous analogue of this system was shown to be active for the same reaction.⁵³⁰ The catalyst for this system is a MOF which incorporated cationic copper(I) centers and can be readily reused, albeit with slightly diminishing performance. More recently, copper(I) systems based on tripodal phosphine ligands have been employed in the catalytic hydroboration of CO₂ using 9-BBN giving mixtures of CH₂(O-BBN)₂, MeO-BBN, and HCO₂BBN in varying selectivity.^{531,532} A heterobimetallic copper/gold system was also found capable of reducing CO₂ using 9-BBN, with good selectivity for the boryl formate derivative, but relatively low turnover numbers.⁵³³

Ruthenium complexes have also shown catalytic activity in the reduction of carbon dioxide. The first example came in 2012,⁵³⁴ and is a somewhat unique case in that it is proposed to proceed *via* initial insertion of CO₂ into a ruthenium–phosphorus bond and subsequent hydroboration of the pendant carbon–oxygen bond by HBpin. Reaction with a second equivalent of HBpin affords pinBOBpin and CH₃OBpin. The reaction was found to be quite sluggish (0.1 turnovers per hour), however 9 turnovers can be achieved in 96 hours at 50 °C. A zinc hydridotriphenylborate catalyst supported by a macrocyclic polyamine has been demonstrated to have similar reactivity, generating a 1:1 mixture of pinBOBpin and CH₃OBpin through the hydroboration of CO₂ over 16 hours with 10 mol% catalyst.⁴⁴⁹

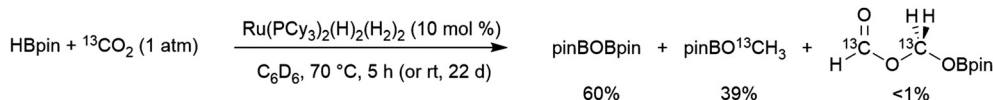
The catalytic hydroboration of CO₂ using other ruthenium complexes has also been reported.⁵³⁵ While pinacolborane was generally completely consumed during the reaction, mixtures of boron-containing products were consistently observed (Scheme 85). It was later confirmed that formaldehyde reacts with borylformate to give pinBOCH₂OCOH.⁵³⁶ Complete consumption of the borylformate product and a larger conversion to pinBOCH₂OCOH was observed upon changing the PCy₃ ligands to P(*c*-C₅H₉)₃ ligands.⁵³⁷ Formaldehyde could be trapped as its corresponding imine in up to 74% yield through the addition of 2,6-diisopropylaniline. A Density Functional Theory (DFT) study of this transformation suggested a ruthenium dihydride carbonyl complex (generated through deoxygenation of CO₂) as the catalytically active complex responsible for the formation of the C₂ species.⁵³⁸

A cationic ruthenium pincer complex in tandem with an alkali metal salt was found to be capable of the transformation of CO₂ to HCO₂Bpin in selectivity as high as 76%.⁵³⁹ The complex was found to be inactive in the absence of the salt, which is proposed to coordinate to HBpin, activating it for



Scheme 84 One pot hydroboration–amination reaction of CO₂.⁹³



Scheme 85 Ruthenium-catalysed hydroboration of CO₂.⁵³⁵

addition to a pendant CO bond in a ruthenium formate intermediate. It was later reported that zinc hydride catalysts were also capable of the selective generation of HCO₂Bpin from CO₂.⁵⁴⁰ In contrast, the use of HBcat generated MeOBcat, while the use of 9-BBN produced a mixture of H₂C(BBN)₂ and MeOBBN.

In an interesting case of ligand-based catalysis, Song and co-workers have demonstrated the ability of ruthenium and zinc diazafluorenyl ligands to add pinacolborane and catecholborane to carbon dioxide.⁵⁴¹ A computational study suggested that the reaction proceeds through a hydride-shuttle mechanism, in which the metal is essentially a spectator while reactivity takes place at the diazafluorenyl C–H bond.⁵⁴²

Palladium catalysts have also shown promise in this transformation. In an elegant study examining the carboxylation of alkynes, a palladium(II) pincer complex was found to be an incredibly active catalyst for the selective reduction of CO₂ to HCO₂Bpin, with turnover numbers of up to 63 500 being observed.⁵⁴³ A molybdenum system was able to catalyse the reduction of CO₂ to H₃COBpin and O(Bpin)₂ using HBpin.⁵⁴⁴ Upon quenching with water, a 58% yield of methanol was obtained. Several Mn(I) catalysts have also been shown to selectively generate methoxyboranes upon hydroboration of CO₂.^{476,545} and the reaction mechanism for this has been elucidated using DFT calculations.⁵⁴⁶

Using Ni and Pd catalysts, Hazari and co-workers studied the effect of varying experimental conditions on the nature of products obtained from the hydroboration of CO₂ with various boranes.⁵²⁸ The authors were able to selectively form products of two (HCO₂BR₂), four (H₂C(OBR₂)₂), and six (MeOBR₂) electron reductions of CO₂ using the same catalyst. Lewis acid additives were found to promote greater reduction of CO₂. Likewise, utilization of catecholborane was found to promote further reduction of CO₂, possibly due to its stronger Lewis acidity (compared to HBpin) and reduced steric bulk (compared to 9-BBN).

Bis-hydroboration of CO₂ using HBpin, HBcat, or 9-BBN, and an iron catalyst has been reported.^{420,547} Most interestingly, they found that the bis-boryl species R₂B–O–CH₂–O–BR₂ are excellent methylene transfer reagents, allowing for the formation of new C–N, C–O, C–C, C=C, and C=N bonds in two-step, one pot protocols. In one such case, L-erythrose was prepared from CO₂ in a chemo-enzymatic cascade.⁵⁴⁸ A cobalt catalyst derived from Co(acac)₃ and Na(HBET₃) was found to reduce CO₂ with a variety of boranes, giving mixtures of products.⁵⁴⁹ With Me₂S–BH₃ for example, (MeOBO)₃ is selectively generated.

The nature of products from the reduction of CO₂ using a copper catalyst system and HBpin could be altered through the nature of a heterobimetallic Cu/M catalyst system.⁵⁵⁰

While some catalyst systems generated HCO₂Bpin, others gave primarily HOBpin or O(Bpin)₂. The authors propose that while copper reduces CO₂ to HCO₂Bpin, the other metal can catalyse further reduction, resulting in the loss of a carbonyl oxygen as O(Bpin)₂.

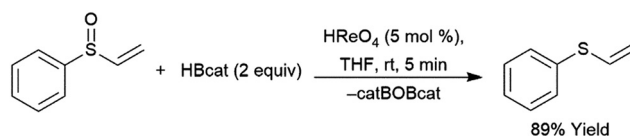
Iridium CNP pincer complexes were able to selectively generate HCO₂Bpin and MeOBcat (and O(Bcat)₂) through the hydroboration of CO₂ with the respective boranes.⁵⁵¹ Rates were enhanced with the addition of water, prompting the authors to suggest that water plays a role in activating the catalyst.

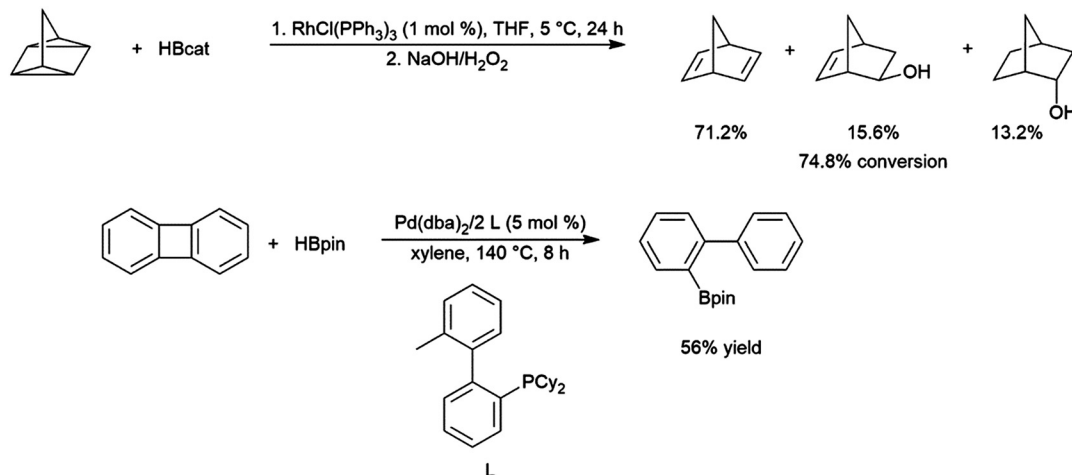
4.23 Sulfoxides and nitro compounds

In chemistry closely related to the reduction of CO₂, which can involve the loss of an oxygen atom as (RO)₂BOB(OR)₂, sulfoxides can be deoxygenated through transition metal-catalysed hydroboration. The reaction was first reported using rhodium(I) catalysts and catecholborane.⁵⁵² Good conversion could also be achieved in the absence of a catalyst, but an excess of borane was required. Subsequent studies showed that rhenium^{553,554} and molybdenum^{554–557} catalysts could also provide the corresponding thioethers in good yields. One advantage to molybdenum and rhenium catalysts is that they are less active as catalysts for the hydroboration of alkenes or alkynes. This allows the selective deoxygenation of sulfoxides with these functional groups (Scheme 86). In a similar fashion, the nitro group in 4-nitroanisole could be reduced to the diboryl amine using an excess of catecholborane and a rhodium(I) catalyst,⁵⁵⁸ to the monoboryl amine using an excess of HBpin and a cobalt(II) catalyst,⁵⁵⁹ or to the amine using HBpin and chromium(0) species.⁵⁶⁰

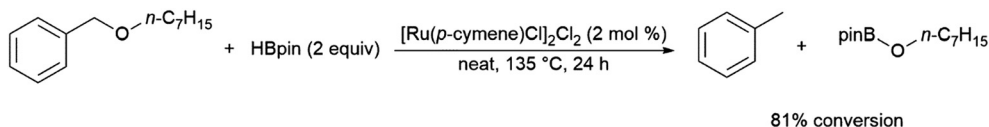
4.24 Other

Partial hydroboration of the strained hydrocarbon quadricyclane has been reported to give norbornenol as part of a mixture of products, with the dominant product being norbornadiene, an isomer of quadricyclane (Scheme 87, top).⁵⁶¹ In a similar fashion, biphenylene can undergo ring-opening reduction using a variety of reducing agents including pinacolborane, formally cleaving a σ-bond to form a borylated 2,2'-biphenyl species (Scheme 87, bottom).⁵⁶² Ring-opening reductions can be performed on cyclopropanes.⁵⁶⁵

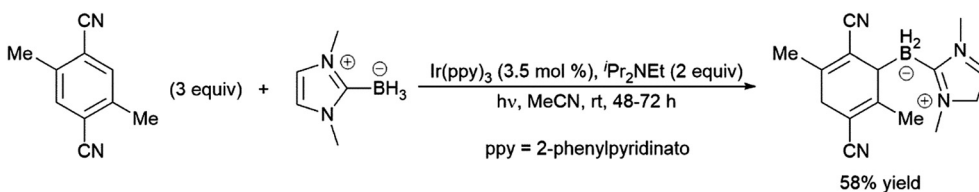
Scheme 86 Rhenium-catalysed deoxygenation of sulfoxides.^{553,554}



Scheme 87 Hydroboration of strained carbon–carbon bonds in quadricyclane (top)⁵⁶¹ and biphenylene (bottom).⁵⁶²



Scheme 88 Ruthenium-catalysed cleavage of ethers.⁵⁶³

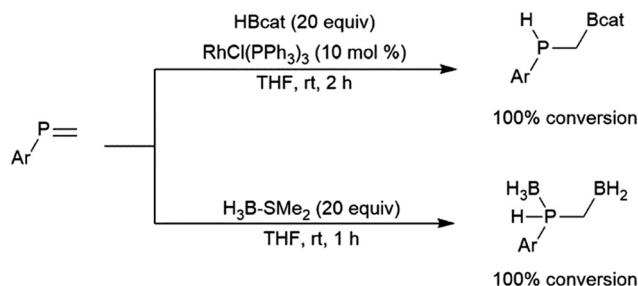


Scheme 89 Hydroboration of an electron-poor aromatic ring using a carbene–borane adduct and an iridium catalyst.⁵⁶⁴

Ring-opening reactions of epoxides have been demonstrated with iron(II)⁵⁶⁶ and nickel(II)⁵⁶⁷ catalyst precursors. While the iron system is believed to break the C–O bond in a ligand-assisted reaction, the nickel system isomerizes the epoxide to the corresponding aldehyde, which then undergoes hydroboration. An yttrium complex was found to catalyse the cleavage of Si–O bonds *via* a hydroboration, which proceeds through a pinacolborane adduct of an yttrium alkoxide complex.⁵⁶⁸ A ruthenium catalyst has been shown to cleave C–O bonds in ethers by hydroboration, under relatively harsh conditions (Scheme 88).⁵⁶³

Electron-poor aromatic rings were shown to undergo 1,4-hydroboration using a carbene–borane adduct and an iridium(III) catalyst in the presence of ethyldiisopropylamine and light (Scheme 89).⁵⁶⁴ A number of other boranes (including pinacolborane) and borane–Lewis base adducts were ineffective in this transformation.

Phosphaalkenes were found to initially form adducts with BH₃; however, when excess Me₂S–BH₃ is added, the adduct undergoes hydroboration (Scheme 90, bottom). Reaction of catecholborane with phosphaalkenes catalysed by RhCl(PPh₃)₃



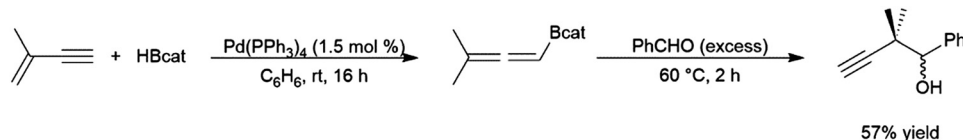
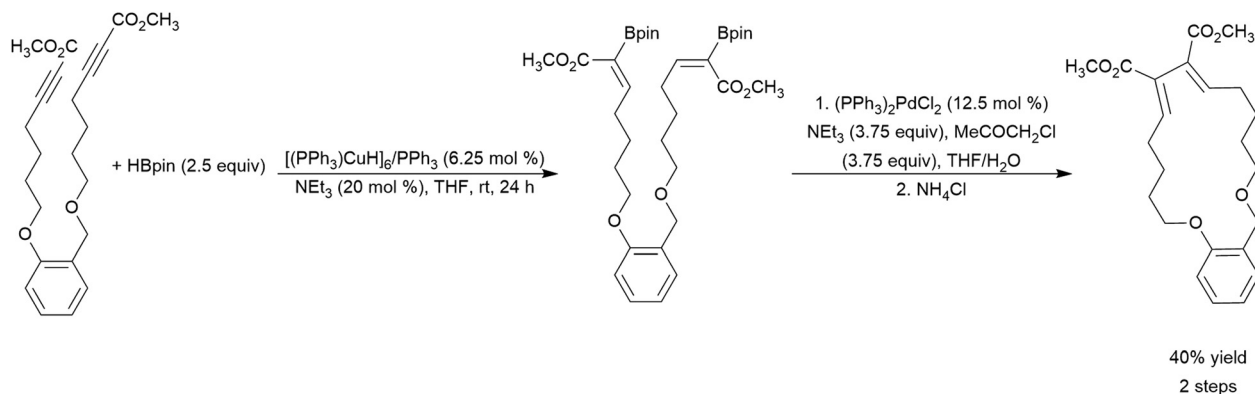
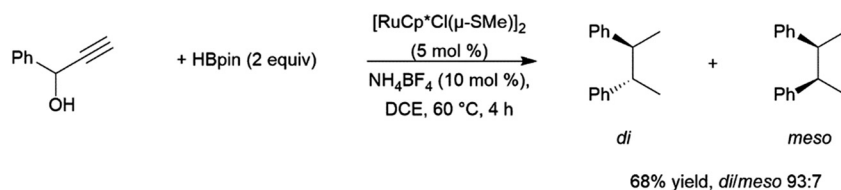
Scheme 90 Hydroboration of phosphaalkenes.⁵⁶⁹

gives the hydroboration product (Scheme 90, top).⁵⁶⁹ With a 1,2-disubstituted phosphaalkene, significant amounts of the hydrolyzed reduction product is also observed.

5 Applications to synthesis

One of the major advantages of the hydroboration reaction is the synthetic versatility of the organoborane product. Though traditionally these products are converted to their corresponding



Scheme 91 Hydroboration as a step in the synthesis of a homoacetylenic alcohol.²¹⁰Scheme 92 Hydroboration-oxidative cyclization of a di-yne.³⁴¹Scheme 93 Hydroboration-homocoupling of a propargylic alcohol.⁵⁷⁰

alcohols *via* oxidative workup, the boryl group can be utilized to install a variety of functional groups. In a one-pot fashion, hydroboration products of dienes^{210,218} and enynes^{210,234} could be added to aldehydes, giving homoallylic and homoacetylenic alcohols respectively (Scheme 91).

Merlic and co-workers prepared a series of bis-vinylboronate species that could undergo oxidative cyclization using palladium(II) catalysts (Scheme 92).³⁴¹

A reductive coupling reaction involving propargylic alcohols, catalysed by a ruthenium complex has been reported (Scheme 93).⁵⁷⁰ The reaction proceeds through initial formation of a ruthenium-allylidene, which undergoes hydroboration with HBpin. The authors hypothesize that trace oxygen generates a radical while eliminating the boryl group. Deprotonation and rearrangement of the radical leads to a ruthenium-alkyne radical, which couples with a second such molecule. The ensuing species is protonated, cleaving the ruthenium-carbon bonds.

5.1 Reactions of boronate esters with organometallic reagents

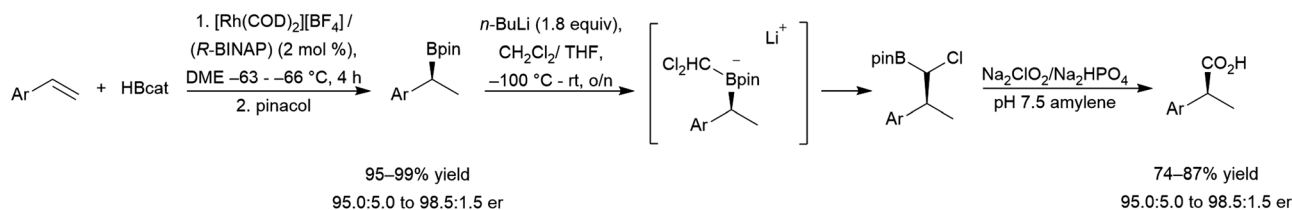
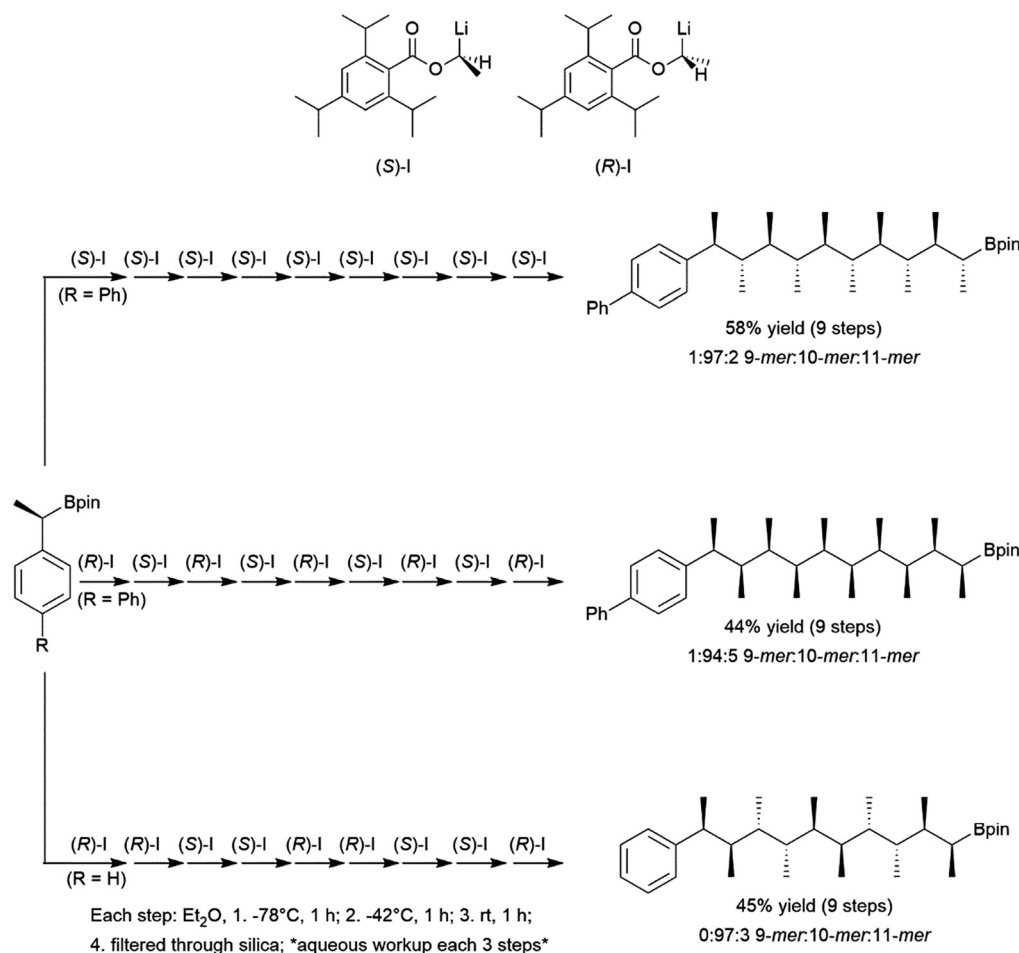
5.1.1 Homologation. Protocols for the homologation of organoboranes have existed for quite some time. Due to their lesser Lewis acidity compared to organoboranes, organoboronate esters require more reactive homologation reagents for the

reaction. Nevertheless, using boronate esters for the reaction offers some advantages, since only the carbon-boron bond can insert the methylene fragment. Using boronate esters for the reaction also allows for the direct homologation of asymmetric boronate ester species following an asymmetric hydroboration. Halomethyl lithium reagents have proven to be effective in the homologation of organoboronate esters. Using a procedure previously developed for homologation,^{572,573} pinacolboronates have been used in the synthesis of chiral 2-arylpropionic acids (Scheme 94), including NaproxenTM and IbuprofenTM (see 5.2 Synthesis of natural products and medicinal compounds).⁵⁷¹

Oxidation of the α -chloroboronate ester with basic hydrogen peroxide provided the corresponding alcohol. An alternative one carbon homologating agent, TMSCHN₂, has also been successfully used to homologate organoboronate esters.⁵⁷⁵ The same reaction has been reported in the reverse order, a one-pot methylenation-hydroboration reaction where a carbonyl group is converted to a terminal alkene using TMSCHN₂ under Rh-catalysis, then catecholborane is added to hydroborate the terminal alkene.⁵⁷⁶

Multiple homologations occur when LiCH₂Br or LiCH₂I are employed in the reaction,⁵⁷⁷ thus LiCH₂Cl is the reagent of choice for the homologation reaction. Multiple homologation



Scheme 94 A hydroboration-homologation-oxidation reaction sequence.⁵⁷¹Scheme 95 Multiple homologation reaction sequence, starting with the product of a chiral hydroboration.⁵⁷⁴

reactions using chiral lithium reagents have been employed to elegantly generate extended chain asymmetric boronate esters and alcohols.⁵⁷⁴ The study showed that the stepwise addition of chiral lithium salts to a chiral biphenylboronate could generate a tailor-made extended chain boronate ester, and the boronate ester could then be readily converted to alcohols or protected alcohols (Scheme 95).

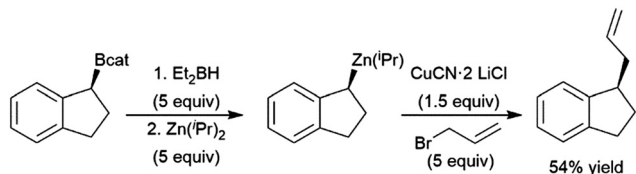
A related carbon–carbon bond forming reaction was used to prepare amino acid derivatives.⁵⁷⁸ In this case the boronate ester must first be converted to a more reactive 9-BBN derivative, prior to homologation and chiral protonation giving the chiral imine ester compound.

5.1.2 Transmetalation. The exchange of boron for zinc has been utilized to functionalize the chiral center of the

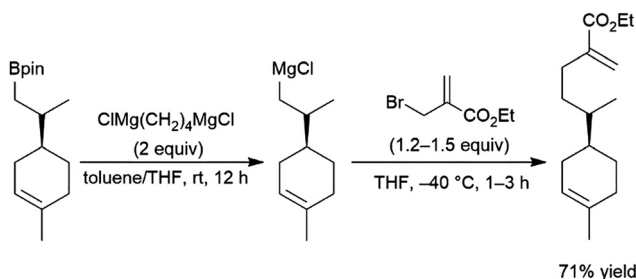
organoboronate hydroboration product.⁵⁷⁹ Following hydroboration, secondary boronate esters must first be alkylated prior to transmetalation with diisopropylzinc, while primary boronate esters can react directly with the zinc reagent.¹⁴⁹ Both pathways preserve the stereochemistry of the hydroboration reaction. Initially the copper(I)-mediated addition to alkyl halides was used in tandem with the transmetalation reaction (Scheme 96), but the straightforward preparation of organozinc compounds also opens the door to other functionalization as well.

Alkylmagnesium species are more nucleophilic and thus potentially more synthetically useful than organozinc compounds, thus there has been an effort to prepare them from organoboronate esters. A method developed for the exchange of





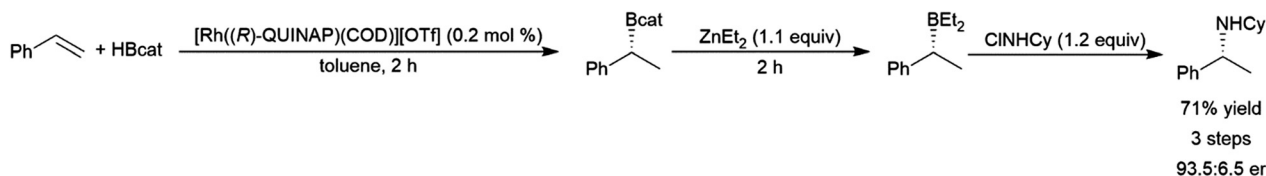
Scheme 96 Zinc transmetalation-alkylation reaction sequence of a boronate ester.¹⁴⁹



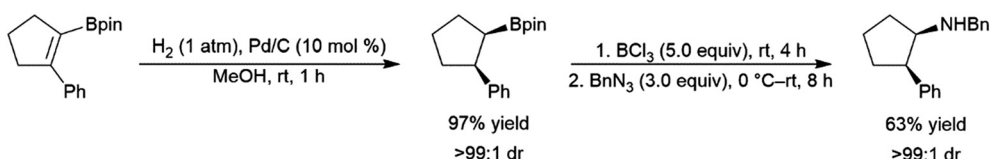
Scheme 97 Magnesium transmetalation-alkylation reaction sequence.¹⁵⁶

magnesium for trialkyl boranes⁵⁸⁰ was later modified to include pinacolboronate esters.¹⁵⁶ These organomagnesium salts were then used in palladium and copper catalysed cross-coupling reactions, 1,2-addition reactions, and alkylations (Scheme 97).

5.1.3 Synthesis of amines. Organoboronate esters are not sufficiently reactive to directly react with an amine, but the boryl group can be readily replaced with an amine upon the generation of a trialkylborane using dialkylzinc or Grignard reagents. The most commonly used reagents for the transformation are $\text{H}_2\text{NSO}_3\text{H}$ and ClNHR (Scheme 98).^{300,581} Notably, only the more favoured migration of the benzyl group occurs in the case of the benzylic diethylborane. The stereochemistry is preserved throughout the reaction. In an effort to generate the tertiary amine, the use of Et_2NCl provided a racemic product in low yields. The reaction has been used as part of the synthesis of Sertraline, a powerful antidepressant often prescribed for depression, anxiety, and other mental conditions.⁵⁸²



Scheme 98 Hydroboration-amination reaction sequence.¹³⁰



Scheme 99 Hydrogenation-amination of a vinyl boronate ester.⁵⁸³

An alternative approach to the same reaction has been published, where the boronate ester is first converted to the RBCl_2 derivative through reaction with BCl_3 , prior to addition of benzyl azide to generate the amine (Scheme 99).⁵⁸³ A very similar intramolecular amination was reported, where an organic azide containing a pendant boronate ester group reacts following the conversion of the boronate ester to a difluoroborane.⁵⁸⁴

Using rhodium-catalysed hydroboration, alkylboronate esters were prepared and were found to be suitable radical precursors for addition to methyl acrylate. In addition to a protected cyclohexenol derivative (Scheme 100), (*S*)-(-)-limonene and norbornene were suitable starting materials for the multistep synthesis.¹⁵⁵

5.2 Synthesis of natural products and medicinal compounds

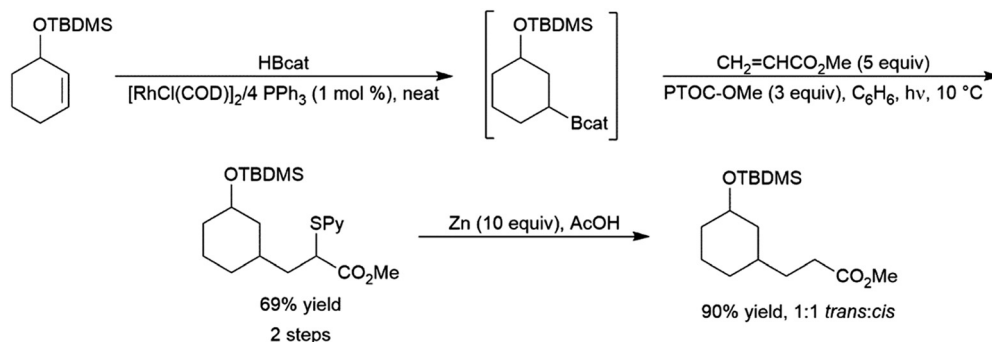
The asymmetric hydroboration of aryl alkenes has been exploited in the synthesis of Ibuprofen[™] and Naproxen[™], two popular anti-inflammatory drugs. An asymmetric hydroboration, followed by homologation gave Ibuprofen[™] in 74% overall yield, with 96.5:3.5 er (Scheme 101).⁵⁷¹ A similar protocol gave Naproxen[™] (Scheme 101, right) in 66% yield with 94:6 er.¹¹⁶ An attempt was made to use a stereoselective rhodium catalysed hydroboration in the preparation of (+)-macbecin I, a compound with antibiotic and antitumor properties, however the predominant isomer was not the desired product.⁵⁸⁵

In a similar fashion, the asymmetric hydroboration of imines was used in the synthesis of (*R*)-Fendiline and (*R*)-Tecalcat, compounds showing promise in the treatment of coronary heart disease and hyperparathyroidism respectively (Scheme 102).⁵⁰⁸

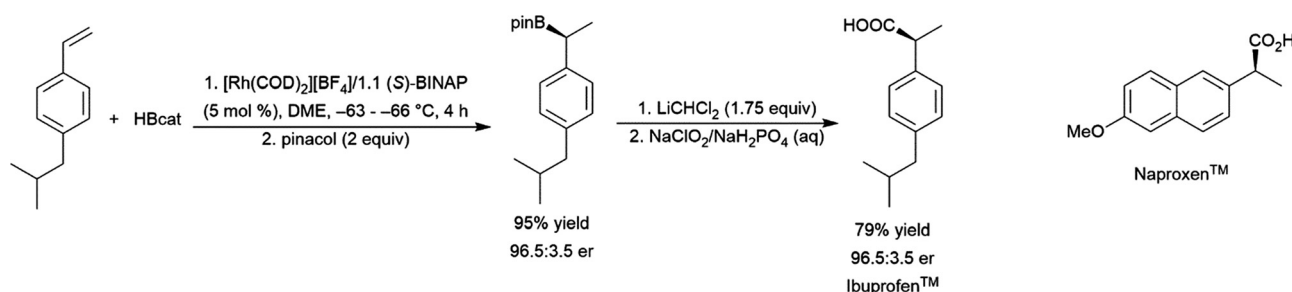
5.2.1 Sertraline. Sertraline was prepared as the minor component of a mixture of *cis*- and *trans*-isomers, following kinetic resolution of the starting racemic dihydronaphthalene starting material *via* asymmetric hydroboration (Scheme 103).⁵⁸² The product was prepared using asymmetric hydroboration of the enantiomerically enriched dihydronaphthalene followed by amination.

5.2.2 Bafilomycin A. A simple rhodium-catalysed hydroboration of a terminal alkene was used to generate the terminal

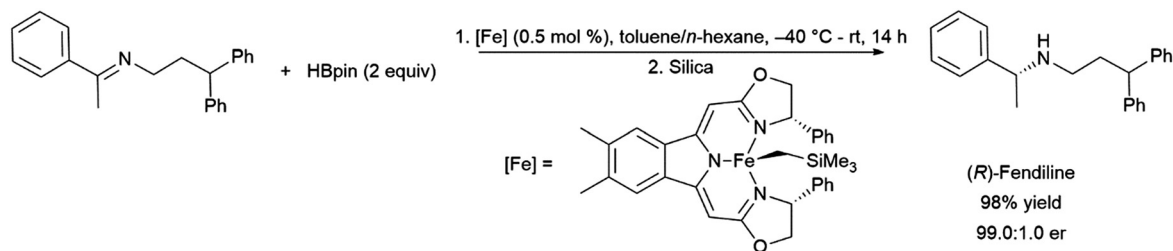




Scheme 100 Addition of methyl acrylate to an alkylboronate ester (PTOC-OMe = *N*-methoxycarbonyloxypyridine-2-thione).¹⁵⁵



Scheme 101 Preparation of Ibuprofen™ from its corresponding styrene.⁵⁷¹



Scheme 102 Preparation of (*R*)-Fendiline via asymmetric hydroboration of an imine.⁵⁰⁸

boronate ester and then the corresponding alcohol as part of the total synthesis of Bafilomycin A, a natural product isolated from *Streptomyces griseus* which has shown antibacterial, antifungal, and immunosuppressing properties.⁵⁸⁹

5.2.3 (+)-Catalponol. A stereoselective palladium-catalysed hydroboration of a 1,3-diene was used as the final step in a catalytic asymmetric synthesis of (+)-catalponol, a natural product exhibiting antitermitic activity isolated from *Catalpa ovata* (Scheme 104).⁵⁸⁶ Interestingly, conversion and selectivity in this reaction was improved by using catecholborane instead of pinacolborane.

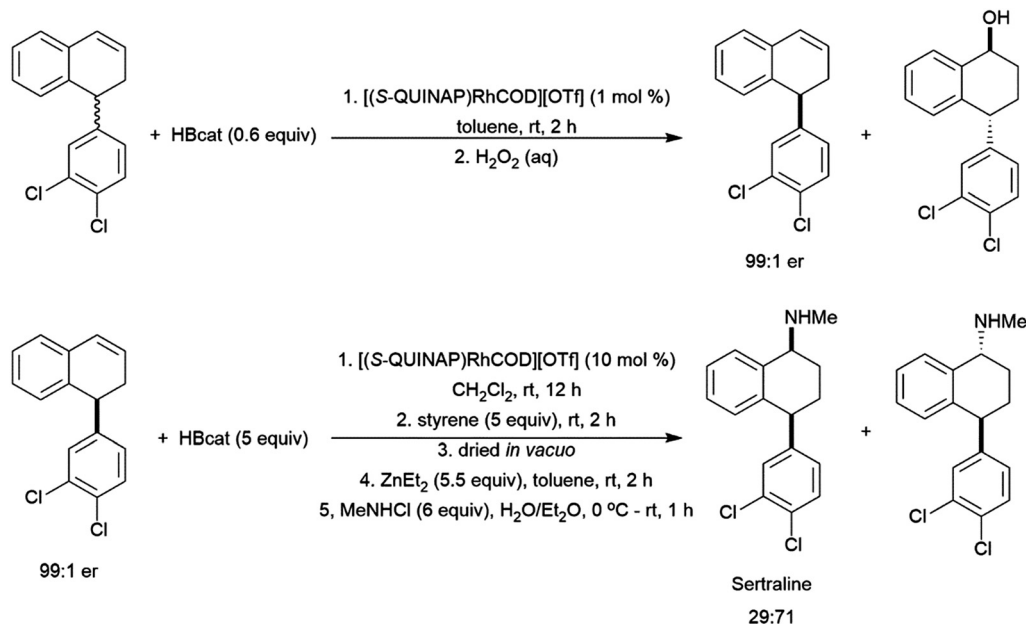
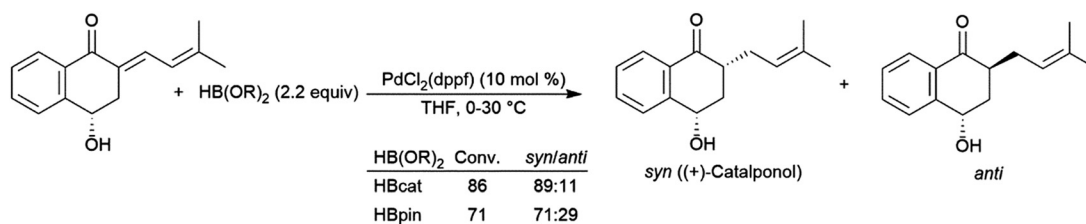
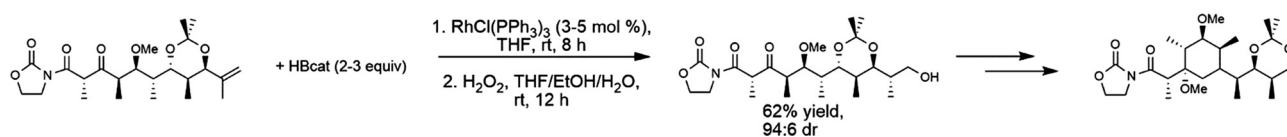
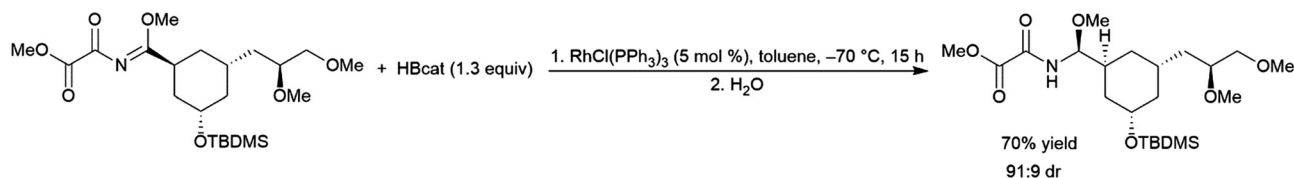
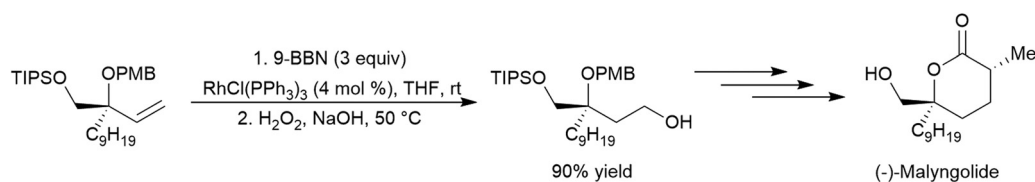
5.2.4 Lonomycin A. A diastereoselective hydroboration of 1,1-disubstituted alkenes was employed for the preparation of a synthon of Lonomycin A (Scheme 105), a complex antibiotic with 23 stereogenic centers.¹⁴⁷ The reaction, catalysed by Wilkinson's complex, proved to be highly diastereoselective and complementary to selectivity obtained in an uncatalysed variant using diisiamylborane. The rhodium-catalysed version gave the desired isomer in 94:6 diastereoselectivity.

5.2.5 Pederin. Pederin, a compound isolated from beetles of the genus *Paederus*, has been found to block mitosis, inhibiting protein and DNA replication, and shows promise in anticancer applications. A complete synthesis of pederin incorporating a stereoselective 1,4-hydroboration of an *N*-acylimide as a key step has been published (Scheme 106).⁵⁸⁷ Other hydroboration procedures and hydrogenations that were attempted failed to produce the desired diastereomer in good selectivity.

5.2.6 (–)-Malngolide. A potent antibacterial compound, (–)-malngolide, was prepared via a route which incorporated a rare rhodium-catalysed hydroboration of an alkene using 9-BBN (Scheme 107).⁵⁸⁸

5.2.7 (+)-Discodermolide. Several borylation steps form part of a total synthesis of (+)-discodermolide (Fig. 2), a polyketide with anticancer properties isolated from a deep-sea sponge.²²¹ A key step in the synthesis is a nickel-catalysed hydroboration of a diene (Scheme 108). Several borylations



Scheme 103 Preparation of sertraline, including kinetic resolution of the starting alkene through asymmetric hydroboration.⁵⁸²Scheme 104 Preparation of (+)-catalponol through hydroboration.⁵⁸⁶Scheme 105 Preparation of a synthon of Lonomycin A, the hydroboration-oxidation of an alkene.¹⁴⁷Scheme 106 The hydroboration of an *N*-acyl imidate included in the synthesis of pederin.⁵⁸⁷Scheme 107 Catalytic hydroboration of an alkene as part of the synthesis of (-)-malyngolide.⁵⁸⁸

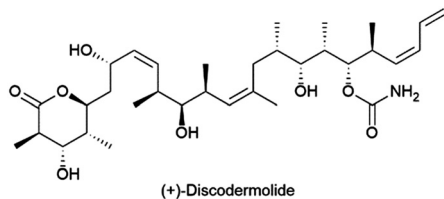
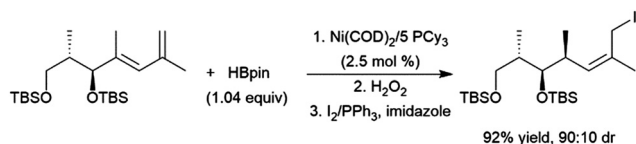
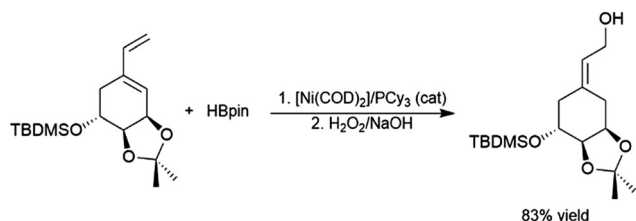


Fig. 2 (+)-Discodermolide.

Scheme 108 Hydroboration of a diene as a step in the preparation of an intermediate in the preparation of (+)-discodermolide.²²¹Scheme 109 Nickel-catalysed hydroboration-oxidation in the preparation of an intermediate en route to vitamin D₃.⁵⁹⁰

using B₂pin₂ were also used in the synthesis, as was an iridium-catalysed hydroboration of a terminal alkene.

5.2.8 Vitamin D₃. The nickel-catalysed 1,4-hydroboration of dienes has been employed in the synthesis of a precursor for a fragment of vitamin D₃ (Scheme 109). This procedure shows promise in the synthesis of analogues of these highly bioactive molecules.⁵⁹⁰

6 Comparison with other methods

6.1 Other hydroborations

The uncatalysed hydroboration reaction has been mentioned extensively in this chapter and is obviously closely related to the transition metal-catalysed variant. The biggest downside to the uncatalysed version is that more reactive boranes and/or harsher reaction conditions are required in general, and the selectivity can be somewhat limited. Catalysis by transition metals can offer complementary and often superior selectivity, and also asymmetric induction through the use of chiral catalysts. Catalysis can allow for more stable boranes to be used, facilitating isolation (for example, pinacolborane-derived products are often stable to column chromatography).

Other catalysts have also been used in catalytic hydroborations, including lanthanides,^{76,77,515,591} magnesium^{592–596} and, more recently, frustrated Lewis pairs.^{597–602} While these catalysts are effective and often quite selective, the lack of

participation from d-orbitals makes selectivity generally similar to uncatalysed hydroborations.

Recent reviews have covered alkali and alkaline earth-catalysed hydroborations,⁶⁰³ organolanthanide- and organo-actinide-catalysed hydroborations,⁶⁰⁴ and aluminum-catalysed hydroborations.⁶⁰⁵

6.2 Reactions of B₂(OR)₄

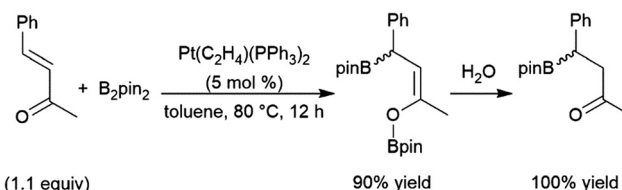
Recent years have seen a rapid expansion in the exploration of the chemistry of B₂(OR)₄ reagents, in particular B₂pin₂. Among the most relevant developments include transition metal-catalysed diboration and boryl addition reactions. This area has recently been reviewed.⁶⁰⁶

Diborations catalysed by zero-valent platinum complexes tend to proceed *via* a catalytic cycle involving oxidative addition of the B–B bond in a manner very similar to rhodium-catalysed hydroborations.^{607–609} Copper-catalysed diborations are also common and the metathesis pathway is similar to that proposed for copper-catalysed hydroborations.^{610–612} The most obvious difference between diboration and hydroboration is the functionalization at two sites; in 1,2-diborations of simple monosubstituted alkenes, a chiral center is always generated. A comparison of asymmetric cationic rhodium-catalysed generation of 1,2-diboryl alkenes from 1,2-diboration of alkenes and from dihydroboration of alkynes found far superior selectivity for the dihydroboration reaction.³⁷⁵ Although diboration reactions are somewhat new in comparison to hydroborations, they have been studied quite extensively and good asymmetric inductions have been achieved in some cases. For a more detailed description and comparison of the syntheses of multi(boronate) esters from diboration of hydroboration please see recent reviews from Xia, Wu and co-workers,³⁷⁰ and Salvado and Fernandez.⁶¹³

Boryl addition reactions can result in a formal hydroboration. These reactions involve the addition of an electrophilic boryl group followed by quenching with a proton source, which is often methanol. Thus, selectivity in these reactions can often be complementary to that observed in hydroborations. For example, the boryl addition to α,β-unsaturated carbonyls can give the β-boryl carbonyl (Scheme 110).⁶¹⁴

6.3 Hydrosilylation

Silanes are like boranes in a number of ways, perhaps not surprising given their diagonal relationship on the periodic table. Like boranes, silanes possess an E–H bond that is polarized towards the hydrogen atom. Similar catalyst systems

Scheme 110 Platinum-catalysed diboration-protonation of an α,β-unsaturated ketone.⁶¹⁴

to those used in hydroborations are frequently used in hydrosilylations.^{615–617} As is the case with hydroborations, side reactions can occur, including dehydrogenative silylation and hydrogenation. Complete regioselectivity and good asymmetric induction have been elusive.⁶¹⁸

7 Challenges and future directions

The main challenges of hydroboration reactivity include the water sensitivity of reagents and products, competitive reactions that reduce the yield of the desired products (*e.g.*, dehydrogenative borylation),⁶¹⁹ and competing catalytic pathways achieved by other boranes formed *in situ*.^{89,620} Development of methodology which reduces or prevents the occurrence of these challenges would be a beneficial development to this field. Future directions will include continued development of earth-abundant catalysts for reactions with boron reagents, including B₂(OR)₄ species as outlined in the comparison with other methods section.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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