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Hydroboration of allenes: Catalytic and non-catalytic strategies for selective functionalization

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ABSTRACT

Hydroboration of allenes is a useful method for the synthesis of unsaturated organoboron compounds, which serve as versatile intermediates in organic chemistry. The transformation presents notable challenges arising from competing regio- and stereoselective pathways, potential rearrangements, and the risk of overreduction. This review presents a systematic overview of both non-catalytic and transition metal-catalyzed hydroboration of allenes, emphasizing mechanistic features and selectivity trends. Non-catalytic approaches using highly reactive boranes allow for efficient transformations, while catalytic systems offer broader structural diversity and improved control through ligand and metal tuning. The current limitations and synthetic potential of each approach are discussed in the context of their applicability to organic synthesis.

1. Introduction

Allenes, characterized by two contiguous (cumulated) carbon-carbon double bonds, exhibit unique electronic and steric properties that distinguish them from typical isolated alkenes, alkynes or 1,3-conjugated dienes and diynes. Their orthogonal π-orbitals allow for diverse reactivity patterns, rendering allenes valuable intermediates in the synthesis of complex molecules. In particular, hydroboration—the addition of boron-hydrogen species across unsaturated bonds—has emerged as a powerful strategy for functionalizing allenes, providing access to synthetically valuable unsaturated organoboron compounds. These unsaturated organoboron species serve as key intermediates in downstream derivatizations. Importantly, allene hydroboration has found utility in the total synthesis of natural products, antibiotics, and anticancer agents, underscoring its significance in medicinal and synthetic organic chemistry. [1–14] As illustrated in Fig. 1, several important pharmaceuticals and bioactive molecules have been synthesized using allene hydroboration as a key transformation.

Despite the utility of allene hydroboration, achieving selective transformations remains a significant challenge due to several competing factors. Owing to the presence of two double bonds, process requires precise regioselectivity, as boron may add either to the terminal (γ), or internal β- or α-carbon atoms (Scheme 1a). Additionally, stereoselectivity must be controlled, as hydroboration can occur from different facial orientations, leading to the formation of (*E*)- or (*Z*)-configured allylboranes (Scheme 1b). [15] Additionally, undesired overreduction processes can complicate product isolation and reduce overall selectivity. Furthermore, kinetic versus thermodynamic control plays a crucial role, as initially formed hydroboration products can undergo [1,3]-boratropic rearrangement affecting the distribution of final products (Scheme 1c). The ability to control these selectivities is highly dependent on the steric and electronic effects of the substituents in allene moiety, the choice of hydroborating reagent, the reaction conditions, and the presence of a catalyst. Collectively, these parameters affect the process efficiency and selectivity, and dictate the outcome of allene hydroboration.

Despite the considerable amount of work on allene hydroboration, it has been only briefly and incompletely covered in other reviews focusing on the C—C bond hydroboration. [16–18]. Very recently, Sun published a review about hydroboration of allenes but only regarding transition-metal catalyzed processes. [19] To date, there have been no reviews focusing on both non-catalytic and catalytic allene

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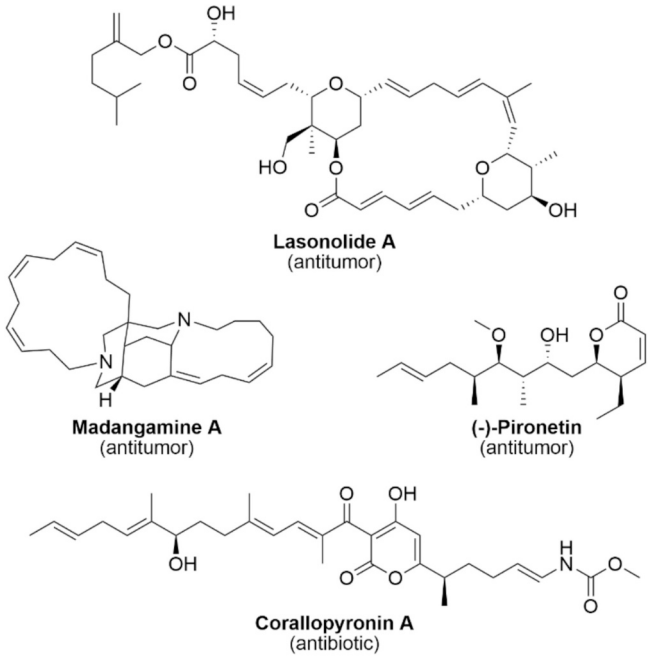
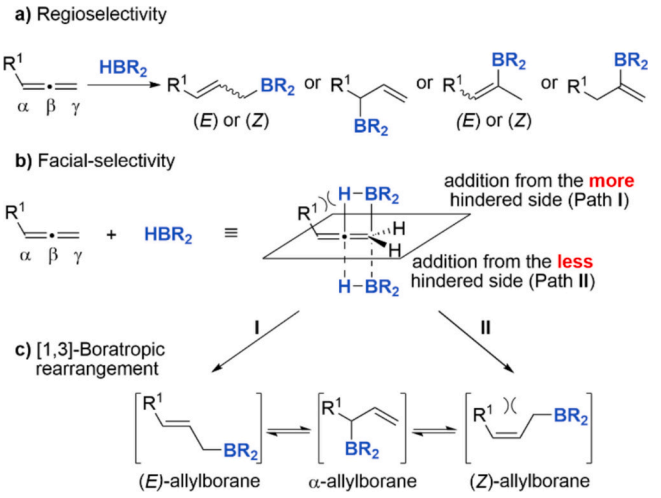


Fig. 1. Selected molecules synthesized via hydroboration of allenes as a key step in their synthetic pathway.



Scheme 1. Hydroboration of allenes.

hydroboration procedures. To address this gap, this review provides a comprehensive analysis of allene hydroboration, with a particular emphasis on selectivity-determining factors, mechanistic insights, and synthetic applications. The discussion is divided into two main sections: non-catalytic and catalytic hydroboration methodologies, each highlighting key advancements in the field, with an additional brief section on hydroboration/dimerization methodologies.

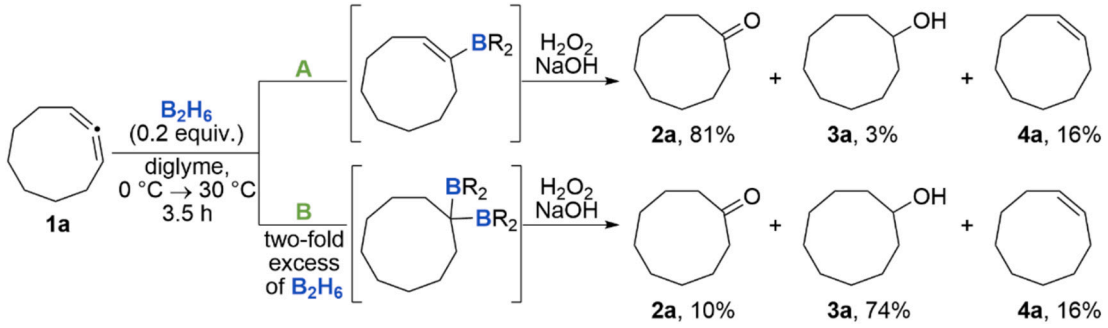
1.1. *Catalyst-free hydroboration of allenes*

The hydroboration of allenes under non-catalytic conditions remains an essential approach for selective syntheses of allylboranes. Early studies on non-catalytic hydroboration focused on the reactivity of simple allenes with dialkyl hydroboranes, revealing fundamental aspects of regio- and stereoselectivity. These findings laid the groundwork for the development of more refined methodologies that leverage steric and electronic effects to control the formation of desired products.

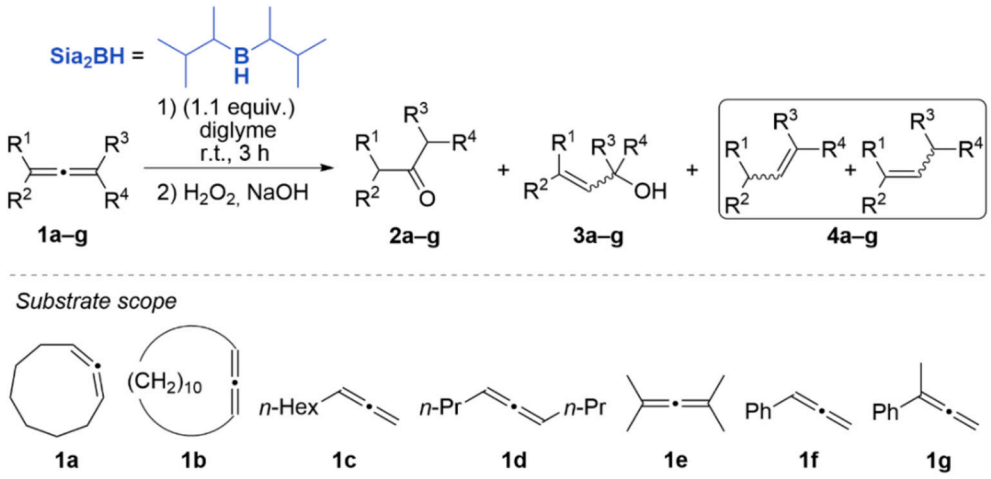
Unlike catalytic hydroboration reactions that generally show catalyst-controlled selectivity, the selectivity of non-catalytic hydroboration relies on the intrinsic reactivity of the allene and the hydroborating reagent. Factors such as reagent sterics, electronic effects, kinetic vs thermodynamic-dependent rearrangements all contribute to the distribution of final products.

In 1963, Devaprabhakara's group reported the first hydroboration of 1,2-cyclononadiene (**1a**) in the absence of a catalyst. [20] Oxidation of the resulting organoborane intermediate yielded cyclononanone (**2a**) as the primary product, along with smaller amounts of cyclononanol (**3a**) and *cis*-cyclononene (**4a**) (Scheme 2, path A). When 1,2-cyclononadiene (**1a**) was treated with a two-fold excess of diborane, the product distribution shifted, favoring the formation of alcohol **3a** as the major product, while the yields of ketone **2a** and alkene **4a** decreased correspondingly (Scheme 2, path B). The authors concluded that diborane predominantly attacks the β-carbon atom of the allenic moiety. Similar results were obtained for the hydroboration of 1,2-cyclodecadiene.

The same group further extended their research by investigating the hydroboration of 1,2-cyclononadiene (**1a**) and 1,2-cyclotridecadiene (**1b**) using disiamylborane (Sia_2BH), a hydroborating reagent which provides greater steric control compared to diborane (Scheme 3). [21] Application of 9- or 13-membered rings explained the influence of the ring size on the reactivity and selectivity of the hydroboration reaction. Since the monohydroboration of allenes can proceed through monoalkyl-, dialkyl-, and trialkylborane intermediates, the distribution of electrophilic attacks by diborane on the α-, β- or γ- (α = γ) carbon atoms of the allenic structure is controlled by the cumulative steric effects arising from the ring size and the intermediate organoboranes. In contrast, the percentage of electrophilic attacks by Sia_2BH is determined solely by the steric effects imposed by the ring size of the allene. For 1,2-cyclononadiene (**1a**), 83% of boron addition occurred at the β-carbon



Scheme 2. Hydroboration of 1,2-cyclononadiene (**1a**) with diborane followed by oxidation.

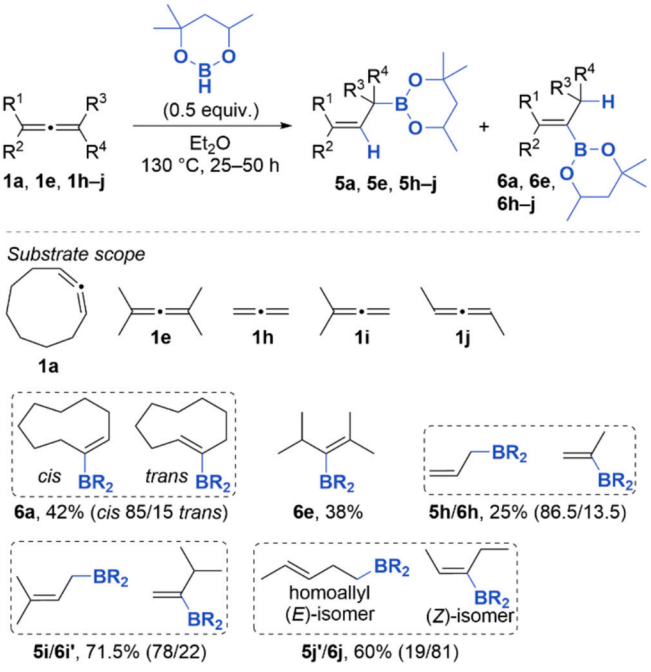


Entry	Allene	Conversion of allene [%]	% Electrophilic addition of borane		Selectivity (**2**/**3**/**4**) [%]
			β-carbon atom	α and γ carbon atom	
1	**1a**	78	83	17	83/12/5
2	**1b**	>99	62	38	61/30/9
3	**1c**	>99	22	78	22/50/28
4	**1d**	>99	67	33	67/23/10
5	**1e**	73.1	>99	-	>99/-/-
6	**1f**	>99	20	80	20/-/80
7	**1g**	>99	12	88	12/-/88

Scheme 3. Hydroboration of allenes (**1a**–**g**) with Sia_2BH followed by oxidation.

atom and 17% at the γ-carbon atom. For the larger 1,2-cyclotridecadiene (**1b**), the regioselectivity shifted to 62% β-carbon and 38% γ-carbon addition (Scheme 3, entries 1–2). In continuation of this study, Devaprabhakara's group also studied the hydroboration of acyclic allenes **1c**–**g** (Scheme 3, entries 3–7). [22] The analysis of products revealed a preferential electrophilic attack of boron on the least hindered γ-carbon atom in terminal allenes **1c**, **1f**, and **1g**. In contrast, boron addition mainly targeted the β-carbon atom in acylic internal allene **1d**, particularly with an exclusive β-addition to tetramethylallene (**1e**).

In 1968, Fish reported the hydroboration of allenes with an air-stable hydroborating reagent – TMDB (4,6,6-trimethyl-1,3,2-dioxaborinane), demonstrating the significant influence of both steric and electronic effects on the regioselectivity and stereochemistry of allene hydroboration. [23] The addition of TMDB to allenes enabled the isolation of stable organoboronates instead of oxidized products. It also revealed that boron addition predominantly occurred at the terminal γ-carbon atom of unsubstituted allenes propadiene (**1h**) and 3-methyl-1,2-butadiene (**1i**) (Scheme 4). In contrary, allenes bearing substituents at both 1- and 3-positions, e.g., 1,2-cyclononadiene (**1a**), 2,4-dimethyl-2,3-pentadiene (**1e**) and 2,3-pentadiene (**1j**), underwent preferential hydroboration at the β-carbon atom. In the case of **1e**, only a single product was isolated, whereas the reaction of 1,2-cyclononadiene (**1a**) yielded a mixture of *cis* and *trans* isomers of **6a**. The product resulting from terminal addition to 2,3-pentadiene (**1j**) was not isolated, however its homoallylic isomer **5j'** was successfully obtained. In the unsymmetrical allene – 3-methyl-1,2-butadiene (**1i**), boron addition on the β-carbon accounted for 22% of the product distribution. The study highlighted that terminally unsubstituted allenic positions are sterically



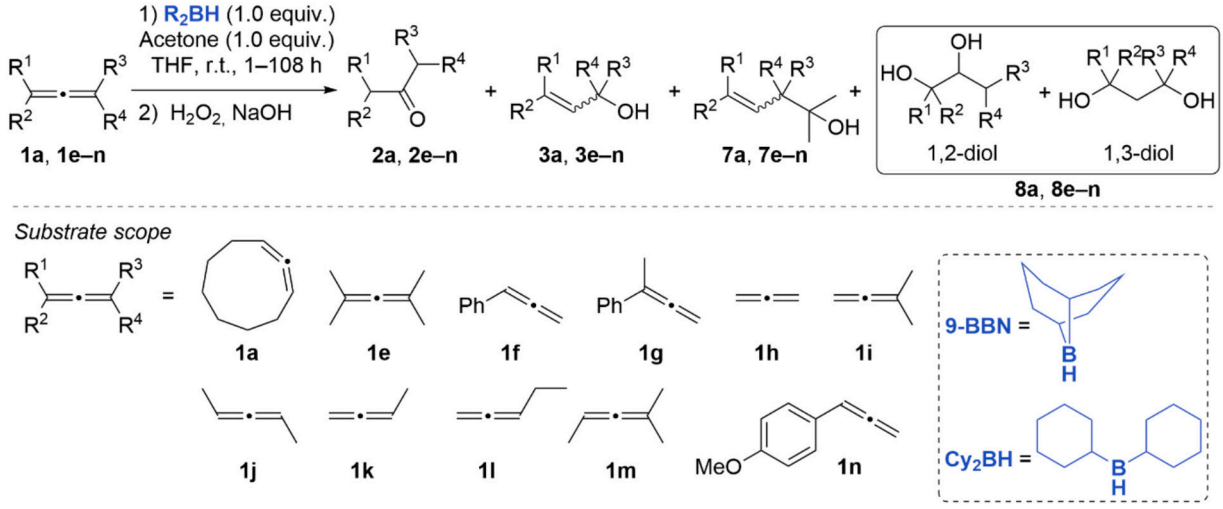
Scheme 4. Hydroboration of allenes (**1a**, **1e**, **1 h**–**j**) with TMDB.

preferred for boron addition, whereas substituted allenic moieties exhibit a stronger influence of electronic effects. The author claimed that this preference can be attributed to the hyperconjugative effect of methyl substituents, which increases the electrophilic predisposition of the central β-carbon atom.

In 1979, Brown et al. described pioneering work on the regioselective hydroboration of allenes with 9-BBN (9-borabicyclo[3.3.1]nonane). [24] The authors showed that 9-BBN predominantly adds to the terminal carbon atom of allenes to form allylborane products, which were subsequently employed in situ in allylboration reactions with acetone and then oxidized to afford the corresponding alcohols. In the case of unsymmetrical allenes, such as 3-phenyl-1,2-butadiene (**1g**), 3-methyl-1,2-butadiene (**1i**), 1,2-pentadiene (**1l**), and 2-methyl-2,3-pentadiene (**1m**), boron-addition occurred selectively to the less substituted allene side (γ-carbon atom) (Scheme 5). This selectivity was attributed to a [1,3]-boratropic allylic rearrangement, facilitating boron migration to the less substituted site. [25] Brown's findings underscored the unique selectivity profile of 9-BBN compared to other dialkylboranes, such as Sia_2BH and Cy_2BH (Scheme 5, entries 12–14), offering an efficient route to allyl derivatives and showcasing the critical role of steric and electronic effects in the hydroboration of allenes.

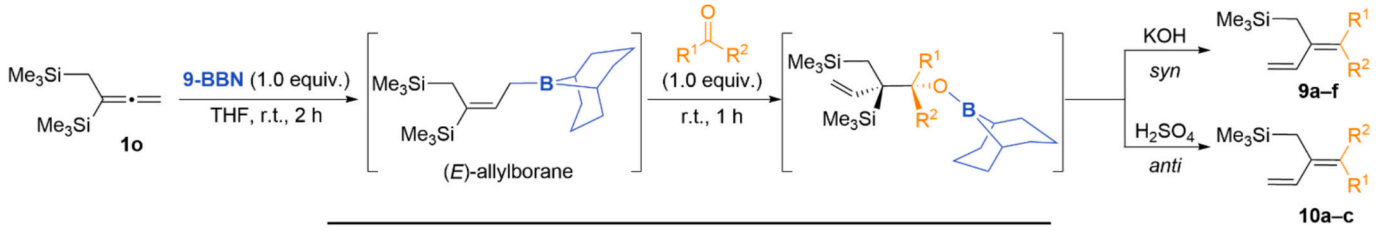
In 1986, Wang et al. disclosed that (*E*)-allylborane, readily prepared through the hydroboration of 1,2-bis(trimethylsilyl)-2,3-butadiene (**1o**) with 9-BBN, could be efficiently condensed with aldehydes and ketones (Scheme 6). [26] The subsequent basic or acidic work-up led to a series of 2-[(trimethylsilyl)methyl]-1,3-butadienes (**9** or **10**) with high isomeric purity. Although the authors did not determine the specific isomer (*E* or *Z*) of the allylborane intermediates, it was later found that the hydroboration of allenes with 9-BBN yields (*Z*)-allylboranes predominantly. These intermediates then undergo rapid thermodynamically controlled (*Z*) to (*E*) isomerization via [1,3]-boratropic allylic rearrangement. [25,27,28]

Four years later, the same group reported the hydroboration of 2-(trimethylsilyl)-2,3-pentadiene (**1p**) and 4-(trimethylsilyl)-2,3-octadiene (**1q**) using 9-BBN and Cy_2BH (Scheme 7). [29] The resulting trimethylsilyl-substituted allylboranes underwent condensation with aldehydes, followed by elimination of hydroxytrimethylsilane under either basic or acidic conditions. These sequential reactions afforded a variety of internal 1,3-butadienes with high isomeric purity. A key aspect of their work was the ability to achieve high diastereoselectivity during the condensation step. By selecting suitable hydroborating reagents and work-up conditions, the geometry of both double bonds in the resulting dienes could be precisely controlled. For example, hydroboration with 9-BBN and Cy_2BH allowed for selective control of the geometry of one double bond, while the Peterson olefination reaction under acidic or basic conditions controlled the geometry of the other



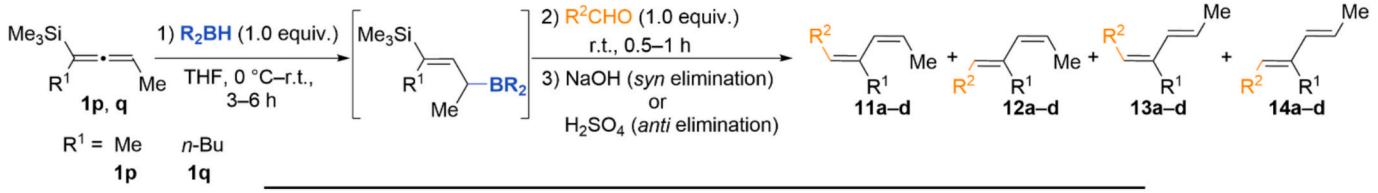
Entry	Allene	R_2BH	Reaction time [h]	Conversion of allene [%]	Selectivity (**2**/**3**/**7**/**8**)
1	**1a**	9-BBN	1	>99	17/-/83/-
2	**1e**		108	92	-/>99/-/-
3	**1f**		4	88.5	8/-/86/6
4	**1g**		4	>99	-/-/93/7
5	**1h**		2.5	50	-/-/-/>99
6	**1i**		2.5	>99	-/-/>99/-
7	**1j**		2	95	-/-/86/14
8	**1k**		1.5	93	-/-/86/14
9	**1l**		1.5	96	2/-/92/6
10	**1m**		No data given	No data given	-/-/>99/-
11	**1n**		4	96	-/-/93/7
12	**1h**	Cy_2BH	3	98	38/-/35/27
13	**1e**		3	97	95/-/-/5
14	**1e**	Sia_2BH	14	97	90/-/5/5

Scheme 5. Hydroboration of allenes (**1a**, **1e**–**n**) followed by allylboration with acetone and oxidation.



Entry	R^1	R^2	Diene	Isolated yield [%]	Selectivity (**9**/**10**)
1	H	Me	**9a**	61	98/2
2	H	*n*-Pent	**9b**	82	97/3
3	H	Ph	**9c**	88	98/2
4	H	(*E*)-CH_3CH=CH	**9d**	59	98/2
5		–$(CH_2)_5$–	**9e**	58	-
6	Me	*n*-Pr	**9f**	68	55/45
7	H	Me	**10a**	50	2/98
8	H	*n*-Pent	**10b**	87	0.5/99.5
9	H	Ph	**10c**	83	2/98

Scheme 6. Stereoselective synthesis of 2-[(trimethylsilyl)methyl]-1,3-butadienes (**9** and **10**).

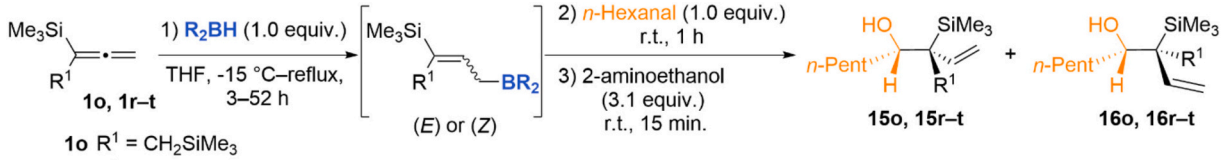


Entry	R_2BH	Work-up conditions	R^1	R^2	Diene	Isolated yield [%]	Selectivity (**11**/**12**/**13**/**14**)
1	9-BBN	NaOH	Me	*n*-Pent	**11a**	77	94/1/4/1
2		H_2SO_4			**12a**	80	1/90/3/6
3	Cy_2BH	NaOH			**13a**	78	-/-/98/2
4		H_2SO_4			**14a**	70	-/-/8/92
5	9-BBN	NaOH	Me	Ph	**11b**	86	92/1/5/2
6		H_2SO_4			**12b**	87	1/91/2/6
7	Cy_2BH	NaOH			**13b**	83	-/-/97/3
8		H_2SO_4			**14b**	82	-/-/5/95
9	9-BBN	NaOH	*n*-Bu	*n*-Pent	**11c**	68	97/1/2/-
10		H_2SO_4			**12c**	65	1/93/2/4
11	Cy_2BH	NaOH			**13c**	77	-/-/97/3
12		H_2SO_4			**14c**	73	-/-/9/91
13	9-BBN	NaOH	*n*-Bu	Ph	**11d**	83	92/1/4/2
14		H_2SO_4			**12d**	86	1/92/2/5
15	Cy_2BH	NaOH			**13d**	85	-/-/97/3
16		H_2SO_4			**14d**	79	-/-/3/97

Scheme 7. Stereoselective synthesis of internal 1,3-dienes by the condensation reaction of aldehydes with the γ-trimethylsilyl-substituted allylboranes.

double bond. This approach enabled the synthesis of all four geometric isomers of various internal 1,3-dienes (**11**–**14**).

Wang et al. also described the stereoselective hydroboration of allenylsilanes, emphasizing the temperature dependence of the product distribution and the ability to synthesize both (*Z*)- and (*E*)-isomers selectively. [27] Hydroboration with Cy_2BH at low temperatures predominantly yielded kinetically favored (*Z*)-isomers (Scheme 8). However, longer reaction times or higher temperatures facilitated allylic rearrangement, resulting in the thermodynamically preferred (*E*)-isomers. The authors demonstrated that the steric factors of the substituents significantly influenced the rate of isomerization. For example, the (*Z*)-allylborane product from the hydroboration of 2-(trimethylsilyl)-2,3-pentadiene (**1r**) readily isomerized to the corresponding (*E*)-allylborane, whereas the (*Z*)-allylboranes from hydroboration of bulkier allenes like **1s** was more stable even at higher temperatures (Scheme 8, entry 9). The control over isomerization allowed selective condensation of the (*Z*)-isomers with aldehydes to afford specific diastereomers with high stereoselectivity. Conversely, allowing the reaction to proceed to equilibrium produced the (*E*)-isomers, which could then undergo condensation to yield the complementary set of



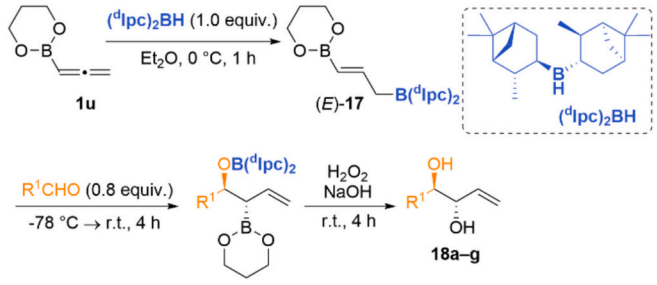
1o $R^1 = CH_2SiMe_3$
1r R^1 = Me
1s R^1 = *i*-Pr
1t R^1 = *n*-Bu

Entry	R_2BH	Allene	Temperature [°C]	Time [h]	Isolated yield [%]	Selectivity (**15**/**16**)
1	9-BBN	**1o**	r.t.	4	93	>99/1
2		**1r**	r.t.	3	89	98/2
3		**1s**	r.t.	24	75	88/12
4		**1t**	r.t.	4	89	97/3
5	Cy_2BH	**1o**	0	4	81	6/94
6			50	20	78	83/17
7			reflux	52	73	94/6
8		**1r**	r.t.	3	93	97/3
9		**1s**	r.t.	4	92	3/97
10		**1t**	-15	6	90	4/96
11			r.t.	3	86	30/70
12			50	7	91	91/9

Scheme 8. Stereoselective synthesis of allylsilanes (**15** and **16**) by hydroboration and the diastereoselective condensations with *n*-hexanal.

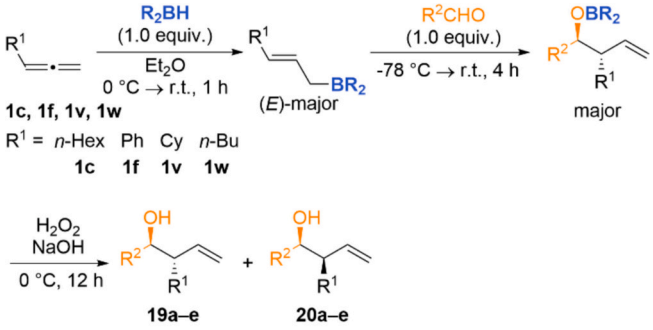
diastereomers. This methodology provided a versatile tool for synthesizing both diastereomers of allylic silanes with high isomeric purity. By adjusting the reaction temperature and hydroborating reagent, Wang et al. successfully demonstrated precise control over the reaction outcome, expanding the utility of hydroboration of allenes in the stereoselective synthesis of complex molecules.

In 1961, Brown and Zweifel reported the synthesis of chiral organoborane – $(^dIpc)_2BH$ (di*iso*pinocampheylborane, see Scheme 9 for its structure). [30] However, its application in the hydroboration of allenes was not realized until 1995, when Brown et al. employed $(^dIpc)_2BH$ for the enantioselective hydroboration of allenylboronate (**1u**) to prepare chiral γ-boryl-(*E*)-allylborane (**17**). This reagent was utilized for the synthesis of enantioenriched *anti*-1,2-diols (**18a–g**) via stereospecific condensation of chiral allylborane **17** with aldehydes (Scheme 9). [31] Hydroboration of allenylboronate (**1u**) with $(^dIpc)_2BH$ initially forms γ-boryl-(*Z*)-allylborane as the kinetic product, which then isomerizes through rapid [1,3]-boratropic allylic rearrangement to yield the thermodynamically favored (*E*)-isomer **17**. The use of $(^dIpc)_2BH$ in this particular context underscores its pivotal role in achieving high diastereo- and enantioselectivity in the synthesis of *anti*-1,2-diols (**18a–g**). Building on this foundational work, in 2002, Flamme and Roush advanced the method by developing a diastereo- and enantioselective synthesis of 1,5-pentenediols via one-pot double allylboration strategy wherein the boronic ester was replaced for tetraphenylethane-1,2-diol moiety. [32] In 2013, they refined this approach further by substituting the boronate unit with a 2,2-dimethylpropanediol ester, enabling the



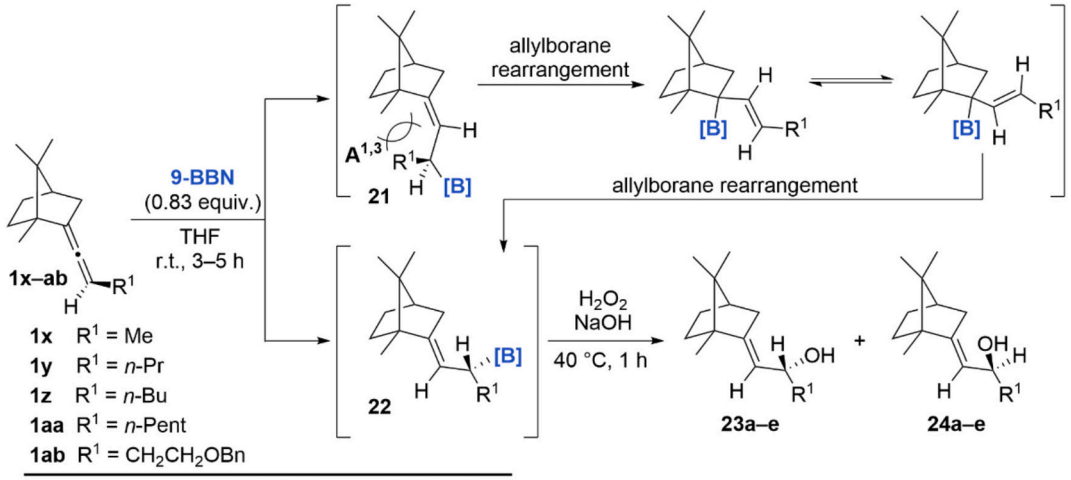
Entry	R^1CHO	Diol	Isolated yield [%]	*ee* [%]	Configuration
1	MeCHO	**18a**	75	92	3*S*, 4*R*
2	EtCHO	**18b**	67	90	3*S*, 4*R*
3	CyCHO	**18c**	70	94	3*S*, 4*R*
4	PhCHO	**18d**	76	95	3*S*, 4*R*
5	PhCHO	**18e**	80	95	3*S*, 4*R*
6	*t*-BuCHO	**18f**	59	95	3*S*, 4*R*
7	CH_2=CHCHO	**18g**	63	-	meso

Scheme 9. Synthesis of *anti*-1,2-diols from the hydroboration of **1u** and subsequent reaction of **17** with representative aldehydes.



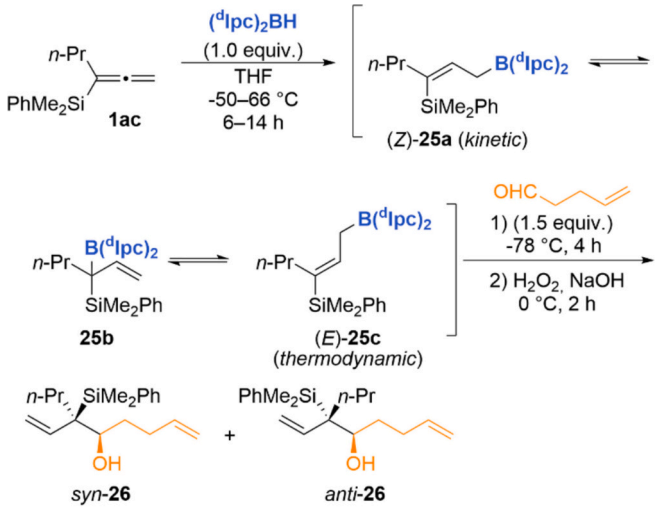
Entry	R_2BH	Allene	R^2	*Anti*/*Syn* [%]	Product *Anti*	Isolated yield [%]	Configuration (*ee*) [%]
1	Cy_2BH	**1c**	Ph	88/12	**19a**	82	-
2		**1f**	Ph	>99/0	**19b**	90	-
3		**1f**	Me	>99/0	**19e**	82	-
4		**1v**	Ph	96/4	**19c**	77	-
5		**1w**	Ph	86/13	**19d**	81	-
6	$(^dIpc)_2BH$	**1c**	Ph	90/10	**19a**	81	3*S*, 4*R* (74)
7		**1f**	Ph	>99/0	**19b**	84	3*S*, 4*R* (84)
8		**1f**	Me	>99/0	**19e**	75	3*S*, 4*R* (80)
9		**1v**	Ph	80/20	**19c**	75	3*S*, 4*R* (80)
10		**1w**	Ph	88/12	**19d**	78	3*S*, 4*R* (78)

Scheme 10. Synthesis of homoallylic alcohols (**19** and **20**) via hydroboration of mono-substituted allenes.



Entry	Allene	Isolated yield (**23**+**24**) [%]	Selectivity (**23**/**24**) (% de)
1	**1x**	66	6/1 (72)
2	**1y**	80	15/1 (88)
3	**1z**	82	15/1 (88)
4	**1aa**	77	18/1 (89)
5	**1ab**	71	15/1 (88)

Scheme 11. Synthesis of allylic alcohols **23** and **24** via hydroboration-oxidation of chiral allenes with 9-BBN.

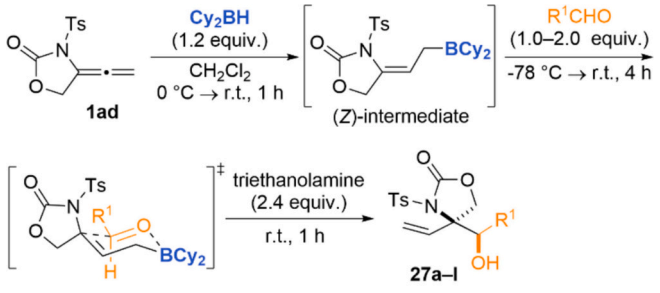


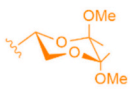
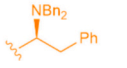
Entry	Temp [°C]	Time [h]	*Syn*/*Anti*	Isolated yield [%]
1	-50	14	10/1	67
2	-20	6	8/1	79
3	25	6	6/1	77
4	66	6	3/1	76

Scheme 12. Synthesis of β-hydroxyallylsilanes **26**.

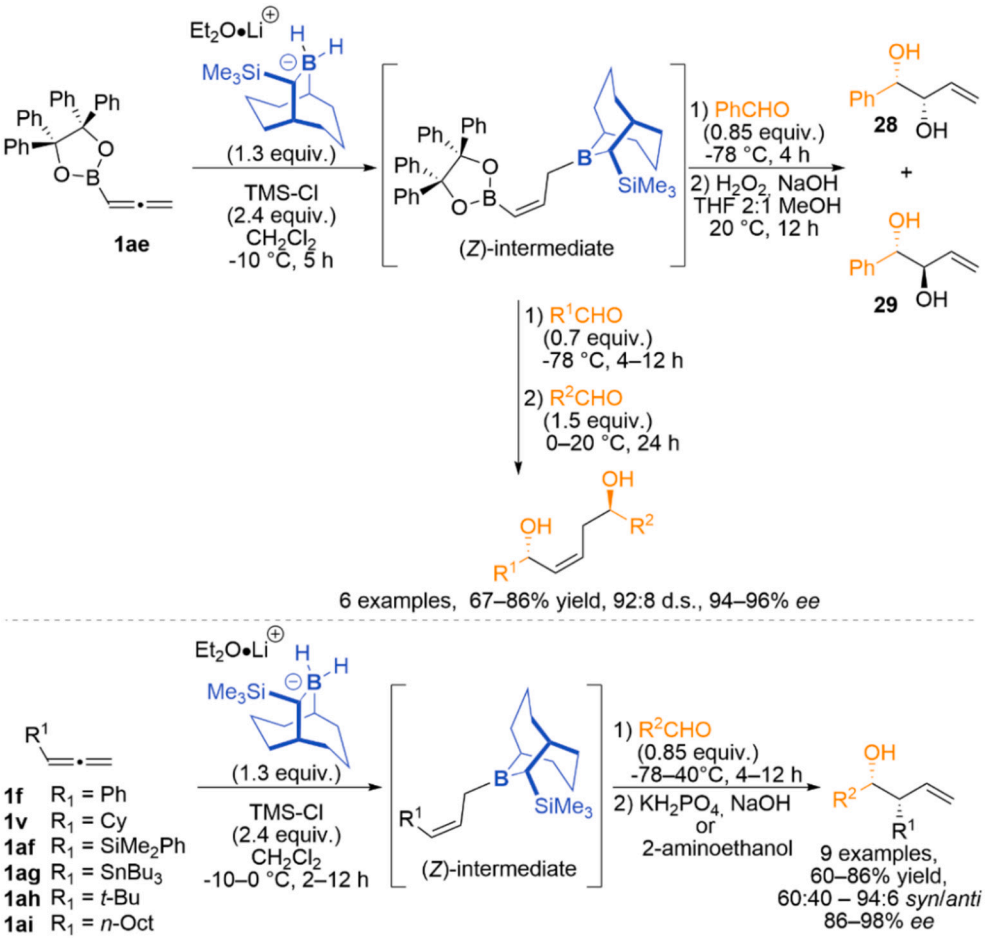
selective synthesis of (*Z*)- and (*E*)-2-methyl-1,5-*anti*-pentenediols. [33]

In 1997, Brown et al. developed a robust method for the synthesis of (*E*)-crotylboranes via the hydroboration of monosubstituted allenes using either Cy_2BH or $(^dIpc)_2BH$. [34] These (*E*)-crotylboranes efficiently condensed with aldehydes to yield homoallylic alcohols (**19** and **20**) with high diastereoselectivity (Scheme 10). By employing $(^dIpc)_2BH$ as the hydroborating reagent, the reaction was further optimized to produce optically active products with good enantioselectivity (74–84%



Entry	R_1CHO	Homoallylic alcohol	Isolated yield [%]
1	*i*-Pr	**27a**	74
2	Et	**27b**	81
3	Ph	**27c**	70
4	2-furyl	**27d**	66
5	$CH{=}CH_2$	**27e**	80
6	$C{\equiv}C\text{-}C_5H_{11}$	**27f**	81
7	CH_2OBn	**27g**	78
8	H	**27h**	60
9		**27i**	95
10		**27j**	90
11		**27k**	80
12		**27l**	74

Scheme 13. Hydroboration of **1ad** and addition of aldehydes to yield protected amino diols **27a**–**l**. Ts = 4-toluenesulfonyl, TBDPS = *tert*-butyldiphenylsilyl.

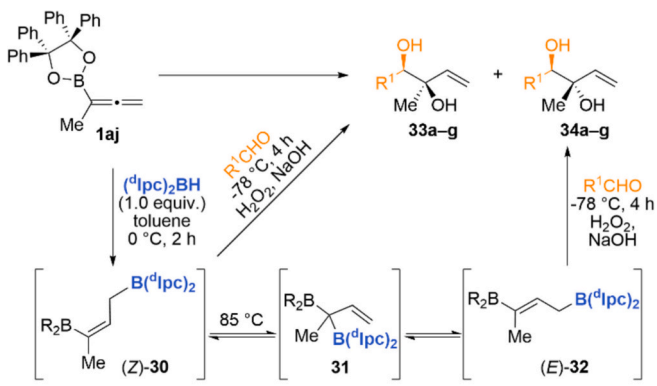


Scheme 14. Kinetically controlled hydroboration-allylboration of allenes with Soderquist borane.

ee). The study revealed that phenylallene (**1f**) provided nearly perfect diastereoselectivity (>99% *anti*), while aliphatic allenes, such as 1,2-heptadiene (**1w**) and 1,2-nonadiene (**1c**), delivered *anti* products with moderate selectivity (87–90%). Cyclohexylallene (**1v**) exhibited a high *anti*:*syn* ratio (96:4) with Cy_2BH, though the selectivity decreased to 80:20 with the bulkier $(^dIpc)_2BH$. This one-step methodology offered a straightforward and efficient route for synthesizing homoallylic alcohols (**19** and **20**) with stereochemical control. The ability to fine-tune both diastereo- and enantioselectivity by varying the hydroborating reagent highlighted its applicability in the synthesis of complex natural products.

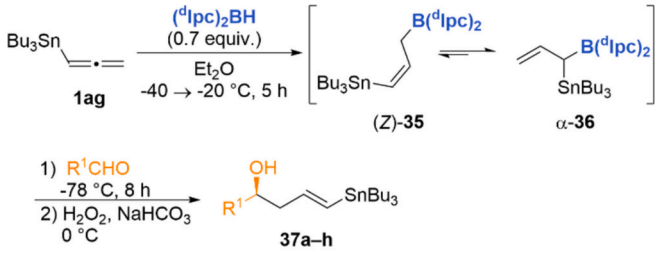
In 2002, Uang and co-workers described a diastereoselective synthesis of (1*R*)-(+)-camphor-based chiral allenes and their hydroboration reactions with 9-BBN. [35] Hydroboration of camphor-based chiral allenes (**1x**–**ab**) with 9-BBN, followed by oxidative work-up, proceeded with high diastereoselectivity and yielded allylic alcohols **23a**–**e** and **24a**–**e** in ratios ranging from 6:1 to 18:1, depending on the substituents (Scheme 11). The authors suggested that when the less-substituted double bond of the allene reacted with 9-BBN, the facial selectivity was influenced by the steric bulk of the substituents on the more-substituted double bond. Two possible pathways were suggested for the formation of **23**. The first one involved direct addition of 9-BBN from the *si* face of the allene, while the second one involved initial addition from the *re* face to form allylborane **21**. This intermediate would then undergo allylborane rearrangement, bond rotation, and a second rearrangement to produce allylborane **22**, which was oxidized to yield allylic alcohol **23**. However, temperature-dependent experiments showed no evidence of such rearrangements, supporting the direct *si* face addition as the primary pathway. The mechanism for the formation of the minor allylic alcohol **24** was less clear, and the authors speculated that it might have resulted from epimerization of either allylborane **22** or allylic alcohol **23** during the reaction. This work highlighted the role of steric effects in controlling face-selectivity in the hydroboration of allenes.

Building on the earlier works [26,27,29] of Wang et al., Roush and co-workers explored the hydroboration of allenylsilanes with $(^dIpc)_2BH$. [36] The reaction selectively produced (*Z*)-γ-silylallylborane intermediates, which were subsequently used in aldehyde addition reactions to yield β-hydroxyallylsilanes (**26**) (Scheme 12). The authors observed that the ratio of *syn*-**26** to *anti*-**26** isomers was strongly dependent on the hydroboration temperature. At lower temperatures, such as −50 °C, the formation of the kinetically favored (*Z*)-isomer (**25a**) dominated, resulting in a higher *syn*-**26**/*anti*-**26** ratio compared to the reaction carried out at room temperature (Scheme 11, entry 3). The authors proposed that the (*Z*)-γ-silylallylborane (**25a**) could isomerize to the thermodynamically favored (*E*)-isomer (**25c**) via a boron allylic migration pathway. However, the steric bulk of the $(^dIpc)_2B$ substituent appeared to limit this isomerization, allowing the *syn* product to remain predominant, even under conditions that might otherwise favour isomerization (Scheme 12, entry 4). Roush et al. further extended this procedure to a series of chiral aldehydes and applied it in the synthesis of *Durhamycin A*, a member of the aureolic acid family known for its broad-



Entry	R^1CHO	Temp. [°C]	Product	*Syn*/*Anti*	*ee* [%]	Isolated yield [%]
1	$Ph(CH_2)_2CHO$	0	**33a**	20/1	92	72
2		85	**34a**	1/17	89	76
3	$PhCH_2CHO$	0	**33b**	20/1	85	71
4		85	**34b**	1/12	87	67
5	PhCHO	0	**33c**	20/1	86	82
6		85	**34c**	1/15	84	77
7	$BnO(CH_2)_2CHO$	0	**33d**	20/1	89	69
8		85	**34d**	1/14	85	66
9	$BnOCH_2CHO$	0	**33e**	20/1	88	79
10		85	**34e**	1/14	85	72
11	PhCH=CHCHO	0	**33f**	20/1	90	75
12		85	**34f**	1/15	82	71
13	$PMBOCH_2C(CH_3)_2CHO$	0	**33g**	20/1	88	56
14		85	**34g**	1/12	80	51

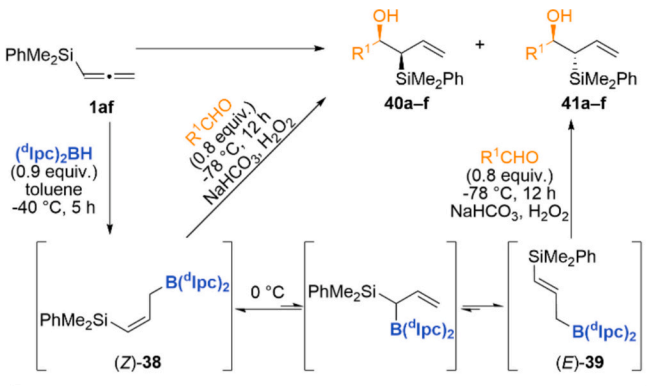
Scheme 15. Synthesis of *syn*/*anti*-1,2-diols (**33**/**34**) via hydroboration of **1aj** with $(^dIpc)_2BH$. PMB = *p*-methoxybenzyl.



Entry	R^1CHO	Product	Isolated yield [%]	*ee* [%]
1	$Ph(CH_2)_2CHO$	**37a**	64	95
2	$PhCH_2CHO$	**37b**	67	95
3	PhCHO	**37c**	78	93
4	$BnO(CH_2)_2CHO$	**37d**	68	95
5	$BnOCH_2CHO$	**37e**	71	95
6	PhCH=CHCHO	**37f**	73	95
7	CyCHO	**37g**	55	92
8	*t*-BuCHO	**37h**	51	94
9[a]	$Ph(CH_2)_2CHO$	*ent*-**37a**	71	94
10[b]	$Ph(CH_2)_2CHO$	*ent*-**37a**	73	30

[a] $(^lIpc)_2BH$ was used. [b] $(^dIpc)_2BH$ in Et_2O at 0 °C.

Scheme 16. Synthesis of δ-stannyl homoallylic alcohols **37a**–**h** via kinetically controlled hydroboration-allylborane isomerization.



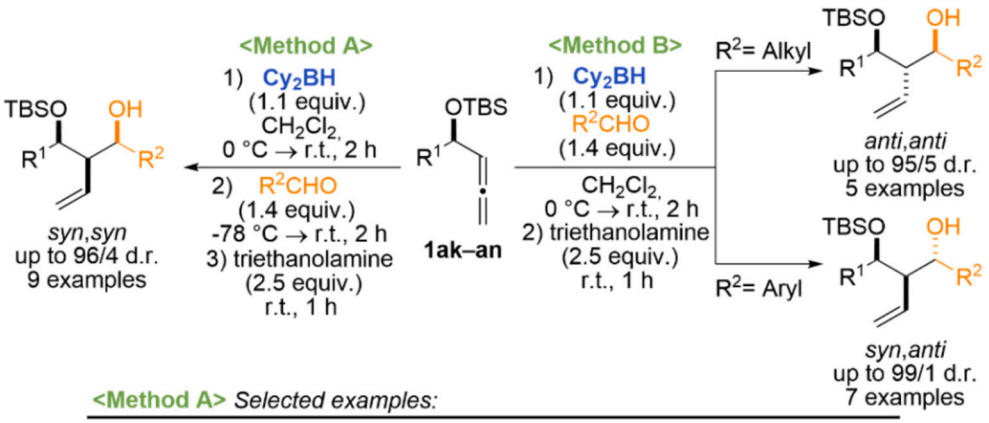
Entry	R^1CHO	Temp. [°C]	Product	*Syn*/*Anti*	*ee* [%]	Isolated yield [%]
1	$Ph(CH_2)_2CHO$	-40	**40a**	14/1	87	76
2		>-40	**41a**	1/20	86	87
3	$PhCH_2CHO$	-40	**40b**	12/1	87	70
4		>-40	**41b**	1/20	87	90
5	PhCHO	-40	**40c**	18/1	86	80
6		>-40	**41c**	1/20	83	83
7	CyCHO	-40	**40d**	20/1	84	67
8		>-40	**41d**	1/20	86	80
9	$TBSO(CH_2)_2CHO$	-40	**40e**	15/1	84	71
10		>-40	**41e**	1/20	85	91
11	$TBSOCH_2CHO$	-40	**40f**	14/1	87	72
12		>-40	**41f**	1/20	84	87

Scheme 17. Synthesis of *syn*/*anti*-β-hydroxyallylsilanes via hydroboration and allylborane isomerization.

spectrum antibacterial and antitumor activities and its role as an inhibitor of HIV Tat-dependent transactivation. [37,38]

Ariza et al. reported a stereoselective hydroboration methodology for allenes, aiming at the synthesis of highly functionalized homoallylic alcohols. [39] In their study, hydroboration of allene **1ad** with dicyclohexylborane (Cy_2BH) in dichloromethane at room temperature yielded a single stereoisomer of the (*Z*)-allyldicyclohexylborane intermediate (Scheme 13). Subsequent reaction of this intermediate with aldehydes at low temperature (−78 °C) afforded the corresponding homoallylic alcohols in 60–74% yield with high diastereomeric purity. The stereochemical outcome was attributed to steric interactions arising from the bulky Cy_2BH reagent and the significant steric hindrance provided by the substituents on the more substituted double bond of the allene moiety. These combined steric effects directed the boron addition to the less hindered side of the allene and prevented isomerization of the (*Z*)-allylborane intermediate to its (*E*)-isomer, even under reflux conditions. The steric bulk further influenced the aldehyde addition step, ensuring high diastereoselectivity by favoring a single diastereomer. The methodology consistently provided homoallylic alcohols (**27a**–**l**) with good to excellent yields and high diastereomeric purity. This work underscored the critical role of steric effects, not only from the hydroborating reagent but also from the allene substrate, in stabilizing the (*Z*)-allylborane intermediate and guiding the regio- and stereoselectivity of the reaction. The established methodology was further extended by the same group to the stereoselective synthesis of protected quaternary 2-amino-2-vinyl-1,3-diols. [40]

In 2009, Roush et al. reported the kinetically controlled hydroboration of monosubstituted allenes [41] using Soderquist borane (10-TMS-9-BBD-H, see Scheme 14 for its structure). [42,43] This approach enabled the selective formation of (*Z*)-γ-substituted allylboranes without significant isomerization to the thermodynamically preferable product. [41] The authors optimized the hydroboration conditions using a model allene substrate **1ae** and found that the reaction conducted at −10 °C for 5 h in dichloromethane yielded the (*Z*)-allylborane intermediate



<Method A> *Selected examples:*

Entry	R^1	R^2	Major product	Facial selectivity[a]	*E*/*Z*[b]	Isolated yield [%]
1	Me	Et	*syn*,*syn*	93/7	95/5	54
2	*i*-Pr	Ph	*syn*,*syn*	96/4	96/4	65
3	Ph	*i*-Pr	*syn*,*syn*	95/5	95/5	79

[a]*syn*,*syn*/*anti*,*syn* ratio. [b](*syn*,*syn* + *anti*,*syn*)/(*anti*,*anti* + *syn*,*anti*) ratio.

<Method B> *Selected examples:*

Entry	R^1	R^2	Major product	Facial selectivity[a]	*E*/*Z*[b]	Isolated yield [%]
1	*n*-Pent	Et	*anti*,*anti*	6/94	84/14	65
2	Ph	*i*-Pr	*anti*,*anti*	11/89	85/15	60
3	*i*-Pr	Ph	*syn*,*anti*	99/1	91/9	65
4	*i*-Pr	*p*-NO_2-Ph	*syn*,*anti*	99/1	84/16	56

[a]*syn*,*anti*/*anti*,*anti* ratio. [b](*anti*,*anti* + *syn*,*anti*)/(*syn*,*syn* + *anti*,*syn*) ratio.

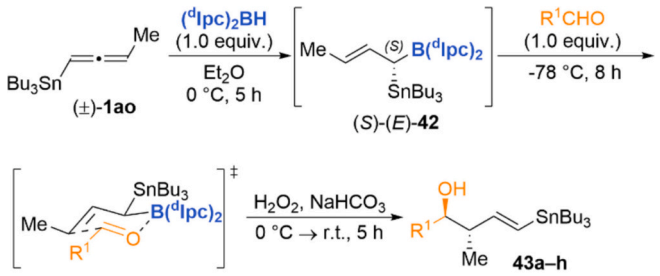
Scheme 18. Hydroboration of allenes **1ak-an** with Cy_2BH followed by isolated or tandem addition of aldehydes

selectively, which upon allylboration and oxidation, produced a 1,2-diol (**28**) with a 91:9 diastereomeric ratio in 75% yield (Scheme 14). The authors attributed this kinetic selectivity to steric interactions between the TMS group of Soderquist's borane and the π-allyl fragment of the (*Z*)-allylborane intermediate, which raised the energy barrier for [1,3]-boratropic shifts and suppressed isomerization to the thermodynamically favored (*E*)-isomer. Computational studies further supported that these steric effects were highly substrate-dependent, with 1,1-disubstituted allenes exhibiting increased kinetic control due to greater steric hindrance in the transition states. [28] The obtained (*Z*)-intermediates were utilized in subsequent double allylboration reactions with aldehydes to afford (*Z*)-1,5-diols with good yields (67–86%) and enantioselectivities (94–96% ee). The methodology was further extended to various allenes, although each allene required specific reaction conditions to achieve optimal selectivity and yield. This study demonstrated the unique capability of Soderquist's borane to kinetically control allene hydroboration. The stereochemically defined (*Z*)-allylboranes from these hydroboration reactions are challenging to access using previously reported methods. Beyond expanding the synthetic utility of allylboranes, this work underscored the importance of precise control of reaction conditions and reagent design in overcoming isomerization challenges inherent to non-catalytic allene hydroboration.

In the same year, Roush and co-workers reported a stereoselective hydroboration methodology for

1-methyl-allenylboronate (**1aj**) using $(^dIpc)_2BH$, demonstrating temperature-dependent control of intermediates formation. [44] Hydroboration of **1aj** at 0 °C yielded the kinetic product (*Z*)-γ-boryl-allylborane (**30**), which retained its stereochemical integrity due to steric hindrance in the transition state preventing the formation of 1,1-diboryl species (**31**) via [1,3]-boratropic shifts (Scheme 15). Intermediate **30** could react with aldehydes, upon subsequent oxidation, to produce 1,2-*syn*-diols (**33**) with excellent diastereo- and enantioselectivity (20/1 *syn*/*anti*, 85–92% *ee*). However, at elevated temperatures (85 °C), the (*Z*)-γ-boryl-allylborane intermediate **30** underwent thermodynamically driven isomerization to (*E*)-γ-boryl-allylborane (**32**). This thermodynamic intermediate enabled the selective synthesis of 1,2-*anti*-diols (**33a–g**) upon the reaction with aldehydes, featuring high diastereoselectivity (>12/1 *anti*/*syn*) and enantiocontrol (80–89% *ee*). The study highlighted the pivotal role of temperature in dictating the stereochemical outcome of allene hydroboration and provided a flexible strategy for the synthesis of both 1,2-*syn*- and 1,2-*anti*-diols from the same substrate under controlled conditions. The use of 1-methyl-allenylboronate (**1aj**) as a substrate, together with temperature-controlled access to specific diastereomers, distinguishes this work from earlier studies by Brown. [24,25]

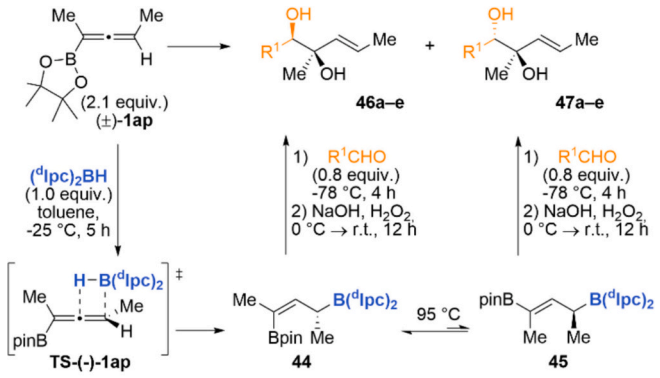
In 2010, Roush et al. extended the scope of their hydroboration studies to allenylstannane **1ag**, further demonstrating the versatility of $(^dIpc)_2BH$ in controlling stereoselectivity. [45] The hydroboration of allenylstannane (**1ag**) with $(^dIpc)_2BH$ at −40 °C initially formed the kinetic product (*Z*)-γ-stannylallylborane (**35**) (Scheme 16). However,



Entry	R^1CHO	Product	Isolated yield [%]	*ee* [%]
1	$Ph(CH_2)_2CHO$	**43a**	71	92
2[a]	$Ph(CH_2)_2CHO$	*ent*-**43a**	67	88
3	$PhCH_2CHO$	**43b**	69	92
4	PhCHO	**43c**	67	89
5	$BnO(CH_2)_2CHO$	**43d**	73	94
6	$BnOCH_2CHO$	**43e**	70	90
7	PhCH=CHCHO	**43f**	71	92
8	CyCHO	**43g**	64	93
9[b]	*t*-BuCHO	**43h**	56	90

[a] $(^lIpc)_2BH$ was used. [b] -78 °C → r.t.

Scheme 19. Enantioconvergent hydroboration of racemic allene **1ao** with $(^dIpc)_2BH$ followed by crotylboration of aldehydes and subsequent oxidation

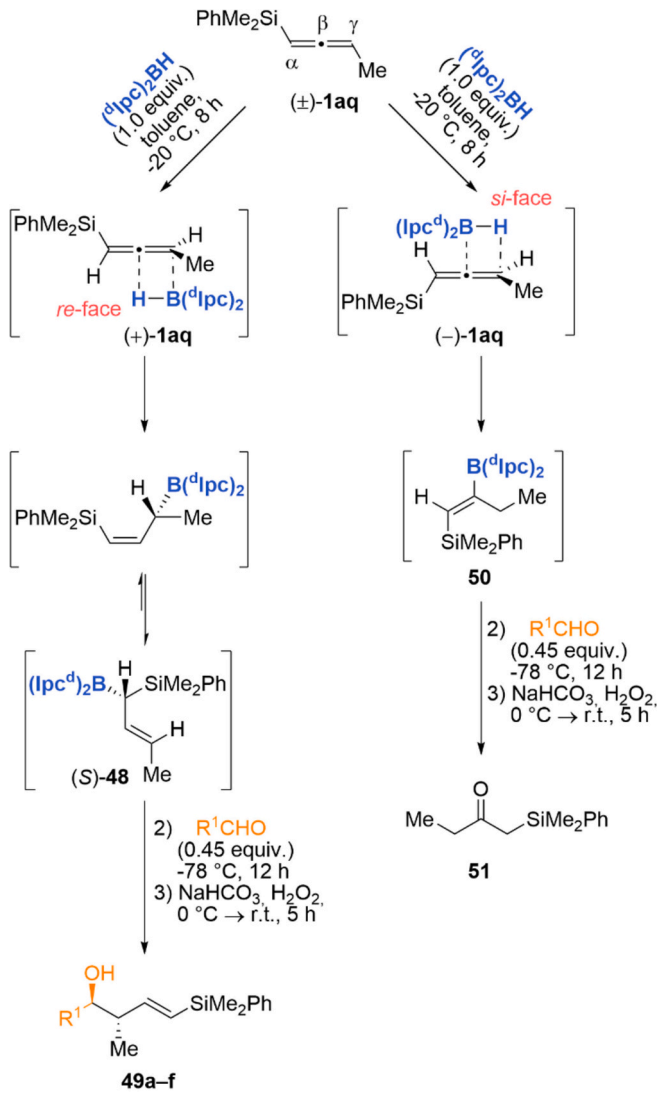


Selected examples:

Entry	R^1CHO	Temp. [°C]	Product	*Syn*/*Anti*	*ee* [%]	Isolated yield [%]
1	$Ph(CH_2)_2CHO$	-25	**46a**	20/1	90	75
2		95	**47a**	1/7	87	89
3	$BnO(CH_2)_2CHO$	-25	**46b**	20/1	90	72
4		95	**47b**	1/10	92	84
5	PhCHO	-25	**46c**	20/1	93	63
6		95	**47c**	1/10	88	80
7	CyCHO	-25	**46d**	20/1	94	73
8		95	**47d**	1/6	90	87
9	PhCH=CHCHO	-25	**46e**	10/1	92	74
10		95	**47e**	1/15	87	86

Scheme 20. Diastereo- and enantioselective synthesis of (*E*)-2-methyl-1,2-*syn*-3-pentenediols (**46a**–**e**) and (*E*)-2-methyl-1,2-*anti*-3-pentenediols (**47a**–**e**) via allenylboronate (±)-**1ap** kinetic resolution with $(^dIpc)_2BH$ and aldehyde allylboration.

upon increasing the temperature above −40 °C, **35** underwent a [1,3]-boratropic shift reaction, producing the thermodynamically stable α-stannylallylborane **36**. The formation of **36** was unique compared to previously described hydroboration procedures, further illustrating how

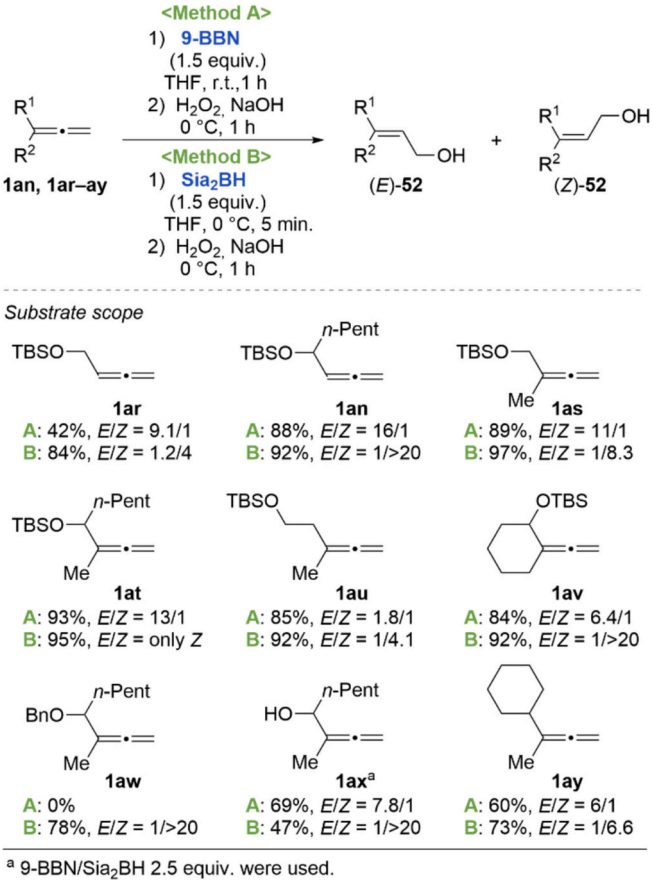


Entry	R^1CHO	Product	*ee* [%]	Isolated yield [%]
1	PhCHO	**49a**	95	85
2[a]	PhCHO	*ent*-**49a**	94	82
3	PhCH=CHCHO	**49b**	95	78
4	$Ph(CH_2)_2CHO$	**49c**	93	89
5	CyCHO	**49d**	94	71
6	$TBSO(CH_2)_2CHO$	**49e**	95	72
7	$BnO(CH_2)_2CHO$	**49f**	96	75

[a] $(^lIpc)_2BH$ was used.

Scheme 21. Enantioselective synthesis of (*E*)-δ-Silyl-*anti*-homoallylic alcohols (**49a**–**f**) via an enantiodivergent hydroboration-crotylboration reaction of a racemic allenylsilane (±)-(**1aq**) with $(^dIpc)_2BH$.

different substituents in allene moiety can influence the selectivity of the reaction. Computational calculations suggested that the hyperconjugative interactions between the -$SnBu_3$ and the -$B(^dIpc)_2$ groups were critical in governing the equilibrium and stereochemical outcome of the reaction. [46] The length of Sn—C bond could also be beneficial. This highly controlled hydroboration-allylborane isomerization enabled the synthesis of α-stannylallylborane **36**, which subsequently underwent allylboration with representative aldehydes and oxidation to produce (*E*)-δ-stannyl homoallylic alcohols (**37a**–**h**) with excellent



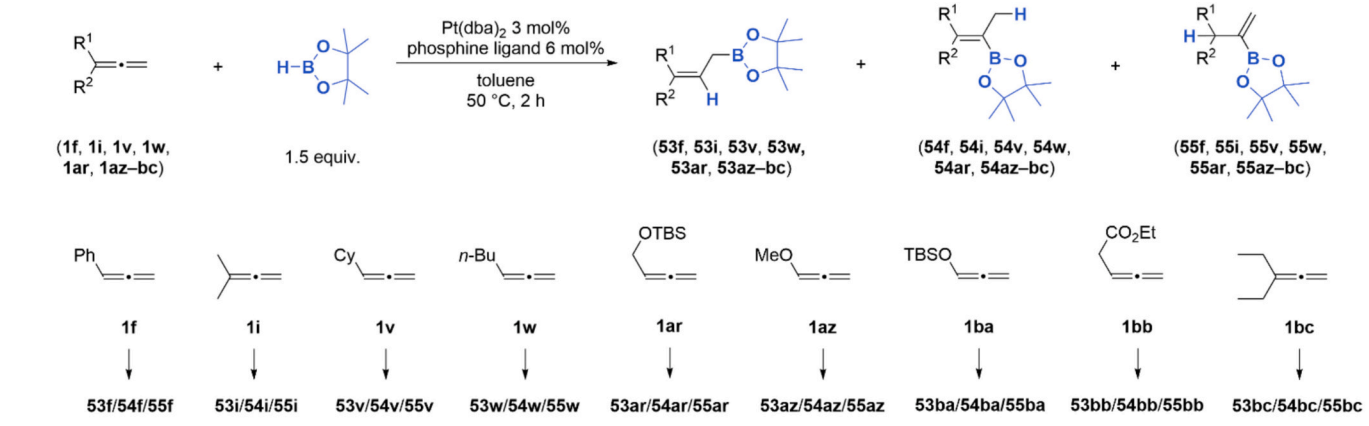
Scheme 22. Hydroboration-oxidation of allenes with 9-BBN and Sia_2BH.

enantioselectivities (>95% *ee* in most cases). The authors highlighted the significance of this approach for its ability to generate δ-stannyl homoallylic alcohols directly, obviating the need for multistep modification of terminal vinyl group.

Building on their earlier work with allenylstannane **1ag**, Roush and co-workers extended their hydroboration studies to allenylsilane **1af**, further investigating how different substituents in the allene moiety influence the selectivity and outcome of the hydroboration reaction. [47] At −40 °C, the hydroboration proceeded under kinetic control to yield (*Z*)-γ-silylallylborane (**38**). However, once the reaction temperature increased above −40 °C, **38** underwent a [1,3]-boratropic shift reaction to form the thermodynamically stable (*E*)-γ-silylallylborane (**39**). This hydroboration-isomerization sequence allowed access to various β-hydroxyallylsilanes, depending on the allylborane intermediate used. Allylboration of aldehydes with **38** at −78 °C selectively afforded *syn*-β-hydroxyallylsilanes (**40**) with high diastereo- and enantioselectivities (up to 18:1 *syn/anti*, 87% *ee*). In contrast, reactions with **39** gave *anti*-β-hydroxyallylsilanes (**41**) with 20:1 *anti*/syn diastereoselectivity and enantiomeric excesses of 83–87% (Scheme 17). The study also highlighted the influence of steric and electronic effects on the equilibrium between *Z* and *E* intermediates. Unlike their earlier work on the hydroboration of allenylstannane **1ag**, where thermodynamic equilibrium favored

α-stannylallylborane (**36**), the shorter Si—C bond in allenylsilane **1af** (relative to Sn—C) contributed to the preference for (*Z*)- or (*E*)-γ-silylallylboranes. This difference underscores the importance of substrate-specific factors in determining the selectivity of allene hydroboration. While (*Z*)-γ-substituted allylboranes have previously been obtained by hydroboration of monosubstituted allenes with Soderquist's borane, this study is the first example of achieving a good *Z/E* ratio using a simpler dialkylborane, such as $(^dIpc)_2BH$.

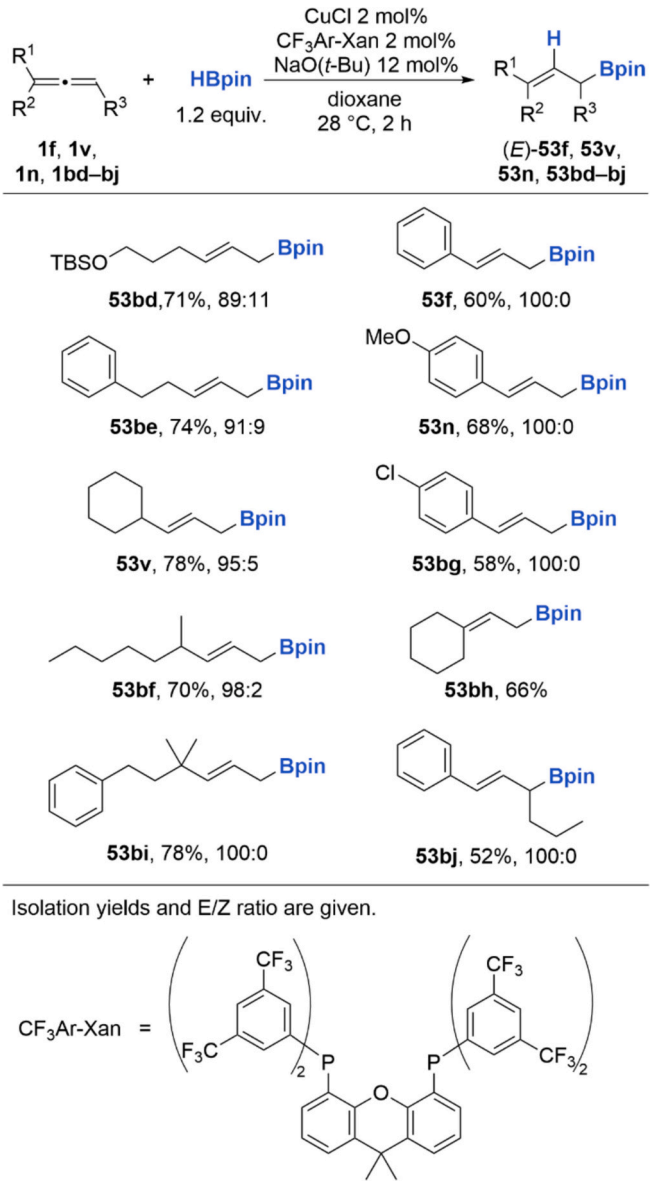
In 2010, Ariza et al. demonstrated a versatile approach to the hydroboration of 4-silyloxy-1,2-allenes with Cy_2BH, allowing the synthesis of three out of four possible stereoisomers of 2-vinyl-1,3-diols from a single allene precursor (Scheme 18). [48] Consistent with previous reports, [27,36] the hydroboration of allenes **1ak**–**an** generated either (*Z*)- or (*E*)-allylboron intermediates depending on the reaction conditions, with the (*Z*)-intermediate favored at lower temperatures. The stereochemical outcome of obtained 1,3-diols was determined by the reaction conditions, in particular the order of reagent addition and the type of aldehyde used. Allylboration carried out after hydroboration, produced *syn*,*syn*-configured 1,3-diols (Method A, Scheme 18). However, when the hydroboration was performed in the presence of an aldehyde, a tandem hydroboration-allylboration pathway ensued, yielding 1,3-diols with high facial selectivity, depending on the type of aldehyde used (Method B, Scheme 18). Aliphatic aldehydes favored the



	1f	1i	1v	1w	1ar	1az	1ba	1bb	1bc
PCy_3	-	33/0/67 63%	-	0/0/100 79%	-	100[a]/0/0 65%	100[b]/0/0 77%	-	56/0/44 70%
$P(t\text{-}Bu)_3$	0/0/100 97%	6/0/94 53%	0/0/100 91%	0/0/100 79%	0/0/100 76%	-	100[c]/0/0 86%	0/0/100 60%	1/0/99 96%
TTMPP	0/57/43 63%[d]	0/95/5 76%	0/91/9 76%	0/100/0 58%	0/39/61 76%	-	0/100/0 76%	0/0/100 49%	0/100/0 76%

[a] E/Z = 16/84. [b] E/Z = 9/91. [c] E/Z = 10/90. [d] 16 h.

Scheme 23. Allenes hydroboration catalyzed by $Pt(dba)_2$ and different phosphine ligands.

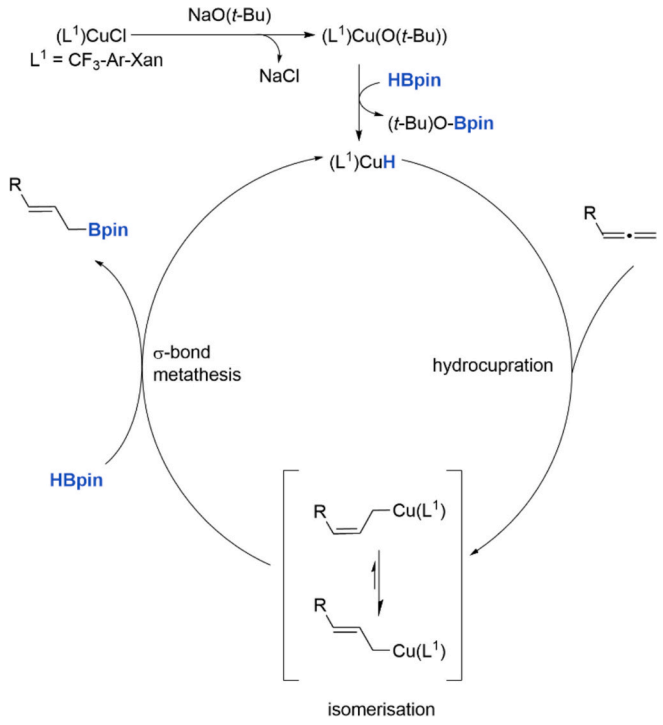


Scheme 24. Allenes hydroboration in the presence of CuCl, NaO(*t*-Bu) and bidentate phosphine ligand.

formation of *anti*,*anti*-1,3-diols, whereas aromatic aldehydes reacted to provide 1,3-diols with opposite facial bias (*syn*,*anti*-products). This stereodivergent methodology demonstrates the ability to precisely control the stereochemical outcome of hydroboration-allylboration reactions by adjusting the order of reagent addition and reaction conditions.

In 1968 and 1973, Caserio and Moore reported their attempts to achieve the kinetic resolution of 2,3-pentadiene (**1j**) via hydroboration with $(Ipc)_2BH$, although low levels of enantioselectivity were obtained. [49,50] To the best of our knowledge, no further studies on enantioselective hydroboration of racemic allenes were conducted until 2011, when Roush et al. described the enantioconvergent hydroboration of a racemic allenylstannane (±)-**1ao**, representing a significant advancement in asymmetric allene hydroboration (Scheme 19). [51] Using $(^dIpc)_2BH$ as the hydroborating reagent, the authors demonstrated that both enantiomers of racemic allenylstannane (+)-**1ao** and

(−)-**1ao** converged to a single enantiomerically enriched crotylborane intermediate (*S*)-*E*-**42** through distinct, kinetically controlled pathways. This transformation was driven by the stereochemical influence of the bulky $(^dIpc)_2BH$ and presumably by the ability of the C—Sn bond to

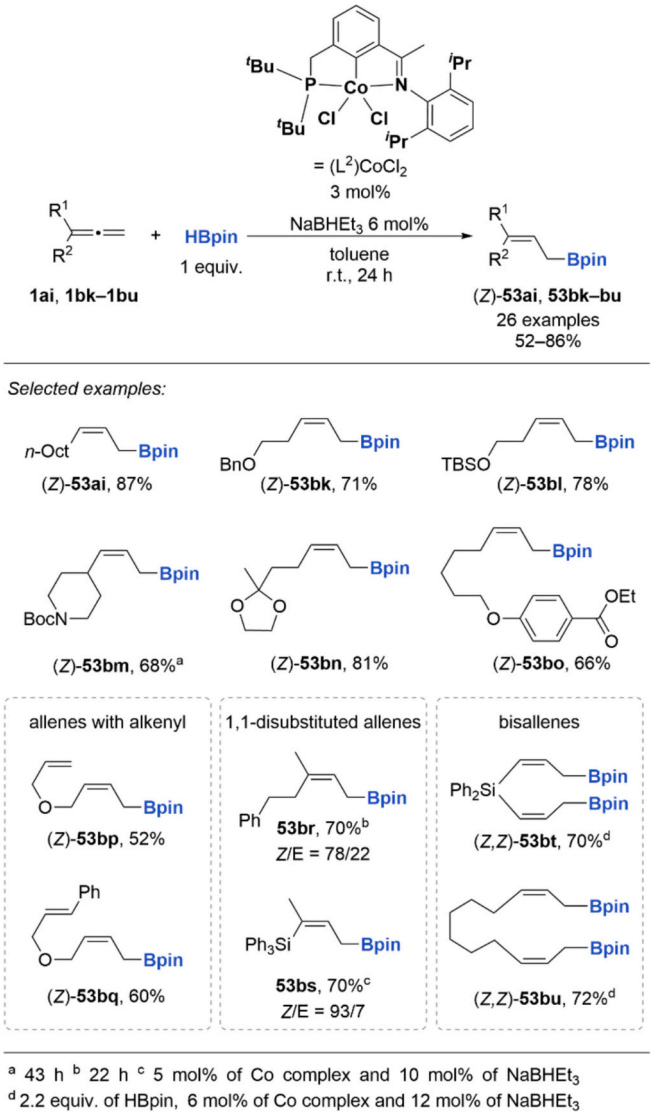


Scheme 25. Proposed mechanism for the hydroboration of allenes in the presence of CuCl, NaO(*t*-Bu) and the bidentate phosphine ligand.

interact with the empty p orbital on the boron atom, facilitating suprafacial [1,3]-boratropic shifts. [46,47] Subsequent crotylboration of aldehydes with (*S*)-(*E*)-**42** yielded (*E*)-δ-stannyl-*anti*-homoallylic alcohols (**43a**–**h**) in good yields (56–73%) and with excellent enantioselectivities (88–94% *ee*). Importantly, this enantioconvergent process did not involve racemization or kinetic resolution, enabling efficient utilization of racemic allene substrates.

Building upon their earlier findings, Roush and co-workers extended their investigations to the diastereo- and enantioselective hydroboration of the racemic allenylboronate (±)-**1ap** and demonstrated an alternative approach involving kinetic resolution. [52] Hydroboration of racemic allenylboronate (±)-**1ap** with $(^dIpc)_2BH$ at −25 °C selectively yielded the kinetic product (*R*)-(*Z*)-γ-borylallylborane (**44**) via **TS-(−)-1ap** involving direct addition of $(^dIpc)_2BH$ from the *re* face of the allenylboronate (−)-**1ap** (Scheme 20). Subsequent allylboration of aldehydes with **44** at −78 °C furnished 1,2-*syn*-diols (**46**) with high diastereoselectivity (>10:1) and enantioselectivity (90–94% *ee*). Heating **44** to 95 °C induced a [1,3]-boratropic shift to form thermodynamically more stable (*S*)-(*E*)-γ-borylallylborane (**45**). Allylboration of aldehydes with **45** afforded 1,2-*anti*-diols (**47**) with moderate diastereoselectivity (15:1) and high enantioselectivity (87–92% *ee*).

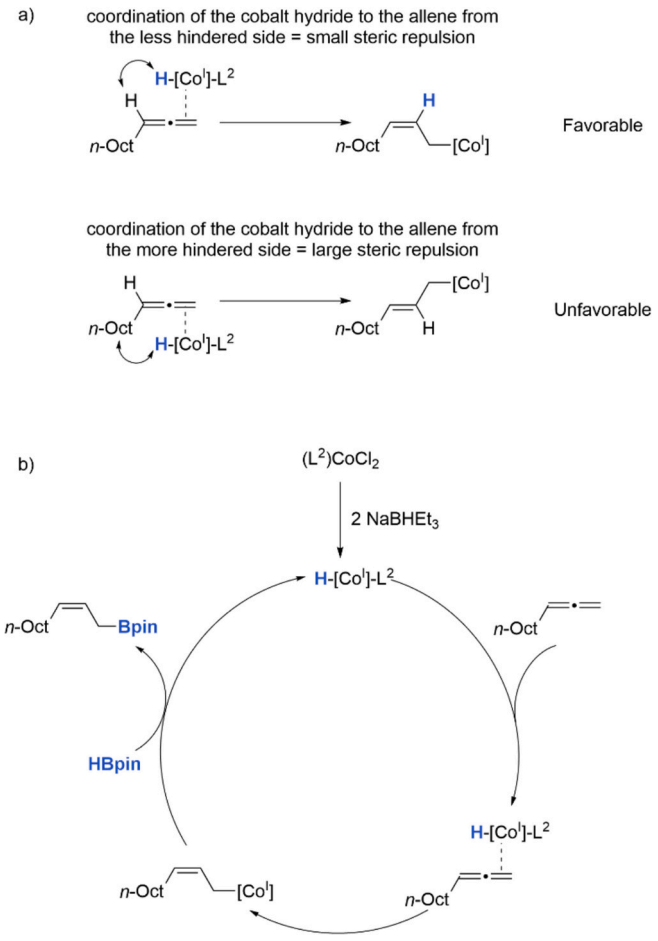
Following their studies on enantioconvergent hydroboration of racemic allenylstannanes, Roush et al. reported the hydroboration of racemic allenylsilanes, revealing an enantiodivergent pathway distinct from their previous works. [53,54] Treatment of racemic allenylsilane (±)-(**1aq**) with $(^dIpc)_2BH$ led to different reaction pathways for each enantiomer, resulting in the formation of two structurally distinct intermediates (Scheme 21). Hydroboration of (+)-**1aq** proceeded via selective addition of boron to the allene carbon atom adjacent to the methyl group, generating crotylborane (*S*)-*E*-**48** through a [1,3]-boratropic shift. In contrast, hydroboration of (−)-**1aq** favored boron addition at the β-carbon atom, producing vinylborane **50**, which was oxidized to ketone **51** rather than participating in the crotylboration step. This enantiodivergent reactivity resulted in the selective formation of (*E*)-δ-silyl-*anti*-homoallylic alcohols (**49**), upon crotylboration of aldehydes, in high yields (71–89%) and with excellent enantioselectivities



Scheme 26. Hydroboration of terminal allenes in the presence of pincer-ligand-based cobalt complex and $NaBHEt_3$.

(93–96% *ee*). Unlike the previous enantioconvergent hydroboration of allenylstannanes, which led to both enantiomers to a single product, this study showed that racemic allenylsilanes undergo hydroboration via distinct regio- and stereoselective pathways, yielding different intermediates depending on the enantiomer involved.

Chida et al. developed a stereodivergent hydroboration of allenes, demonstrating that the stereochemical outcome of the transformation is critically dependent on the choice of borane reagent. [15] Hydroboration with 9-BBN resulted in thermodynamically favored (*E*)-allylic boranes due to rapid [1,3]-boratropic shift, whereas Sia_2BH provided kinetically controlled (*Z*)-allylic boranes. As illustrated in Scheme 22, the hydroboration of allenes with Sia_2BH or 9-BBN and subsequent oxidation led to distinct (*E*)- or (*Z*)-allylalcohols (**52**). This study highlighted the impact of steric bulk on the rate of isomerization. The application of bulky Sia_2BH slowed the rearrangement and allowed the retention of the (*Z*)-configuration. The developed method was further extended to the synthesis of trisubstituted olefins, skipped dienes, and allylbenzenes – structural motifs frequently found in biologically active compounds. The work of Chida et al. underscored how reagent selection enables precise control over stereoselectivity in allene hydroboration.

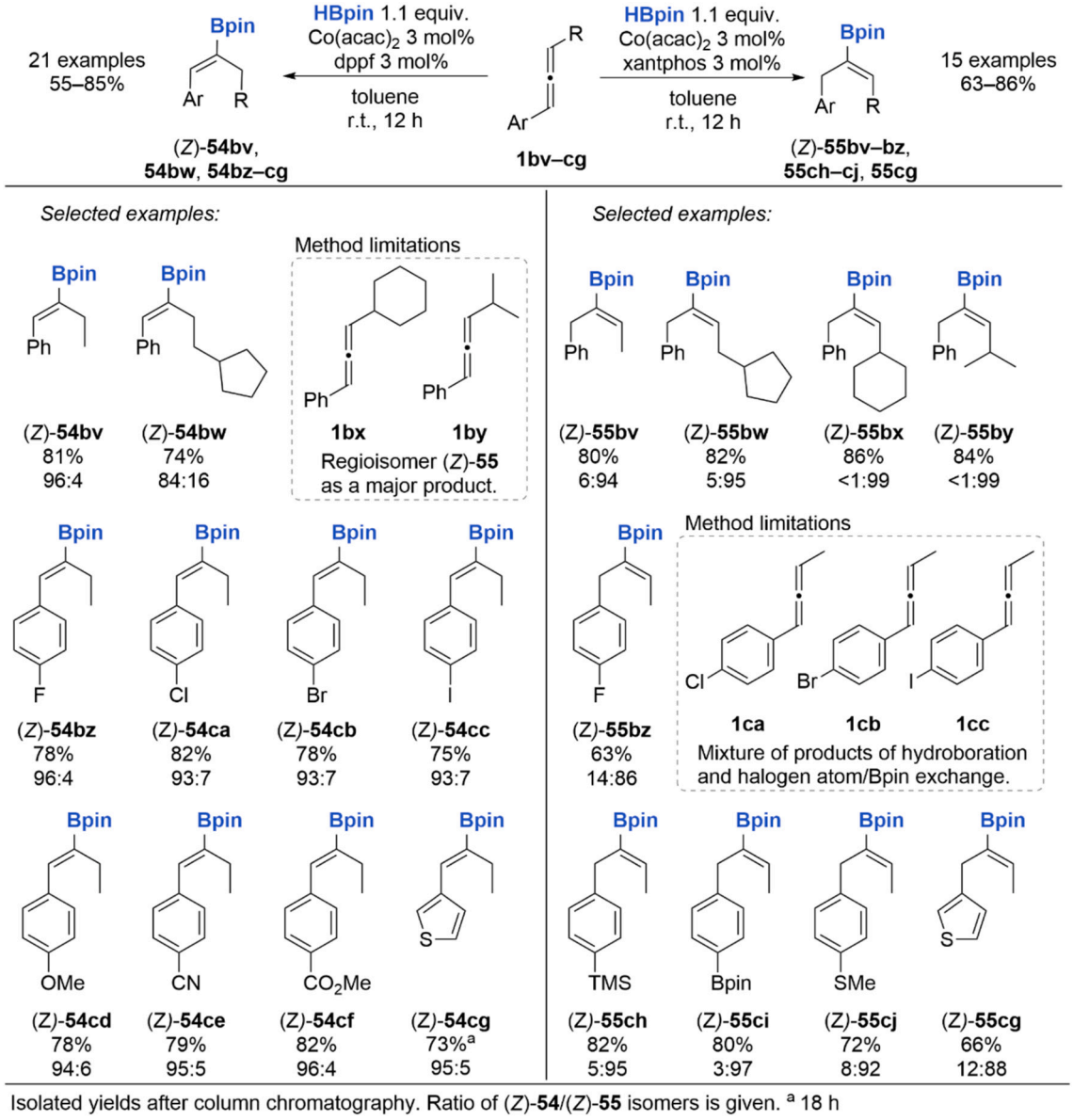


Scheme 27. a) Differences in the steric repulsion depending on the side of coordination of the Co—H to the allene. b) Proposed catalytic cycle for the hydroboration of allenes in the presence of pincer-ligand-based cobalt complex and $NaBHEt_3$.

1.2. Catalytic hydroboration of allenes

Although allene hydroboration can proceed in the absence of a catalyst, the catalytic addition of boranes to allenes offers several significant advantages. Foremost among these, it facilitates conducting the reactions under milder conditions with more stable alkoxyboranes such as pinacolborane (HBpin). It allows direct isolation of stable organoboron products, without the necessity to convert them to more stable derivatives such as alcohols. Moreover, appropriate choice of the catalyst enables the attainment of a wide range of products with great regio- and stereoselectivity, which are not accessible through the non-catalytic pathway. The catalytic hydroboration of allenes is limited to transition-metal complexes, particularly cobalt and nickel, however there are also catalysts based on platinum, ruthenium or copper.

It should be noted that alternative processes, such as diboration or protoboration, could also be employed in the borylation of allenes and often lead to the same product as hydroboration. In the literature, we can find papers about catalytic borylation of allenes (sometimes referring to this process as a hydroboration) but with diboron (e.g. B_2pin_2) used as an borylating agent together with some proton source (e.g., MeOH). [55–57] In these protoboration reactions, only one boryl moiety from diboron reagents is incorporated into the final product structure. While these methodologies are scientifically valuable and often synthetically useful, they suffer from reduced atom economy, which is a key consideration in the design of sustainable chemical processes. Therefore, in this article, we will restrict our discussion to hydroboration reactions

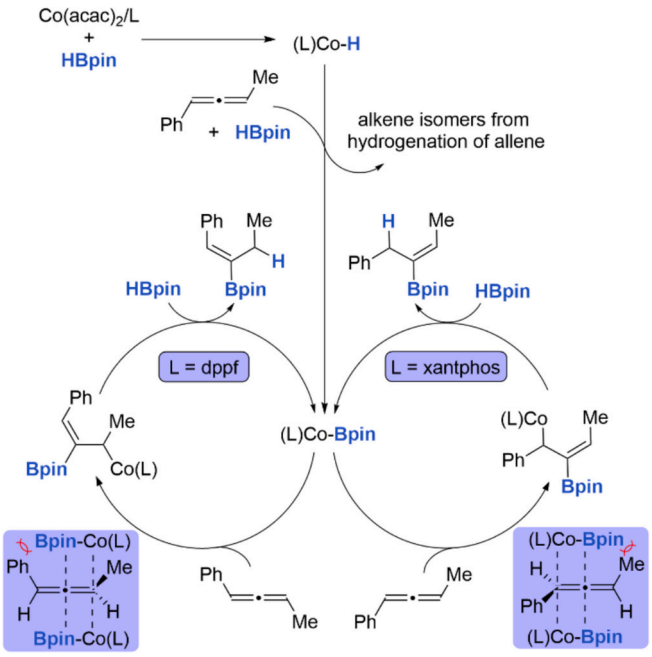


Scheme 28. Hydroboration of 1-aryl-3-alkyl-substituted allenes in the presence of $Co(acac)_2$ and dppf (1,1-bis(diphenylphosphino)ferrocene) or xantphos ((9,9-dimethyl-9H-xanthene-4,5-diyl)bis(diphenylphosphane)).

involving the direct addition of the B—H bond from borane reagents to allenes. These processes offer superior atom efficiency and align with the principles of green chemistry and economically viable synthesis.

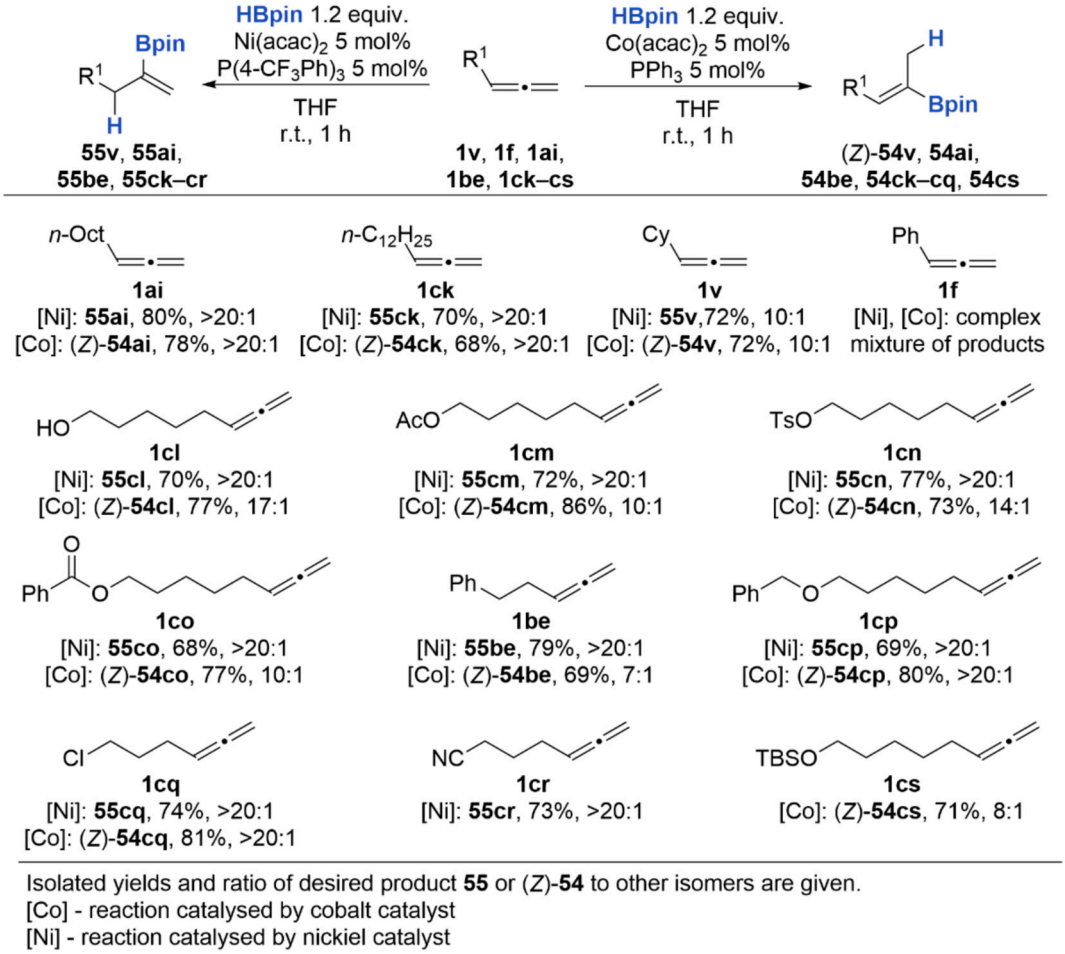
In the 1999, Yamamoto et al. reported for the first time the catalytic hydroboration of terminal allenes. [58] Reaction between hepta-1,2-diene (**1w**) and HBpin was conducted with platinum or rhodium catalyst: $Pt(dba)_2$ (dba = dibenzylideneacetone) and $[RhCl(COD)]_2$ (COD = cyclooctadiene) with various phosphine ligands. They found that platinum catalysts showed higher activity and ligands had prominent impact on the regioselectivity of the process. Moreover, hydroboration of structurally diverse mono- and disubstituted allenes in the presence of Pt $(dba)_2$ and PCy_3, P(*t*-Bu)$_3$ or TTMPP (tris(2,4,6-trimethoxyphenyl) phosphine) showed that the allene structure also strongly influences the selectivity of these hydroboration reactions. Appropriate tuning of the steric and electronical properties of the substrate can completely reverse regioselectivity, despite the use of the same ligand. Adjustment of allene's structure and appropriate choice of the phosphine ligand enabled the formation of three distinct products with moderate to high yields: *anti*-Markovnikov addition of HBpin to the terminal C=C bond (**53**), Markovnikov addition of HBpin to terminal C=C bond (**54**) and addition of HBpin to internal C=C bond with boron atom attached to the β-carbon of substrate (**55**) (Scheme 23). Based on these observations, a possible mechanism comprising three steps was proposed: (i) oxidative addition of HBpin to platinum(0) leading to H-Pt-Bpin, (ii) insertion of allene, and (iii) reductive elimination to release product. In this scenario, the second step is crucial for determining the reaction selectivity, since allene may insert into either H—Pt bond or into Pt-Bpin bond. The nature of TTMPP is likely to induce the latter possibility, whereas other phosphines tend to promote the insertion into the H—Pt bond, which can explain their influence on the regioselectivity of the reaction.

Surprisingly, after Yamomoto's pioneering work, the catalytic hydroboration of allenes remained unexplored until 2013, when the

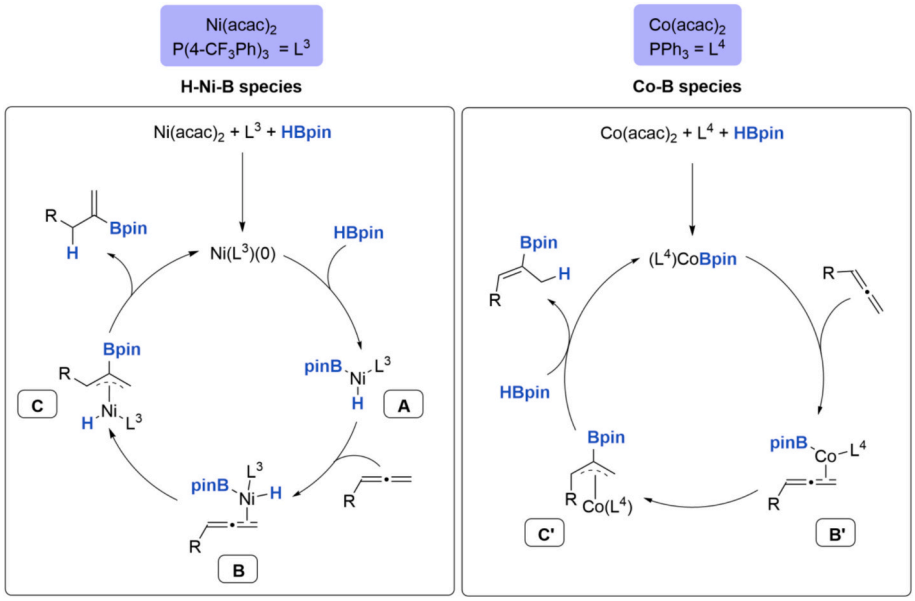


Scheme 29. Proposed catalytic cycles for the hydroboration of allenes catalyzed by $Co(acac)_2$ and biphosphine dppf or xantphos ligands.

Tsuji group reported a copper-catalyzed process employing CuCl, Xantphos-type phosphine ligand and NaO(*t*-Bu) as a base. [59] The optimal ligand was identified by screening various ligands in a model reaction between cyclohexylallene and pinacolborane. Monodentate phosphines such as PPh_3 and PCy_3 proved ineffective, yielding almost none of the targeted allylboronate product. In contrast, bidentate phosphines (e.g., dppbz, Xantphos, and related Xantphos-type ligands) dramatically enhanced both yield and selectivity, giving the allylboronate as the major product with high *E*-stereoselectivity. Other hydroboration products, regarding regio- and stereoselectivity, were not observed. N-Heterocyclic carbene (NHC) ligands were also evaluated, but poor *E/Z* selectivity and lower yields were obtained, underscoring the superior performance of phosphines in this Cu-catalyzed borylation. Using optimized conditions, several terminal allenes substituted with aliphatic and aromatic moieties were exclusively converted into allyl boronates via *anti*-Markovnikow addition of HBpin within 2 h under ambient conditions (Scheme 24). The products were predominantly obtained as (*E*) isomers, with a visible influence of the steric effect of the substrate substituents. For allenes containing aliphatic group(s), the selectivity toward (*E*)-isomer increased in the order: primary (**1bd**, **1de**) < secondary (**1v**, **1bf**) < tertiary (**1bi**) alkyl moiety, whereas substrates **1f**, **1n**, **1bg** and **1bj** bearing aryl groups led to (*E*)-allyl boronates. Notably, the reaction maintained high efficiency with the unsymmetrical 1,3-disubstituted allene **1bj**. According to the authors, it was the first reported example of transition metal-catalyzed hydroboration of internal allene. The proposed catalyst activation starts with the formation of $(L^1)CuCl$ (L^1 = CF_3Ar-Xan) and subsequent chloride substitution with $^{-}$O(*t*-Bu) anion to form copper alkoxide, which then reacts with HBpin



Scheme 30. Substrate scope of $Ni(acac)_2/P(4\text{-}CF_3Ph)_3$ and $Co(acac)_2/PPh_3$ catalyzed hydroboration of terminal allenes.

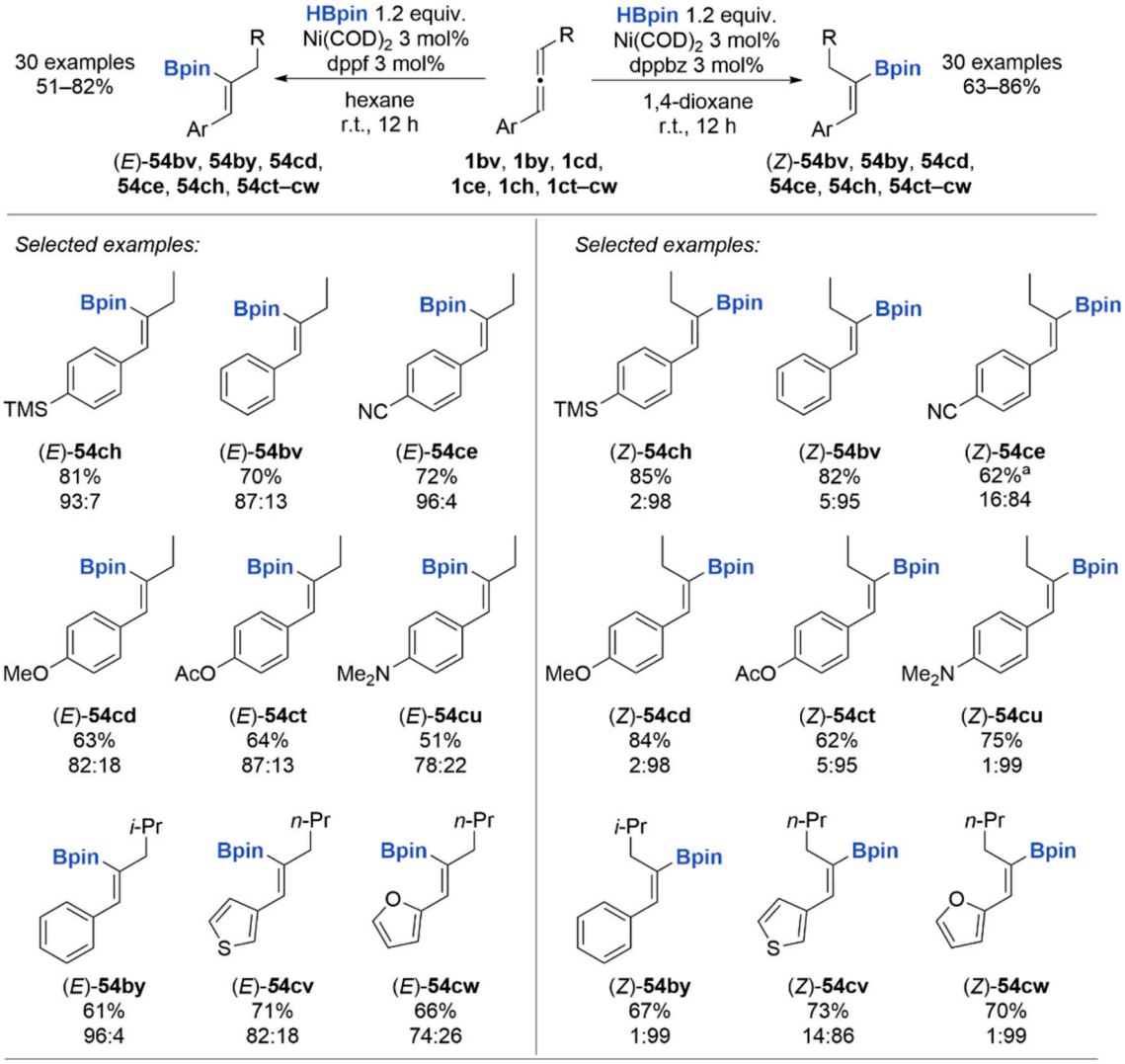


Scheme 31. Proposed catalytic cycles for allenes hydroboration catalyzed by $Ni(acac)_2/P(4\text{-}CF_3Ph)_3$ and $Co(acac)_2/PPh_3$.

to generate the catalytically active copper hydride $(L^1)CuH$. The catalytic cycle begins with the insertion of the Cu—H bond into an allene from its less sterically hindered side. This leads to the formation of a kinetic product - (*Z*)-σ-allylic copper species, which then isomerises into the corresponding thermodynamically stable (*E*)-σ-allylic copper intermediate. Finally, σ-bond metathesis with HBpin releases the final product and regenerates copper hydride (Scheme 25). In the same work, authors also presented protoboration of allenes employing B_2pin_2 and MeOH in the presence of a different copper complex. In this case, regioselectivity was completely reversed compared to hydroboration process described above.

In 2020, Ma et al. developed a cobalt-catalyzed hydroboration reaction of terminal allenes in the presence of pincer ligand and $NaBHEt_3$ (activator) to access (*Z*)-allyl boronate products. [60] The procedure was effective for both monosubstituted, disubstituted allenes as well as bisallenes bearing various functional groups such as ester, benzyloxy, N-heterocycles, OTBS (OTBS = O(Si(Me)$_2$*t*-Bu) and ketal. Moreover, the procedure exhibited excellent chemoselectivity for allenes with additional isolated double C═C bond in the structure (enallens **1bp** and **1bq**) leading to HBpin addition to π-conjugated double bonds, whereas the alkene moiety was intact (Scheme 26). Obtained (*Z*)-allylboronates have also been used as effective building blocks in organic synthesis. For instance, **(*Z*)-53ai** successfully underwent Suzuki-Miyuara coupling, allylborylation of benzaldehyde and conversion to linear or branched allylic alcohol by the reaction with different oxidants. The mechanism of this cobalt-catalyzed allene hydroboration was investigated using SAESI-MS/MS experiments with allene **1ai** as a substrate to confirm hypothesized intermediates. Optimization of the reaction conditions revealed that activation of the cobalt precatalyst with $NaBHEt_3$ was essential to generate the catalytically active species: Co(I) hydride. In the next step of the catalytic cycle, active form of the catalyst coordinates to the terminal C═C bond of allene from the less hindered side. The same double bond is then inserted into the Co—H bond leading to the (*Z*)-allylic cobalt intermediate. Catalytic cycle is finished when (*Z*)-allylic cobalt species reacts with HBpin, either by σ-bond metathesis or by oxidative addition and reductive elimination, to give final product and regenerate cobalt-hydride species (Scheme 27). It should be noted that, unlike (*Z*)-σ-allylic copper species described by the Tsuji group, (*Z*)-σ-allylic cobalt species do not isomerize to the corresponding (*E*)-isomer.

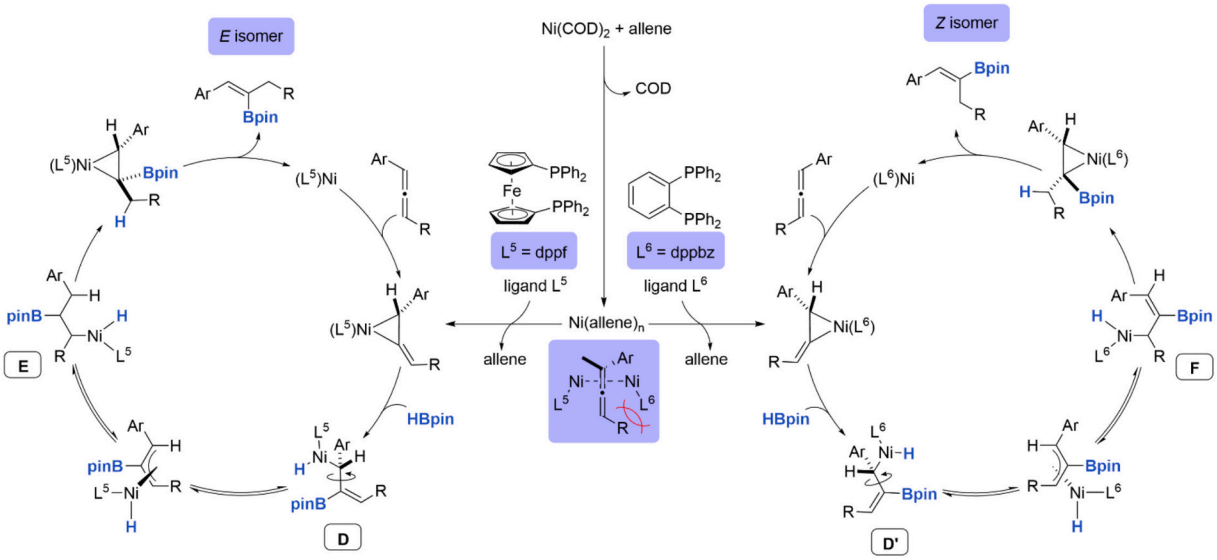
Independently, the Ge group reported the ligand-controlled cobalt-catalyzed regiodivergent hydroboration of internal allenes. [61] Their findings, in line with Yamamoto's earlier studies, demonstrated that the regioselectivity of hydroboration can be finely tuned by the strategic selection of ligands coordinated to the cobalt catalyst. Specifically, the choice of biphosphine ligands dictates which of the two C═C bonds in the allene undergoes borylation. At the outset, 13 biphosphine ligands were evaluated in hydroboration of buta-1,2-dien-1-ylbenzene with HBpin in the presence of $Co(acac)_2$, uncovering a compelling trend correlated with the bite angles of the ligands. When bisphosphines with medium bite angles (such as 98° for dppb and 96° for dppf) were employed, HBpin was selectively added to the alkyl-substituted double bond. Conversely, ligands with larger bite angles (such as 111° for xantphos and 114° for Nixantphos) facilitated selective addition to the aryl-substituted double bond. Notably, ligand selection influenced only the regioselectivity, with no effect on stereoselectivity affording (*Z*)-isomer exclusively. These results showed that the regioselectivity of the reaction is governed by a synergy of the ligand bite angle and steric or electronic effects of the substrate. Ligands with medium bite angles favour steric control, preferentially directing borylation toward the more sterically accessible alkyl-substituted C═C bond. In contrast, when ligands with larger bite angles are used, electronic activation of an allene is dominant, promoting hydroboration at the more sterically hindered but electronically activated phenyl-substituted C═C bond. The hydroboration of 1-aryl-3-alkyl-disubstituted allenes in ambient conditions, provided deeper insight into regioselectivity, highlighting the interplay between substrate structure and biphosphine ligands. Using $Co(acac)_2$ and dppf (with medium bite angle) hydroboration predominantly occurred at the alkyl-substituted C═C bond (21 examples) (Scheme 28). However, for bulkier alkyl groups (*i*-Pr in **1by** or cyclohexyl in **1bx**), steric hindrance redirected borylation to the aryl-substituted bond (Scheme 28). The process tolerated diverse functional groups including ether, halogen, trimethylsilyl, cyano, ester attached to aromatic ring as well as sulfur- and oxygen-containing heteroaryl rings. Switching to $Co(acac)_2$ and xantphos (with large bite angle) selectively promoted hydroboration at the aryl-substituted C═C bond, confirming ligand's influence on regioselectivity, due to dominance of electronic effects (Scheme 28). However, most of halogens (Cl, Br and I) were incompatible in the process, as they were replaced by the Bpin moiety (Scheme 28). A series of control experiments were performed to investigate the mechanism. For catalyst activation, HBpin reacts with $Co(acac)_2$ in the presence of bisphosphine ligands to produce the Co—H species. Nevertheless, unlike Li's earlier findings, this cobalt intermediate does not



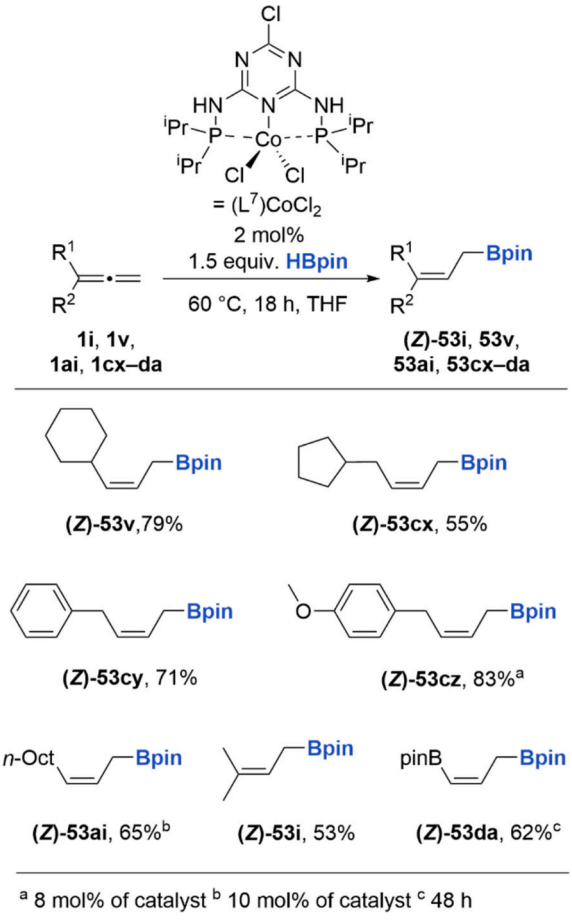
Scheme 32. Hydroboration of allenes in the presence of $Ni(COD)_2$ and dppf or dppbz.

directly participate in the catalytic cycle. Instead, it reacts with allene and second molecule of HBpin, leading to hydrogenation of allene and the formation of catalytically active Co-Bpin species. Subsequently, migratory insertion of allene into this Co-Bpin intermediate generates an allyl cobalt species, whose structure depends on the biphosphine ligand. This species then reacts with HBpin, releasing the final product and regenerating the Co-Bpin catalyst. (Scheme 29) The proposed mechanism suggested that the Co-catalyzed regiodivergent hydroboration would not occur for alkyl,alkyl-1,3-disubstituted allenes with similar steric hindrance at both double bonds. However, increasing bulkiness of one group or utility of terminal allene could enable selective hydroboration on the less hindered site, which indeed was confirmed by experiments.

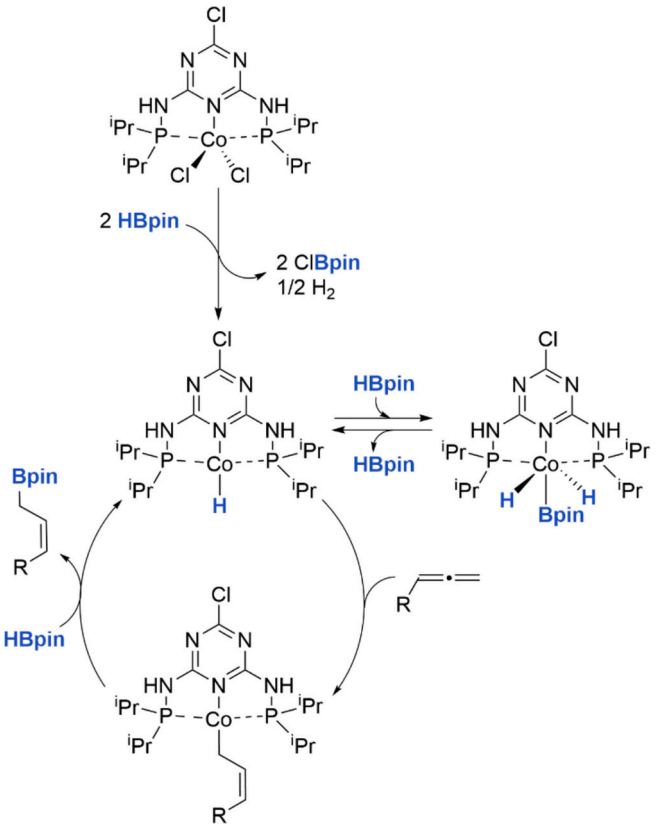
One year later, Zhan and his coworkers reported regiodivergent HBpin addition to terminal 1,2-dienes using cobalt and, for the first time, nickel catalytic systems in the presence of simple phosphines. [62] A wide range of alkyl-substituted allenes underwent selective hydroboration at internal C═C bond catalyzed by $Ni(acac)_2/P(4\text{-}CF_3Ph)_3$, whereas $Co(acac)_2/PPh_3$ promoted hydroboration at the terminal C═C bond (Scheme 30). For both catalytic systems, boryl group was attached to the β-carbon of allene to yield *gem*- or (*Z*)-isomers, respectively. The reactions proceeded under mild conditions and tolerated various functional groups including carboxylic ester, ether, alcohol and chloro moieties. However, aryl-substituted allenes were not appropriate substrates since they led to complex mixture of products, likely due to their higher reactivity. The regioselectivity differences were attributed to distinct catalytic mechanisms of cobalt and nickel. Building on their previous work on allene hydrosilylation and related studies, [63–66] along with control experiments using $Ni(COD)_2$, the authors proposed a catalytic cycle involving Ni(0) species. Accordingly, the nickel-catalyzed allene hydroboration, as depicted in Scheme 31, begins with in situ reduction of the Ni precursor with HBpin to form a Ni(0) species. Oxidative addition of HBpin to Ni(0) generates a proposed H–Ni–Bpin species (**A**). Subsequent coordination of the allene to nickel affords intermediate **B**. Migratory insertion of the coordinated allene into the Ni—H bond then gives an π-allyl intermediate (**C**), which undergoes further transformation to furnish the vinylborane product and regenerate Ni(0). The formation of the catalytically active species in cobalt-



Scheme 33. Proposed catalytic cycles for allenes hydroboration catalyzed by $Ni(COD)_2$ and dppf or dppbz.

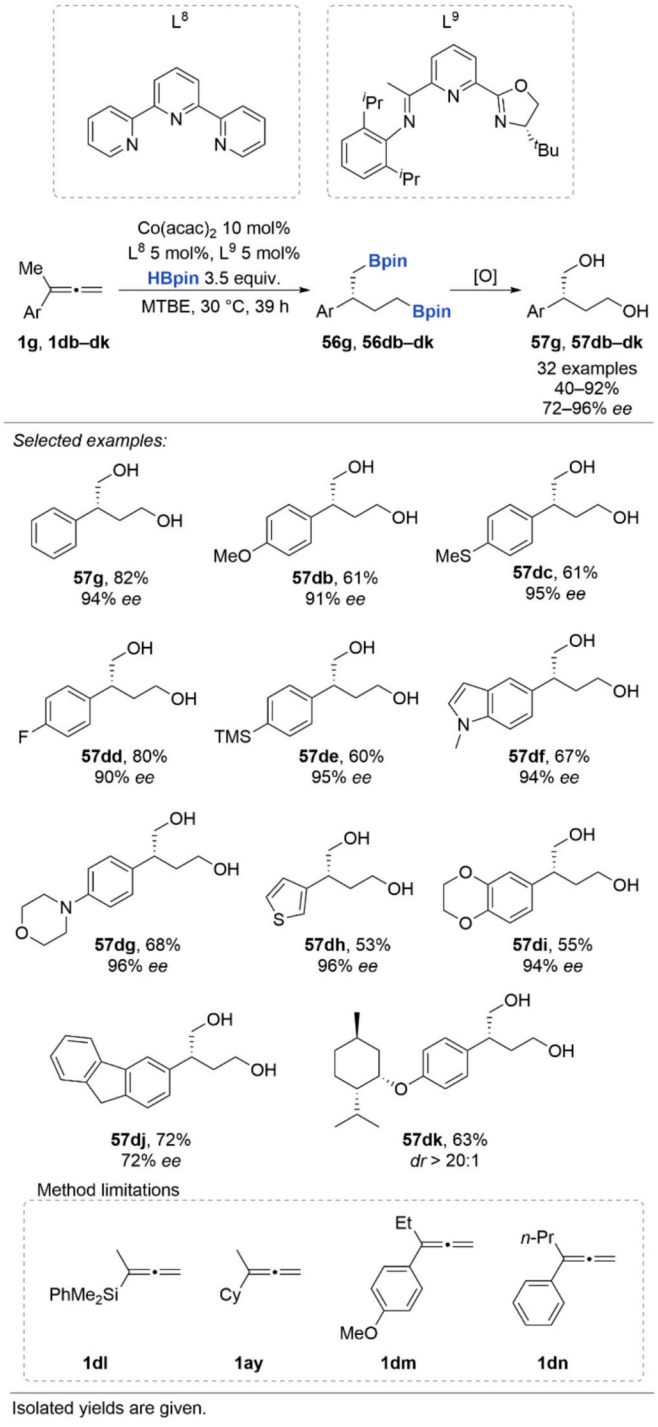


Scheme 34. Hydroboration of allenes in the presence of cobalt pincer complex.



Scheme 35. Proposed mechanism for allenes hydroboration with the cobalt pincer complex.

catalyzed hydroboration of allenes was proposed based on the mechanistic insights from Ge's work. [61] The active (L^4)Co–Bpin complex is generated through the reduction of $Co(acac)_2$ by HBpin in the presence of a phosphine ligand L^4. Coordination of the allene to the (L^4)Co–Bpin complex yields intermediate **B′**, which is proposed to evolve to a π-allyl cobalt species **C′**. Subsequent reaction of **C′** with HBpin releases the (*Z*)-alkenylboronate product and regenerates the active (L^4)Co–Bpin species. A plausible explanation for the divergent regioselectivity of cobalt



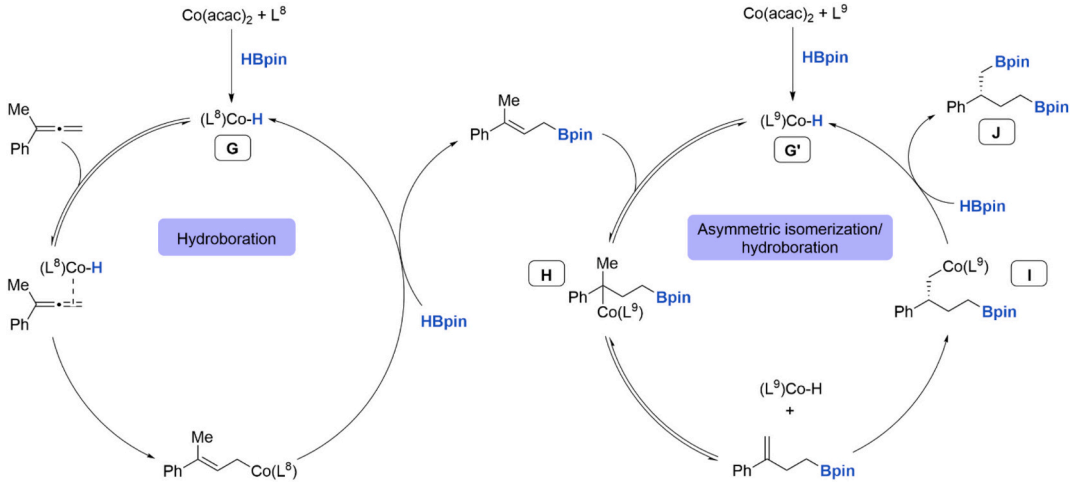
Scheme 36. Dihydroboration of 1,1-methyl-aryl-disubstituted allenes in the presence of $Co(acac)_2$, tpy (L^8) and chiral oxazoline iminopyridine (L^9).

and nickel systems lies in different structures of catalytic active species (ligand-metal-Bpin or metal-ligand, respectively). In the cobalt system, the catalytically active species is proposed to be a (L^4)Co–Bpin complex, and regioselectivity is established during reaction of the π-allyl cobalt species **C′** and second molecule of HBpin resulting in intermolecular addition of hydrogen atom at the terminal position (γ-position) of the initial allene framework. In contrast, in the nickel system, the catalytically active species is proposed to be a Ni(L^3)(0), which then reacts with HBpin resulting in H-Ni-Bpin intermediate **A**. Due to this fact, the π-allyl nickel species **C**, formed during catalytic cycle, consists of Ni—H bond and undergoes reductive elimination and intramolecular addition of hydrogen atom at α-position of the initial allene framework.

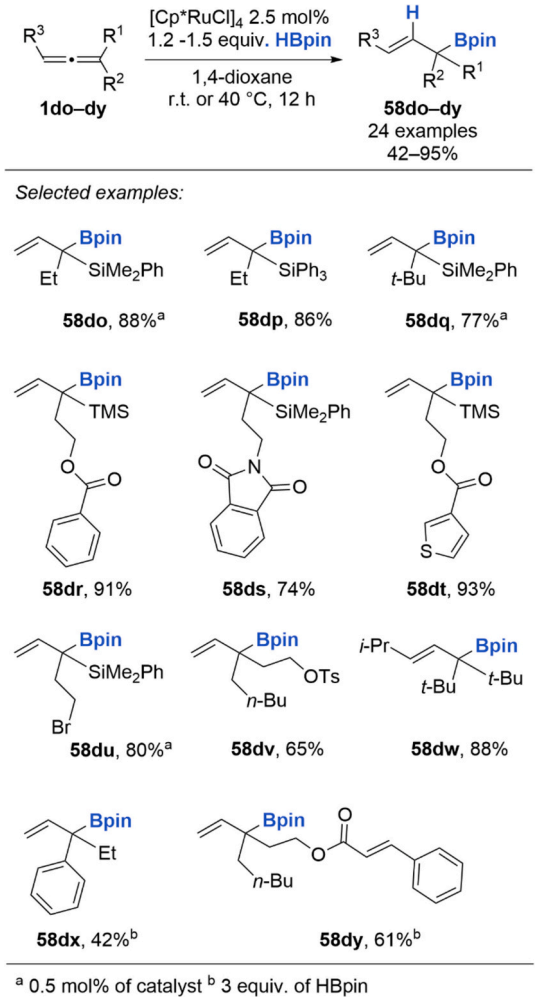
In 2023, the Ge group revisited the hydroboration of allenes and reported a comprehensive study focused on stereoselectivity control using nickel-based catalytic system. [67] By employing $Ni(COD)_2$ as a catalyst precursor with different phosphine ligands, either (*E*)- or (*Z*)-alkenylboronates were selectively produced. While preserving regioselectivity, the choice of ligand allowed to control the stereoselectivity of this nickel-catalyzed allene hydroboration – (*E*)- or (*Z*)-alkenylboronates were synthesized using dppf or dppbz, respectively. A variety of internal allenes including aryl,alkyl-, diaryl- and dialkyl-substitued (30 examples in total) were converted to the corresponding stereodefined alkenylboronates under ambient conditions, with moderate to high yields (Scheme 32). The process was tolerant to a wide range of functionalities such as silyl, cyano, ether, sulphide, fluoro, chloro, ester, amine and amide moieties. Nevertheless, both electronic and steric properties of the allene substituents influenced the *E/Z* selectivity. In the presence of $Ni(COD)_2$ and dppf, (*E*)-selectivity increased, when allene with electron-deficient aryl groups were used, and decreased for electron-rich aromatic rings substituents. Conversely, (*Z*)-favoring $Ni(COD)_2$/dppbz system showed enhanced selectivity with electron-donating aryl groups and lower selectivity with electron-withdrawing substituents. Steric effects were significant only in the $Ni(COD)_2$/dppf system – substrates with bulkier moieties enhanced (*E*)-selectivity. In contrast, the stereoselectivity of the $Ni(COD)_2$/dppbz system was largely unaffected by alkyl group size. To explain observed selectivity and elucidate the reaction mechanism, the authors conducted a wide range of experiments including synthesis and isolation of nickel intermediates, stoichiometric transformations, kinetic studies and deuterium-labelling experiments. Based on these investigations, plausible mechanism was proposed (Scheme 33). It begins with ligand exchange between $Ni(cod)_2$ and allene, giving allene-ligated nickel(0) species $Ni(allene)_n$, which reacts with bisphosphine ligand to form bisphosphine-coordinated nickel-allene complex. Subsequently, σ-bond metathesis with HBpin gives η^1–allyl nickel intermediate **D** or **D′**, which then undergoes ligand-controlled σ-π-σ isomerization producing either nickel intermediate **E** or **F**, which corresponds to (*E*)- or (*Z*)-alkenylboronates, respectively. Reductive C—H elimination from these intermediates, accompanied by coordination of the C═C bond to nickel, gives nickel-olefin complexes. Dissociation of the alkenylboronate product regenerates unsaturated nickel species (L^5)Ni(0) or (L^6)Ni(0), which reacts with another allene substrate to re-enter the catalytic cycle.

In 2024, three additional reports on the hydroborations of allenes were published. In first of these, Lewandowski and Hreczycho investigated the cobalt-catalyzed addition of HBpin to terminal allenes leading to (*Z*)-isomer of allylic boronates. [68] Although the same type of products were obtained in Li's earlier work using cobalt-based catalyst as well, Lewandowski proposed a procedure in which external activators were not needed. However, the reaction was carried out with an excess of HBpin and elevated temperature (60 °C). The method showed good efficiency for alkyl-substituted allenes but was not compatible with aryl-substituted analogues, which reacted to yield the mixture of various products (Scheme 34). Based on the NMR experiments and literature reports, the authors proposed a plausible mechanism of the process (Scheme 35). In the initial step, HBpin reacts with precatalyst (L^7)$CoCl_2$ to generate a mixture of Co(I) and Co(III) species in equilibrium. Both species are proposed to be catalytically active, although primary catalytic activity is attributed to Co(I) species. The next step involves the insertion of the allene into Co—H bond, followed by transmetallation with HBpin to yield the allylboronate product and regenerate the active cobalt catalyst.

In the same year, the Zhao group reported the first example of dihydroboration of 1,1-disubstituted allenes using a cobalt catalyst system comprising $Co(acac)_2$ and two simple ligands—one achiral and one chiral. [69] This method enabled the synthesis of asymmetric organodiboron compounds **56**, which, after oxidative workup, furnished a library of 32 chiral diols **57** (Scheme 36). The reaction proceeded



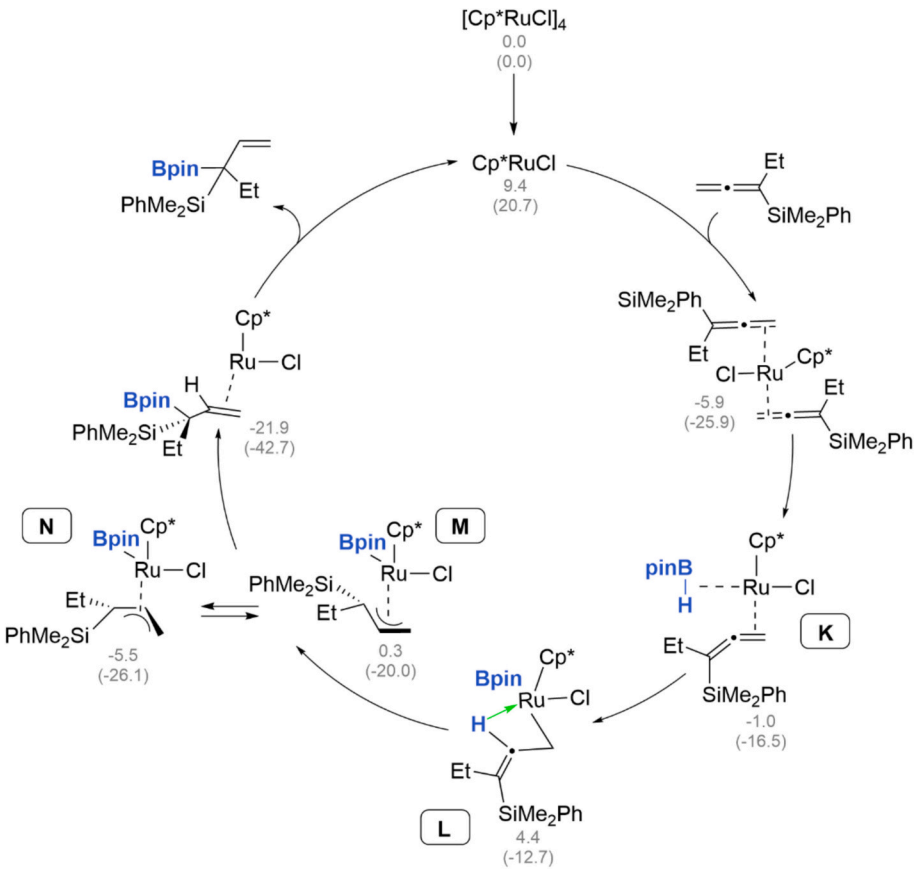
Scheme 37. Plausible mechanism of dihydroboration of 1,1-methyl-aryl-disubstituted allenes in the presence of $Co(acac)_2$, tpy (L^8) and chiral oxazoline iminopyridine (L^9).



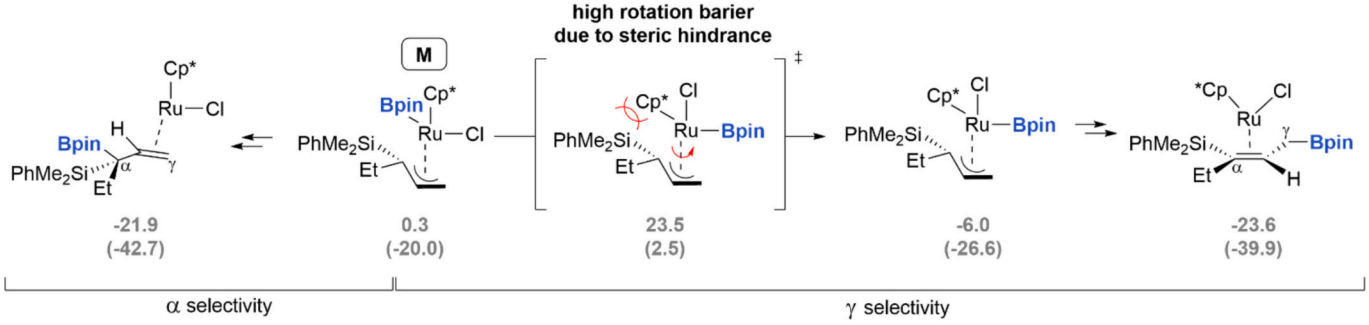
Scheme 38. α-Regioselective hydroboration of allenes in the presence of $[Cp^*RuCl]_4$.

smoothly with a wide range of 1,1-disubstituted allenes bearing methyl and aryl substituents and displayed excellent tolerance toward various functional groups on the aryl ring including trifluoromethyl, ether, thiol, ester and hydroxyl moieties. Additionally, allenes substituted with methyl group and aromatic heterocycle were also compatible with the reaction conditions. In contrast, substrates bearing larger alkyl substituents, such as ethyl (**1dm**), propyl (**1dn**), silyl (**1dl**), and dialkyl (**1ay**), did not furnish desired dihydroboration products (Scheme 35). To elucidate the reaction mechanism, the authors performed a series of control experiments, which suggested that this cobalt-catalyzed allene dihydroboration proceeds via a ligand relay catalysis. In this system, the first ligand L^8, 2,2′:6′,2″-terpyridine (tpy), facilitates the selective formation of an achiral allylic boronate intermediate from the allene and HBpin. The second ligand, a chiral oxazoline iminopyridine (L^9), promotes enantioselective addition of the borane to the remaining C═C bond. The mechanism proceeds through two interconnected catalytic cycles (Scheme 37). In the first one, the cobalt hydride species (L^8)Co–H (**G**) is generated in situ from $Co(acac)_2$, tpy (L^8), and HBpin. Coordination of the allene to the cobalt center is followed by hydrometallation, yielding a π-allyl-cobalt species, which reacts with HBpin, likely via σ-bond metathesis or oxidative addition/reductive elimination, to regenerate the cobalt hydride species and release the (*E*)-allylic boronate intermediate. The second catalytic cycle involves migratory insertion of the allylboronate intermediate into the (L^9)Co–H (**G'**) to form intermediate **H**. Subsequent β-H elimination followed by second migratory insertion leads to the chiral alkyl Co species **I**. Final reaction with HBpin regenerates the cobalt hydride species **G'** and releases the final product **J** (Scheme 37).

In 2025, a unique α-regioselective hydroboration of 1,1-disubstituted allenes was reported by Sun and his coworkers. In their study, the addition of HBpin to a 1,2-diene in the presence of a ruthenium catalyst, specifically $[Cp^*RuCl]_4$, exclusively afforded unusual, highly sterically hindered α-boration products. [70] The reaction proceeded under mild conditions and exhibited high regio- and chemoselectivity. In addition, this ruthenium-catalyzed hydroboration tolerates a broad range of functional groups, such as imide, silyl ether, halide, heterocycle, tosylate, and carboxylic esters (Scheme 38). Among the tested substrates, 1,1-silyl,alkyl-disubstituted allenes gave the best results. 1,1-Dialkyl and 1-alkyl-1-aryl- substituted allenes were also compatible, but higher equivalents of HBpin were necessary to achieve high conversions of these allene substrates. In contrast, monosubstituted allenes were unreactive under their identified conditions. Notably, trisubstituted allenes underwent the addition of HBpin with the same regioselectivity as observed for 1,1-disubstituted analogues. To rationalize the unusual regioselectivity, specifically, the attachment of the boryl group to the more sterically hindered α-position of the allene, the authors investigated the reaction mechanism. A combination of deuterium labelling and kinetic isotope effect (KIE) experiments, together with DFT



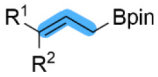
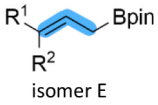
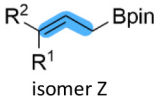
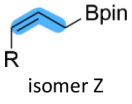
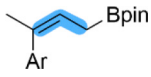
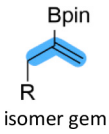
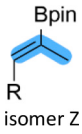
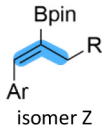
Scheme 39. Plausible catalytic cycle for the α-hydroboration of allenes in the presence of $[Cp^*RuCl]_4$ with calculated relative Gibbs free energies and electronic energies, ΔG_{sol} (ΔE_{sol}) respectively in kcal/mol.



Scheme 40. Energy profile for reductive elimination from intermediate M at α- and γ-positions. Calculated relative Gibbs free energies and electronic energies, ΔG_{sol} (ΔE_{sol}) respectively in kcal/mol are given.

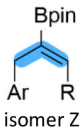
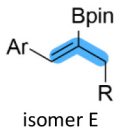
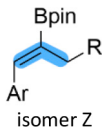
calculations, was employed. The proposed catalytic cycle, as depicted in Scheme 39, begins with the dissociation of $[Cp^*RuCl]_4$ into its monomeric form Cp*RuCl, a 14-electron complex, which then coordinates two allene molecules as it is thermodynamically favorable. One allene ligand is subsequently replaced by HBpin, generating a key intermediate **K**. Oxidative migratory insertion results in the addition of hydrogen atom to β-carbon of allene and the formation of intermediate **L**, which is stabilized by an agostic interaction with the vinylic hydrogen. Moreover, this interaction acts as a counteraction of forming transition state for direct reductive elimination, which would otherwise be anticipated as a low-barrier step toward direct γ-boration. Upon rotation along the C_γ–C_β bond, agostic attraction is released and two π-allyl intermediates (**M** or **N**) are formed, depending on direction of the rotation. They can be considered as *pseudo* diastereoisomers to each other and they both lead to the same final α-borylated product via reductive elimination, while regenerating the active catalyst form Cp*RuCl. In the context of unusual regioselectivity of this reaction, the most crucial step of its mechanism is connected to the formation of π-allyl intermediate **M** or **N** and specific structures that they possess. Although its open γ-position seems more accessible for Bpin group to attach, α-position is favored in fact. The exclusive formation of the α-borylated regioisomer can be rationalized by several factors. The Bpin group in the π-allyl intermediate (**M** or **N**) is inherently oriented toward the α-carbon, and a favorable but weak H···O interaction exists between the vinylic hydrogen and an oxygen atom of the Bpin unit. These features facilitate direct reductive elimination to form the C_α–B bond. In contrast, a γ-selective elimination would require an additional rotation of the Cp*RuCl(Bpin) moiety relative to the π-allyl ligand to orient the Bpin toward the terminal γ-carbon. DFT calculations indicate that this reorientation has a prohibitively high energy barrier (23.5 kcal/mol) due to severe steric repulsion between the bulky Cp*

Table 1
Comparative overview of selected catalytic systems for allene hydroboration.

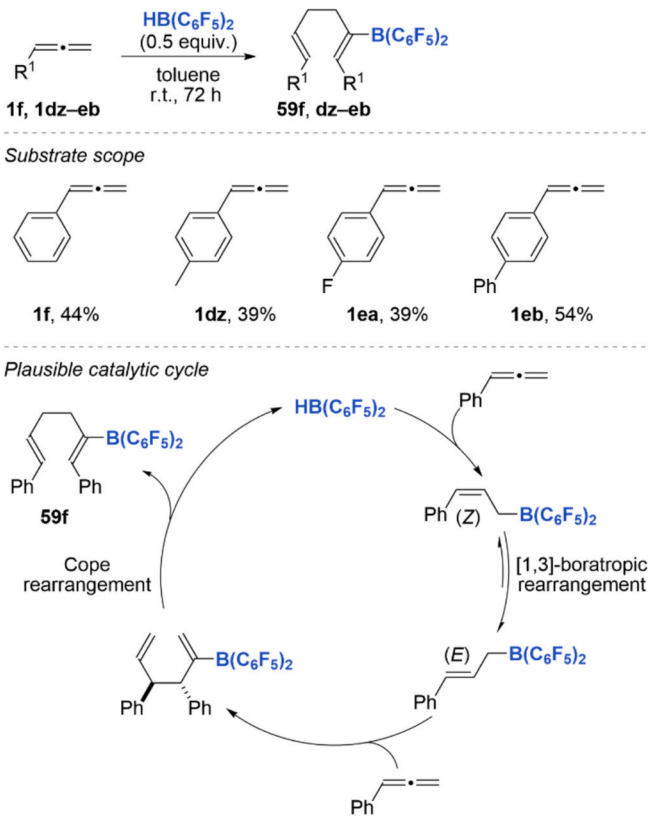
Catalytic system	Allene type	Reactions conditions	Type of product(s)	Advantages	Limitations	Key mechanistic feature	Ref.
							
$Pt(dba)_2$/ phosphine ligand[a]	Terminal	50 °C, 2 h, toluene 1.5 equiv. of HBpin		Early precedent; operational simplicity	Moderate selectivity; limited scope	Allene insertion into either H—Pt bond or into Pt–Bpin bond depending on phosphine used	[58]
							
$CuCl/CF_3$Ar-Xan/NaO(t-Bu)	Terminal	28 °C, 2 h, dioxane 1.2 equiv. of HBpin		High *E*-selectivity; mild conditions	Mainly terminal allenes; reduced E/Z for some alkyl substrates	Allene insertion into Cu—H bond and generating σ-allyl–Cu intermediate	[59]
$(L^2)CoCl_2$ / $NaBHEt_3$	Terminal	r.t., 24 h, toluene 1 equiv. of HBpin		Excellent regio- and *Z*-control; broad FG tolerance	Requires hydride activator; longer reaction time	Allene insertion into Co—H bond and generating σ-allyl–Co intermediate	[60]
$(L^7)CoCl_2$	Terminal	60 °C, 18 h, THF 1.5 equiv. of HBpin		No external activator; high Z-control	Elevated temperature; narrower scope	Allene insertion into Co—H bond and generating σ-allyl–Co intermediate	[68]
$Co(acac)_2$/tpy	Terminal (1,1-disubstituted)	30°C, 1.5 h, MTBE 1.5 equiv. of HBpin		Broad substrate scope, high selectivity	Higher catalyst loading	Allene insertion into Co—H bond and generating σ-allyl–Co intermediate	[69][b]
$Co(acac)_2$/ PPh_3						Allene insertion into Co–Bpin bond; intermolecular addition	
$Ni(acac)_2$/ $P(4\text{-}CF_3Ph)_3$	Terminal	r.t., 1 h, THF 1.2 equiv. of HBpin		Complementary regioselectivity under mild conditions	Not appropriate for aryl allenes (due to complex mixtures of products)	Ni(0) insertion into HBpin bond; intramolecular addition	[62]
$[Cp^*RuCl]_4$	Terminal (1,1-disubstituted)	r.t. or 40 °C, 12 h, 1,4-dioxane 1.2–1.5 equiv. of HBpin		Unique α-selectivity; complements other systems	Demonstrated mainly for sterically biased substrates	Ru–allene coordination; π-allyl Ru intermediate; selectivity set at reductive elimination	[70]
$Co(acac)_2$/ dppf	Internal	r.t., 12 h, toluene 1.1 equiv. of HBpin		Ligand-controlled regioselectivity and high *Z*-selectivity	Regiodivergence largely restricted to aryl/alkyl internal allenes; reduced for alkyl/alkyl substrates	Allene insertion into Co–Bpin; ligand-controlled insertion site and thus regioselectivity	[61]

(*continued on next page*)

Table 1 (*continued*)

Catalytic system	Allene type	Reactions conditions	Type of product(s)	Advantages	Limitations	Key mechanistic feature	Ref.
$Co(acac)_2$/ xantphos	Internal	r.t., 12 h, hexane 1.2 equiv. of HBpin	 isomer Z	Ligand-controlled stereoselectivity and high regioselectivity	Demonstrated only for internal allenes	Ni(0)–allene coordination; coordination-controlled stereochemistry	[67]
$Ni(COD)_2$/ dppf			 isomer E				
$Ni(COD)_2$/ dppbz		r.t., 12 h, 1,4-dioxane 1.2 equiv. of HBpin	 isomer Z				

General conditions of reactions are given. [a] PCy_3 or $P(t\text{-}Bu)_3$ or TTMPP; type of product is dependent on both the ligand and allene structure. [b] Presented conditions are regarding to the first step (hydroboration of allene) of the sequential hydroboration/ isomerization/ asymmetric hydroboration process.

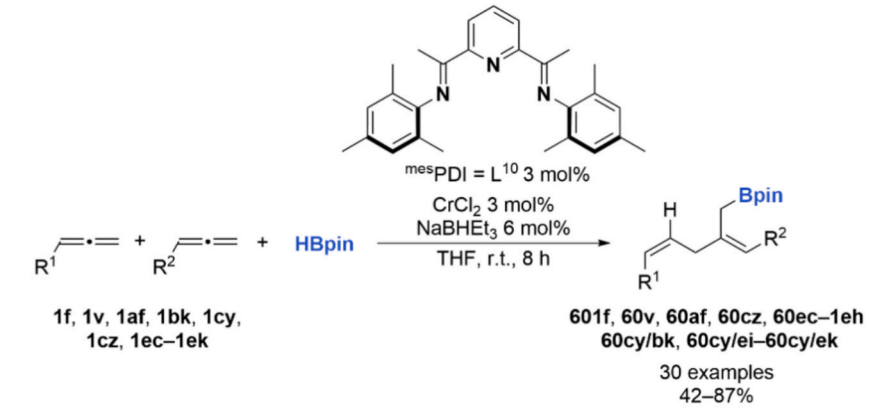


Scheme 41. Hydroboration/dimerization of arylallenes with Piers' borane.

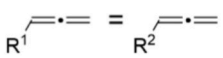
ligand and the substituents at C_α (Scheme 40). Thus, the pathway to γ-boration is rendered kinetically inaccessible and the reaction proceeds exclusively via α-boration, despite the greater steric hindrance at the allene's α-position.

Table 1 summarizes the catalytic systems reported for the hydroboration of allenes and highlights the principal trends observed across different metal platforms. In most cases, the reactions proceed under mild conditions, typically at room temperature or with mild heating, and require only a small excess of HBpin. As demonstrated in Yamamoto's pioneering work on Pt complexes, [58] the structure of the hydroboration product may depend on the substitution pattern of the allene. However, in the systems collected here, the dominant factors controlling regio- and stereochemical outcome are the metal center and, in particular, the ligand environment. This is especially evident when comparing cobalt- and nickel-based catalysts. Cobalt complexes bearing pincer ligands preferentially afford products in which the boryl group is introduced at the terminal carbon of the allene framework, leading to allylboranes, [60,68,69] whereas cobalt catalysts coordinated by mono- or bidentate phosphines favour formation of alkenylboranes with the Bpin group located at the internal carbon. [61,62] In contrast, nickel catalysts provide exclusively alkenylboranes; nevertheless, appropriate ligand tuning enables the control over the position of the double bond or its geometric configuration in the final product. [62,67]

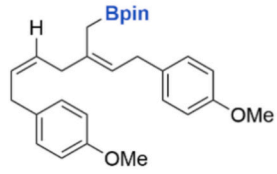
The origin of regioselectivity can be rationalized by considering the initial steps of the catalytic cycle. In several systems operating on terminal allenes, such as those based on Cu [59] and selected Co catalysts, [60,68,69] the cycle is proposed to begin with formation of a metal hydride species generated from the metal precursor and HBpin (or via base-assisted activation). Subsequent insertion of the terminal C═C bond into the M–H bond gives a σ-allyl–metal intermediate, which then reacts with HBpin to furnish the corresponding allylborane and regenerate the active hydride species. In other systems, particularly those involving phosphine-ligated cobalt complexes, [61,62] the catalytically active species is proposed to contain a metal–boryl unit (Co–Bpin), and insertion of the allene into the M–B bond leads to alkenylborane products. Nickel catalysts described by Zhan and co-workers [62] are proposed to operate through a Ni(0)-mediated pathway involving oxidative addition and reductive elimination, while the stereodivergent $Ni(COD)_2$ /dppf and dppbz systems [67] as well as the Ru catalyst $[Cp^*RuCl]_4$ [70] involve initial coordination of the allene to the metal center, with subsequent steps within the coordinated complex determining the final regio- or stereochemical outcome.



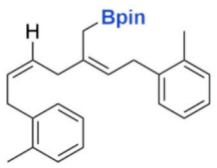
Homodimerization/hydroboration



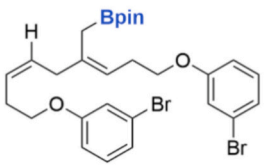
Selected examples:



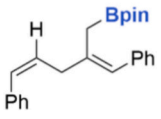
60cz, 76%



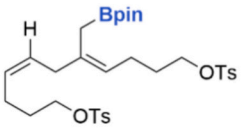
60ec, 78%



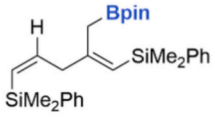
60ed, 67%



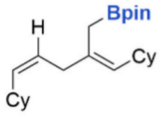
60f, 62%



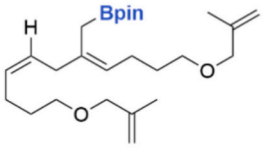
60ee, 52%[a]



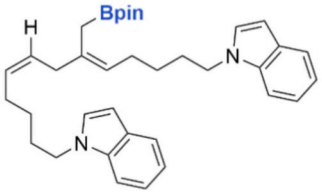
60af, 62%



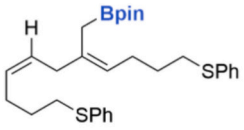
60v, 87%



60ef, 73% [b]

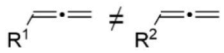


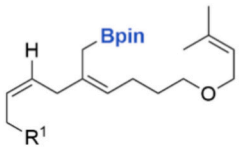
60eg, 60%



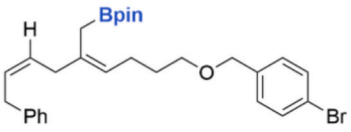
60eh, 66%

Crossdimerization/hydroboration

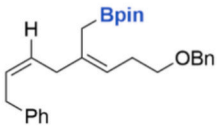




R^1 = Ph, **60cy/ei,** 45%
R^1 = Bn, **60cy/ej,** 40%



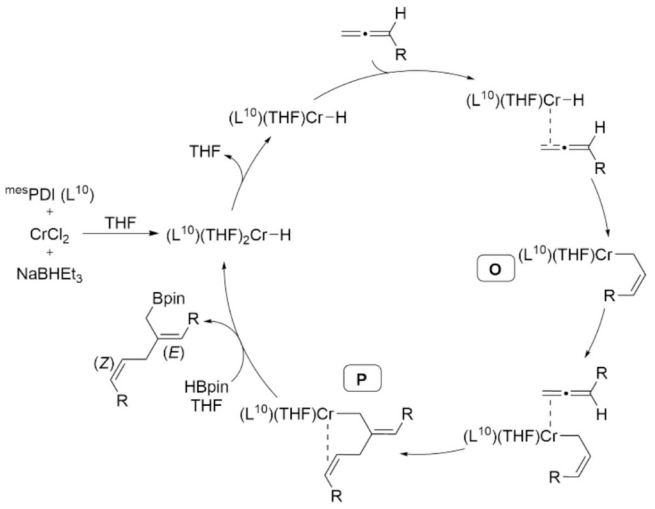
60cy/ek, 51%



60cy/bk, 42%

Isolated yields are given. Homodimerization/hydroboration: allene (1 equiv.), HBpin (0.6 equiv.)
Crossdimerization/hydroboration: allene R^1 (2 equiv.), allene R^2 (1 equiv.), HBpin (0.6 equiv.)
[a] 50 °C [b] 40 °C

Scheme 42. Chromium-catalyzed dimerization/hydroboration of allenes.



Scheme 43. Mechanism of chromium-catalyzed dimerization/hydroboration of allenes.

1.3. Hydroboration/dimerization of allenes

Broad scope of terminal and internal allenes has been transformed to allyl or alkenylboronates via addition of pinacolborane in the presence of metal catalysts or using higly reactive alkylboranes eg., 9-BBN, $(^{d}Ipc)_2BH$. However, Erker's and Ge's groups discovered that the reaction of borane and allenes can proceed via a process combining both hydroboration and dimerization reactions, leading to boryl-functionalized skipped dienes. [71,72]

In 2018, Erker and coworkers reported a dimerization of arylallenes induced by Piers' borane ($HB(C_6F_5)_2$). [71] The reaction between two equivalents of an arylallene and $HB(C_6F_5)_2$ led to the formation of a boryl-substituted 1,6-diaryl-1,5-hexadienes (Scheme 41). The transformation initiates with a *Z*-selective 2,3-hydroboration of the allene, followed by a [1,3]-boratropic shift to generate an *E*-allylborane intermediate. [73] Subsequent allylboration with a second equivalent of arylallene affords the boryl-substituted diene, which then undergoes a boryl-enabled Cope rearrangement. Notably, the entire sequence occurs at room temperature, whereas similar Cope rearrangements typically require heating to around 100 °C, [74] highlighting the role of the electrophilic boryl group in facilitating the rearrangement. Furthermore, Gellrich and coworkers later demonstrated that such bis (pentafluorophenyl)borane-substituted products can undergo transborylation with HBpin to afford bench-stable boronate derivatives. [75]

Two years later, the Ge's group reported a study focused on syntheses of boryl-substituted (*E,Z*)-1,4-dienes via chromium-catalyzed dimerization/hydroboration of allenes. [72] The developed process proceeds at room temperature, in the presence of $CrCl_2$, pyridine-2,6-diimine ligand ^{mes}PDI, and $NaBHEt_3$ as an activator. Except substrates with ketone or aldehyde moieties, which were not tolerated in this process, a wide range of terminal allenes with different functionalities, such as ether, halide, tosylate, silyl, silyl ether, terminal alkene, and thioether groups, were transformed to the desired products in modest to high isolated yields (Scheme 41). Moreover, the developed transformation proceeded either via homo- or cross-dimerization/hydroboration when employing one type of allene or two different allenes, respectively (Scheme 42). To investigate mechanism of this process, the authors examined solvent effects and conducted EPR spectroscopic analysis, control experiments, and kinetic studies. The obtained results suggested that $CrCl_2$ is activated with $NaBHEt_3$ in the presence of ^{mes}PDI (L^{10}) in THF to generate a Cr(I) hydride $(L^{10})(THF)_2Cr–H$, which begins the catalytic cycle. Then, after the dissociation of one THF molecule, sterically and electronically unsaturated Cr(I) hydride species $(L^{10})(THF)Cr–H$ is formed and then coordinated with allene. Subsequent migratory insertion results in allylchromium intermediate **O**, which coordinates with second molecule of allene. Then next insertion occurs and new C—C bond between two allenes molecules is formed, leading to allylchromium species **P**. Its further migratory insertion reactions with allenes are probably inhibited by the intramolecular coordination of the *cis*-C=C bond. The last step of the catalytic cycle is the reaction of intermediate **P** and HBpin, resulting in the regeneration of $(L^{10})(THF)_2Cr–H$ and the formation of final product. Its (*E,Z*) isomerism can be explained by steric hindrance between chromium catalyst and R substituent when allene coordinates to the chromium center – specific reaction geometry is promoted to minimize their repulsion (Scheme 43).

2. Conclusions and outlook

The hydroboration of allenes has been extensively studied, revealing a diverse range of mechanistic pathways and selectivity-determining factors. Non-catalytic hydroboration, employing various dialkylboranes, has enabled the straightforward synthesis of organoboron compounds under mild conditions, frequently affording high regio- and stereoselectivity. However, these transformations typically rely on highly reactive alkylboranes, which are used in situ without the isolation of boron-containing products. In contrast, recent advances in transition metal-catalyzed hydroboration of allenes have significantly broadened the synthetic utility of this transformation, enabling the selective formation of structurally diverse and reasonably stable organoboron compounds that are inaccessible under catalyst-free conditions. Remarkably, distinct selectivity patterns can be achieved using the same metal complex and under comparable or even identical conditions, by appropriate choice of the ligand. Furthermore, a key advantage of catalytic approaches lies in their ability to generate isolable organoboranes under mild conditions, which can be employed in downstream transformations with greater control over stereochemistry and functional group compatibility. Despite these developments, the application of metal-catalyzed allene hydroboration in the synthesis of pharmaceuticals and other complex bioactive molecules remains unexplored, presenting vast opportunities for its strategic integration into modern synthetic planning. In particular, the incorporation of allene hydroboration into sequential or tandem catalytic processes represents a domain with high-potential. The in situ generation of functionalized organoboron intermediates could enable one-pot hydroboration and cross-coupling sequences, cascade cyclizations, or multicomponent transformations, thereby facilitating the construction of structurally complex molecules. [76–79]

Looking ahead, the development of sustainable and energy-efficient catalytic systems remains a critical challenge. Continued efforts should be directed toward catalytic platforms based on earth-abundant metals such as iron, cobalt, manganese, or copper, especially those operating under ambient conditions and at low catalyst loadings. [80–83] In this regard, the recent emergence of Single-Atom Catalysts (SACs) in hydroboration and related hydrofunctionalization reactions may provide an additional opportunity to combine high activity with well-defined catalytic sites. [84–86] In parallel, the development of photocatalytic and radical-mediated hydroboration strategies in related unsaturated systems suggests that analogous approaches for allenes may unlock complementary reactivity and selectivity profiles under exceptionally mild conditions. [87–90] From both environmental and economic perspectives, the exploration of organocatalysts and main group element-based catalysts represents an exciting and underexplored area of research, as these catalytic systems have been extensively studied in hydroboration reactions of alkenes, alkynes, dienes, diynes, enynes and many other unsaturated bonds. [91–100] These catalysts offer key advantages including low toxicity, earth abundance, and unique reactivity. We hope that this review stimulates interest from the community of photocatalysis, organocatalysis, and organometallic catalysis and encourages synthetic chemists to develop elegant transition metal-free catalytic systems for the divergent hydroboration of allenes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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