APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 327–345

Review

Recent developments in bisdiborane chemistry: B–C–B, B–C–C–B, B–C=C–B and B–C≡C–B compounds†

Valery M. Dembitsky, Hijazi Abu Ali and Morris Srebnik*

Department of Medicinal Chemistry & Natural Products, School of Pharmacy, PO Box 12065, Hebrew University of Jerusalem, Jerusalem 91120, Israel

Received 18 November 2002; Revised 27 November 2002; Accepted 13 January 2003

An overview of the development of new strategies in organic synthesis with a minimum of chemical steps is becoming increasingly necessary for the efficient assembly of complex molecular structures. Therefore, the combination of multiple reactions in a single operation represents a particularly efficient approach. Among these strategies, the synthesis and reactivity of bisdiboranes has never been reviewed although its popularity for the synthesis of complex architectural molecules has been steadily increasing during the last decade. This review is intended to highlight the use of partly geminated boranes (B–C–B), and also bisdiborane reagents (B–C–C–B, B–C=C–B, B–C≡C–B). Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: bisdiborane; geminated boranes; tetraorganodiborane; bis(pinacolato) diborane(4); bis(catecholato) diborane(4); diazoalkanes; insertions; hydroboration; dihydroboration; carbenoids; bis(boryl)alkenes; vinylphosphonates; 1-alkynylboronates; diboration; thermolysis

INTRODUCTION

Bisdiborane derivatives are an important class of compounds in boron chemistry. The addition of diboranes ($X_2B–BX_2$) to unsaturated hydrocarbons, first discovered by Schlesinger and coworkers in 1954,[1] is an attractive and straightforward method to introduce two boryl units into organic molecules.[2–4] Diborane itself, B_2H_4, is stable only when complexed by Lewis base ligands such as amines or phosphines. Although the tetrahalides, B_2X_4 ($X = F$, Cl, Br, I), have a reasonably well-established chemistry, they suffer from low thermal stability (with the exception of B_2F_4) and preparative difficulties. Tetraorganodiborane compounds, B_2R_4, are stable only when substituted with sterically demanding R groups such as *t-Bu,* CH_2–*t*-Bu, and mesityl. The most stable derivatives are those in which good π-donor groups are present such as amido (NR_2) or alkoxy (OR).[5,6] More recently, as part of the interest in the oxidative addition chemistry of the B–B bond and metal-catalyzed diborations of alkenes[7–10] and alkynes,[11–16] synthesis of stable, crystalline bis(pinacolato) and bis(catecholato) diborane(4) derivatives have been reported.[17,18]

The development of new strategies in organic synthesis with a minimum of chemical steps is becoming increasingly important for the efficient assembly of complex molecular structures.[19,20] The combination of multiple reactions in a single operation represents a particularly efficient approach. Among these strategies,[21] geminated organobismetallic derivatives (1,1-bis anions) are becoming increasingly useful.[22] During the past decades considerable efforts have been made to find new routes for the preparation of geminated sp^2 organobismetallic derivatives and for their selective reactions with several electrophiles.[22,23]

This review will concentrate primarily on features of the chemistry of diborane compounds with particular structures: B–C–B, B–C–C–B, B–C=C–B, and B–C≡C–B. We will also survey some of the chemistry of organoboron compounds derived from diborane precursors.

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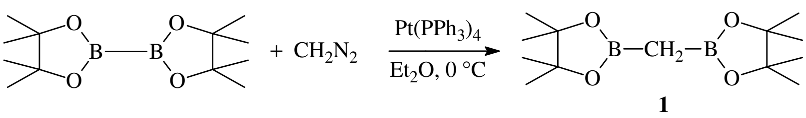
*Correspondence to: Morris Srebnik, Department of Medicinal Chemistry & Natural Products, School of Pharmacy, PO Box 12065, Hebrew University of Jerusalem, Jerusalem 91120, Israel.
E-mail: msrebni@md2.huji.ac.il

†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.



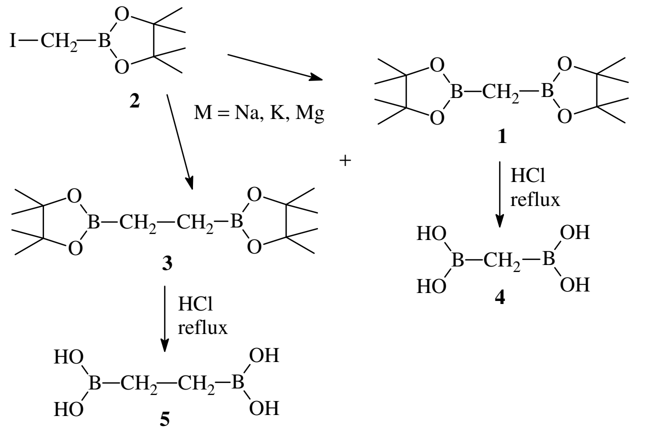
Scheme 1.

FORMATION OF B–C–B COMPOUNDS

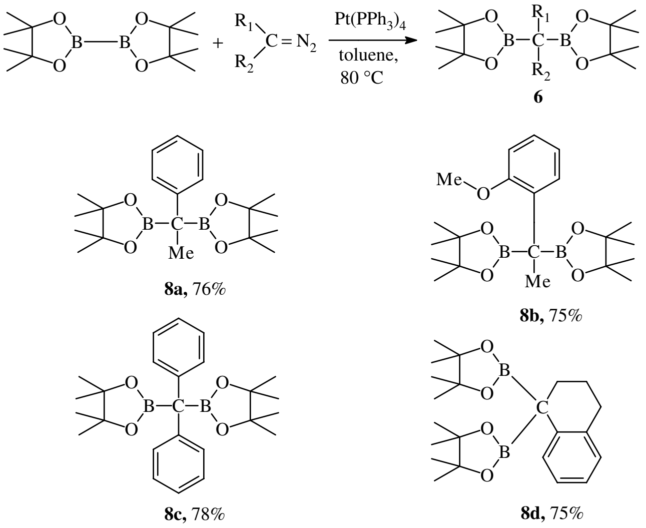
Bisdiborane, BCB, compounds are usually prepared by double hydroboration of terminal alkynes with dialkylboranes.[24–26] They are interesting precursors to *gem*-bimetallics such as BCLi[27–30] and BCMgX.[31] Recently, we reported that the parent compound (pinacolato)$_2$BCH$_2$B (**1**) can be prepared in high yield by reaction of bis(pinacolato)diborane(4) with diazomethane (Scheme 1).[32] This reaction gave good results and had not been described before.

Insertions into (R$_2$N)$_2$B–B(NR$_2$)$_2$, where R = Me, Et, *n*-Pr, were not successful. Two mechanisms for the insertion are possible: (a) addition/1,2-migration to and from boron as in the Hooz reaction[33–35] or (b) oxidative addition of B–B to a Platinum(0) complex, insertion of CH$_2$ into the Pt-B bond, migration, and reductive elimination.[36] Alternatively, formation of **1** from (pin)BCH$_2$I by coupling with metals has been reported.[32] Reflux of **1** and **3** with HCl gave the stable boronic acids **4** and **5** respectively (Scheme 2).

Novel C1-bridged bisboronate derivatives **8a–d** have recently been reported by insertion of diazoalkanes into bis(pinacolato)diborane(4) by Abu Ali *et al.*[37] (Scheme 3) and the proposed catalytic cycle is shown in Fig. 1. A view of **8d** is shown in Fig. 2.



Scheme 2.



Scheme 3.

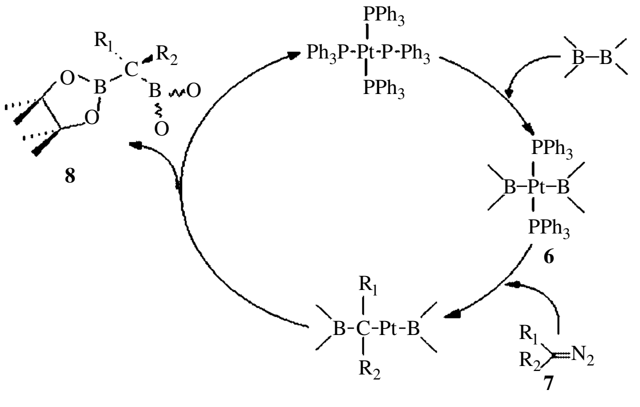


Figure 1. The proposed catalytic cycle for formation of B–C–B compounds.

Preparation of 1,4-dibora-2,5-cyclohexadienes (**10a–c**) have been demonstrated by Wrackmeyer and Kehr.[38] Organoboration of tetrakis(alkynyl)stannanes leads to the spiro-cyclic compound **9** in high yield. The reactions of **9** with MeBBr$_2$, *i*-PrBBr$_2$, and PhBCl$_2$ in dichloromethane between −78 and +25 °C give B–C=C–B (**10a–c**) compounds. Interconversion of these compounds gives compounds with B–C–B structures **11–13** (Scheme 4).

B–C–B compounds **15** and **16**[39] could be synthesized from compound **14**, and **18**[40] from compound **17** (Scheme 5). Formation of a 2,5-diborabicyclo[2.1.1]-hexane **20** and its conversion product tetracarbahexaborane (**19**), which also have a B–C–B structure, have been reported by Enders *et al.*[40] Synthesis of carbaboron compounds has also been reviewed recently.[41]

The 1,1′-spirobistannoles (**22a–d**) are an intermediate for synthesis of borolenes (**23**); and compounds **24a,b** with the

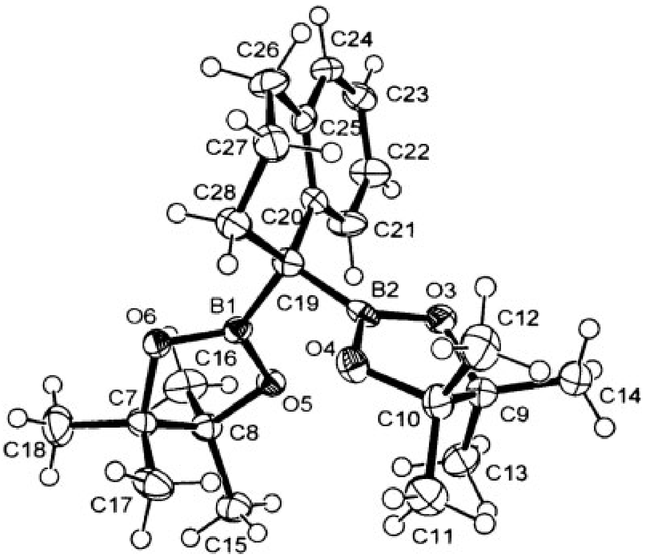
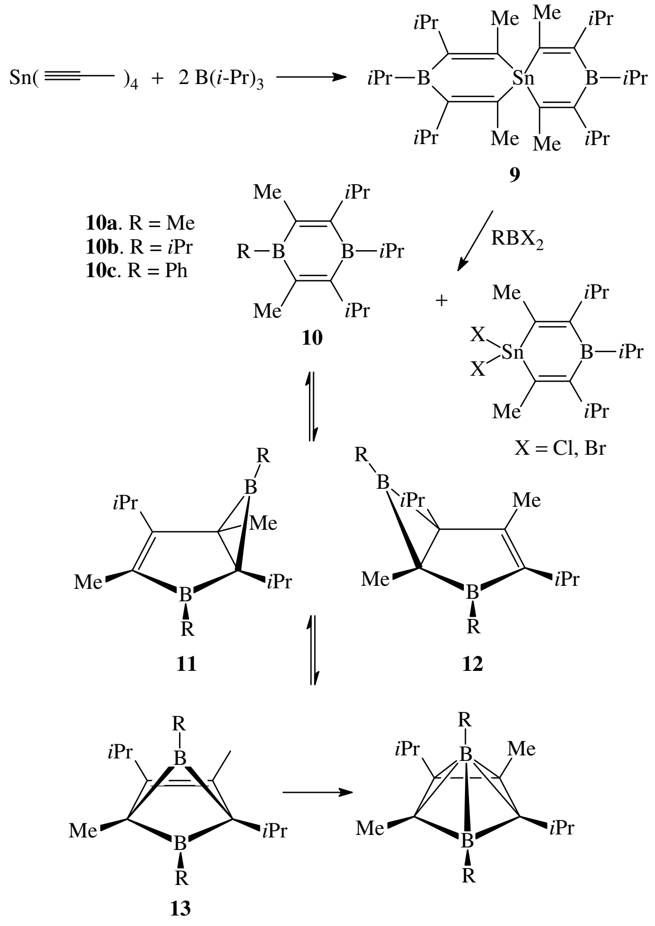
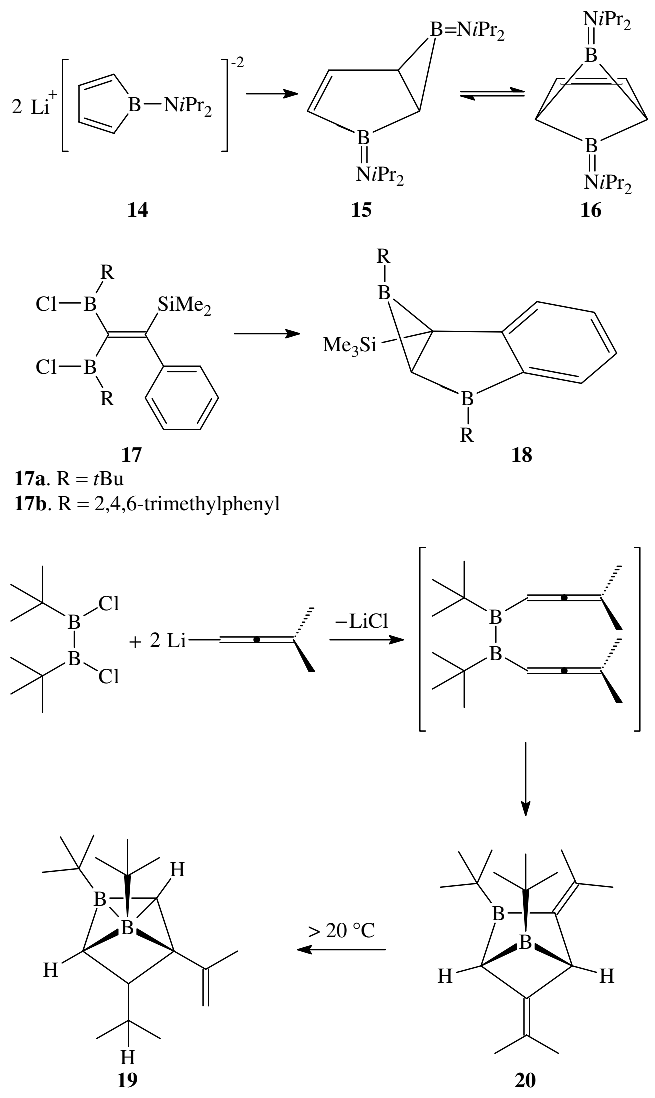


Figure 2. The proposed view of the geminal organoboron compound **8d**, showing the atom-numbering scheme.



Scheme 4.



Scheme 5.

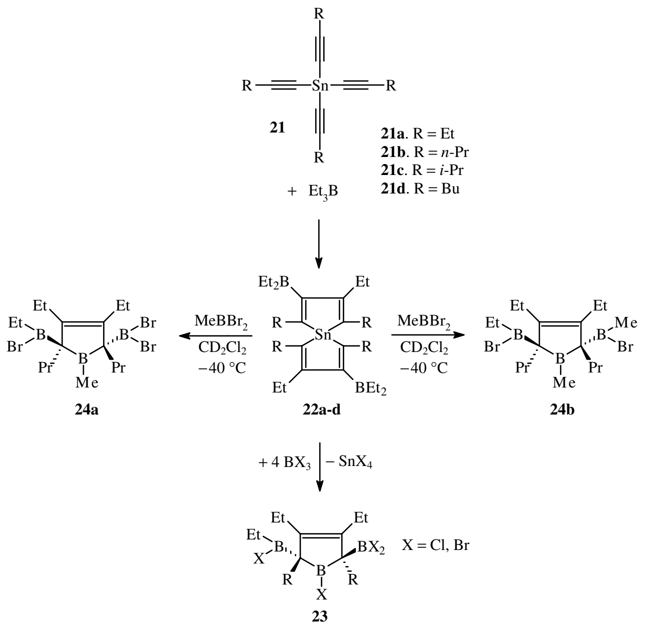
B–C–B structure were prepared from the reaction of tetra-1-alkynyltin (**21**) with triethylborane (Scheme 6).[42]

Another B–C–B compound, 2,5-diborylated 3-borolene (**26**) could be obtained by reacting **25** and $MeBBr_2$ in a 1 : 2 ratio (Scheme 7).[42]

The synthesis of heterodiborolanes **27** and **28** with a B–C–B structure has been demonstrated in the papers by Siebert and coworkers (Scheme 8).[43,44]

GEMINAL ORGANOBORON COMPOUNDS

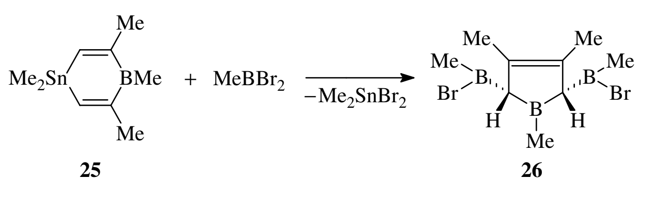
The chemistry of geminated boron compounds has been reviewed recently.[22,23] The synthesis of (diethylcyclopropyl)borane or cyclopropyl-9-BBN was performed by dihydroboration of either propargyl chloride or bromide, followed by the addition of methyllithium to the resulting 1,1-diborio compound **29** (Scheme 9).[24] Also, the *gem*-diboron **30** could



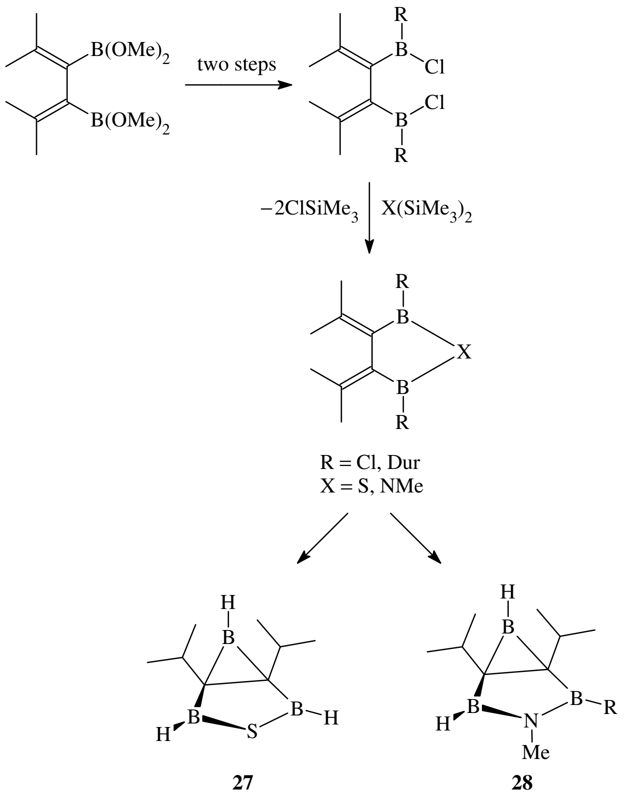
Scheme 6.

be obtained if tosylate was chosen as the leaving group.[11] The best synthesis of (*E*)-alkenyl-9-BBN compounds is an indirect route involving oxidative elimination of one boron from the easily formed diboryl intermediate **31**.[45]

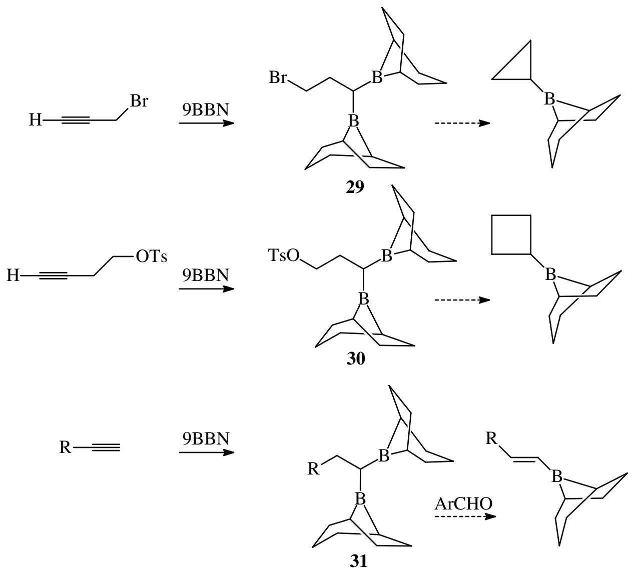
The dihydroboration of 1-hexyne with diborane results in the formation of a highly branched, polymeric product. Since it was anticipated that the reaction product would contain the two boron atoms either on adjacent carbon atoms or on the same carbon, oxidation with alkaline hydrogen peroxide should lead either to 1,2-hexanediol or ω-hexaldehyde respectively. Unexpectedly, however, oxidation of the dihydroborated 1-hexyne gave, in addition, 1-hexanol as the major product. The formation of 1-hexanol from the dihydroboration intermediate can be rationalized in terms of a rapid hydrolysis of one boron–carbon bond of either the 1,1- (**32**) or the 1,2-diboron (**33**) compounds prior to the oxidation step (Scheme 10).[25] The only reasonable explanation for the high yield of primary alcohol is that the hydroboration product, whatever its structure, undergoes a rapid hydrolysis to lose one of the two boron–carbon bonds prior to oxidation. Since the alkaline hydrolysis involves an attack by a base on the electrophilic boron atom, these substituents, which decrease the acidity of the boron atom, should greatly reduce the hydrolytic stability of the 1,1-diborio derivative. So, the diborioalkane was hydrolyzed first and oxidized in a second step with alkaline hydrogen peroxide at pH 8, to give the aldehyde in 68% yield.[26]



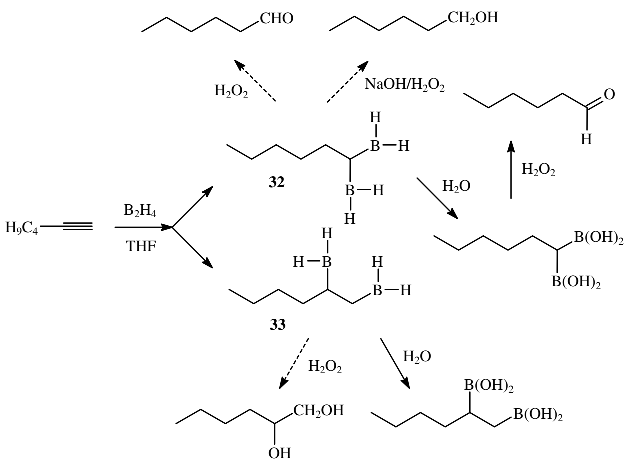
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

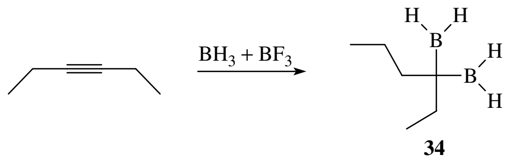
The double hydroboration of 3-hexyne was examined first with an excess of diborane,[46,47] but the oxidation of the product from dihydroboration of 3-hexyne gave 1,1-diborioalkane (**34**) as the major product[46] (Scheme 11).

The hydroboration of 1-hexyne produced *gem*-1,1-bis(dichloroboryl)hexane (**35**), which could be converted to the well-known 1,1-bis[2-(1,3,2-dioxaborinyl)]hexane (**36**) (Scheme 12).[48]

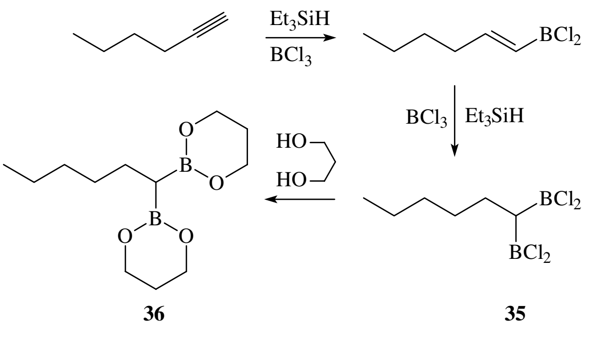
3-Butyn-1-ol tosylate can be converted by 9-BBN to 9-cyclobutyl-9-bora-bicyclo[3.3.1]nonane (**38**) via geminal compound **37**, which is oxidized to cyclobutanol (**39**) (Scheme 13).[49]

Tetracyclohexyldiborane adds to 1-hexenyldicyclohexylborane mainly with the formation of the geminal 1,1-diborane **40** compound (Scheme 14).[50] Cainelli *et al.*[51] found that the 1,1-diborane compounds **41** formed by the dihydroboration of 1-hexyne, 1-decyne, or phenylacetylene with tetracyclohexyldiborane undergo transmetalation by the action of two equivalents of butyllithium in heptane at −70 °C to form mixed 1-bora-1-lithium compounds.

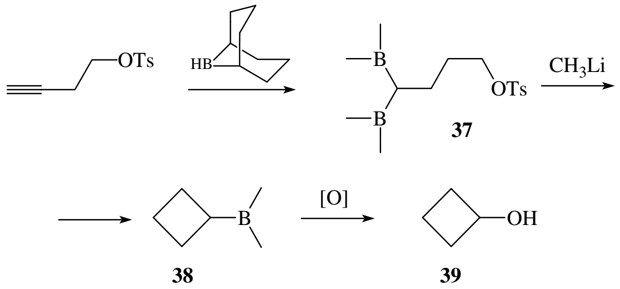
Binder and Köster[52] have found that hydroboration of 3-chloro-1-propenyl-dialkylborane gave *gem*-1,1-bis(dialkylboryl)-3-chloropropane (**42**). When **42** was heated with sodium tetraethyl borate, it cyclized to cyclopropyldialkylborane (**43**; Scheme 15). **43** in the presence of



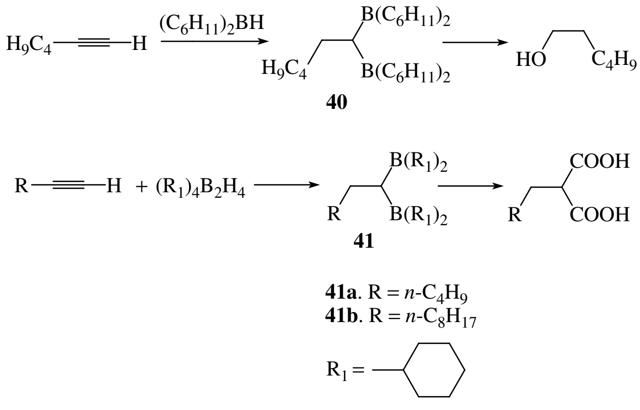
Scheme 11.



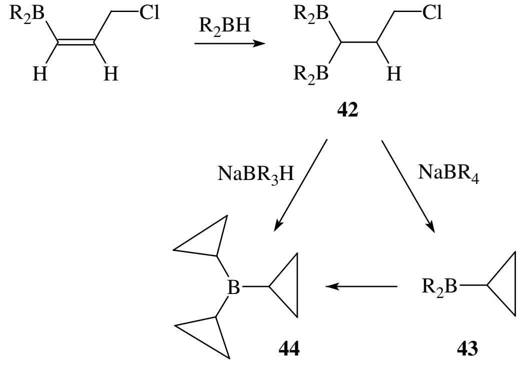
Scheme 12.



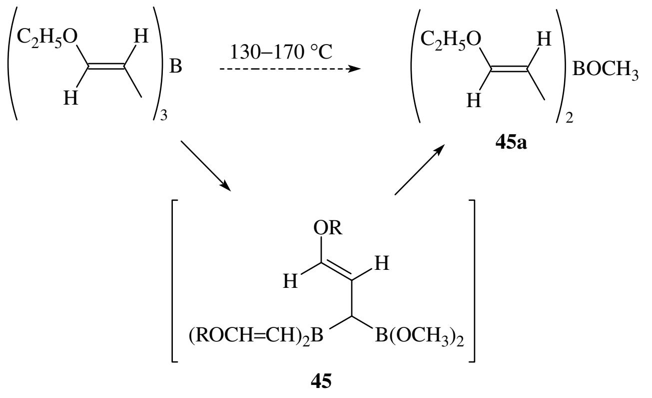
Scheme 13.



Scheme 14.



Scheme 15.

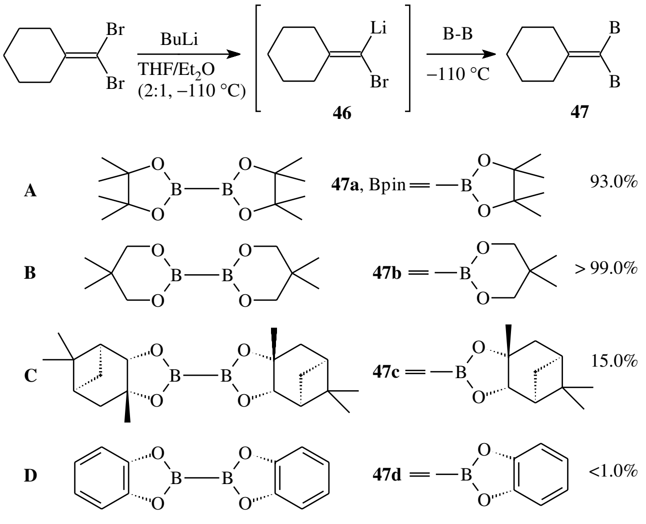


Scheme 16.

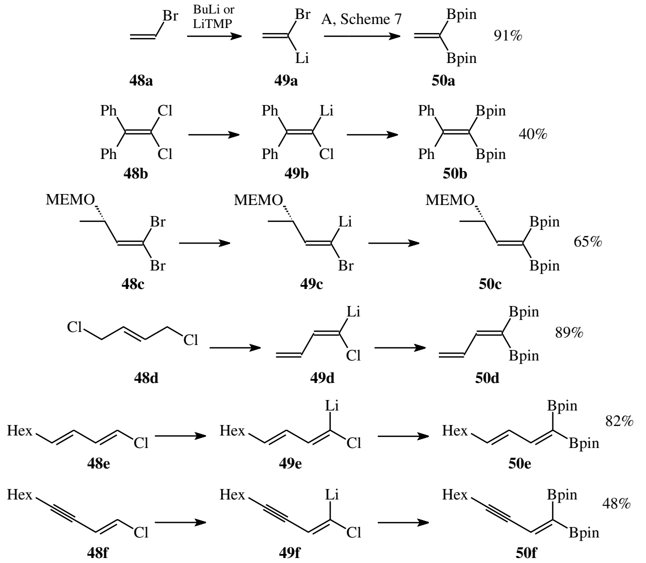
compounds with B–H bonds symmetrizes to tricyclepropylborane (**44**). Later, **44** was formed directly from **42** by reaction with $NaBR_3H$.[49]

Geminated compound **45A** could be formed during the exchange reactions between alkoxyvinylboranes and an alkyl borate, apparently proceeding via the formation of intermediate **45** (Scheme 16).[53]

A novel and efficient method for *gem*-dimetalation of carbenoids has been reported by Shimizu and coworkers.[54] Treatment of alkylidene-type lithium carbenoids with interelement compounds, such as silylborane or diborane to generate the corresponding borate complex, followed by warming to room temperature, induced migration of the silyl or boryl group from a negatively charged boron atom to the carbenoid carbon to afford 1-boryl-1-silyl-1-alkenes or 1,1-diboryl-1-alkenes in good yields. Carbon–carbon-bond forming transformations of the *gem*-dimetalated compounds mediated by boron or silicon is also described. *gem*-Diborylation of alkylidene-type carbenoids with diboranes has been demonstrated. Thus, commercially available diboranes **A**–**D** were used in the reactions (Scheme 17). Bis(pinacolato)diborane (**A**) and optically active bis[(+)-pinanediolato]-diborane (**B**) reacted with **46** to give *gem*-diborylated compounds **47a** and **47b** in high yields. In contrast, reaction with bis(neopentanediolato)diborane (**C**) resulted in low yield of **47c** due, probably, to its low solubility under the reaction conditions, whereas no desired diborylated compound was obtained when bis(catecholato)diborane (**D**) was employed.



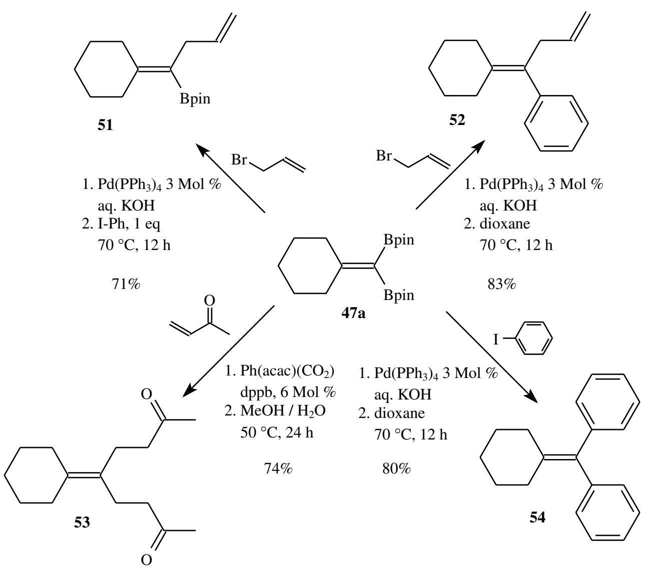
Scheme 17.



Scheme 18.

By use of **A** (Scheme 17), various kinds of alkylidene-type carbenoid **49a–f** were *gem*-diborylated, as shown in Scheme 18. Unsubstituted and 2,2-disubstituted carbenoid **49a** gave 1,1-diborylalkene (**50a**) in high yields. Dichloroalkene (**48b**) could also be used, which, after chlorine–lithium exchange, underwent *gem*-diborylation, giving rise to **50b** in 40% yield, whereas optically active 1,1-diborylalkene (**50c**) was obtained from the corresponding dibromide **48c** in 65% yield. Double deprotonation of **48d** generated **49d**, which reacts with **A** to afford 1,1-diborylbutadiene (**50d**) in 89% yield. *gem*-Diborylation of lithium carbenoids **49e** and **49f** prepared from conjugated chloroalkenes **48e** and **48f** proceeded smoothly, producing conjugated compounds **50e** and **50f** bearing two boryl groups at the terminal positions.[54]

Some synthetic applications of *gem*-bismetallic compounds shown in Scheme 19. When an equimolar amount of allyl bromide was used as the coupling partner, stepwise coupling was possible. Thus, when **47a** was treated with an equimolar amount of allyl bromide, the allylated alkenylboronate **51** was obtained. Furthermore, the allylation followed by coupling with iodobenzene in one pot gave the corresponding bis-coupled product **52** in a good overall yield. Rhodium-catalyzed Michael-type addition reaction of **47a** to methyl vinyl ketone proceeded smoothly to give diketone **53** in 74% yield.[55] Two C–B bonds in

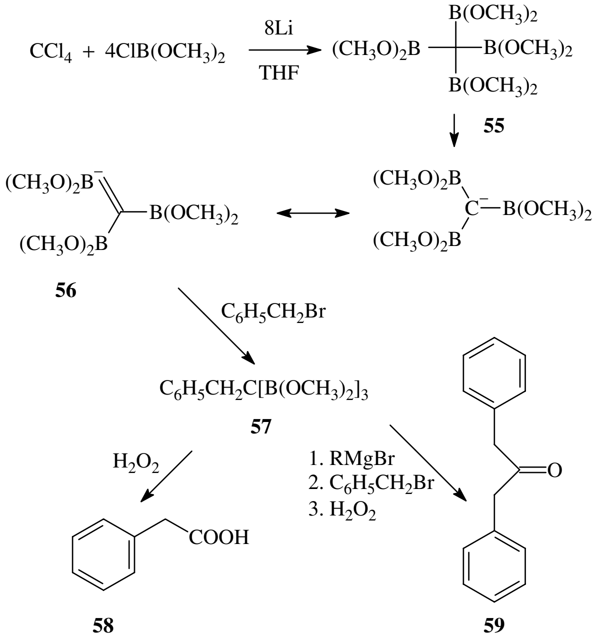


Scheme 19.

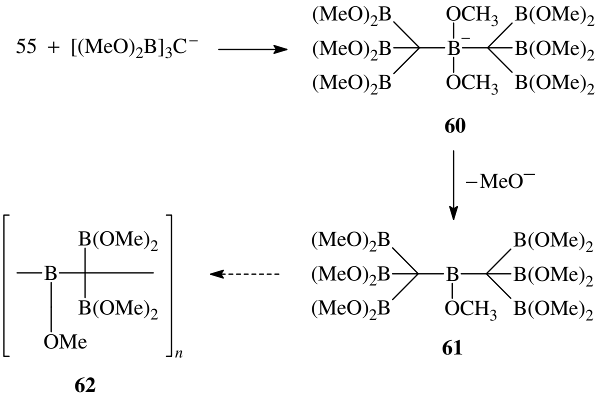
47a were simultaneously converted into two C–C bonds, as exemplified by the Palladium-catalyzed cross-coupling reaction, with iodobenzene giving rise to **54**.

Castle and Matteson reported the successful preparation of the 1,1,1-triboryl compounds **55** (Scheme 20).[56] Octamethyl methanetetraboronate (**55**) appears stable indefinitely in neutral methanol, and with NaOH it degraded to **56**, which under H_2O_2 conditions transformed to **58** and **59** via **57**.

According to Castle and Matteson,[57] **55** reacts with carbanion $[(MeO)_2B]_3C^-$ to form methanetetraboronic ester (**60**). The resulting adduct **60** might then lose methoxide, add another carbanion, and continue the process to form polymer **62** via **61** with a C–B–C–B–C... backbone (Scheme 21).



Scheme 20.

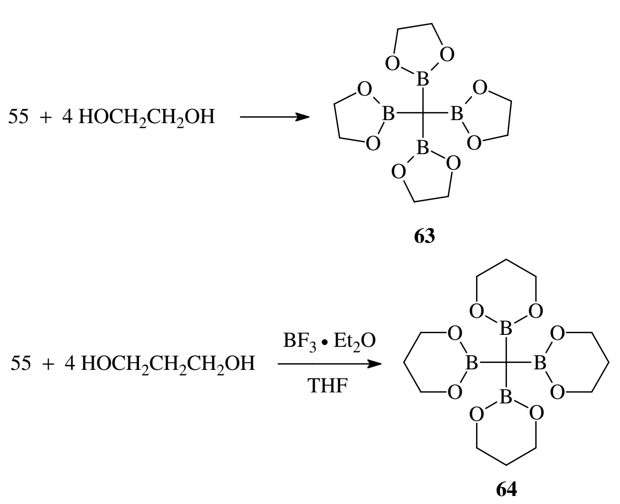


Scheme 21.

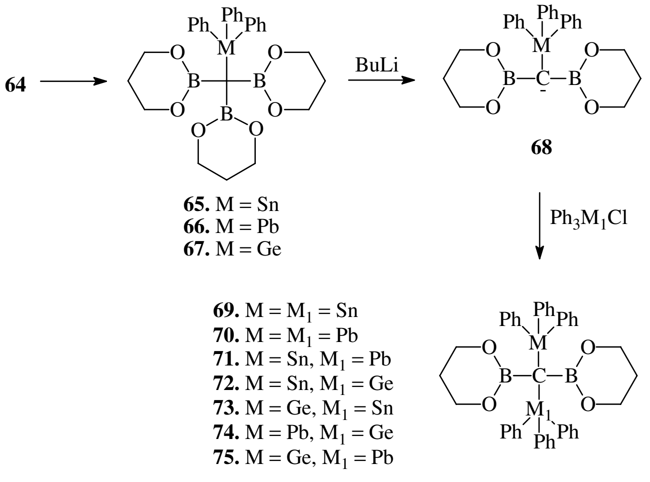
The syntheses of cyclic boronic esters **63** and **64** containing B–C–B bonds (Scheme 22) and tetrametallomethanes containing Group IV metals have been reported by Matteson and Wilcsek.[58]

Reaction of **64** with butyllithium followed by Ph_3SnCl gave good yields of **65, 66** and **67** (Scheme 23).[58] Compounds **69–75** could be prepared via carbanion **68** with two different metal atoms M and M_1 if base-catalyzed disproportionation of **65–67** occurred. The ditin (**69**), dilead (**70**), tin–lead (**71**), tin–germanium **72**, and lead–germanium (**74**) compounds were synthesized in good yields.[58,59]

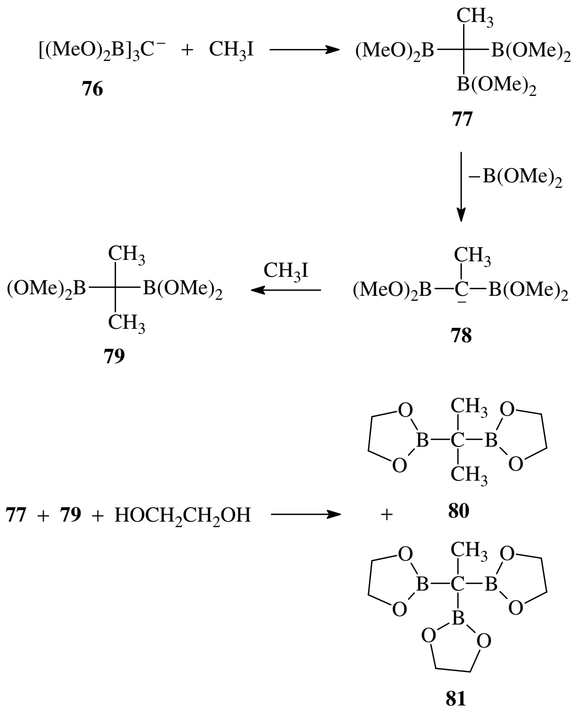
Treatment of tetrakis(dimethoxyboryl)methane (**62**) with bases such as methyllithium or lithium methoxide leads to the tris(dimethoxyboryl)methide ion **76** (Scheme 24),[60] which reacted with methyl iodine to give the monomethylation product **77**. Loss of a dimethoxyboryl



Scheme 22.



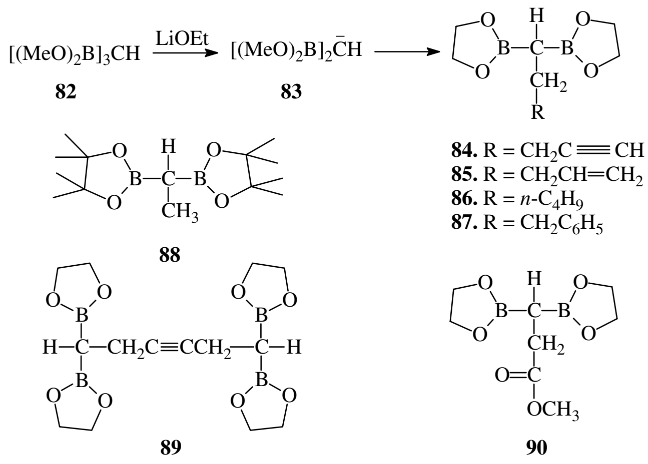
Scheme 23.



Scheme 24.

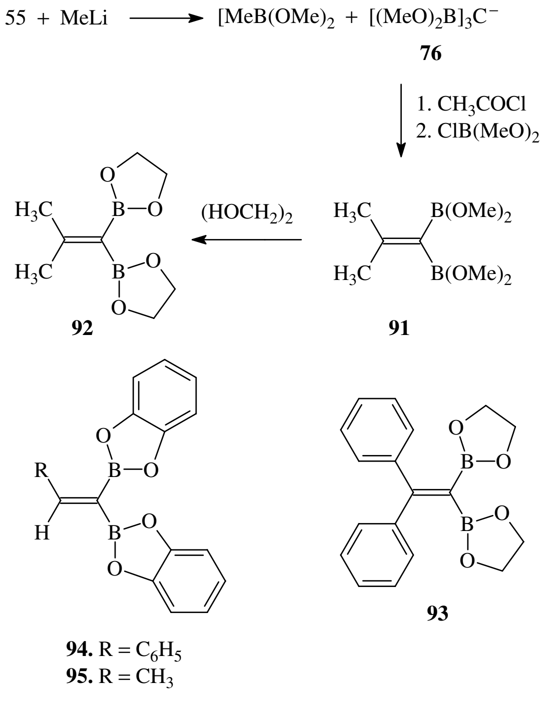
group from monomethylation product **77** gave 1,1-bis(dimethoxyboryl)ethide ion **78**, which reacted with methyliodide to form 2,2-bis(dimethoxyboryl)propane (**79**). Approximately equimolar mixtures of di- (**80**) and monomethylation (**81**) were obtained in about 50% total yield when methyliodide was added to a mixture of **77** and **79** in the presence of ethylene glycol.

Alkylation of tris(dimethoxyboryl)methane **82** by LiOEt and removal of one dimethoxyboryl cation gave bis(dimethoxyboryl)methide ion **83** (Scheme 25) or its borate ester complex.[60] The reaction with allyl bromide lead smoothly to 4,4-bis(1,3,2-dioxaborol-2-yl)-1-butene (**85**). Other alkyl halides reacted with **82** to give the B–C–B products **84, 86, 87, and 88–90**. [60]



Scheme 25.

Also, octamethyl methanetetraboronate (**55**) and methyllithium in tetrahydrofuran (THF) served as a source of tris(dimethoxyboryl)methide ion **76**, which reacts with dimethoxyboron chloride to give tetramethyl 2-methylpropane-1,1-diboronate (**91**; Scheme 26);[61] reaction of **91** with ethylene glycol forms the geminated boron compound **92**. Refluxing benzophenone with **76** for 6 h followed by additional ethylene glycol formed **93** in 48% yield.



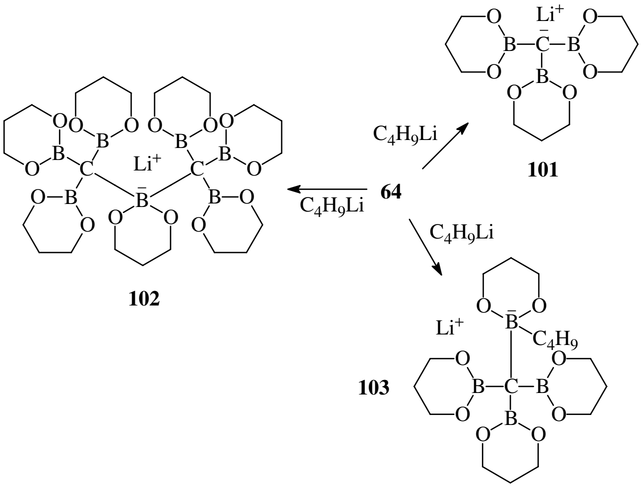
Scheme 26.

Benzaldehyde led to styrene-β, β-diboronic acid, which reacts with catechol in benzene to form the catechol esters **94** and **95**.[61]

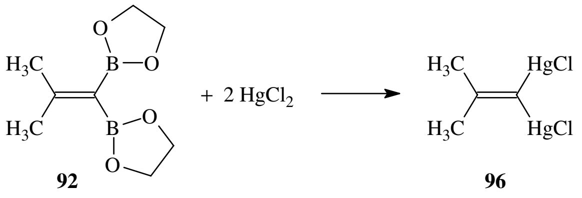
Electrophilic displacement of the boronic ester group occurred in the reaction of **92** with two equivalents of mercuric chloride, and sodium acetate in methanol gave 2-methylpropene-1,1-dimercuric chloride (**96**; Scheme 27).[61]

Deprotonation of bis(trimethylenedioxyboryl)methane (**97**) with lithium 2,2,6,6-tetra-methylpiperidine yielded the diborylcarbanion **98**, which reacts with alkyl halides to give high yields of *gem*-diboronic esters **99**, which also could be deprotonated and alkylated to give **100** (Scheme 28).[62] Carbanion **98a** reacts with aldehydes and ketones to form enol borate intermediates, which hydrolyzed to ketones.

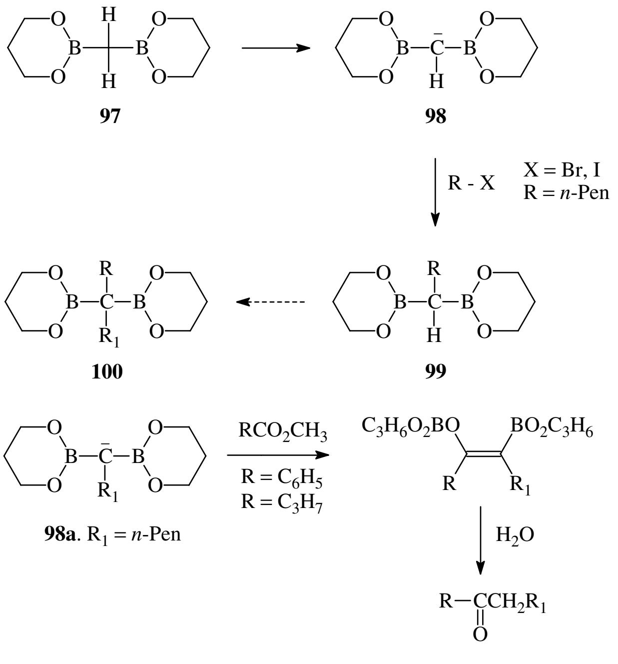
Anionic bisdiborane compounds derived from methanetetraboronic (**64**) and methanetriboronic esters,[57–63] *gem*-diborylalkanes,[26,29,64] and deprotonation of trialkylboranes[65,66] have been found useful in a variety of syntheses, including condensation with aldehydes and ketones, and alkylation by alkyl halides.[67] Matteson *et al.*[68] found that the lithium salts of some bisdiborane compounds (**101**–**103**) could be obtained from **64** with LiBu (Scheme 29). The salt **101** is a very strong base and abstracts protons from dimethyl sulfoxide, in which it is soluble.



Scheme 29.



Scheme 27.

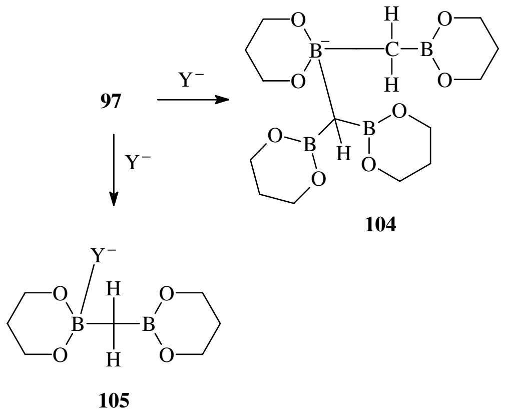


Scheme 28.

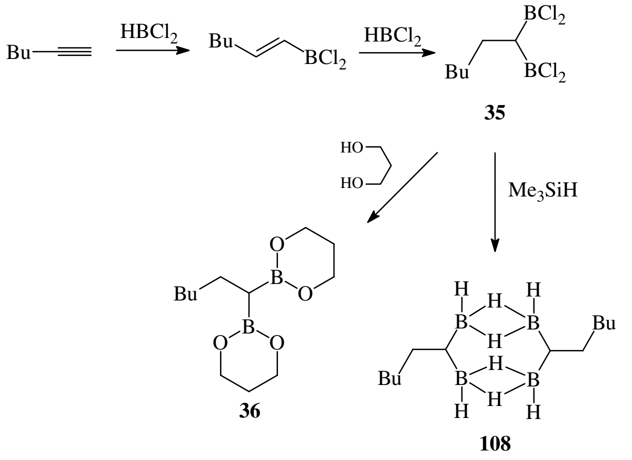
The lithium salt of **98** is a slightly soluble in THF and precipitates, giving an apparent increase of the acidity of **97**, which reacts with bases Y^- to form borate complexes **105** or the self-condensation product **104** (Scheme 30).[69]

Hydroboration of 1-hexyne leads to 1,1-bis(dichloroboryl)-hexane (**35**; Scheme 31)[70] and could be converted to **36**.[69] Treatment of **35** with trimethylsilane yielded 1,1-bis-(diborylhexane)dimer **108**.

The first reported synthesis of a bidentate borane (B–C–B) incorporating C_6F_5 groups (**109**) came from the Marks group in 1994.[71] The borane t-$BuCH_2CH[B(C_6F_5)_2]_2$ (**109**) was prepared by the metathetical route shown in Scheme 32. Also, **110** can be prepared via dihydroboration of terminal alkynes using the hydroboration reagent $HB(C_6F_5)_2$.[72] As an alternative to diborate formation **112a–c**, retrohydroboration can be precluded by incorporating unsaturation in the backbone using tin–boron (**111**) exchange/hydroboration as shown in Scheme 32.[73]



Scheme 30.



Scheme 31.

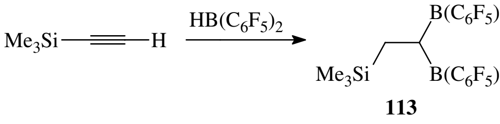
Piers and co-workers[72,74] found that the 1,1-diboryl alkane (**113**) formed upon double hydroboration of $Me_3SiC\equiv CH$ (Scheme 33).

Geminal organoboron compounds **115**–**118** can also be prepared using 4-vinyl-anisol (**114**) and $HB\text{-}1,2\text{-}O_2C_6H_4$ with rhodium(I) as catalysts (Scheme 34).[4,75]

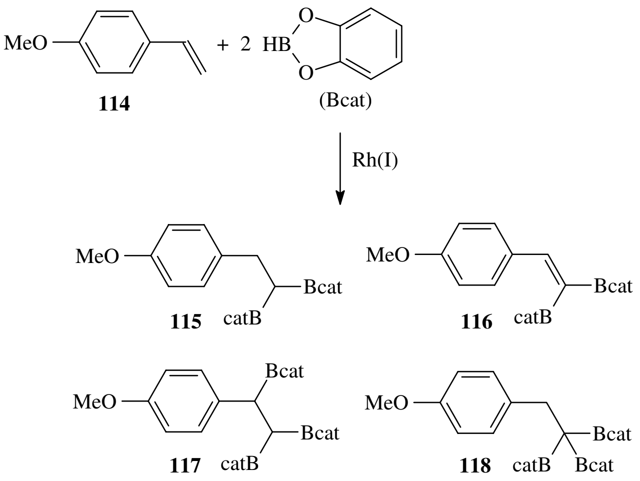
Reaction of the boriranyllideneboranes **119**–**121** with tetrahalodiboranes(4) leads to two types of product: **122, 123** and **124, 125** (Scheme 35).[76,77] Compounds **119**–**121** were first prepared by Berndt more then 20 years ago.[78] Treatment of **122** with four equivalents of dimethylaminotrimethylsilane gave **126a**–**c**.

FORMATION AND REACTIVITY OF B–C–C–B, B–C=C–B, AND B–C≡C–B COMPOUNDS

Formation of BCCB alkanes **3** and **5** (see Scheme 2) from $(pin)BCH_2I$ by coupling with metals has been reported.[32,63,79]



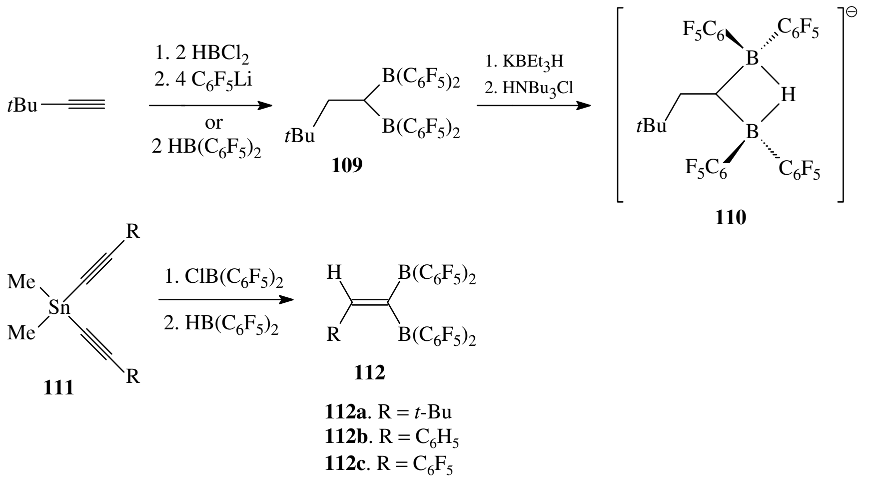
Scheme 33.



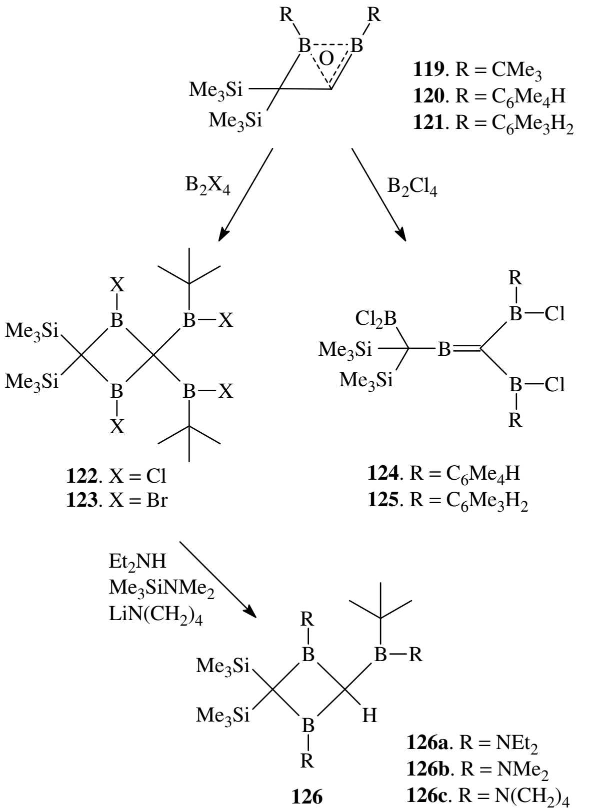
Scheme 34.

The quantity, the solvent and the metal determine the ratio of BCCB/BCB, varying from 96 : 4 (with sodium excess 35%, and yield 94%) to 34 : 66 (sodium excess 15%, yield 94%) in benzene.[32] Hydroboration of 1,3-butadiene in ether (diene : BH_3 = 5 : 2) produces a mixture of compounds, where **128** and 1,2-bis-(1-boronyl)butane (**127**) were also found (Scheme 36).[80,81] When heating **128** at 140–170 °C it isomerizes to geminal 1,1-bis(1-boronyl)butane (**129**).[82]

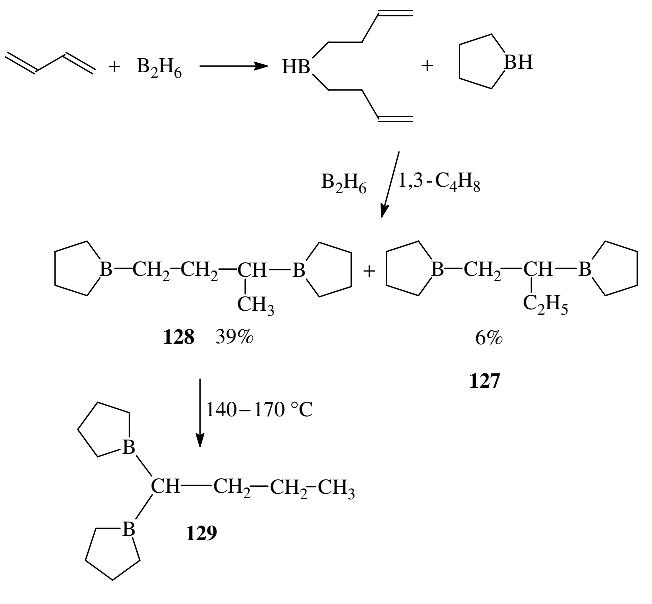
B–CC–B compounds **130** and **131** can be obtained from the addition of alkenylboronates to diborane (Scheme 37); hydrolysis of **130** by hydrochloric acid,



Scheme 32.



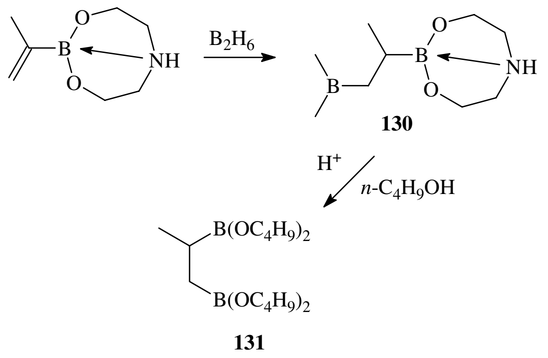
Scheme 35.



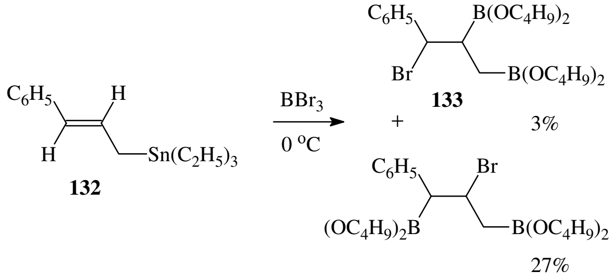
Scheme 36.

followed by esterification with butanol, gave tetrabutyl 1,2-propanediboronate (**131**).[83]

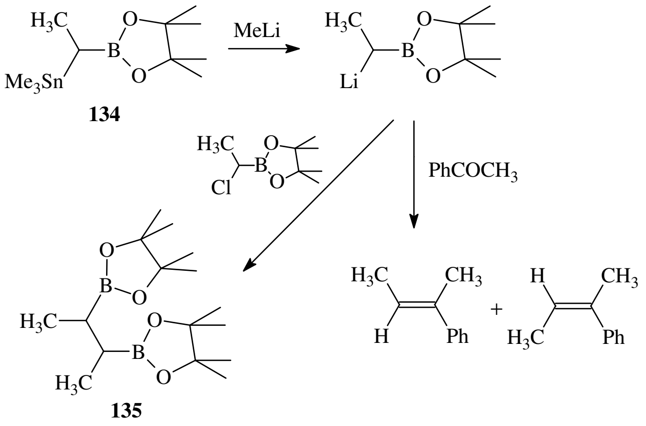
Reaction of **132** with tribromoborane at 0 °C forms a mixture of two products, one of which has B-CC-B structure (**133**; Scheme 38).[84]



Scheme 37.



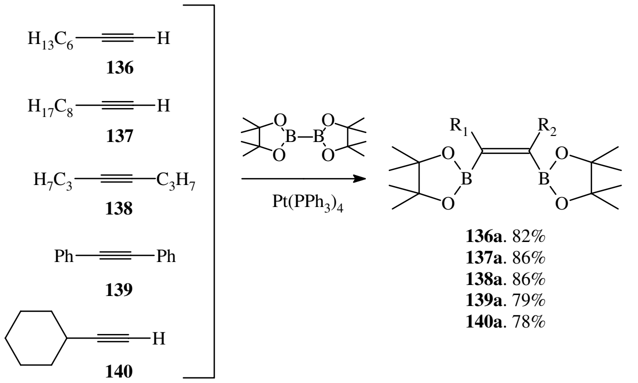
Scheme 38.



Scheme 39.

B–CC–B compound **135** can also be obtained by destannylation of trimethyltin (**134**) according to Scheme 39.[85]

In 1993, Ishiyama *et al.*[86] reported the synthesis of isomerically pure *cis*-1,2-bis(boryl)alkenes **136a**–**140a** from their corresponding alkynes **136**–**140** (Scheme 40)[86,87] via platinum complexes. The solvents did not play an important role in the reaction, but a comparison of the reaction rates at 50 °C revealed that the addition was apparently accelerated in polar solvents: e.g. DMF > CH_3CN > THF > toluene. Synthesis of *trans*-1-organo-1-alkenyl-boronates was reported when palladium(0) was used as catalyst.[88]

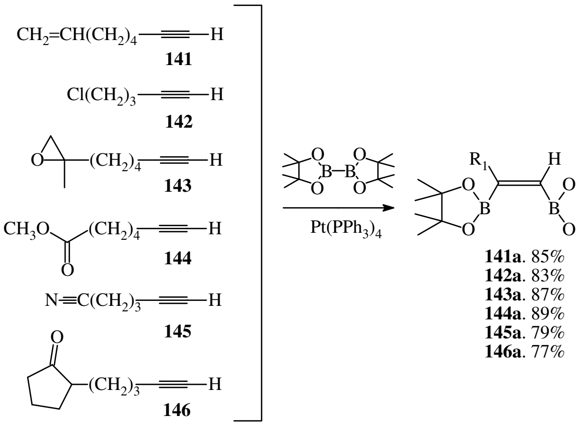


Scheme 40.

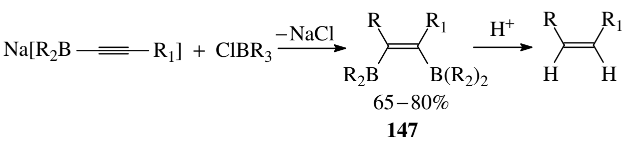
The same reaction produced different alkynes **141–146** (Scheme 41).[89] These reactions were not catalyzed by rhodium(I) or palladium(0).

The borates react with chlorodialkylboranes in a sterically selective manner, forming with good yields *cis*-1,2-bis(dialkylboryl)alkenes (**147**), the protonolysis of which with water or alcohols produces *cis*-olefins (Scheme 42).[90]

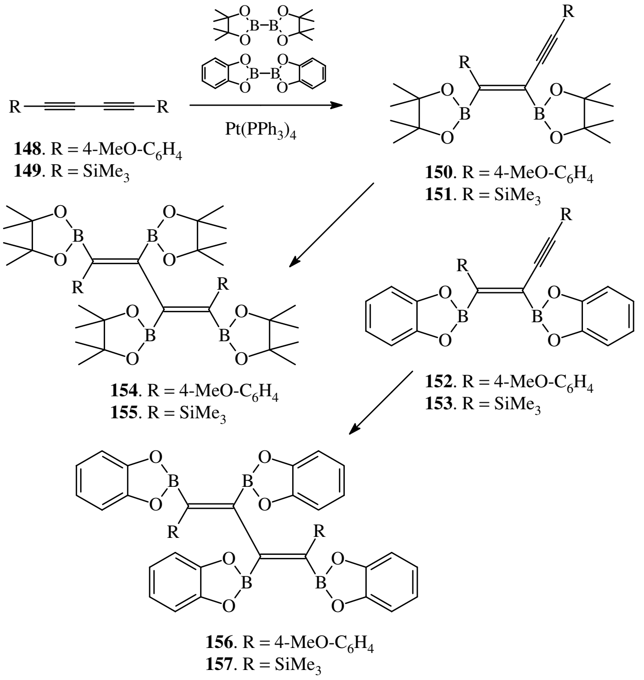
The formation of B–C=C–B compounds **150–153** has been demonstrated with the use of 1,3-diynes via platinum(II) anions.[91] The addition of (pin)B–B(pin) and (cat)B–B(cat) to 4-MeOC$_6$H$_4$C≡CC≡CC$_6$H$_4$-4-OMe and SiMe$_3$C≡CC≡CSiMe$_3$ proceeded smoothly to gave the novel tetrakis(boronate ester) compounds **154–157** respectively (Scheme 43). An important step in the catalyzed diboration of alkynes appears to be the dissociation of phosphine from the [(PPh$_3$)$_n$Pt(η-alkyne)] complexes, giving rise to a mono(phosphine)Pt intermediate, which serves as the active catalyst in these systems.



Scheme 41.



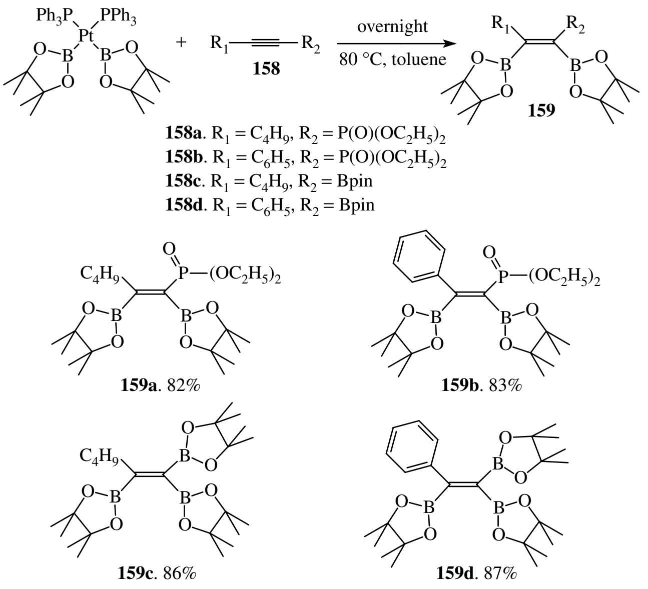
Scheme 42.



Scheme 43.

The diboration reaction of bis(pinacolato)diborane(4) with diethyl 1-hexynyl-phosphonate (**158a**), diethyl phenylethynyl phosphonate (**158b**), 1-hexynylpinacolato borane (**158c**), and phenylethynylpinacolatoborane (**158d**) in the presence of a catalytic amount of Pt(PPh$_3$)$_4$ (3 mol%) in toluene at 80 °C overnight gave the desired novel *cis*-1,2-diboronated vinylphosphonate and trisboronated alkene addition products **159a, 159b, 159c** and **159d** respectively in high yields (Scheme 44).[92]

The structure of **159d** was found to be fully isomorphous to that of **159c**, with the C$_6$H$_5$ ring located in place of the C$_4$H$_9$ residue. The reaction was efficiently catalyzed by Pt(PPh$_3$)$_4$ in toluene at 80 °C. The apparent hydroboration followed by deboronation when the B–B and platinum compounds are not pre-equilibrated may be due to either water or other such protic impurities, since it is known that 1-alkynylboronates are very susceptible to cleavage by water. Pre-equilibration of Pt(PPh$_3$)$_4$ plus excess B–B would lead to (PPh$_3$)$_2$Pt(B)$_2$. If excess water were present, (PPh$_3$)Pt(B)$_2$ would react with H$_2$O to give (PPh$_3$)PtH$_2$ + B–O–B. (PPh$_3$)$_2$PtH$_2$ would lose hydrogen and with excess B–B give more (PPh$_3$)$_2$Pt(B)$_2$, which, using PPh$_3$ and B-B, is in equilibrium with (PPh$_3$)$_3$Pt or (PPh$_3$)$_4$Pt + B–B, by the way, as well as with the (PPh$_3$)Pt(B)$_2$ species. So, in effect, platinum can catalyze the hydrolysis of the B–B bond. The desired products **159a–d** were produced in 100% conversion yields and high isolated yields.

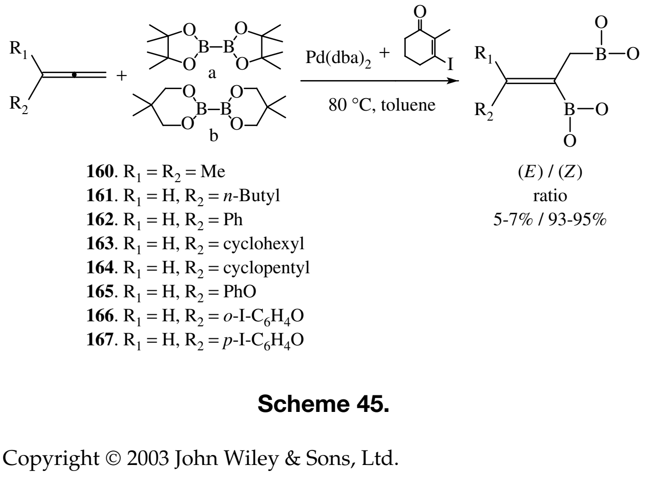


158a. $R_1 = C_4H_9$, $R_2 = P(O)(OC_2H_5)_2$
158b. $R_1 = C_6H_5$, $R_2 = P(O)(OC_2H_5)_2$
158c. $R_1 = C_4H_9$, $R_2 = Bpin$
158d. $R_1 = C_6H_5$, $R_2 = Bpin$

Scheme 44.

Unusual diboration of allenes catalyzed by palladium complexes formed novel B–C–C–B compounds **160**–**167**.[93] A new catalytic pathway other than one involving the oxidative addition of diborane to palladium(0) species operates in this new palladium-catalyzed reaction. The observation that an aryl-, alkenyl iodide, or I_2 was required to initiate the present catalytic reaction is interesting and vital to the understanding of the catalytic mechanism (Scheme 45).

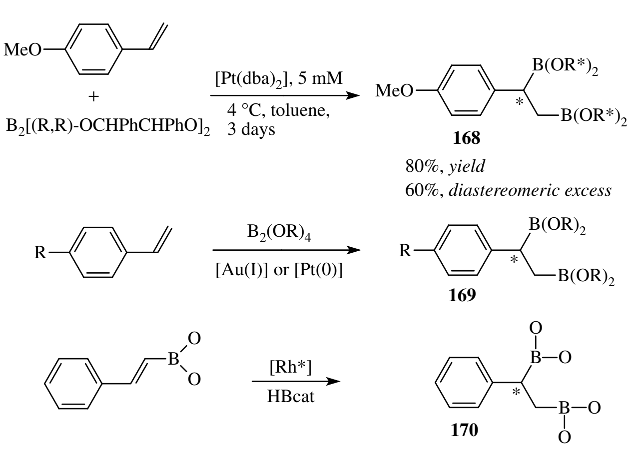
Platinum complexes also catalyzed diboration of terminal alkenes with chiral diborane compounds.[9,75] It has recently been shown that addition of certain enantiomerically pure chiral diborane compounds, such as $B_2[(R,R)\text{-}OCHPhCHPhO]_2$, to 4-vinylanisole using the Miyaura[86] $[Pt(dba)_2]$ (dba: dibenzylidene acetone) catalyst system provides chiral 1,2-diborane ester **168** with up to 60% diastereometric excess (Scheme 46). Similarly, and based on earlier stoichiometric data (*vide supra*) Iverson and Smith[94] reported that $[Pt(NBE)_3]$ and $[Pt(COD)_2]$ catalyzed the addition of B_2cat_2 to terminal alkenes giving 1,2-diborane ester **169**.



160. $R_1 = R_2 = Me$
161. $R_1 = H$, $R_2 = n\text{-Butyl}$
162. $R_1 = H$, $R_2 = Ph$
163. $R_1 = H$, $R_2 =$ cyclohexyl
164. $R_1 = H$, $R_2 =$ cyclopentyl
165. $R_1 = H$, $R_2 = PhO$
166. $R_1 = H$, $R_2 = o\text{-}I\text{-}C_6H_4O$
167. $R_1 = H$, $R_2 = p\text{-}I\text{-}C_6H_4O$

(*E*) / (*Z*) ratio 5-7% / 93-95%

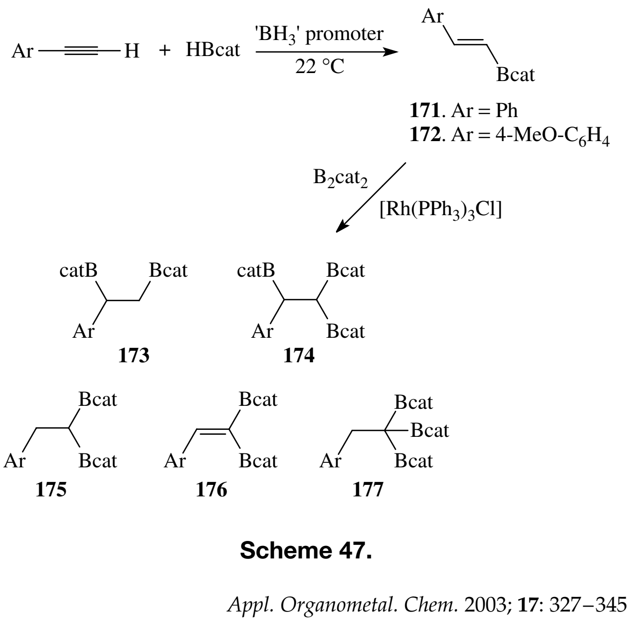
Scheme 45.



Scheme 46.

Also, saturated bisdiborane **170** with 72% enantiomeric excess (13% yield) could be obtained at −20 °C using a catalyst system composed of $[Rh(NBD_2)ClO_4/S,S$-chiraphos] [NBD: norbornadiene; chiraphos: 2,3-bis(diphenylphosphino)-butane].[95]

The synthesis of B–C–C–B compounds **173** and **174**, and also geminal boron compounds **175**–**177** using rhodium catalysts, have been reported recently.[96] Diboration of the styrylboronate esters with B_2cat_2 in the presence of a variety of rhodium phosphine catalysts gives predominantly either $p\text{-}R\text{-}C_6H_4\text{-}CH_2C(Bcat)_3$ (**177**), which contains three boronate ester groups on one carbon atom, or its isomer $p\text{-}R\text{-}C_6H_4\text{-}CH(Bcat)CH(Bcat)_2$ (**174**; Scheme 47). The formation of **173** apparently involves regiospecific insertion of the vinylboronates into an Rh–B bond followed by β-hydride elimination, another regiospecific insertion of the 2,2-vinyl bis(boronate) into the remaining Rh–B bond followed by



171. Ar = Ph
172. Ar = 4-MeO-C_6H_4

Scheme 47.

C–H reductive elimination leading to 2,2-diboration and a 1,2-hydrogen shift. Wilkinson's catalyst [Rh(PPh$_3$)$_3$Cl] gives the highest yields of **177** with 75% and 71% yields from **171** and **172** respectively, and [Rh(COE)$_2$(μ-Cl)]$_2$ with two equivalents of P(*o*-Tol)$_3$ gave **174** in best yield with 50% and 49% from **171** and **172** respectively.

Tetra(chloro)diborane reacts with acetylene to yield (*Z*)-1,2-bis(dichloroboryl)ethane (**178**)[97–99] and cyclopentene forms *cis*-1,2-bis(dichloroboryl)cyclopentene (**179**; Scheme 48).[100]

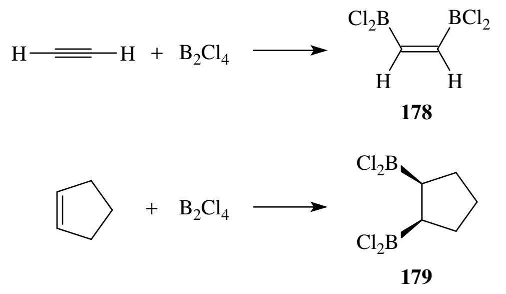
Diphenylacetylene reacts with dibromophenylborane to form *cis*-β-bromovinylborane, which when reacts with lithium leads to hexaphenyl-1,4-diboracyclohexadiene (**180**), the deuterolysis of which by deuteroacetic acid leads to *cis*-dideuterostilbene (Scheme 49).[101]

Singleton and Redman[102] have found that 1,2-diborylethylenes **182**, **183** and **184** were readily generated from the reaction of *trans*-1,2-bis(tributylstannyl)ethylene (**181**) with haloboranes (Scheme 50).[103]

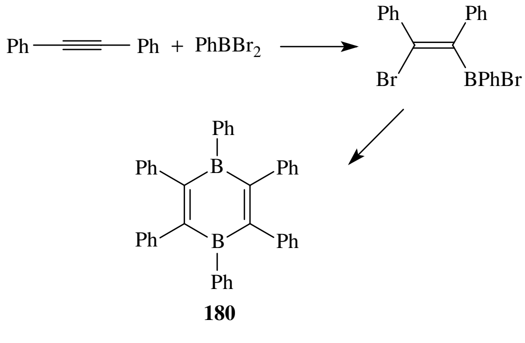
Formation of B–C–C–B compounds belonging to the bidentate Lewis acid was conducted by Biallas and coworkers more then 30 years ago.[104–106] The reactions of a bidentate version of the quintessential boron-based Lewis acid (BF$_3$) with simple Lewis bases and anions have been investigated. Thus, F$_2$BCH$_2$CH$_2$BF$_2$ (**135**) was prepared by mixing ethylene and B$_2$F$_4$ at low temperature (Scheme 51).[107] To obtain diboryl derivative **136** with strongly Lewis acidic boron centers, a weakly basic reagents such as Ph$_3$COMe was required.

Treatment of the known compound 1,2-(BCl$_2$)$_2$C$_6$H$_4$[108] with slightly more than two equivalents of Zn(C$_6$F$_5$)$_2$ led to smooth conversion to the desired 1,2-diborane **187** (Scheme 52).[109] Reaction of **187** with potassium salts of OH$^-$ and F$^-$ in the presence 18-crown-6 produces borate anions **188** and **189** when X is chelated between the two boron centers.

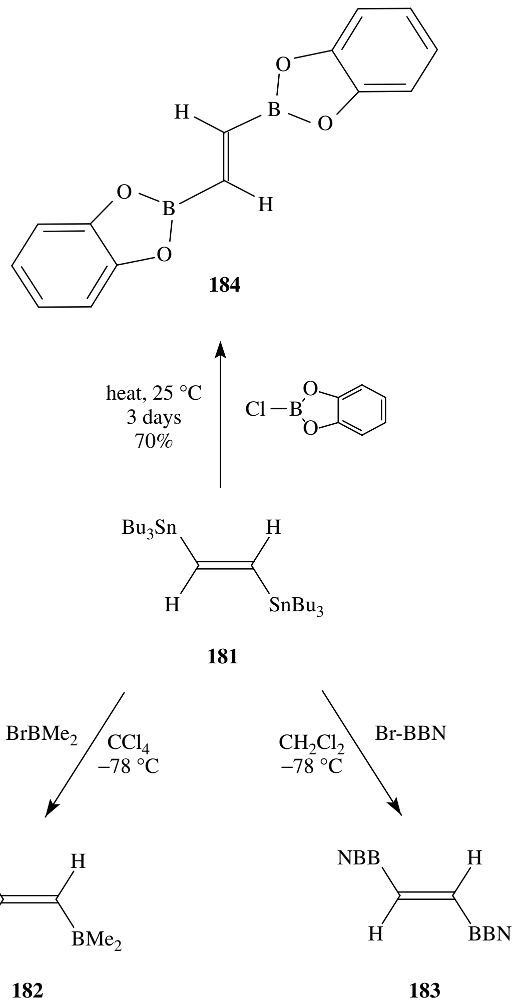
Two different routes, by Piers and coworkers[109] and Marks and coworkers[110] independently, reported recently, the formation of compound **190**. Marks and coworkers[110] treated the organotin precursor 1,2-C$_6$F$_4$(SnMe$_3$)$_2$ with excess BCl$_3$ at high temperatures (Scheme 53). For conversion to **191**, organotin C$_6$F$_5$ transfer agent [(C$_6$F$_5$)$_2$SnMe$_2$][111] or Zn(C$_6$F$_5$)$_2$ reagents were used.[109]



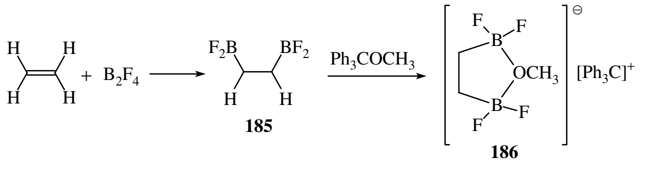
Scheme 48.



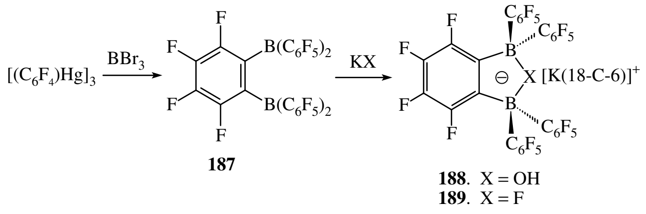
Scheme 49.



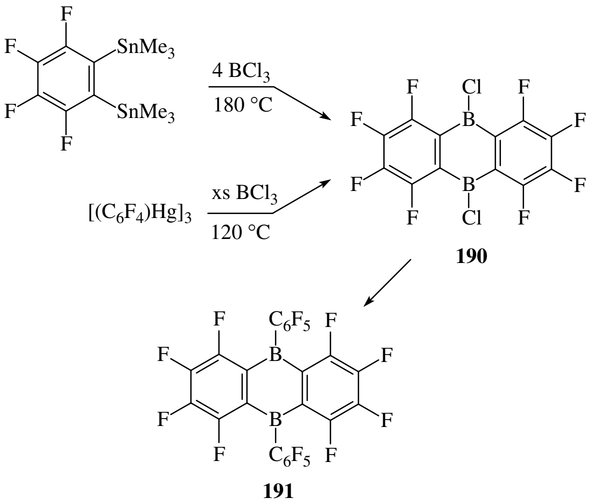
Scheme 50.



Scheme 51.



Scheme 52.

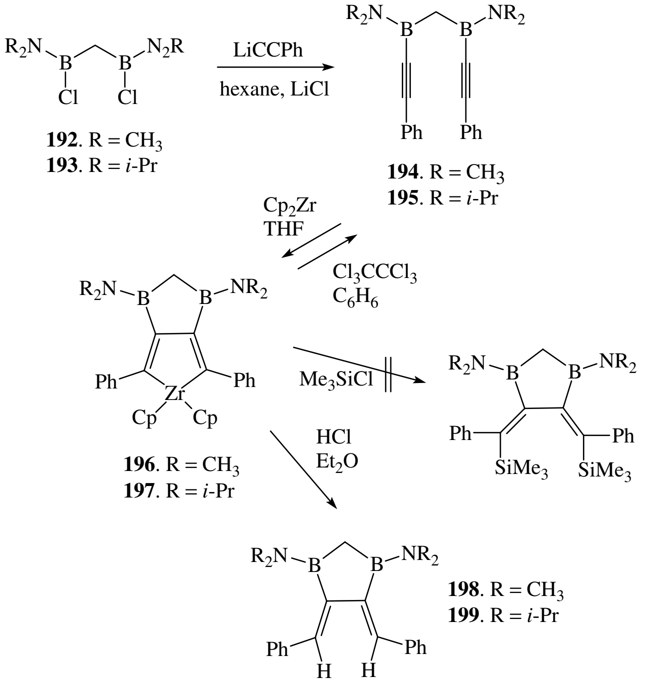


Scheme 53.

It is known that zirconocenes mediate cyclization.[22] Metzler *et al.*[112] synthesized *cis*-bis(4,5-phenylmethylidene)-1,3-bis(dialkylamino)-1,3-boranes **198** and **199** with almost quantitative yield (Scheme 54) via zirconocene species **196** and **197**. Bis[(dialkylamino)(phenylethynyl)boryl]methanes **194** and **195** were obtained in good yields by reacting lithium phenylacetylide with **192** and **193**.

The hexaborylbenzene derivatives **202** and **203** have been obtained by transition-metal-catalyzed {[CpCo(CO)$_2$], [Co$_2$(CO)$_8$], [Ni(cod)$_2$]} cyclotrimerization of bis(1,3,2-benzodioxaborol-2-yl)acetylene (**200**) and bis[1,3,2-(2,3-naphtho)-dioxaborol-2-yl] acetylene (**201**; Scheme 55).[113] AlMe$_3$ and AlEt$_3$ were found to react with **202** and **203** to furnish $C_6(BMe_2)_6$ (**204**) and $C_6(BEt_2)_6$ (**205**) respectively. With pyridine, the hexafunctional Lewis acid **204** formed the crystalline bis(pyridine) adduct $C_6(BMe_2)_6 \cdot 2(NC_5H_5)$ (**206**). Thermolysis of $C_6(BEt_2)_6$ (**205**) resulted in the intramolecular elimination of ethane to give the 1,2,3,4-bis(29,39-dihydro-19,39-diborole)-5,6-bis(diethylboryl)-benzene compound **207** (Scheme 55).

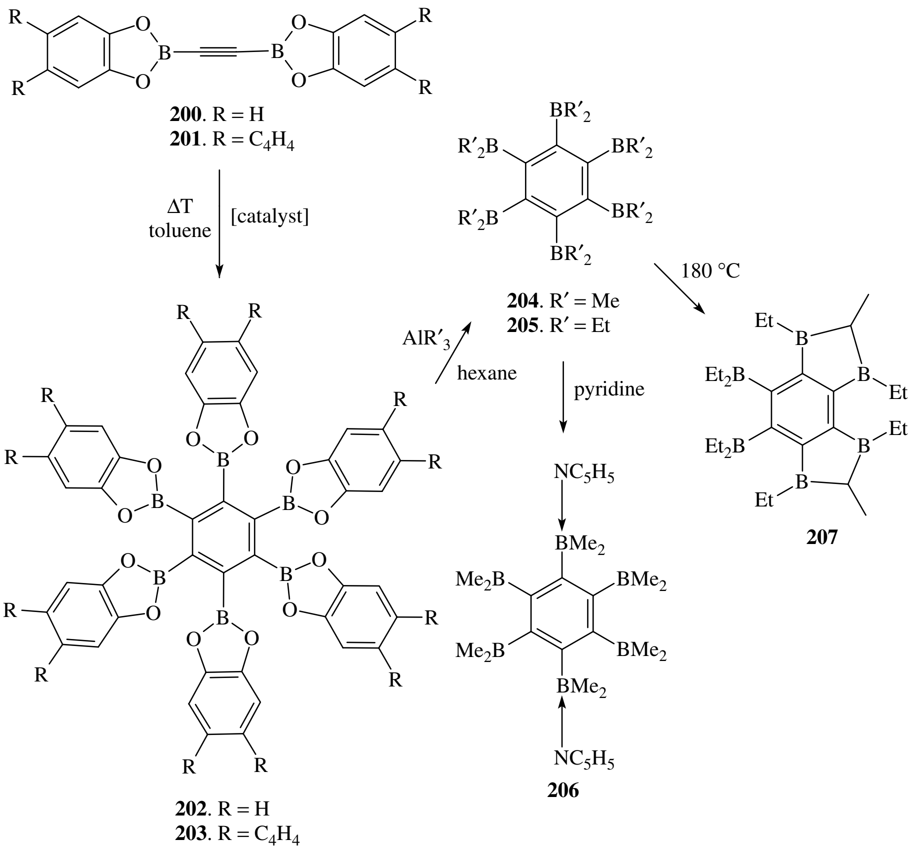
Reaction of [Co$_2$(CO)$_8$] with **200** yielded the bis(1,3,2-dioxaborol-2-yl) dicobaltatetrahedron derivative **208**. Reaction of stoichiometric amounts of **208** and diphenylacetylene gives the bis(boryl)tetraphenylbenzene derivative **209**, and reaction of **208** and mono(1,3,2-benzodioxaborol-2-yl)acetylene gives the tetraborylbenzene derivative **210** (Scheme 56).[113]



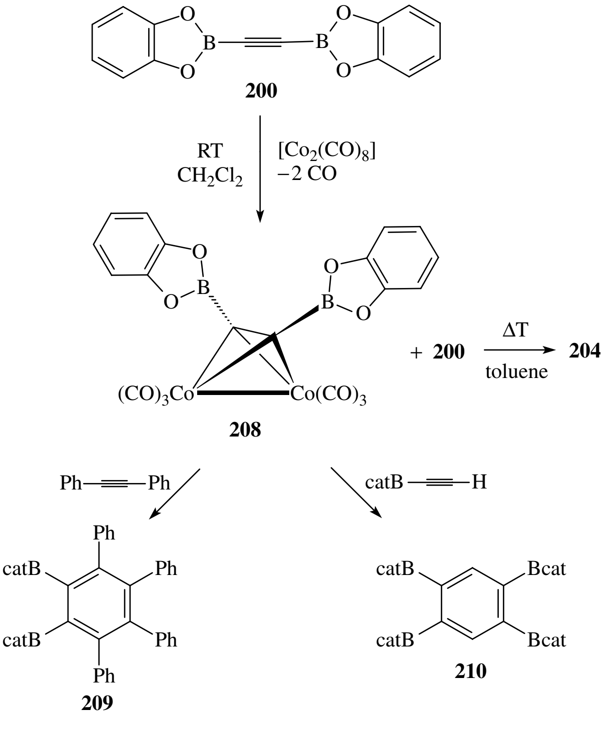
Scheme 54.

The catechol-substituted diborane(4) **200** was reacted with diborylacetylene in the presence of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] to gave **211** in 71% yield (Scheme 57).[114] Catechol-substituted diborylacetylenes **200** or **201** in the presence of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] or [Pt(PPh$_3$)$_4$] gave tetra- and the RHF/3–21G-optimized geometries of **212** and **213** and reveal intramolecular stabilization of the boron p_z orbital. When [Pt(cod)$_2$] is used as catalyst, the tetraborylethene **213** is formed exclusively.[114]

Derivatives of lithium and tin can be used in the preparation of B–C=C–B **215**–**217**, **219**, **221**, **222** and B–C≡C–B **214** and **220** compounds (Scheme 58). By preparing mono- and bi-dentate organoboron Lewis acids, the scope and limitations of synthesizing the requisite organoboranes by the boron–tin exchange between a boron halide and the appropriate organostannane have been observed.[115] Also, organotin derivatives can be obtained either from the corresponding RMgBr or RLi reagent and Me$_n$SnCl$_{4-n}$ or from a Barbier procedure using the organic halide, Me$_3$SnCl and magnesium metal: 1,2-bis(trimethylstannyl)ethyne, *o*-, *m*-, and *p*-bis(trimethylstannyl) benzenes, α,*o*-bis(trimethylstannyl)toluene, α,α-bis-(trimethylstannyl)-*o*-xylene, and 2,2-dimethyl-2-stannaindane.[115] Studies of the properties of these organoboranes have identified the heightened Lewis acidity of 1,2-bis(diethylboryl)ethyne and the π-electron delocalization involving the 2p_z-boron orbitals in the 9,10-dihydro- (**216**) and 9,10-dibora-anthracene (**217**)



Scheme 55.

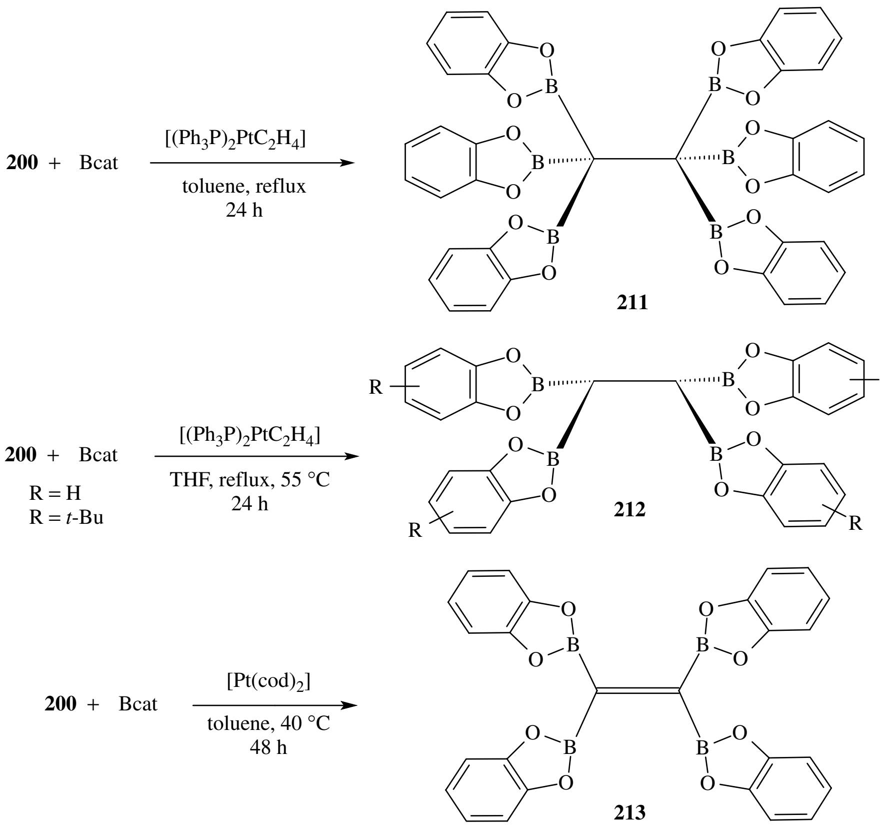


Scheme 56.

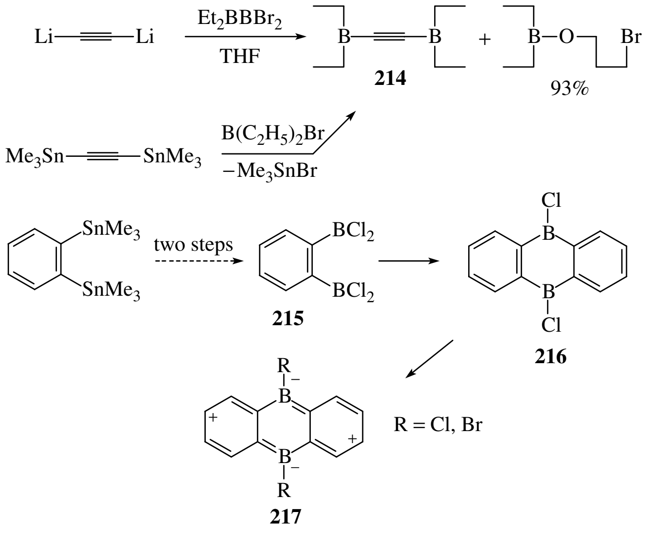
systems. Finally, an electronic mechanism for the boron–tin exchange has been developed to account for the selectivity of boron halide attack at unsaturated carbon–tin bonds.

The thermolysis of boranes **214** led variously to definite dimers or ill-defined oligomers with B–C=C–B structure **219** (Scheme 59). 1,2-Bis(diethylboryl)ethyne (**214**) was heated to 120 °C and the liquid evolved was permitted to reflux for 2 h. Evaporation of the liquid evolved under reduced pressure allowed the condensation of 1.0 equivalent of Et_3B and a red–brown viscous oil remained (**218**). Subsequent heating up to 700 °C in a thermogravimetric analysis apparatus left a shiny black residue of empirical formula of $C_3B_2H_4$ (**219**).[115]

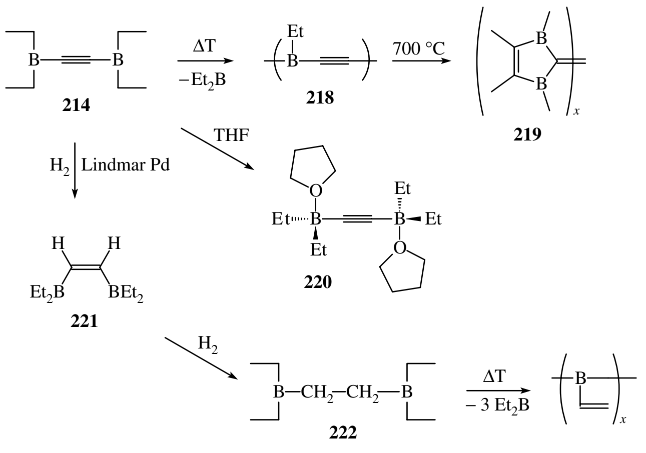
Recently, Ishiyama and Miyaura[116] published an article where they reviewed the metal-catalyzed borylation of alkenes, alkynes, and organic electrophiles with B–B compounds. They also reported that the platinum(0)-catalyzed addition of bis(pinacolato)diborane to alkenes and alkynes stereoselectively yielded *cis*-bis(boryl)alkanes or *cis*-bis(boryl)alkenes; and the addition of diborane to 1,3-dienes with a platinum(0) complex afforded a new access to the *cis*-1,4-bis(boryl)butene derivatives, which are a versatile reagent for diastereoselective allylboration of carbonyl compounds. The mechanisms and the synthetic applications of these reactions have also been discussed.



Scheme 57.



Scheme 58.



Scheme 59.

REFERENCES

1. Urry G, Kerrigan J, Parsons TD, Schlesinger HI. *J. Am. Chem. Soc.* 1954; **76**: 5299.
2. Onak T. *Organoboron Chemistry*. Academic Press: New York, 1975; 38–40.
3. Coyle TD, Ritter JJ. *Adv. Organometal. Chem.* 1972; **10**: 237.
4. Muetterlies EL. *The Chemistry of Boron and its Compounds*. Wiley: New York, 1967; 398–399.
5. Abu Ali H, Goldberg I, Srebnik M. *Eur. J. Inorg. Chem.* 2002; **73**.
6. Brotherton RJ, McCloskey JL, Petterson LL, Steinberg H. *J. Am. Chem. Soc.* 1960; **82**: 6242.
7. Baker RT, Nguyen P, Marder TB, Westcott SA. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 1336.
8. Ishiyama T, Yamamoto M, Miyaura N. *Chem. Commun.* 1997; 689.
9. Marder TB, Norman NC, Rice CR. *Tetrahedron Lett.* 1998; **39**: 155.

10. Iverson CN, Smith MR. *Organometallics* 1997; **16**: 2575.
11. Ishiyama T, Matsuda N, Murata M, Ozawa F, Suzuki A, Miyaura N. *Organometallics* 1996; **15**: 713.
12. Iverson CN, Smith MR. *J. Am. Chem. Soc.* 1995; **117**: 4403.
13. Cui Q, Musaev DGM, Morokuma K. *Organometallics* 1998; **17**: 742.
14. Cui Q, Musaev DGM, Morokuma K. *Organometallics* 1998; **17**: 1383.
15. Siebert W, Pritzkow H, Maderna A. *Angew. Chem. Int. Ed. Engl.* 1996; **35**: 1501.
16. Clegg W, Scott AJ, Lesley G, Marder TB, Norman NC. *Acta Crystallogr. Sect. C* 1996; **52**: 1989, 1991.
17. Nöth H. Z. *Naturforsch. Teil B* 1984; **39**: 1463.
18. Lawlor FJ, Norman NC, Pickett NL, Robins EG. *Inorg. Chem.* 1998; **37**: 1777.
19. Dembitsky VM, Tolstikov GA, Srebnik M. *Eurasian Chem. Technol. J.* 2002; **4**: 87.
20. Corey EJ, Cheng X. *The Logic of Chemical Synthesis*. Wiley–Interscience: New York, 1989.
21. Wender PA (ed). Frontiers in Organic Synthesis thematic issue. *Chem. Rev.* 1996; **96**: 1.
22. Dembitsky VM, Srebnik M. In *Titanium and Zirconium in Organic Synthesis*, Marek I (ed.). Wiley–VCH Verlag: Weinheim, 2002; 230–281.
23. Marek I. *Chem. Rev.* 2000; **100**: 2887.
24. Binger P, Köster R. *Angew. Chem.* 1962; **7**: 652.
25. Brown HC, Rhodes SP. *J. Am. Chem. Soc.* 1969; **91**: 4306.
26. Zweifel G, Arzoumanian H. *J. Am. Chem. Soc.* 1967; **89**: 291.
27. Zweifel G, Fischer RP, Horng A. *Synthesis* 1973; 37.
28. Ashe III AJ, Shu P. *J. Am. Chem. Soc.* 1971; **93**: 1804.
29. Cainelli G, Dal Bello G, Zubiani G. *Tetrahedron Lett.* 1966; 4315.
30. Mukaiyama T, Murakami M, Oriyami T, Yamaguchi M. *Chem. Lett.* 1981; 1193.
31. Reddy CK, Periasamy M. *Tetrahedron Lett.* 1993; **49**: 8877.
32. Abu Ali H, Goldberg I, Srebnik M. *Organometallics* 2001; **20**: 3962.
33. Hooz J, Morrison GF. *Can. J. Chem.* 1970; **48**: 868.
34. Hooz J, Gunn DM, Kono H. *Can. J. Chem.* 1971; **49**: 2371.
35. Hooz J, Gunn DM. *Tetrahedron Lett.* 1969; 3455.
36. Ishiyama T, Momota S, Miyaura N. *Synlett* 1999; **11**: 1790.
37. Abu Ali H, Goldberg I, Kaufmann D, Burmeister C, Srebnik M. *Organometallics* 2002; **21**: 1870.
38. Wrackmeyer B, Kehr G. *Polyhedron* 1991; **10**: 1497.
39. Herberich GE, Ohst H, Mayer H. *Angew. Chem. Int. Ed. Engl.* 1983; **23**: 969.
40. Enders M, Pritzkow H, Siebert W. *Angew. Chem. Int. Ed. Engl.* 1992; **31**: 606.
41. Eosch JJ. *J. Organometal. Chem.* 1995; **500**: 101.
42. Wrackmeyer B, Kehr G. *J. Organometal. Chem.* 1995; **501**: 87.
43. Greiwe P, Beez V, Pritzkow H, Siebert W. *Eur. J. Inorg. Chem.* 2001; 381.
44. Beez V, Greiwe P, Pritzkow H, Hofmann M, Schleyer PvR, Siebert W. *Eur. J. Inorg. Chem.* 1998; 1775.
45. Colberg JC, Rane A, Vaquer J, Soderquist JA. *J. Am. Chem. Soc.* 1993; **115**: 6065.
46. Dulou R, Chretien-Bessiere Y. *Bull. Soc. Chim. Fr.* 1959; 1362.
47. Brown HC, Zweifel G. *J. Am. Chem. Soc.* 1961; **83**: 3834.
48. Soundararajan R, Matteson DS. *J. Org. Chem.* 1990; **55**: 2274.
49. Brown HC, Rhodes SP. *J. Am. Chem. Soc.* 1969; **91**: 4306.
50. Zweifel G, Arzoumanian H. *J. Am. Chem. Soc.* 1967; **89**: 291.
51. Cainelli G, Dal Bello G, Zubiani G. *Tetrahedron Lett.* 1965; 3429.
52. Binder P, Köster R. *Angew. Chem.* 1962; **74**: 652.
53. Bubnov YuN, Bogdanov VS, Yakovlev IP, Mikhailov BM. *Zh. Obsch. Khim. (SSSR)* 1972; **42**: 1313.
54. Kurahashi T, Hata T, Masai H, Kitagawa H, Shimizu M, Hiyama T. *Tetrahedron* 2002; **58**: 6381.
55. Sakai M, Hayashi H, Miyaura N. *Organometallics* 1997; **16**: 4229.
56. Castle RB, Matteson DS. *J. Am. Chem. Soc.* 1968; **90**: 2194.
57. Castle RB, Matteson DS. *J. Organometal. Chem.* 1969; **20**: 19.
58. Matteson DS, Wilcsek RJ. *J. Organometal. Chem.* 1973; **57**: 231.
59. Matteson DS, Larson GL. *J. Organometal. Chem.* 1973; **57**: 225.
60. Matteson DS, Thomas JR. *J. Organometal. Chem.* 1970; **24**: 263.
61. Matteson DS, Tripathy PB. *J. Organometal. Chem.* 1970; **21**: P6.
62. Matteson DS, Moody RJ. *J. Am. Chem. Soc.* 1977; **99**: 3196.
63. Matteson DS. *Stereodirected Synthesis with Organoboranes*. Springer: Berlin, 1995.
64. Cainelli G, Dal Bello G, Zubiani G. *Tetrahedron Lett.* 1966; 4329.
65. Rathke MW, Kow R. *J. Am. Chem. Soc.* 1972; **94**: 6854.
66. Kow R, Rathke MW. *J. Am. Chem. Soc.* 1973; **95**: 2715.
67. Ashe AJ, Shu P. *J Am. Chem. Soc.* 1971; **93**: 1804.
68. Matteson DS, Hagelee LA, Wilcsek RJ. *J. Am. Chem. Soc.* 1973; **95**: 5096.
69. Matteson DS, Moody RJ. *Organometallics* 1982; **1**: 20.
70. Soundararajan R, Matteson DS. *Organometallics* 1995; **14**: 4157.
71. Jia L, Yang X, Stern CL, Marks TJ. *Organometallics* 1994; **13**: 3755.
72. Parks DJ, Spence RE, Spence H, Piers WE. *Angew. Chem. Int. Ed. Engl.* 1995; **34**: 809.
73. Kohler K, Piers WE, Jarvis AP, Xin S, Feng Y, Bravakis AM, Collins S, Clegg W, Yap GPA, Marder TB. *Organometallics* 1998; **17**: 3557.
74. Piers WE, Irvine GJ, Williams VC. *Eur. J. Inorg. Chem.* 2000; 2131.
75. Marder TB, Norman NC. *Top. Catal.* 1998; **5**: 63.
76. Abu Ali H, Goldberg I, Srebnik M. *Organometallics* 2001; **20**: 3962.
77. Ziegler A, Pritzkow H, Siebert W. *Eur. J. Inorg. Chem.* 2001; 387.
78. Berndt A. *Angew. Chem. Int. Ed. Engl.* 1993; **32**: 985.
79. Matteson DS, Majumdar D. *J. Organometal. Chem.* 1979; **170**: 259.
80. Mikhailov BM, Bezmenov A, Vasil'ev LS, Kiselev VG. *Dokl. Akad. Nauk SSSR* 1964; **155**: 141.
81. Mikhailov BM, Bezmenov A, Vasil'ev LS. *Dokl. Akad. Nauk SSSR* 1966; **167**: 590.
82. Brown HC, Negishi E, Gupta SK. *J. Am. Chem. Soc.* 1970; **92**: 2460.
83. Aronovich PM, Bogdanov VS, Mikhailov BM. *Izv. Akad. Nauk SSSR Ser. Khim.* 1969; 362.
84. Tanigawa Y, Moritaqni I, Nishida S. *J. Organometal. Chem.* 1971; **28**: 73.
85. Matteson DS, Wilson JW. *Organometallics* 1985; **4**: 1690.
86. Ishiyama T, Matsuda N, Miyaura N, Suzuki A. *J. Am. Chem. Soc.* 1993; **115**: 11 018.
87. Miyaura N, Suzuki A. *Chem. Rev.* 1995; **95**: 2457.
88. Ishiyama T, Yamamoto M, Miyaura N. *Chem. Lett.* 1996; 1117.
89. Ishiyama T, Matsuda M, Murata M, Ozawa F, Suzuki A, Miyaura N. *Organometallics* 1996; **15**: 713.
90. Binder P, Köster R. *Tetrahedron Lett.* 1965; 1901.
91. Lesley G, Nguyen P, Taylor J, Marder TB, Scott AJ, Clegg W, Norman NC. *Organometallics* 1996; **15**: 5137.
92. Abu Ali H, Al Quntar AA, Goldberg I, Srebnik M. *Organometallics* 2002; **21**: 4533.
93. Yang FY, Cheng CH. *J. Am. Chem. Soc.* 2001; **123**: 761.
94. Iverson CN, Smith III MR. *Organometallics* 1997; **16**: 2757.
95. Wiessauer C, Weissensteiner W. *Tetrahedron Asymm.* 1996; **7**: 5.
96. Nguyen P, Coapes RB, Woodward AD, Taylor NJ, Burke JM, Howard JAK, Marder TB. *J. Organometal. Chem.* 2002; **652**: 77.
97. Rudolph RW. *J. Am. Chem. Soc.* 1967; **89**: 4216.
98. Zeldin M, Gatti AR, Wartik T. *J. Am. Chem. Soc.* 1967; **89**: 4217.
99. Coyle TD, Ritter JJ. *J. Am. Chem. Soc.* 1967; **89**: 5739.
100. Rozen A, Zeldin M. *J. Organometal. Chem.* 1971; **31**: 319.
101. Eisch JJ, Gonsior LJ. *J. Organometal. Chem.* 1967; **8**: 53.
102. Singleton DA, Redman AM. *Tetrahedron Lett.* 1994; **35**: 509.
103. Corey EJ, Wollenberg RH. *J. Am. Chem. Soc.* 1974; **54**: 5581.
104. Shriver DF, Biallas MJ. *J. Am. Chem. Soc.* 1967; **89**: 1078.
105. Biallas MJ. *J. Am. Chem. Soc.* 1969; **91**: 7290.
106. Biallas MJ. *Inorg. Chem.* 1971; **10**: 1320.
107. Ceron P, Finch A, Frey J, Kerrigan J, Parsons T, Urry G, Schlesinger HI. *J. Am. Chem. Soc.* 1959; **81**: 6368.

108. Kaufmann D. *Chem. Ber.* 1987; **120**: 901.
109. Williams VC, Piers WE, Clegg W, Elsegood MRJ, Collins S, Marder TB. *J. Am. Chem. Soc.* 1999; **121**: 3244.
110. Metz MV, Schwartz DJ, Stern CL, Nickias PN, Marks TJ. *Angew. Chem. Int. Ed. Engl.* 2000; **39**: 1312.
111. Chambers D, Chivers T. *J. Chem. Soc.* 1964; 4782.
112. Metzler N, Nöth H, Thomann M. *Organometallics* 1993; **12**: 2423.
113. Ester C, Maderna A, Pritzkow H, Siebert W. *Eur. J. Inorg. Chem.* 2000; 1177.
114. Bluhm M, Maderna A, Pritzkow H, Bethke S, Gleiter R, Siebert W. *Eur. J. Inorg. Chem.* 1999; 1693.
115. Eisch J, Kotowicz BW. *Eur. J. Inorg. Chem.* 1998; 761.
116. Ishiyama T, Miyaura N. *J. Organometal. Chem.* 2000; **611**: 392.