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Recent advances in syntheses and reaction chemistry of boron and silicon substituted 1,3-dienes

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Contents

1. Introduction

Reports of main group element substituted 1,3-dienes and their reaction chemistry are still fairly rare in organic chemistry. In the present review, we will cover recent advances in the preparation and synthetic uses of boron and silicon substituted 1,3-dienes. Hilt and Bolze authored a review in Synthesis (published in early 2005) that covers the preparation of 1-boron and 2-boron substituted 1,3-dienes that were subsequently used in Diels–Alder reactions.[1] In the current review, we will cover the preparation of boron substituted 1,3-dienes used for studies other than Diels–Alder chemistry from 1998 to 2008 and preparation of boron substituted

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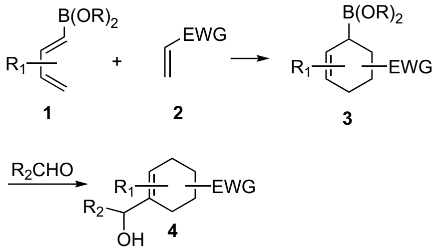
dienes used for Diels–Alder reactions over the same time period but with more emphasis on Diels–Alder chemistry reported since Hilt and Bolze's review (2004–2008). In late 2005, Hansen and Lee submitted an account of the Lee group's work on enyne metathesis to Accounts in Chemical Research.[2] This review covers some of the Lee group's work in tandem dienyne ring-closing metathesis of alkynyl silaketals to make silicon substituted 1,3-dienes. In 2007, Xi published a review of 1-lithio-1,3-dienes.[3] In some cases these lithio dienes have been used to prepare silicon dienes but silicon dienes are not the focus of that review. Marciniec and Pietraszuk authored a review on the preparation of silicon containing compounds using ruthenium catalysts in 2004.[4] There are three references to silicon substituted dienes in this review but diene preparation and use is not the focus of the Pietraszuk review. In the current review we will also cover the preparation of silicon substituted dienes used for Diels–Alder as well as other studies from 1998 to 2008. In the case of the Lee group's work, we will briefly review their publications prior to 2005 and focus on the ones, which have appeared from 2005 to 2008.

2. Brief overview of early work with boron and silicon substituted 1,3-dienes

Most work reported with main group-substituted dienes has been done with the 1-(dialkoxyboryl)-1,3-butadienes (**1**), sometimes termed 1,3-dienyl-1-boronates. These compounds were reported by Vaultier in 1987,[5] and numerous reports of their Diels–Alder chemistry have appeared from the laboratories of Vaultier,[6–9] Lallemand,[7,9–12] and others.[13–15] Most of these reports use the dienylboronates in [4+2]/allylation tandem reactions (**1**–**4**), and this sequence is now often called the Vaultier tandem sequence.



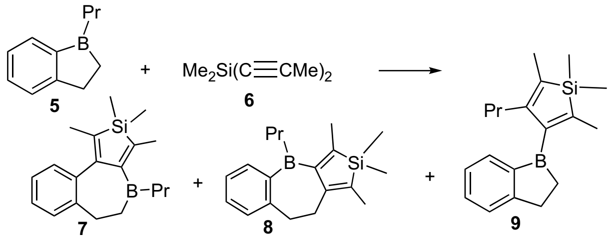
In contrast to the 1,3-dienyl-1-boronates, few reports on the preparation and Diels–Alder chemistry of 1,3-dienyl-2-boronates exist in the literature prior to 1998.[1,16–18] Limited use of early members of this class of compounds is presumably due to their high affinity toward dimerization, even at room temperature.[19]

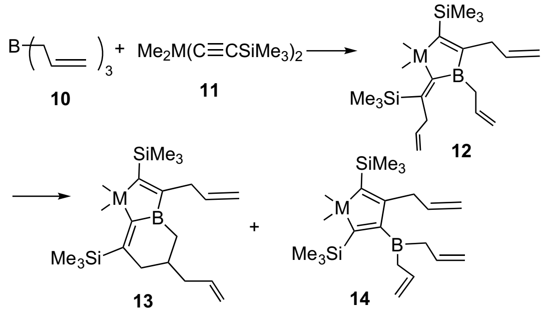
Reports of silicon substituted 1,3-dienes and their reaction chemistry prior to 1998 are also not widespread in organic chemistry. With respect to silyl substituted 1,3-dienes, 1-trimethylsilyl-1,3-butadiene was originally reported and trapped with maleic anhydride in 1957.[20] Fleming and co-workers then reported an alternate preparation of this compound and a number of its Diels–Alder reactions over the 1970s and early 1980s.[21,22] Subsequent to these initial reports a number of 1-silyl-1,3-diene preparations that rely on olefination of α,β-unsaturated aldehydes, nickel catalyzed coupling reactions, etc. have also been reported and reviewed.[23,24] Reports of 2-silyl substituted 1,3-dienes are 3–4 fold less frequent than their 1-substituted counterparts. 2-Triethylsilyl-1,3-butadiene and a few of its Diels–Alder reactions were reported by Ganem and Batt in 1978.[25] Paquette and Daniels reported some 2-silyl substituted-1,3-cyclohexadienes in 1982 but none of their Diels–Alder chemistry.[26] Trost and Mignani reported the Pd catalyzed elimination and cyclization reactions of 3-acetoxy-2-trimethylsilyl-1-butene in 1986.[27] One other report of the preparation of 2-trialkylsilyl-1,3-dienes appeared since a 1995 review[24] but prior to 1998.[28] No Diels–Alder reactions of silicon substituted dienes were reported in that work. Reports of the preparation and use of 2-trialkoxysilyl-1,3-dienes prior to 1998 are extremely rare. We find a report of the use of the Ganem and Batt protocol[25] to make 2-trimethoxysilyl- and 2-triethoxysilyl-1,3-butadiene in 1984 and then a report of the polymerization of these materials in 1989.[29]

3. Preparation and reactions of boron substituted 1,3-dienes

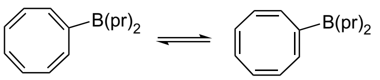
3.1. Preparation and use of boron dienes in structural and noncycloaddition studies

In 1998, Wrackmeyer and Vollrath reported that 1-propyl-1-boroindane (**5**) reacts with dimethyl-di(1-propynyl)silane (**6**) to produce a 1:0.8:0.6 mixture of siloles (**7**–**9**) that can be viewed as 2-boron substituted 1,3-dienyl systems.[30] In 2000, Tok, Wrackmeyer, and Bubnov reported the allylboration of related acetylenic derivatives of both silicon and tin and one of the product (**14**) is a 2-boron substituted 1,3-diene.[31,32] Bis(trimethylsilylethynyl) dimethylsilicon and bis(trimethylsilylethynyl) dimethylstannane were both organoborated to yield heterocycles (**12**) M=Si, Sn, which were then heated to yield B(allyl)$_2$ substituted siloles or stannoles (**14**).





Cyclooctatetraenyl (dipropyl) borane (**15**) was also reported at the conference where the work above was disclosed.[31] The boron in this compound already has a strong orbital interaction with the adjacent double bond so there is no driving force for the borotropic rearrangements needed to account for the production of the boron containing heterocyles reported above. Reversible double bond fluctuation was observed as expected.



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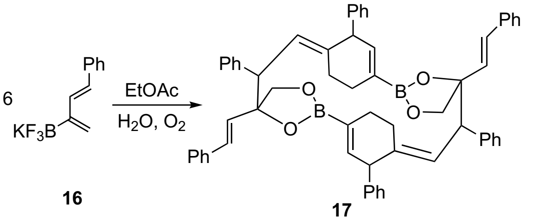
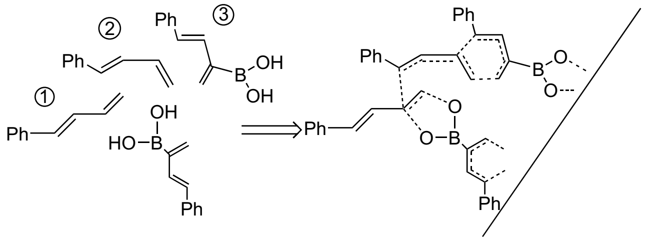
In 2000, Ishiyama and Miyaura published a review, which covered platinum and palladium catalyzed reactions of diborons.[33] One example of the diboration of the yne portion of an enyne to produce a diboron substituted 1,3-diene is reported as well as one example of a 1,2-diboron substituted alkene, which was cross-coupled at the 1-position with *E*-β-bromostyrene to yield a monoborated 1,3-diene. In 2005, Stone and co-workers reported a couple of examples of alkyne coupling that occurred at rhenium monocarborane complexes.[34] The resulting products of these coupling reactions contain a 2-boron substituted 1,3-diene moiety.

In 2007, Welker and co-workers reported an unusual hydrolysis/oligimerization reaction of boron substituted 1,3-diene (**16**). Attempts to grow crystals of BF_3 substituted diene (**16**) in ethyl acetate under atmospheric conditions instead produced a symmetrical structure (**17**) (characterized by X-ray crystallography) derived from six molecules of (**16**).

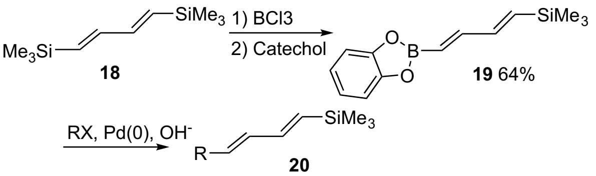


The rationalization of the formation of (**17**) requires protonolysis of some of the boron carbon bonds in (**16**) to generate some 1-phenyl-1,3-butadiene. The terminal double bond of one 1-phenyl-1,3-butadiene molecule (labeled 1 in the figure below) appears to have been oxidized and to have participated in an electrophilic addition reaction with the internal alkene of a second molecule of 1-phenyl-1,3-butadiene (labeled 2 in the figure below). The terminal double bond of this second molecule of 1-phenyl-1,3-butadiene has participated in a Diels–Alder reaction with a boron substituted diene (depicted as the boronic acid substituted diene labeled 3 in the figure below).

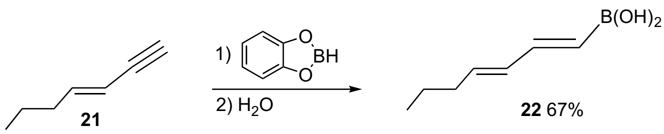


3.2. Preparation and use of boron dienes in cross-coupling and allylation reactions

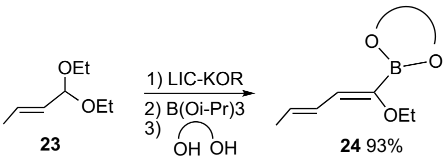
As one might imagine, there have been a number of reports over the last 10 years of the preparation of boron substituted 1,3-dienes, which were subsequently used in cross-coupling reactions. In 1998, Naso and co-workers reported the preparation of a 1-boryl-4-silyl substituted 1,3-diene (**19**) and its use in a variety of cross-coupling reactions with aryl and alkenyl halides.[35]



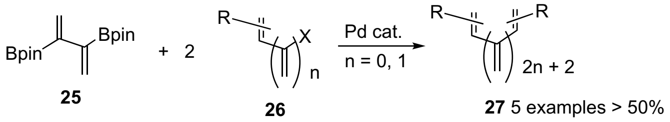
In 1999, Barrett and co-workers reported the hydroboration of heptenyne (**21**) to produce dienyl boronoic acid (**22**), which was subsequently used in a Pd catalyzed cross-coupling reaction leading to a total synthesis of restrictinol.[36]



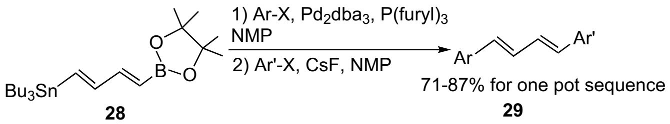
In 2002, Prandi and Venturello and co-workers reported treating crotonaldehyde diethyl acetal with Schlosser's base followed by triisopropylborate and a diol to generate dienyl boronic esters (**24**).[37] Those boronic esters were then cross-coupled with a variety of aryl halides and triflates with aryl iodides and bromides providing significantly higher cross-coupled product yields than the chlorides as expected.



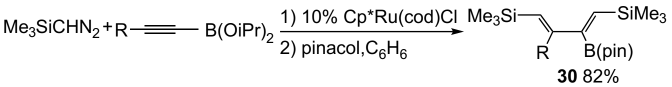
In 2004, Shimizu and co-workers reported the cross-coupling of 2,3-bis(pinacolato)boryl-1,3-butadiene (**25**) to make both symmetrical and unsymmetrical dendralenes (**27**).[38] The scheme below shows the symmetrical dendralene example and in general yields were significantly better for the preparation of symmetrical compared to unsymmetrical substrates. Following this initial communication, a full paper appeared on this chemistry in 2007 and describes the use of these bis-boryl dienes to make a number of lignans.[39]



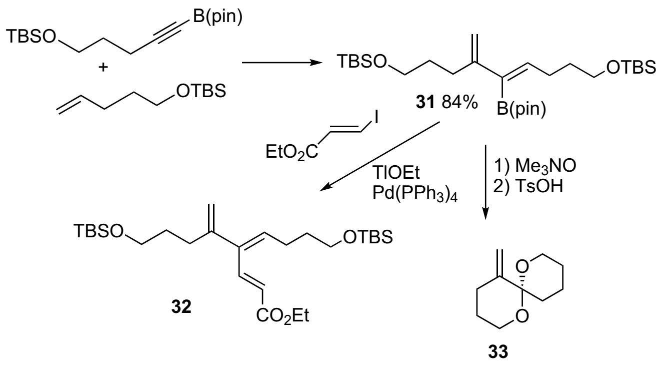
Coleman and Walczak reported the preparation of a hetero-bismetalated diene (**28**) in 2005, which was used in a number of sequential Stille couplings followed by Suzuki–Miyaura cross-coupling reactions.[40] They reported the use of this diene and tandem cross-coupling scheme in a total synthesis of Lucilactaene in 2005 as well.[41]



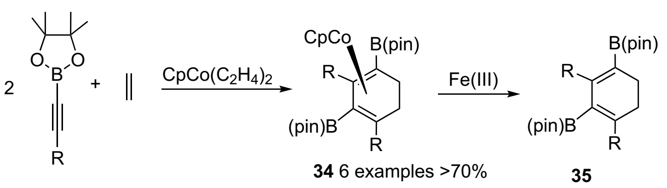
In 2005, Shirakawa and co-workers reported the ruthenium catalyzed double addition of trimethylsilyldiazomethane to alkynylboronates to produce hetero tris-metalated 1,3-dienes, which contained one boron substituent and two silicon substituents (**30**). The carbon boron bonds in the dienes were used in Suzuki–Miyaura couplings whereas the silicons were removed by proteolysis or converted to iodides, which were also used in cross-coupling.[42]



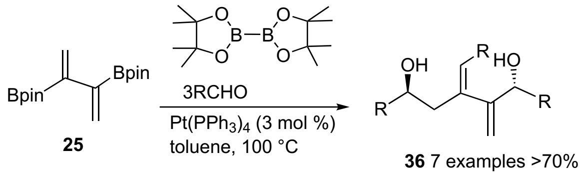
In 2005, Kim and Lee also reported a boron-directed regio- and stereoselective enyne cross-metathesis reaction, which was used to prepare a variety of vinyl boronate containing 1,3-dienes (**31**).[43] In one case, the cross-metathesis was run on a 1 g scale and then the boron diene product was used in both a cross-coupling reaction to produce **32** as well as an oxidation of the dienyl boronate where the ketone was trapped via an acid catalyzed spiroketalization reaction to produce **33**.



In 2007, Malacria, Vollhardt and co-workers reported a cyclopentadienyl cobalt (CpCo) mediated cocyclization of two alkynyl borates with alkenes to produce cobalt complexed diboron substituted cyclohexadienes (**34**).[44] The cyclohexadienes were demetalated oxidatively (**35**) and then used in sequential Suzuki–Miyaura cross-coupling reactions.

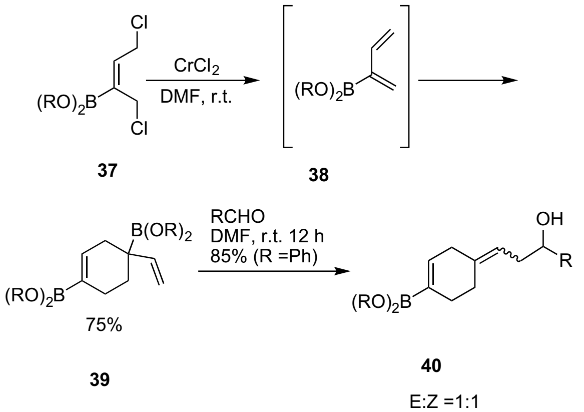


Lastly, in 2007, Shimizu and co-workers reported that the bis(pinacolatoboryl) diene (**25**), which they first reported in 2004 could be treated with bis(pinacolato)diboron and 3 mol equiv of an aldehyde to effect a triple aldehyde addition reaction and the production of 2,3-bis(alkylidene)alkane-1,5-diols (**36**).[45] The triple addition reactions took place for both aryl and alkyl aldehydes and were optimized with $Pt(PPh_3)_4$ as catalyst in toluene at 100 °C.

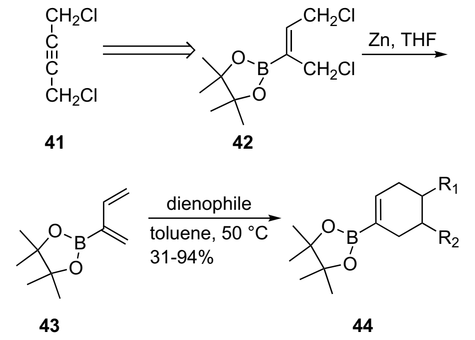


3.3. Preparation and use of boron dienes in Diels–Alder cycloadditions

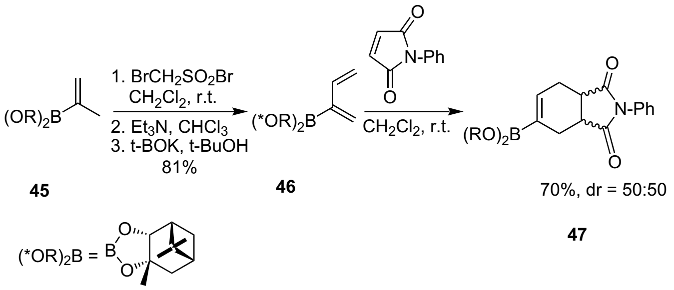
In contrast to the 1,3-dienyl-1-boronates (**1**) mentioned above, few reports on the preparation and Diels–Alder chemistry of 1,3-dienyl-2-boronates exist in the literature prior to 1998.[1,16–18] Limited use of early members of this class of compounds (**38**) is presumably due to their high affinity toward dimerization to **39**, even at room temperature.[19]



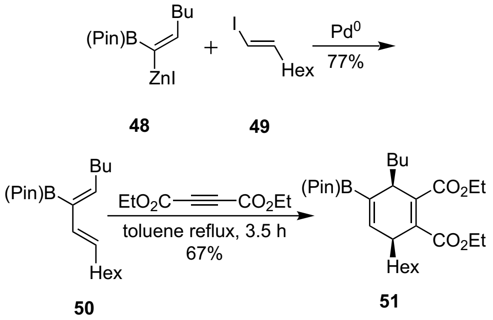
In the early 1990s, Suzuki and co-workers first synthesized the unsubstituted diene (**43**), which could be isolated in a fast trap-to-trap distillation under high vacuum.[17] This diene (**43**) showed reasonable Diels–Alder reactivity with both mono and disubstituted dienophiles at 50 °C.



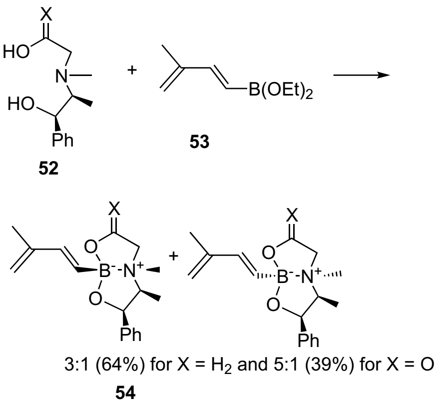
Related chiral diene (**46**) was also synthesized in the early 1990s in high yield (81%) via a free-radical addition of bromomethane sulfonyl bromide to **45** followed by vinylogous Ramberg–Backlund reaction (at room temperature slow dimerization of **46** occurred).[46] An attempted asymmetric version of a Diels–Alder reaction of **46** with *N*-phenyl maleimide produced **47** in a 70% yield with no diastereoselectivity.



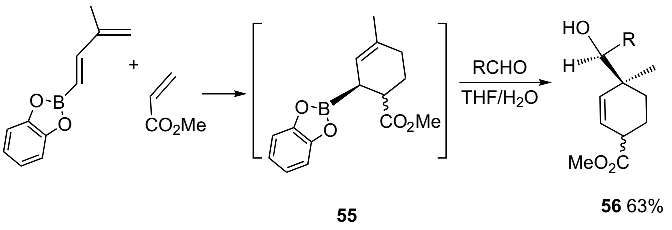
Following a Negishi-type cross-coupling reaction, Knochel and co-workers reported the synthesis of a stereochemically pure 2-boron functionalized 1,3-diene (**50**) and a Diels–Alder example in 1992. The Diels–Alder reaction of diene (**50**) was performed with diethyl acetylene dicarboxylate to afford the cycloadduct (**51**) in 67% yield as a single diastereomer.[47]



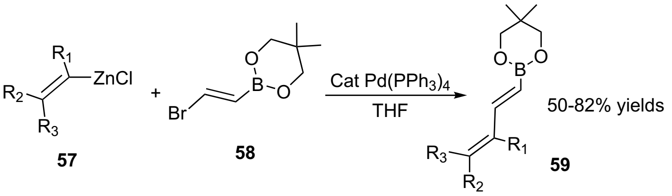
In 1999 Mortier, Vaultier and co-workers reported the preparation and Diels–Alder chemistry of some dienylborates, which contained both chiral boron and nitrogen atoms (**54**).[48] The dienyl complexes were synthesized by chiral ligand exchange on the diethoxy dienyl borate (**53**) and then the mixture of dienyl complex diastereomers was reacted with *N*-phenyl maleimide in Diels–Alder chemistry. Isolation of a pure diastereomer of the X=O diene and reaction with *N*-phenyl maleimide followed by boron carbon bond oxidation with hydrogen peroxide provided a cycloadduct in 12% ee.

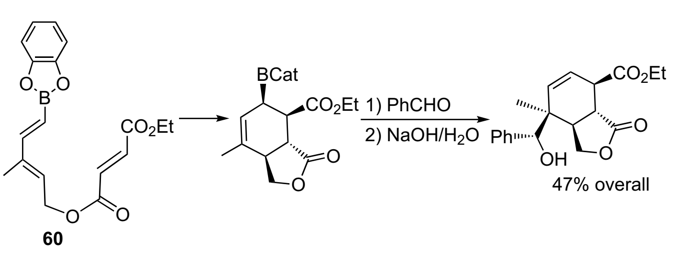


Also in 1999, Six and Lallemand reported a one-pot Diels–Alder/allylation Vaultier sequence for use in a Clerodin synthesis.[9] The initial allyl borate (**55**) formed as a result of the Diels–Alder cycloaddition proved unstable so running the cycloaddition in the presence of the aldehyde allowed the allyl borate to be trapped immediately after formation and provided 22–50% yields of Diels–Alder/allylation products (**56**). The full paper describing the use of this sequence in a synthesis of an advanced Clerodin intermediate appeared in 2002.[7]

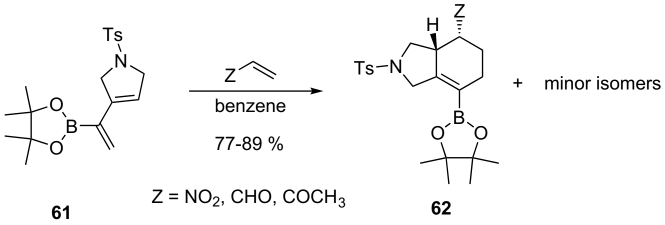


In 2000, Vaultier, Mortier, and co-workers reported a palladium catalyzed cross-coupling of alkenyl zincs (**57**) and bromo boronate alkenes (**58**) to produce boronate-substituted dienes (**59**).[49] Several of these dienes were subjected to a tandem Diels–Alder/allylation sequence to produce bicyclic lactones. A number of additional 1,3-dienylboronates (**60**) prepared by enyne hydroboration were also reported in this manuscript and those dienes were used in both intra and intermolecular Diels–Alder reactions.

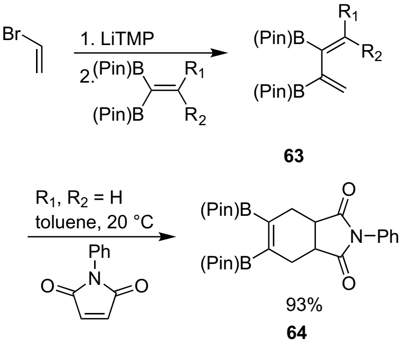




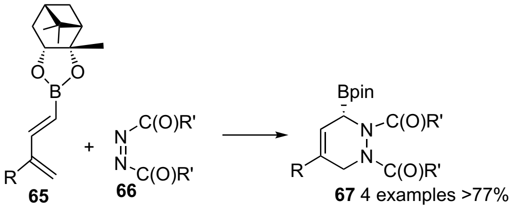
Also in 2000, Renaud and co-workers synthesized highly functionalized 1,3-dienyl-2-boronates (**61**) using enyne ring-closing metathesis reactions of boronate-substituted alkynes. These dienes undergo cycloaddition reactions with electron-deficient dienophiles (nitroethylene, acrolein, MVK) with high regio- and stereoselectivity. Unfortunately, many of these dienes turned out to be unstable due to dimerization.[50]



Diboronyl dienes (**63**) were synthesized by Shimizu and co-workers in a one-pot reaction reported in 2001.[51] Surprisingly, these dienes showed higher reactivity in cycloaddition than the corresponding mono-substituted boron diene (**43**).

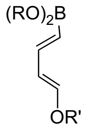


Also in 2001, Jiang and co-workers reported two chiral pinanediol 1,3-dienylboronates (**65**) and their hetero Diels–Alder reactions with some azo compounds (**66**).[14] They were using this asymmetric Diels–Alder reaction of a boron diene to prepare some intermediates (**67**) needed to make a series of thrombin inhibitors.



In 2002, Carreaux, Cossio and co-workers experimentally repeated Suzuki's work, which showed facile Diels–Alder dimerization of diene (**38**).[19] These workers extended that original experimental study by also carrying out a theoretical analysis of a [4+3] versus [4+2] mechanism for this dimerization. Their computational work predicts a transition state structure with nonclassical [4+3] character. However, the calculations predict that as the C–C and C–B distances in the transition state become shorter and shorter, they reach a point where the C–C bond interaction is more stabilizing than the C–B bond interaction leading to the observation of [4+2] rather than [4+3] cycloaddition products.

In 2003, Gao and Hall reported the preparation of two ether substituted 1,3-dienylboronates (**68**, **69**).[15] The hope was that these ether substituted boron dienes would be significantly more reactive in tandem Diels–Alder/allylboration chemistry compared to their nonether substituted counterparts described above. While these dienes participated in those tandem reactions the conditions required were similar to those for less electron rich dienes (80–100 °C for 16–24 h).



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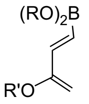

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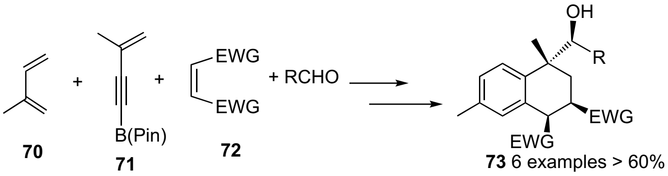
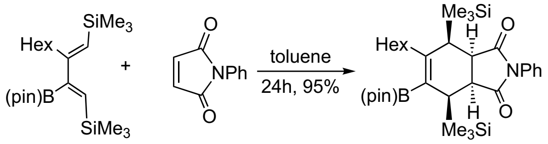
In a late 2004 web release, Hilt and co-workers reported a new route to boron substituted dienes, which involved a cobalt catalyzed Diels–Alder reaction of a diene (**70**) with a boron substituted enyne (**71**).[52] The boron substituted diene product of this Diels–Alder reaction was then subsequently used in a tandem Diels–Alder/allylation (Vaultier) sequence. Two different enynes were used and results from several disubstituted dienophiles were reported. The products (**73**) contain four new stereocenters, one of which is quaternary.



70 **71** **72**

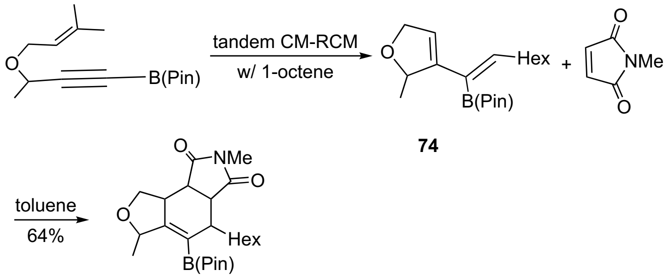
73 6 examples > 60%

Continuing on the topic of uses of alkynylboronates, the work describing ruthenium catalyzed double diazomethane addition to them outlined above also contained one example of the use of this class of boron dienes (**30**, R=Hex) in Diels–Alder reactions.[42]



30 R = Hex

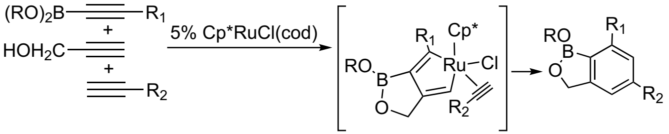
Also in the area of alkynyl boronate chemistry reported in 2005, Lee and co-workers reported the preparation of a number of 2-boron substituted 1,3-dienes (**74**) by enyne cross-metathesis.[43] A Diels–Alder reaction of one of these dienes was reported but the stereochemistry of the product (**75**) of that reaction was not defined.



74

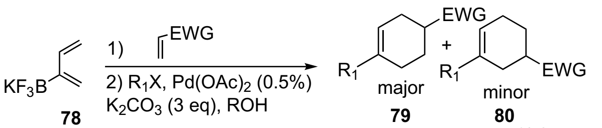
75

Lastly, in the area of alkynyl boronate chemistry reported in 2005, Yamamoto and co-workers disclosed a Cp*RuCl catalyzed cyclotrimerization of three unsymmetrical alkynes, one of which was an alkynyl boronate.[53] Boron substituted dienyl complexes (**76**) were postulated as intermediates in these reactions. The chemistry involved in transforming the proposed intermediate to product is more likely an insertion/reductive elimination sequence than a Diels–Alder/reductive elimination sequence but we include it in this section since it could involve Diels–Alder chemistry of a boron substituted diene. Extension of this chemistry to diynes and an alkynyl boronate was reported in 2006.[54]



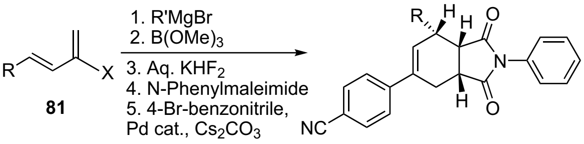
76 **77**

In 2005, we reported the first synthesis of 2-trifluoroborate substituted 1,3-butadienes (**78**) and their use in tandem Diels–Alder/cross-coupling chemistry and then we followed this work with a 2007 report that included the preparation of 4-aryl-2-BF$_3$-substituted 1,3-dienes (**81**) and their tandem Diels–Alder/cross-coupling chemistry.[55,56]



78 **79** **80**

11 examples >50% for 2 steps

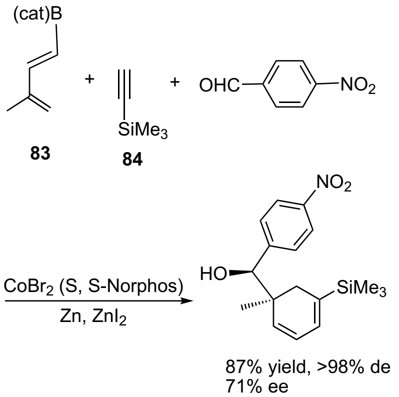


81

Only detected *endo* isomer

82 25% (avg. yield of 63%/step)

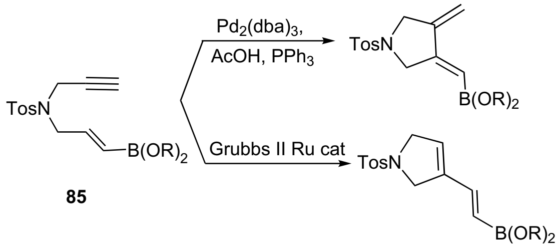
A Diels–Alder/allylation sequence using a boron functionalized diene (**83**) and a silyl alkyne (**84**) as dienophile was reported in 2006. This was cobalt and zinc catalyzed cycloaddition and coupling chemistry, which proceeded with excellent regio- and diastereoselectivity and good enantioselectivity.[57]

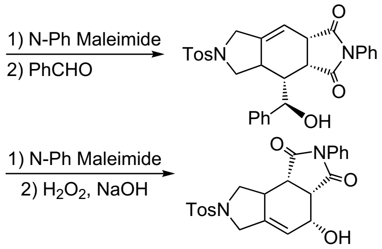


83 **84**

87% yield, >98% de
71% ee

Lastly in this Diels–Alder section, Carboni and co-workers reported a palladium catalyzed cycloisomerization/Diels–Alder/allylation sequence as well as a ruthenium catalyzed cross-metathesis/ring-closing metathesis/Diels–Alder sequence involving 1,3-dienyl-1-boronates in 2007.[58] The substrates for this chemistry (**85**), which were exposed to Grubbs catalyst proved to be complimentary to the ruthenium catalyzed cross-metathesis/ring-closing metathesis chemistry of alkynylboronates reported above with respect to boron diene regiochemistry produced.



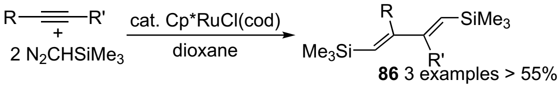


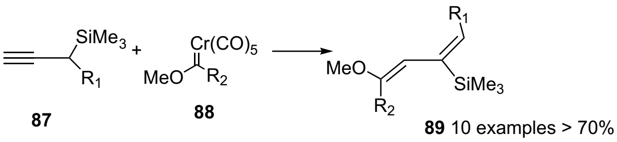
4. Preparation and reactions of silicon substituted 1,3-dienes

4.1. Preparation and use of silicon substituted dienes in reactions other than cycloadditions

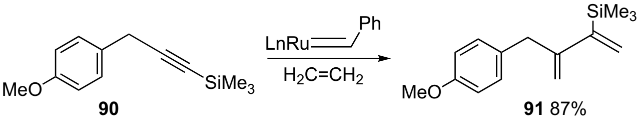
4.1.1. Silicon substituted dienes from reactions of carbenes with alkynes

A number of reports of the preparation of silicon substituted dienes from alkynes have appeared since the late 1990s. Two of the reports involve the addition of carbenes to alkynes and several of the reports involve enyne cross-metathesis. In 2000, Dixneuf and co-workers reported the ruthenium catalyzed double addition of silicon substituted diazo compounds to alkynes to produce 1,4-disilicon substituted 1,3-dienes (**86**). [59] In 2004, Herndon and co-workers reported the coupling of propargyl silanes (**87**) with Fischer carbene chromium complexes (**88**) as a new route for the preparation of 2-silicon substituted 1,3-dienes (**89**).[60]

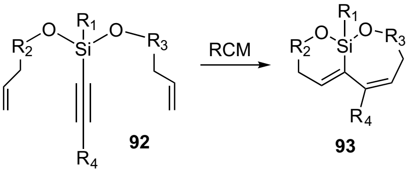




In 2002, Tonogaki and Mori reported an improved 1,3-diene synthesis involving the cross-metathesis reactions between terminal and internal alkynes and ethylene.[61] In one case a silicon substituted alkyne (**90**) was used, which resulted in the production of a 2-silicon substituted 1,3-diene (**91**).

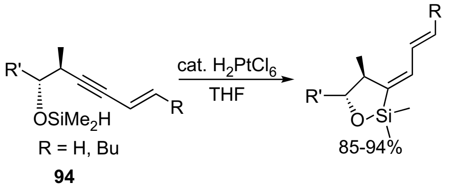


As noted in Section 1, the Lee group has reported a number of examples of both intramolecular and intermolecular cross-metathesis between terminal alkenes and silyl substituted alkynes as well as enynes.[62] The Lee group has also reported examples of a tandem sequence of cross-metathesis ring-closing metathesis reactions of dienynes and endiynes. RCM of alkynyl silaketals (dienynes) (**92**) produced siloxane substituted 1,3-dienes (**93**) [63] and an endiyne substrate was used in a silicon tethered RCM strategy to prepare the framework of Tartolon B.[64]

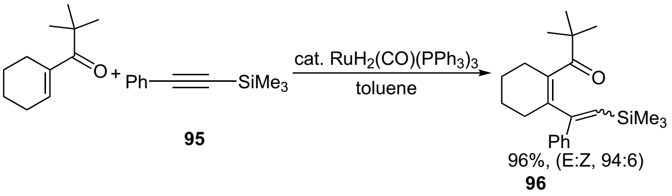


4.1.2. Silicon substituted dienes from X–H addition across an alkyne

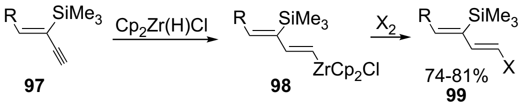
Several reports have appeared recently where silicon substituted 1,3-dienes have been prepared by hydrometalation reactions. In 2001, Marshall and co-workers reported the intramolecular Pt catalyzed hydrosilylation of an enyne (**94**).[65]



In 2004, Murai and co-workers reported a ruthenium catalyzed C–H activation followed by a hydroruthenation of a silyl alkyne (**95**).[66] This reaction sequence leads to a silyl substituted dienone (**96**).

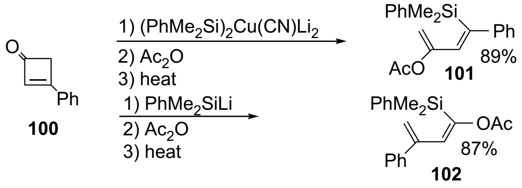


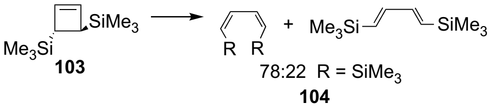
Lastly in 2007, Cai and co-workers reported the hydrozirconation of a silicon substituted enyne (**97**) and the subsequent halogenations (**99**) of the zirconated products.[67]



4.1.3. Silicon substituted dienes from ring opening reactions

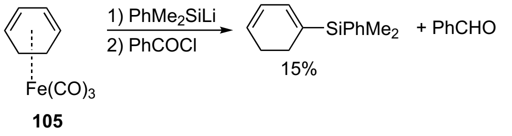
There have been a couple of reports of ring opening reactions of cyclobutenes, which lead to silyl substituted 1,3-dienes. In 2001, Murakami, Ito, and co-workers reported that silyl cuprates participated in 1,4 addition to cyclobutenones (**100**), which were ring opened thermally to produce 1-silyl substituted 1,3-dienes (**101**).[68] This paper also reported that silyl lithium reagents added 1,2 to cyclobutenones and that those addition products also ring opened to produce 1-silyl-1,3-diene isomers (**102**) of the cuprate addition products. In 2004, Murakami and Hasegawa subsequently also reported the synthesis and thermal ring opening of *trans*-3,4-disilylcyclobutene (**103**) to generate *E,E* and *Z,Z*-1,4-ditrimethylsilyl-1,3-butadienes (**104**).[69]

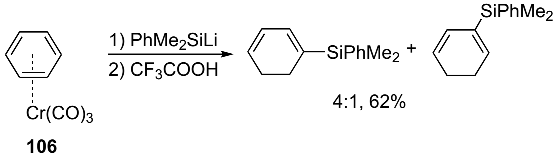




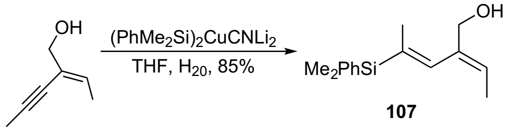
4.1.4. *Silicon substituted dienes from silyl anion additions to electrophiles*

In addition to the silyl anion addition to a cyclobuteneone discussed above, several other examples of silyl anion addition reactions have been used in 1,3-diene preparation. Yeh and co-workers reported the addition of lithiodimethylphenylsilane to (η^4-1,3-diene)-Fe(CO)$_3$ complexes (**105**) and (η^6-arene)Cr(CO)$_3$ complexes (**106**).[70]

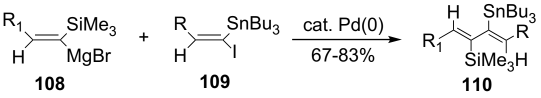




Coleman and co-workers used a silylcupration of an alkyne followed by protonolysis to produce a 1-silyl substituted 1,3-diene (**107**), which was used in a total synthesis of Lucilactaene.[41]



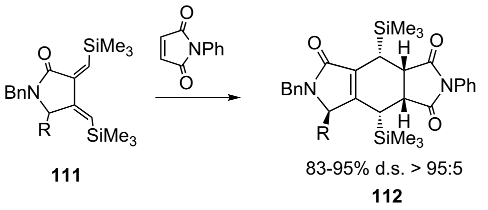
Lastly, in 2006, Cai and co-workers reported the generation of α-silylvinyl Grignard reagents (**108**), which were cross-coupled to α-iodovinylstannanes (**109**) to yield a variety of 2-silyl-3-stannyl substituted 1,3-dienes (**110**).[71]

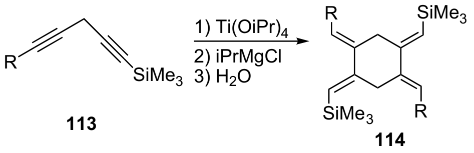


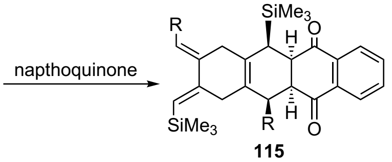
4.2. Preparation and use of silicon dienes in Diels–Alder cycloadditions

4.2.1. *Preparation and use of 1-silicon substituted 1,3-dienes in Diels–Alder cycloadditions*

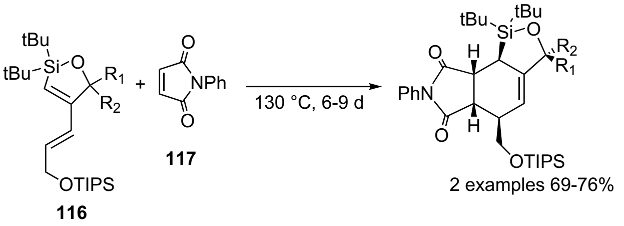
In 2000, Sato and co-workers reported a titanium mediated coupling of bis-acetylenic amides or esters (where all substrates contained at least one silyl substituted alkyne) to generate *exo*-cyclic 1,3-dienes (**111**).[72] Three of these dienes were used in Diels–Alder reactions with ethyl propiolate, an alkynone, or *N*-phenyl maleimide. Cycloadditions with *N*-phenyl maleimide were *endo* selective (**112**). In 2002, they reported the extension of this reaction to diynes (**113**), which were dimerized to yield tetraalkylidene cyclohexanes (**114**), one of which was also used in a Diels–Alder reaction with naphthoquinone to produce **115**.[73]



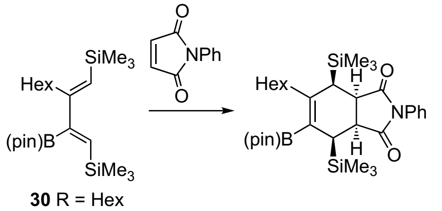




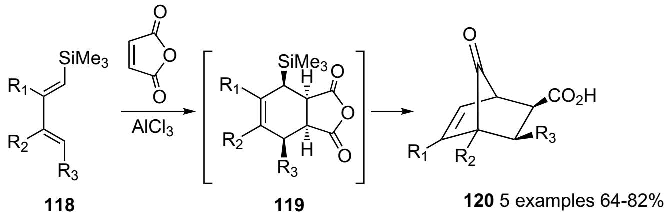
In 2004, Clark and Woerpel reported the reaction of a '*t*-Bu$_2$Si' source with a protected enynol to produce a siloxacyclopentene containing a silicon substituent at the 1-position of a 1,3-diene moiety (**116**).[74] This diene reacted with *N*-phenyl maleimide (**117**) in a Diels–Alder reaction.



Silyl substituted dienes (**30**, R=Hex) made by double addition of trimethylsilyldiazomethane to alkynylboronates described above were also used in one Diels–Alder reaction reported in 2005 and we have included it here as well as above since it is the only example we are aware of where a 1,3-diene substituted by both boron and silicon participates in a Diels–Alder reaction.

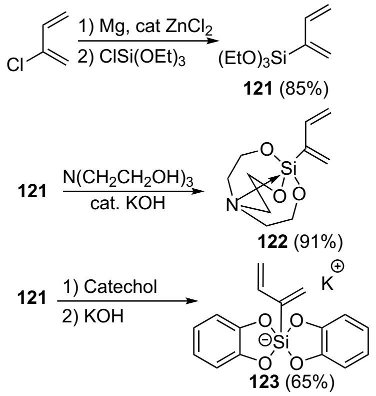


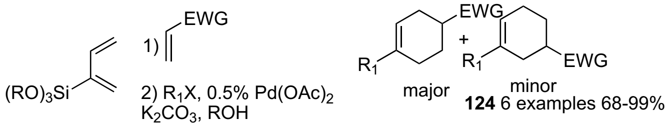
Terminally silylated alkynes undergo regio- and stereoselective coupling on low valent zirconocene species to produce silylated 1,3-dienes.[75] In 2004 and 2006, Xi, Takahashi, and co-workers demonstrated that this zirconocene mediated coupling could be combined with hydrolysis/desilylation and halogenation/desilylation reactions to prepare silylated dienes (**118**), which were not directly available from the Negishi reagent mediated coupling mentioned above.[76,77] In 2007, Xi and co-workers showed that some of these silicon dienes that they had prepared as described above could be used in tandem intermolecular Diels–Alder/intramolecular allylation reactions to produce polysubstituted norbornenones (**120**).[78]



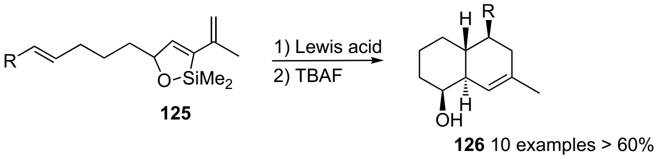
4.2.2. Preparation and use of 2-silicon substituted 1,3-dienes in Diels–Alder cycloadditions

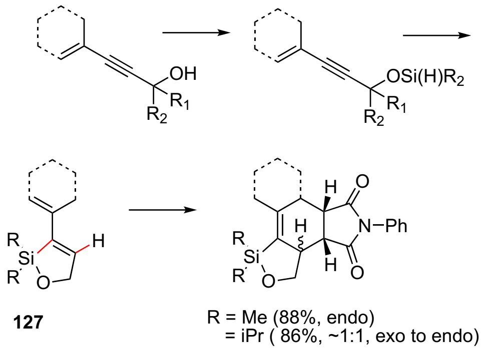
In 2007, we reported the synthesis of two air stable crystalline 2-siloxy substituted 1,3-dienes (**122**, **123**).[79] These diene preparations involved simple ligand exchange reactions of either triethanolamine or catechol with 2-triethoxysilyl-1,3-butadiene (**121**). These dienes were then used in a variety of tandem Diels–Alder/cross-coupling reactions to produce predominantly1,4-disubstituted cyclohexenes (**124**). As was the case in the boron chemistry we reported above for **78** and **81**, the cross-coupling reactions enable these main group element dienes to serve as synthons for a host of carbon substituted dienes.





Later in 2007, Halvorsen and Roush reported using a combination of the Tamao–Ito[80] and Lee protocols[81] to make siloxacyclopentenes containing pendant dienophiles (**125**) and demonstrated that they could be used in intramolecular Diels–Alder reactions, which were followed by protiodesilylation (**126**).[82] We had simultaneously been using a combination of the Tamao–Ito[80] and Lee protocols[81] to make siloxacyclopentenes (**127**), which could participate in intermolecular Diels–Alder reactions.[83]





R = Me (88%, endo)
= iPr (86%, ~1:1, exo to endo)

5. Conclusion

After initial reports of boron and silicon substituted 1,3-diene synthesis 30 or more years ago, they were largely unexplored for their utility in organic methodology through the 1980s and 1990s with the exception of the boron diene Diels–Alder/allylation sequence described above. The last 10 years has seen a number of groups report new synthetic routes to these dienes. The increased emphasis on economy in organic reactions and the search for reactions, which can be run in tandem or longer sequences has also produced a number of reports of new chemistry for these materials. One can anticipate that this trend will continue for main group-substituted dienes since the products of their initial reactions are many times still main group-substituted allylic or alkenyl species capable of further reaction. Many of the dienes described in this review are prepared by transition metal catalyzed reactions of pretty simple organic precursors so we can anticipate one-pot multistep transformations, which involve diene preparation/Diels–Alder/functionalization of main group-substituted alkene sequences. In our case, sequential reaction chemistry of boron and silicon substituted dienes where the initial reactions they participate in are Diels–Alder reactions will continue to occupy considerable synthetic effort on our part for several years to come. The Holy Grail for us will be catalytic *exo* selective and enantioselective Diels–Alder reactions of boron or silicon substituted dienes followed by cross-coupling or hydrolysis reactions to yield enantiomerically pure cyclohexenoids or *cis*-decalins with relative stereochemistries, which are not currently available via classical Diels–Alder chemistry.

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Biographical sketch

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