CHARACTERIZATION OF SEVERAL BORON-HETEROATOM COMPOUNDS AND THEIR REACTIONS WITH CARBONYL ACIDS

By

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ABSTRACT

CHARACTERIZATION OF SEVERAL BORON-HETERATOM COMPOUNDS AND THEIR REACTIONS WITH CARBONYL ACIDS

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The purpose of this research was to study the reactivity of a series of boron - heteroatom compounds towards carbonyl acids. These compounds would serve as boron bases, in order to form boron enolates. The boron compounds synthesized include silylboranes, boron amides and boron phosphides. The ketones used in this investigation were pinacolone and diethyl ketone. The primary method of detection used to monitor the reactions was NMR spectroscopy.

The enolization reaction for boron phosphides 19-21 is in competition with an addition reaction. The addition is a result of a nucleophilic attack of phosphorus on the carbonyl carbon. The extent of enolization for the bases was determined using ^{31}P NMR spectroscopy. The most significant results were observed with compound 22, which showed nearly quantitative enolate formation and no indication of addition products.

To Mom and Dad

ACKNOWLEDGEMENTS

I wish to thank Dr. Michael W. Rathke for his guidance and patience during the course of this research. I also wish to extend my thanks to Robert Elghanian, for putting up with me and assisting me in every possible way.

To my family, Mom and Dad I wish to say THANK YOU. There are no words that can truly express my gratitude for the things you have done over the past several years, and throughout my entire life. To my brothers, Andy and Chris, a sincere thank you goes to you both. Growing up would not have been half as fun - or challenging! - without you.

Finally, I wish to thank my Almighty Father for giving me my family to guide me and help me grow into the person I was made to be.

"All I ever have to be is what you've made me"

Amy Grant

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LIST OF SYMBOLS

I - dimethylaminobis(trifluoromethyl)borane - $(CF_3)_2B{=}NMe_2$

II - bis(trimethylsilyl)aminodifluoroborane - $F_2B\text{-}N(SiMe_3)_2$

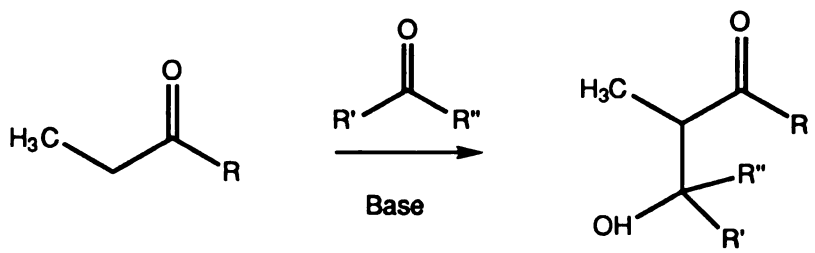
III - bis(trimethylsilyl)aminodichloroborane - $Cl_2B\text{-}N(SiMe_3)_2$

LIST OF ABBREVIATIONS

9-BBN - borabicyclo[3.3.1]nonane
But-Li - Butyl Lithium
Bz - Benzyl group
Dabco - 1,4-diazabicyclo[2.2.2]octane
DBU - 1,8-Diazabicyclo[5.4.0]undec-7-ene
DIP - diisopinocampheyl
DPEA - Diisopropyl ethyl amine
Et - Ethyl group (-CH_2CH_3)
i-Pr - iso-Propyl group
Me - Methyl group (-CH_3)
Mes - Mesityl group
NMR - Nuclear Magnetic Resonance
OTf - Triflate group
Ph - Phenyl group
s-Bu - secondary butyl group
t-Bu - tertiary butyl group
THF - Tetrahydrofuran
TMS - Trimethylsilyl ($SiMe_3$)

INTRODUCTION

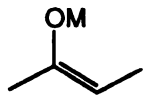
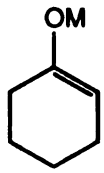
Regiochemistry and stereochemistry both play an important role in the design of synthetic strategies. One well-known carbon - carbon bond forming reaction is the Aldol condensation. The aldol condensation uses an enolate, which is generated by removing an alpha hydrogen from a carbonyl compound with a strong base. The enolate anion then acts as a nucleophile towards a second carbonyl component, as shown in Eq. 1[1].



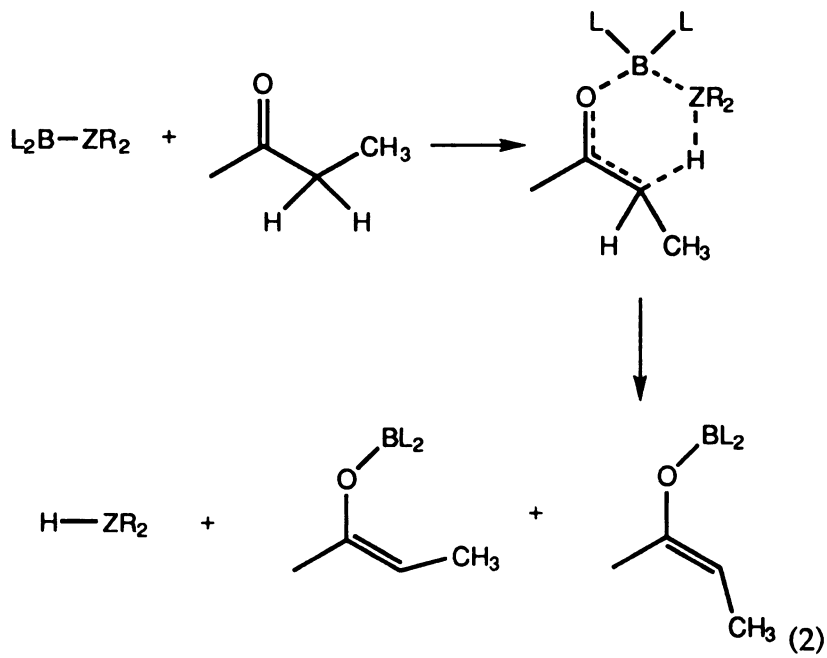
Aldol condensation product (1)

Enolate chemistry is very important in organic synthesis because it offers chemists the ability to control both the regiochemistry and stereochemistry of the newly formed carbon - carbon bond. The goal of this research was to synthesize a boron heteroatom base that would form boron enolates. At present, boron enolates show a greater degree of stereoselectivity, in the aldol condensation, when compared to other metal enolates[2,3].

Table 1: Comparison of Enolate Stereoselectivity with Benzaldehyde

Enolate	Metal (M)	Erythro:Threo
	Li	80 : 20
	$B(C_4H_9)_2$	>97 : 3
	Li	48 : 52
	$B(C_5H_9)C_6H_{13}$	4 : 96
	$Al(C_2H_5)_2$	50 : 50

The general formula for the boron heteroatom bases we examined is $L_2B\text{-}ZR_2$, where Z is the heteroatom (which will be the proton acceptor), R represents various hydrocarbon ligands, and L is either a hydrocarbon or a heteroatom. To be useful bases in the generation of boron enolates three characteristics must be considered. First, the base should be strong enough to generate the enolate. Second, the base should deprotonate the carbonyl fast enough so that enolate equilibration does not compromise stereoselectivity. The third criteria should be a high degree of stereoselectivity in forming the enolate, this can be achieved by a six atom ring transition state, as shown in Eq. 2.

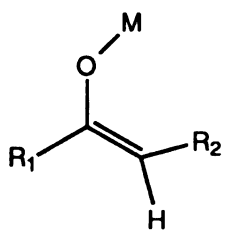


(2)

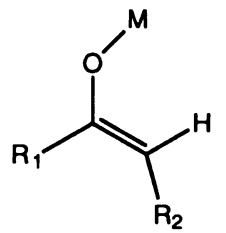
In this project we investigated three general classes of boron heteroatom bases -- silyl boranes (Z = Si), boron amides (Z = N), and boron phosphides (Z = P). The rationale for choosing these three classes is as follows: for the silyl boranes, a driving force for deprotonation would be the replacement of a weak boron - silicon bond with a stronger silicon - hydrogen bond. Boron amides are boron analogs of the widely used lithium amide bases. Boron phosphides have a slightly longer boron heteroatom bond, which indicates less double bond character, when compared with boron amides. The longer bond may enable boron phosphides to be stronger bases than boron amides. This research involved the synthesis and characterization (NMR) of the boron heteroatom bases. Following synthesis was the characterization of the reaction of each boron base with representative carbonyl compounds.

Features of Enolates

Enolates are anions, and can made with various counterions such as Li, Mg, Zn, Al, and B. The convention for assigning enolate geometry, Z or E, depends on the relationship between the α-R group of the enolate and the position of the counterion, Eq. 3 illustrates[4].



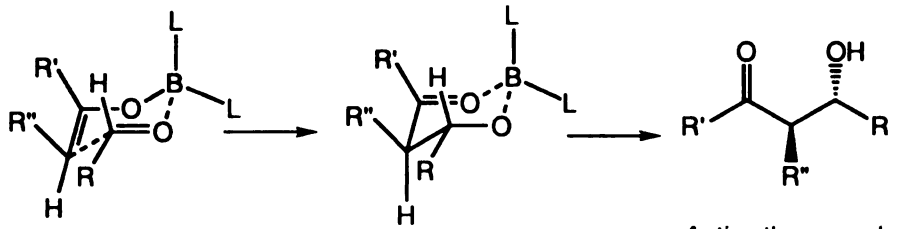
Z



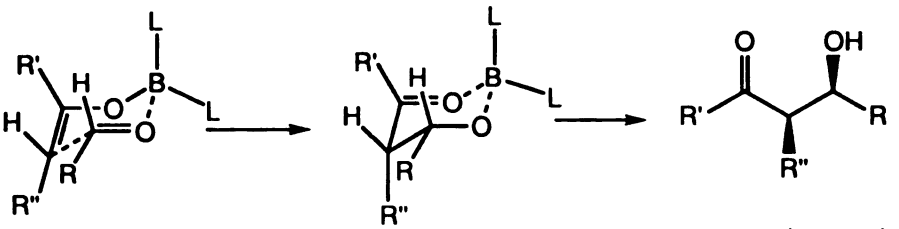
E (3)

As mentioned earlier, among the different metal enolates the boron enolate shows the greatest stereoselectivity[5,6]. The enhancement in stereoselectivity is derived from several different structural features. The boron enolate is unique because it does not exist as an oligomer in solution, like other metal enolates[7]. In addition, the boron aldolates (salt of the aldol) exist in a six-membered ring, Eq. 4 and 5. This transition state is in the chair

conformation and has no aggregation or chelation[6]. Lithium aldolates, which are also cyclic, may not involve covalent bonds between the lithium and oxygen atoms[3]. The short oxygen - boron bond, present in boron aldolates, allows them to be more compact, which enhances the steric interactions that control stereochemistry[6]. The stereochemistry of the aldol products obtained from boron enolates is consistent with the assumed transition state, Eqs. 4 and 5. The E isomer yields the *anti*, or threo, aldol condensation product while the Z isomer gives the *syn*, or erythro, product[4].

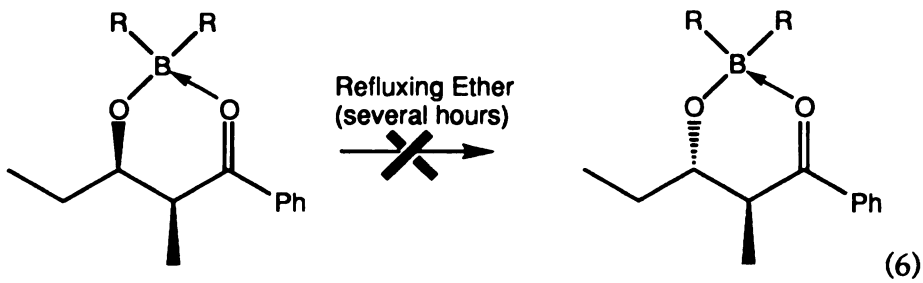


(4)



(5)

Another consequence of the covalent nature of the bonding present in boron enolates is that boron aldolate complexes are stable. The stability of the complexes is reflected in the lack of equilibrium between the threo and erythro diastereomers, in refluxing ether for several hours, Eq. 6 [3,5a]. However, equilibrium between the threo and erythro aldolates is observed when the counterions are lithium, magnesium, potassium, or zinc[3].



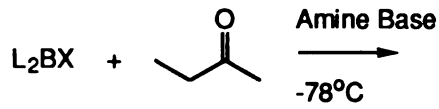
(6)

Equilibration between the threo and erythro diastereomers lowers the stereoselectivity of subsequent reaction steps. The marked enhancement in the stereoselectivity exhibited by boron enolates makes them valuable reagents to chemists.

Review of Boron Enolate Synthesis

Tables 2 and 3, below, show the two most common methods used to synthesize enolates. Both methods use a tertiary amine base, a ketone, and a dialkyl borane with either a halogen or a triflate leaving group.

Table 2: Synthesis of Boron enolates using dialkyl boron triflates



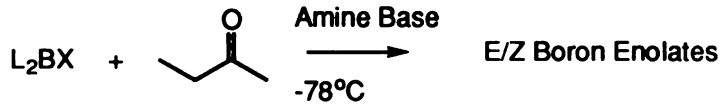
L	X	Bases
n-C_4H_9	O-SO_2CF_3	2,6-lutidine
c-C_5H_9	O-SO_2Me	DPEA[a]
C_2H_5	O-$COCMe_3$	NEt_3
L_1-C_5H_9		pyridine
L_2-C_6H_{13}		Dabco[b]
		DBU[c]
		1,1,3,3-tetramethylguanidine

a) Diisopropyl ethyl amine b) 1,4-Diazabicyclo[2.2.2]octane
c)1,8-Diazabicyclo[5.4.0]undec-7-ene

In table 2, where X = OTf, the ammonium triflate will precipitate out of ethereal and hydrocarbon solvents. The affects of ketone structure, the

tertiary amine base, and the boryl triflate were studied and each individually contributes to the selectivity of the reaction[8].

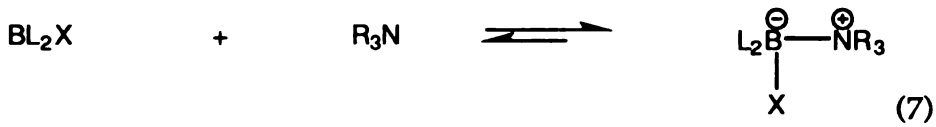
Table 3: Synthesis of Boron enolates using dialkyl boron halides



L	X
9-BBN	Cl
dicyclooctyl	Br
exonorbornyl	I
disiamyl	
2,5-dimethylcyclohexane	

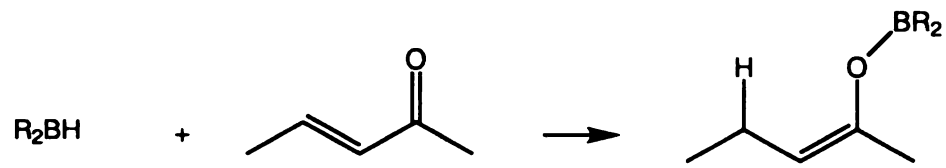
In table 3, where X = halogen, the precipitation of an amine hydrochloride salt is common, in organic solvents. The boryl triflate reagents were reacted with many carbonyl systems including carboxylic acids, anhydrides, acid chlorides, esters, amides, thioesters, and ketoesters[9]. With the exception of acid chlorides, esters, and amides all the above functionality undergoes nearly quantitative enolate formation, the carboxylic acid requires two equivalents of boron reagent[9].

From the reactions described in the tables above, formation of the E enolate is favored in dilute solutions using non-polar solvents, while the formation of the Z enolate is favored in concentrated solutions using more polar solvents[10]. In addition, bulky bases favor the formation of the Z enolate while E enolate formation is favored by less bulky bases[10]. An advantage to the above method is the lack of solvent dependence. A small, but consistent solvent effect was noted, for a given boron ligand. In general, non-polar solvents results in a more compact transition state that enhances the stereoselectivity[8]. A disadvantage for these systems is when a less hindered bases are used there is an irreversible complexation (Eq. 7) between the base and the boron reagent[8]. Because the complexation occurs before enolization the overall enolate yield is low[8].



(7)

The 1,4 hydroboration of an α,β unsaturated acyclic ketone, shown in Eq. 8, is another method used to synthesize boron enolates[11].



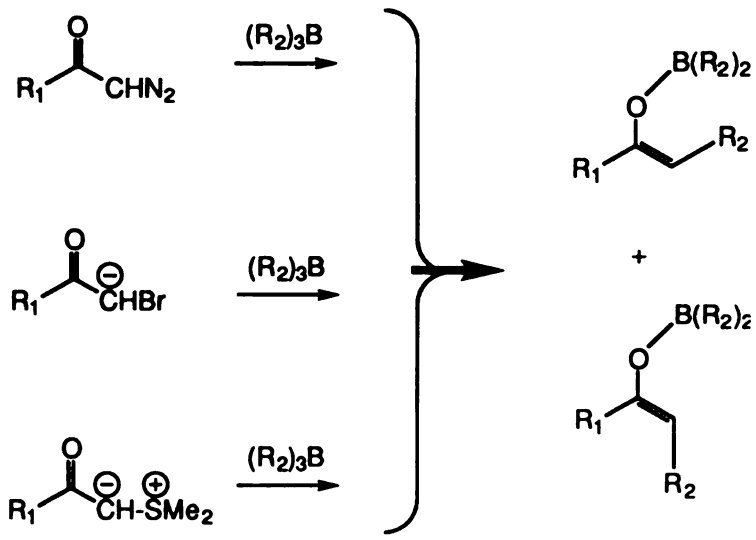
R = disiamyl
dicyclohexyl
diisopinocampheyl
di-2-isocaranyl

(8)

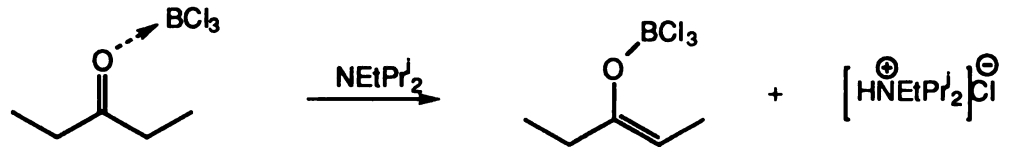
The 1,4 hydroboration reaction allows selective formation of the Z enolate from a variety of E ketones. The transition state is thought to be boat-like[11]. The subsequent aldol condensations are very stereoselective, selectivly giving the expected *syn* isomer[11]. For the reaction shown in Eq. 8, it is also possible to generate boron enolates from amides, imides, and esters using catalytic amounts of $Rh(PPH_3)Cl$[11].

Several indirect methods of generating boron enolates were developed. These methods involve the use of α-diazocarbonyls, halogen-substituted enolates, and sulfur ylides with trialkylboranes, as shown in scheme 1[4]. From these indirect methods is the enolate has incorporated into its own structure one of the ligands from the trialkylborane, this may limit the synthetic utility for these methods depending on what product structure is desired[4].

Scheme 1: Indirect synthesis of Boron enolates

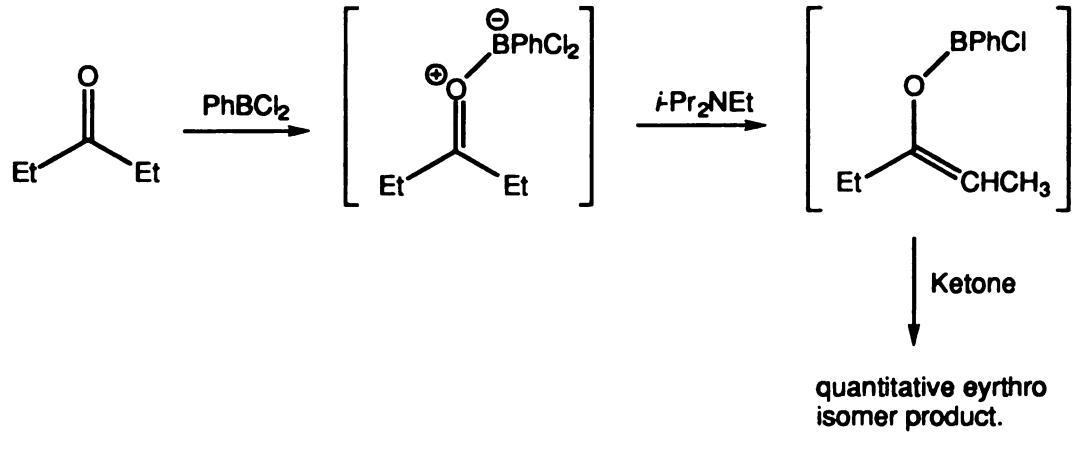


Both BCl_3 and $PhBCl_2$ can also be used to synthesize boron enolates. With BCl_3, to improve the yield of enolate, the ketone and BCl_3 are mixed together before the addition of base, this is done to overcome the boron-amine complexation (Eq 9)[13].



(9)

The erythro, or *syn*, isomer, is selectively generated with $PhBCl_2$, Eq. 10. This reagent is also useful because it is easier to handle than dialkylboron triflates[14].



(10)

The synthesis of a fast acting boron heteroatom base that can quantitatively deprotonate a carbonyl, through a cyclic transition state, that results in a boron enolate was the ultimate goal of this project. There are currently no examples of this kind of base reported in the literature. A boron heteroatom base offers the direct formation of a boron enolate, without the need for any additional reagents, such as excess base or ketone. The reactions of boron heteroatom bases are mild, 1:1 reactions between the base and the carbonyl acid. In addition, the boron enolates generated will offer superior selectivity in the aldol condensation.

CHAPTER 1: SILYLBORANES

Synthesis and Properties of Silylboranes

The synthesis of silylboranes was accomplished, in the literature, using two methods. The first method, shown in Eq. 11, is a salt elimination reaction between a silicon anion and a dialkyl boron chloride species[15a,15b].

$$R_2B\text{-}Cl + LiSiR'_3 \longrightarrow R_2B\text{-}SiR'_3 + LiCl \quad (11)$$

R = Et, NMe_2 R' = Ph, Me, Et

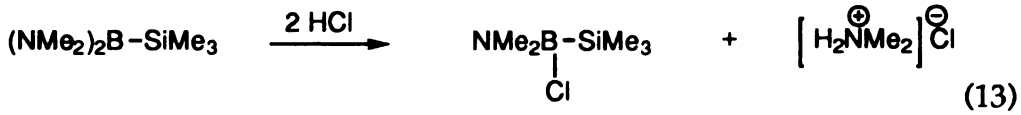
The second method, shown in Eq. 12, is the combination of a dialkylboron chloride, a chlorotrialkylsilicon and two equivalents of an alkali metal[15c].

$$R_2B\text{-}Cl + ClSiR'_3 \xrightarrow{2\,K} R_2B\text{-}SiR'_3 + KCl \quad (12)$$

R = Et, NMe_2 R' = Ph, Me, Et

So far this field of chemistry has focused primarily on the synthesis and characterization of various silylboranes that include -- tris(trimethylsilyl)-boranes[15b], (trimethylsilyl)boranes[15c], (trimethylsilyl)borates[16], and alkoxysilyl(amino)boranes[17]. Characterization of these compounds involved nuclear magnetic resonance (NMR) and mass spectrometry. A limited amount of information is available about the reactions of silylboranes of the type $R_2B\text{-}SiR'_3$. However, the chemistry of trimethylsilylbis-(dimethylamino)borane, $(Me_2N)_2B\text{-}SiMe_3$ is well documented. These reactions allowed us to look at the types of reactions that silylboranes are capable of, and from this information we could determine if silylboranes would be reasonable candidates for our study.

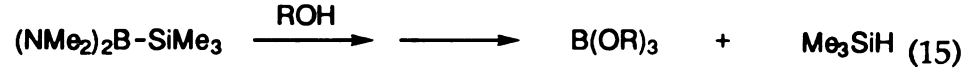
In two separate papers, Noth synthesized trimethylsilylbis-(dimethylamino)borane and then studied the reaction, shown in Eqs. 13 and 14, with hydrochloric acid[15a].



(13)

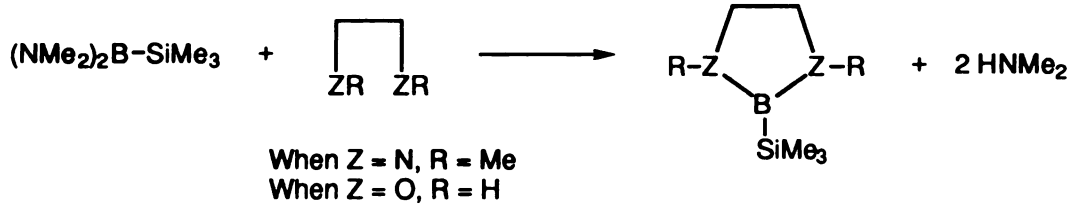
(14)

The reactions shown in Eq. 13 and 14 illustrate the behavior of the silyl boranes in the presence of strong acids. Eq. 15 illustrates the reaction of alcohols with trimethylsilylbis(dimethylamino)borane[15c].



(15)

Noth also reported on the reactions of trimethylsilylbis(dimethylamino)borane with a diol and a diamine, as shown in Eq. 16[15c].



(16)

The above reactions, Eq. 15 and Eq. 16, are analogous to the reaction we want to accomplish. The silylborane dissociates, the boron bonds to an oxygen while the silicon becomes protonated. Our reactions would employ a less acidic carbonyl. However, evidence like the above reactions illustrate the potential silyl boranes have to be boron bases.

Results

We surmised that a silylborane, $R_2B\text{-}SiR'_3$, might function as a boron base towards carbonyl acids. A possible driving force may be the replacement of a weak boron - silicon bond (289 kj/mol) with a strong silicon - hydrogen

bond (531 kj/mol). The compounds shown in Table 4 were synthesized through the reaction of a silicon anion with a dialkylboron chloride.

Table 4: Synthesis of Silyl Boranes

$R_2B\text{-}Cl + LiSiR'_3 \longrightarrow R_2B\text{-}SiR'_3 + LiCl$

Compound	R	R'	R(x) Temp. (°C)
1	o- $C_6H_4O_2$	Me	25[a]
2	Cl	Me	25[b]
3	C_6H_{10}	Me	25[c]
4	Cl	$SiMe_3$	25[b]
5	o-$C_6H_4O_2$	$SiMe_3$	25[a]
6	C_6H_{10}	$SiMe_3$	25[c]

a) solvent : 1:1 Hexane:Benzene
b) solvent : Hexane
c) solvent : Benzene

Compounds 1-6 were characterized by both ^{29}Si and ^{1}H NMR. Their behavior with two representative ketones was monitored with ^{1}H NMR. The results of these studies are summarized in Table 5.

Table 5: Reactions of Silyl Boranes with Ketones

$R_2B\text{-}SiR'_3$ + Ketone ⟶

Compound	pinacolone	diethyl ketone	Time[a]
1[b]	no reaction	no reaction	24 hrs.
2[c]	no reaction	no reaction	24hrs.
3[d]	no reaction	no reaction	24hrs.
4[d]	no reaction	no reaction	24hrs.
5[d]	no reaction	no reaction	24hrs.
6[d]	no reaction	no reaction	24hrs.

a) At room temperature
b) in THF
c) in Hexane
d) in Benzene

As Table 5 shows silyl boranes 1-6 are inert when combined with either a methyl or an ethyl ketone. The ^1H NMR remained unchanged in all cases after a twenty-four hour period. As a result of the inactivity of the silyl boranes we have shown that these compounds do not function as bases to generate boron enolates from ketones.

EXPERIMENTAL

The solvents used - THF, benzene, and hexane - were dried over calcium hydride, distilled and stored in an inert N_2 atmosphere prior to use. All ^{31}P, ^{11}B, ^{29}Si, ^{13}C, ^{1}H NMR data was obtained using the either the Varian 300 MHz or Gemini 300 MHz NMR. The external references for ^{31}P, ^{11}B, ^{29}Si spectra were H_3PO_4, BF_3OEt_2, and TMS respectively. Unless otherwise stated the internal reference for the ^{13}C and ^{1}H data was $CDCl_3$ with TMS. All reagents and reaction products were handled in an inert atmosphere of N_2. NMR samples were sealed in 5mm NMR tubes, capped with a rubber septum and secured with Teflon tape.

Synthesis of tetrakis(trimethylsilyl)silane[18]: 0.914 moles (50% excess) of lithium flatted lithium rods were put into a 500 mL round bottomed flask (equipped with a magnetic stirrer and N_2 inlet/outlet) and washed with dry hexane. The cleaned lithium was then suspened in 100 mL of dry THF and 0.358 moles of TMSCl was added using a syringe.

A 250 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, was charged with 75 mL of dry THF and 75.3 mmoles of $SiCl_4$. Using a syrings 20mL of the $SiCl_4$ solution was added to the lithium metal/TMSCl soution. The mixture warmed slightly and turned dark brown in color, after 4 hours of stirring the remainder of the $SiCl_4$ mixture is added and the mixture is stirred at room temperature overnight.

The solution was filtered into a bed of Celite, in a buchner funnel attached to an aspirator, to remove unreacted lithium metal. The filtrate was then refiltered over a fresh bed of Celite. The filtrate was drowned in 50 mL HCl/150 mL H_2O, at 0^0C. The resulting 2 layers were extracted twice with 100 mL of ether and the ether layer was evaporated under reduced pressure. The yellow solid product was recrystillized using acetone to yield 9.36 g (40%) tetrakis(trimethylsilyl)silane, which is a white solid. The ^{29}Si NMR has resonances at -9.7 ppm (Me_3Si) and -135.5 ppm $(Me_3Si)_4Si$ ppm.

Synthesis of tris(trimethylsilyl)silyl lithium[18]: 6.5 mmoles of tetrakis-(trimethylsilyl)silane was placed in a 50 mL round bottom flask and pumped

dry overnight with a vacuum. The 50 mL round bottom flask was then equipped with a magnetic stirrer and N_2 inlet/outlet line, and charged with 25 mL THF and 6.6 mmoles of methyl lithium. The solution turned bright yellow. After 24 hours the solvents were removed under reduced pressure and the solid residue was stirred in pentane for 2.5 hours. The solution was canula filtered into a new 50 mL flask, that was flushed with N_2 and equipped with a magnetic stirrer and N_2 inlet/outlet line. At -78^{0}C, crystals formed in the flask and the solvents were removed with a syringe. The crystals were then recrystalized with pentane : THF solution. The product (>95% yield) is a pale yellow solid and the ^{29}Si NMR has a single resonance at -5.3 ppm.

Synthesis of B-trimethylsilylcathecolborane (1): A 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, was charged with 3.0 mmol of a 1:1 hexane : benzene solution of cathecol boron chloride. At room temperature, 3.0 mmol of the lithium salt of hexamethyldisilane was added, via syringe. The mixture became slightly warm and a solid precipitate was formed upon completion of addition. The solution was allowed to stir at room temperature for 30 minutes, the solvents were evaporated and NMR analysis was performed.

^{11}B : (C_6D_6) - 19.66, 23.13 ppm

Synthesis of B-trimethylsilyldichloroborane (2): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.5 mmol of a hexane solution of boron trichloride was added. At room temperature, 0.5 mmol of $LiSiMe_3$ was added using a syringe. The solution was allowed to stir at room temperature for 30 minutes, the solvents were evaporated and NMR analysis was performed.

^{11}B : (Hexane : D_2O,external) - 28.75 ppm

Synthesis of B-trimethylsilyldicyclohexylborane (3): In a 5 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of dicyclohexyl boron chloride was dissolved in 0.5 mL of hexane. At room temperature, 1 mmol of $LiSiMe_3$ in benzene, was added with a syringe. The

solution was allowed to stir at room temperature for 30 minutes, the solvents were evaporated and NMR analysis was performed.

^{11}B : (C_6D_6) - 73.45 ppm

Synthesis of B-tris(trimethylsilyl)silyldichloroborane (4): A 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, was charged with 0.6 mmol of a hexane solution of boron trichloride, an additional 0.5 mL of benzene was also introduced. At room temperature, 0.6 mmol of a benzene solution of tris(trimethylsilyl)silyl lithium was added. A salt precipitate was formed upon completion of the addition. The solution was allowed to stir at room temperature for 60 minutes, the solvents were evaporated and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O external) - 10.49 ppm
^{1}H : (C_6D_6) - 0.232 ppm

Synthesis of B-tris(trimethylsilyl)silylcathecolborane (5): In a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.6 mmol of a 1:1 benzene : hexane solution of cathecol boron chloride was dissolved in an additional 0.5 mL of benzene. At room temperature, 0.6 mmol of a benzene solution of tris(trimethylsilyl)silyl lithium was added. A salt precipitate was formed upon the completion of addition. The solution was allowed to stir at room temperature for 60 minutes, the solvents were evaporated and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 39.67, 21.58, 7.75 ppm

Synthesis of B-tris(trimethylsilyl)silyldicyclohexylborane (6): In a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.6 mmol of dicyclohexyl boron chloride was dissolved in 0.5 mL of benzene. At room temperature, 0.6 mmol of a benzene solution of tris(trimethylsilyl)-silyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 60 minutes, the solvents were evaporated and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 51.692, 52.02 ppm (doublet)
^{1}H : (C_6H_6, D_2O, external) - 0.24 ppm

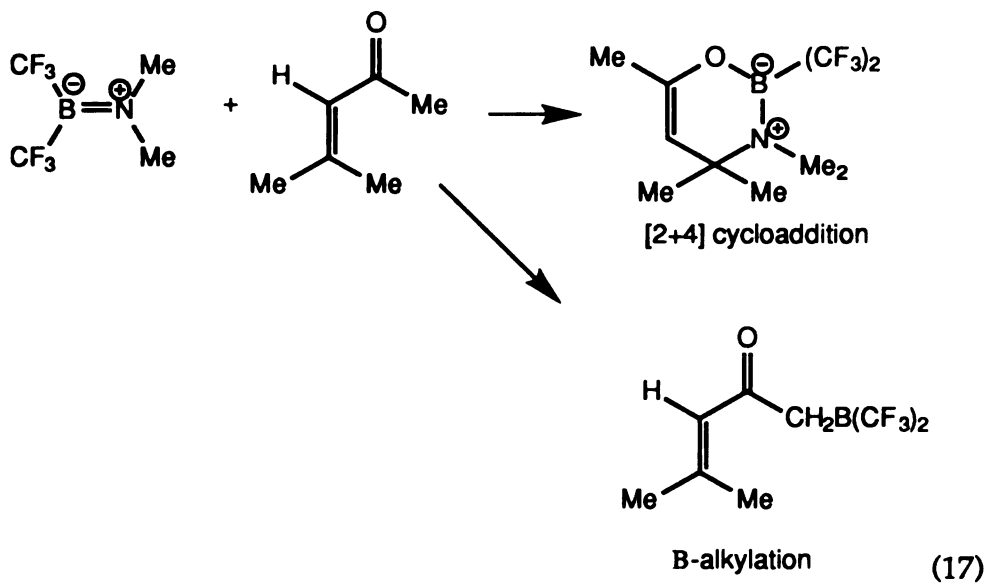
CHAPTER 2: BORON AMIDES

Literature survey of Boron Amides

Boron amides can be viewed as boron analogs of lithium amides, which are very powerful bases. However, electron diffraction data of several boron amides exhibit short boron - nitrogen bonds. The average bond length of a boron amide is 1.41 angstroms while a typical single bond is around 1.58 angstroms[19]. In addition, many unsymmetrical boron amides exhibit restricted boron - nitrogen bond rotation and can exist in cis/trans isomers in solution[19]. The shortened boron - nitrogen bond and the cis/trans isomerization present both imply a strong pi bond moment between boron and nitrogen[19]. Both of these factors may limit how effective these compounds are as boron bases.

Boron amides are well reviewed in the literature. Dimethylamino-bis(trifluoromethyl)borane, $(CF_3)_2B=N(CH_3)_2$, (I), was studied in great detail by Ansorge and co-workers. Dimethylamino-bis(trifluoromethyl)borane is thought to be planar through comparison, by electron diffraction, with other boron amides and from data obtained from theoretical calculations[20]. The data indicate the planarity comes from a boron - nitrogen pi bond[20].

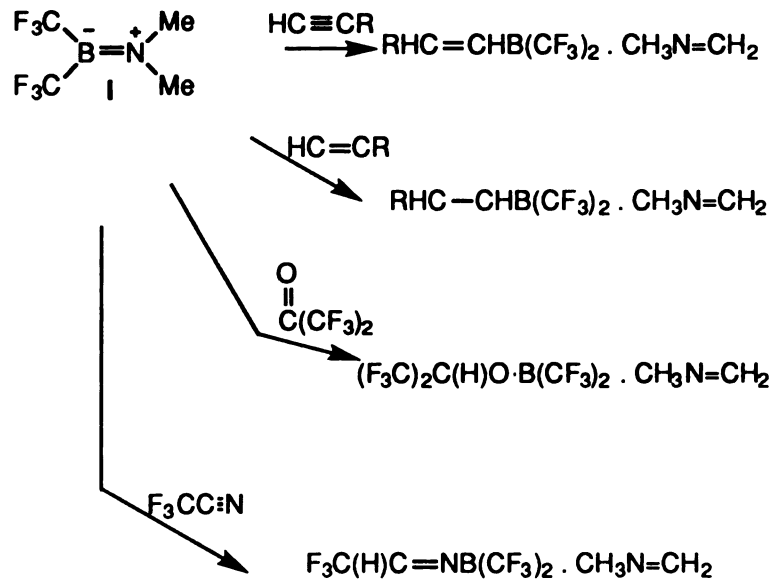
Reaction of (I) with 1,3 dienes and β-unsaturated ketones gave [2+4] cycloaddition and β-alkylation products, shown in Eq. 17[20].



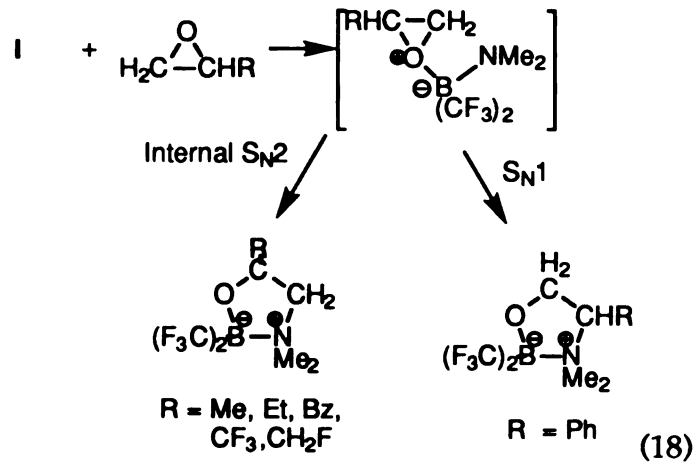
(17)

The reaction of (I) with terminal alkynes and terminal alkenes yields aminoboration products (Scheme 2). For the reactions shown in scheme 2, the methyl group on nitrogen is a hydride source[21].

Scheme 2: Reaction of (I) with various functional groups

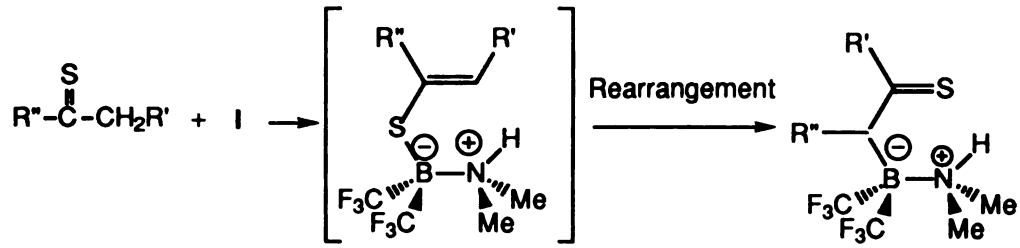


The reaction of (I) with epoxides, (Eq. 18), gave ring expansion. When the epoxide is symmetrical, polymerization results[22].



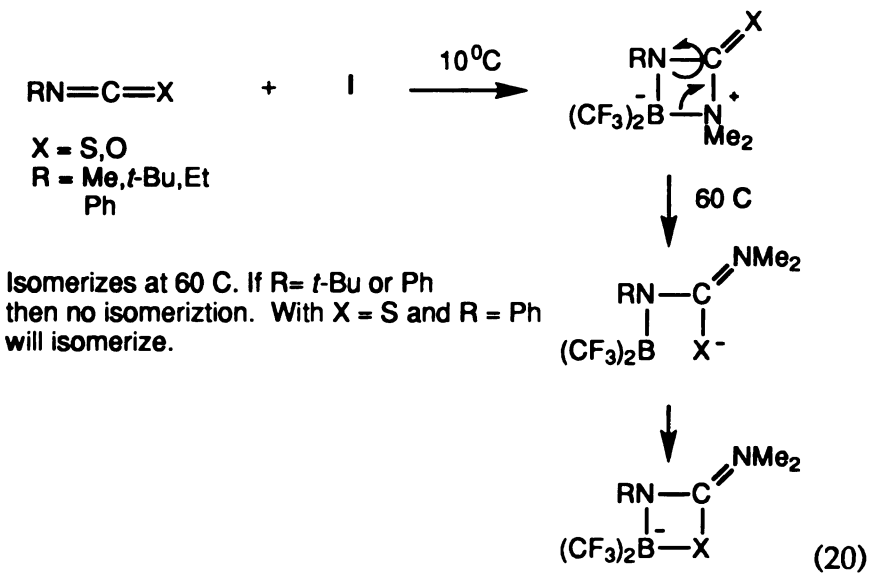
(18)

Eq. 19 shows (I) underwent an ene-type reaction with thiocarbonyl compounds[23].



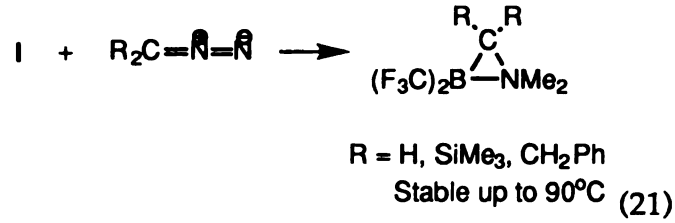
(19)

The type of reaction shown in Eq. 19 is similar to the reaction we plan to explore between boron amides and carbonyls. The enethiol intermediate shown in the above reaction is a sulfur analog of a boron enolate. Ansorge also reported addition of (I) to isocyanates and isothiocyanates, (Eq. 20)[24].



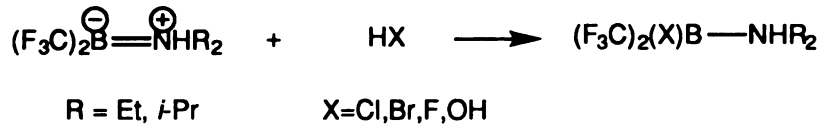
(20)

In 1994, the first boron-nitrogen analogs of cyclopropane were synthesized by the adding (I) to carbenes, shown in Eq. 21[25,26].



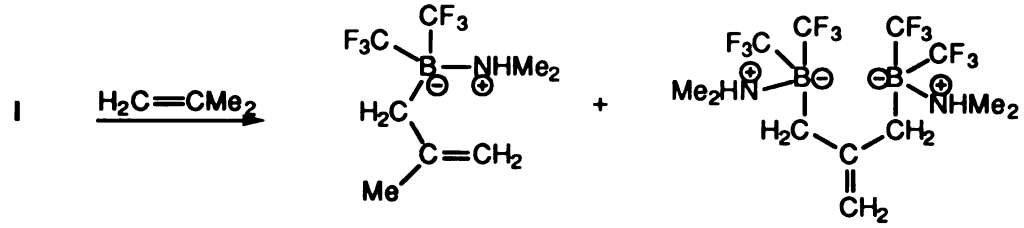
(21)

Brauer, Eq. 22, studied the addition of HX across the boron - nitrogen bond of (I)[27].

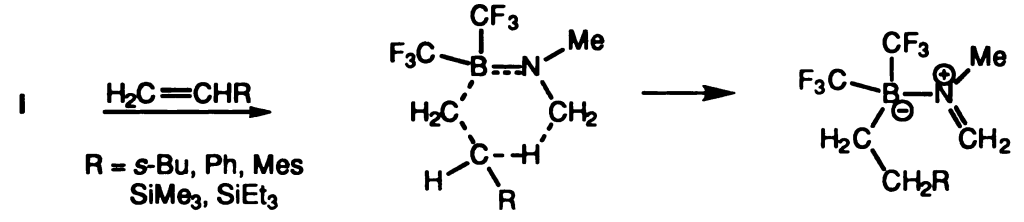


(22)

The reaction shown in Eq. 22 shows the behavior of boron amides with strong acids. We want to get similar results using a less acidic proton on carbonyl compounds. Burger studied, Eq. 23, the alkylation of (I) by 1-alkenes[28]. When a bulky group is placed on the alkene there is a hydride transfer from one of the methyl groups on nitrogen to the olefinic carbon, Eq. 24[28].

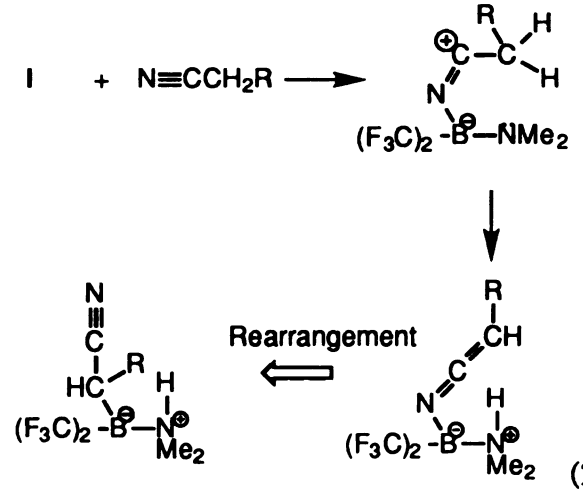


(23)



(24)

Burger also showed that (I) underwent an ene-type reaction with nitriles and carbonyl compounds. Eq. 25 shows the ene-type reaction with a nitrile, which forms in a boron - carbon bond[29].



(25)

The reactivity of (I) with alkenes, nitriles, and carbonyl groups shown in the above equations show the electrophilic nature of the boron as it adds across the multiple bond.

Two of the boron amides studied in this project were also synthesized and studied in the literature, bis(trimethylsilyl)aminodifluoroborane, $F_2B\text{-}N(SiMe_3)_2$ – (II), and bis(trimethylsilyl)aminodichloroborane,

Cl_2B-$N(SiMe_3)_2$ -- (III). Geymayer published a procedure, Eq. 26, for the synthesis of (II)[30a].

$$BF_3.OEt_2 + NaN(SiMe_3)_2 \xrightarrow{-78^0C} F_2B\text{-}N(SiMe_3)_2 \quad (26)$$

Russ synthesized (II), Eq. 27, by heating BF_3 and tris(trimethylsilyl)-amine[31].

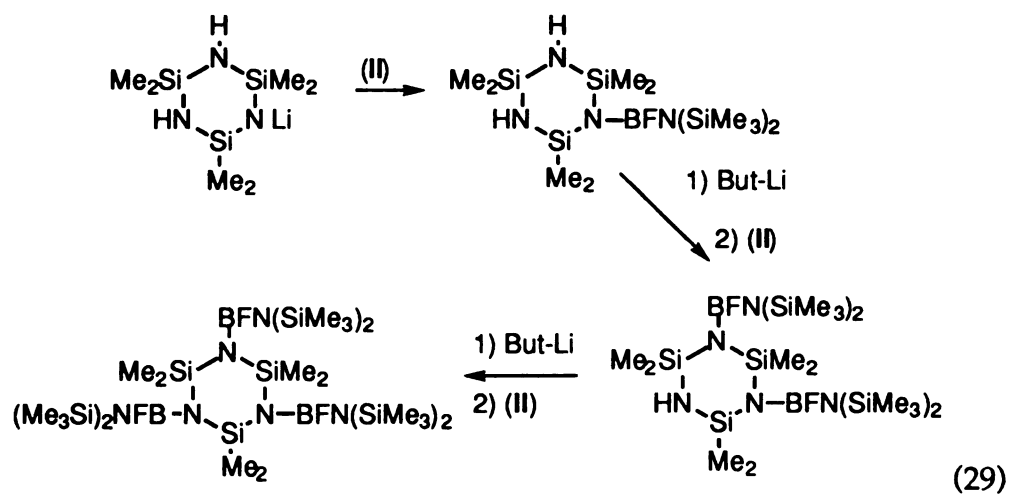
$$BF_3 + N(SiMe_3)_3 \xrightarrow{130^0C} F_2B\text{-}N(SiMe_3)_2 + TMSF \quad (27)$$

In a third publication, Gerrard synthesized (II), Eq. 28, through the loss of HCl from a boron-amine complex using a secondary amine base[32].

$$(Me_3Si)_2NH.BCl_3 \xrightarrow{-HCl \text{ by } R_2NH} (Me_3Si)_2NBCl_2 + [R_2\overset{\oplus}{N}H_2]\overset{\ominus}{Cl} \quad (28)$$

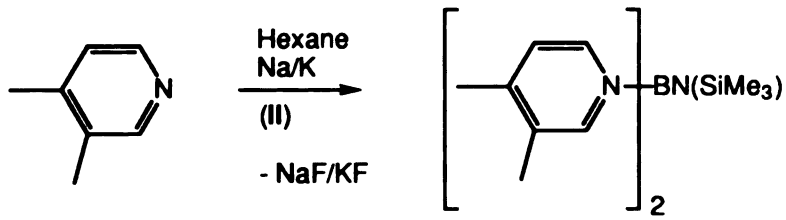
Although many reactions of compounds (II) and (III) are reported in the literature, there are no current reports of any reactions with ketones or aldehydes. However, following reactions of (II) and (III) do indicate the potential these boron amides have to behave as boron bases towards carbonyls. This information encouraged us to study the reactions of these compounds in more detail.

Klingebiel and co-workers investigated the reaction of (II) with the lithium salt of hexamethylcyclotrisilazanes, (Eq. 29)[33].



(29)

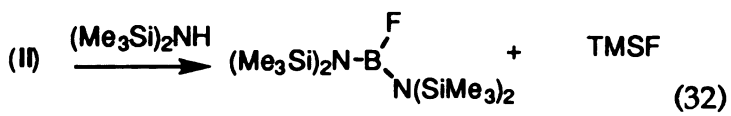
Eq. 30 shows the reaction that Meller studied that involved (II) and 3,4 lutidine[34].



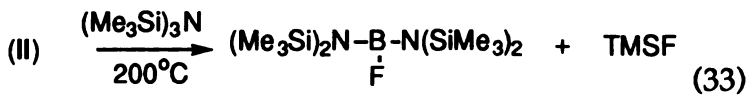
(30)

In a series of reports Elter documented the reactions of (II) with various silylamines, Eqs. 31-36 [35,36].

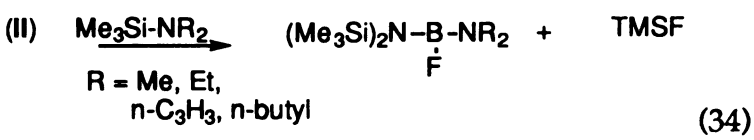
(31)



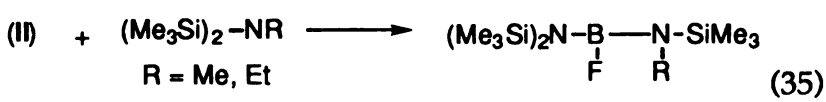
(32)



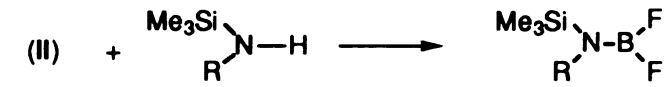
(33)



(34)

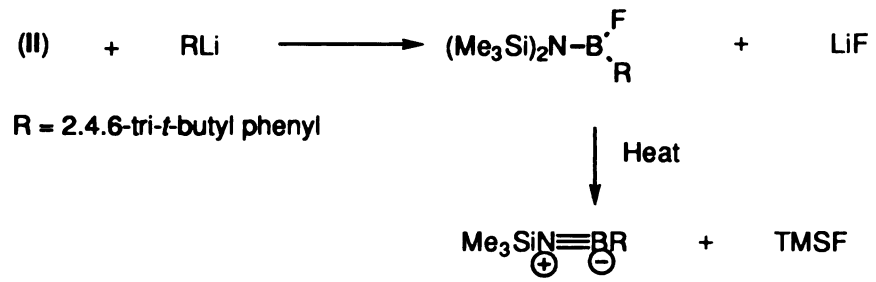


(35)



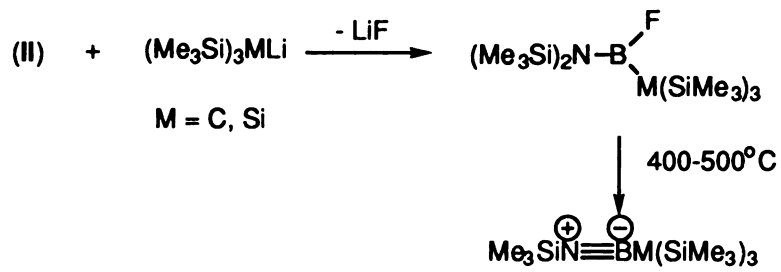
R = *i*-Pr, Me (36)

Elter also disclosed the reaction of (II) with organolithium compounds, shown in Eq. 37[37].



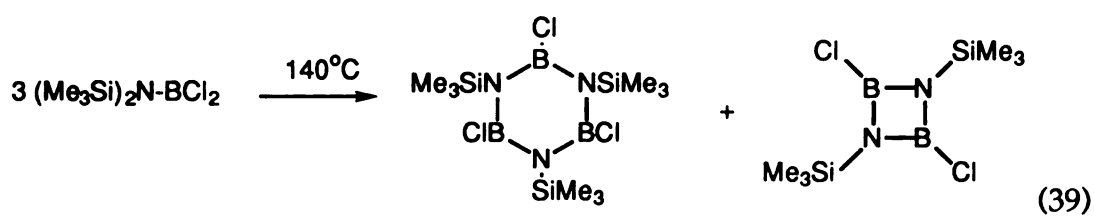
(37)

Klingebiel, in two separate publications, investigated the reaction of (II) with both tris(trimethylsilyl)methane and tris(trimethylsilyl)silane, Eq. 38 [38,39].



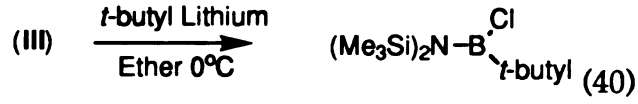
(38)

The chemistry of the dichloro derivative, $Cl_2B\text{-}N(SiMe_3)_2$ – (III) was also studied. Two separate reports showed that when three equivalents of (III) were heated to 140^{0}C the products obtained were the corresponding borazine[40,41] or diazadiboretidine[40], Eq. 39.



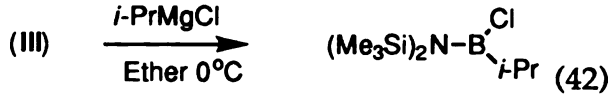
(39)

Neilson studied the reaction of (III) with several nucleophiles, shown in Eq. 40-43[42].

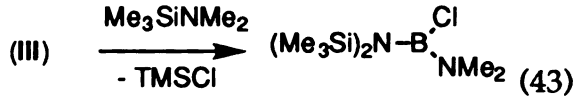


(40)

(41)

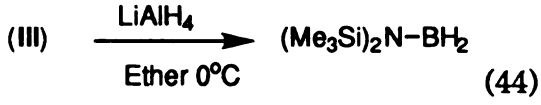


(42)



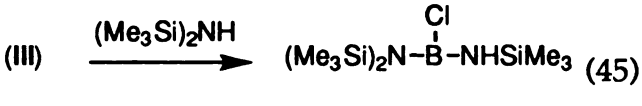
(43)

Wells and co-workers studied the action of lithium aluminum hydride, Eq. 44, on (III)[43].



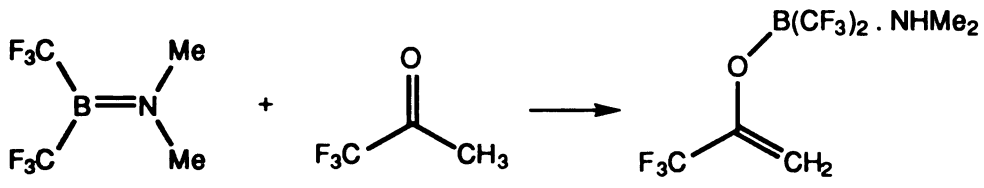
(44)

Wells also studied the reaction of (III) with 1,1,1,3,3,3-hexamethyl-disilazane, Eq. 45[44].

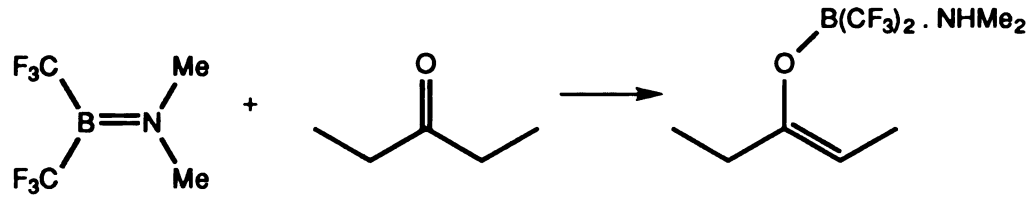


(45)

Currently, there are two papers that report a reaction of (I) with ketones. For these special cases (I) acted like a boron base, Eqs. 46 and 47, and a boron enol derivative is formed, in small yield[23,29].



(46)

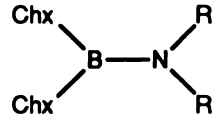


(47)

These reports showed that through modification of the ligands on boron it is possible to synthesize a boron enolate with a boron amide. For the above two examples, it is the action of the CF_3 group on boron that enhances the electron deficiency of the boron, despite the pi bonding from the nitrogen[28]. With this in mind we set out to find other boron amides that could enolize carbonyl acids.

Results

The three boron amides pictured in Eq. 48 were synthesized in our laboratory, through the 1:1 reaction of dicyclohexylboron chloride with the lithium salt of the secondary amine. None of these compounds give boron enolates as products when reacted with ketones. The assumption for the lack of reactivity is the presence of the boron - nitrogen pi bond.



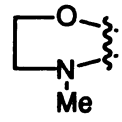
R = Phenyl, isopropyl, and $SiMe_3$

(48)

Because of the reactivity of $(CF_3)_2B\text{-}NMe_2$ we hoped that by further modification of the ligands on both boron and the nitrogen we may be able to synthesize other suitable boron amides that would function as boron bases. Boron amides 7-17, shown in table 6, were synthesized through the action of a lithium dialkylamide on a boron halide.

Table 6: Synthesis of Boron Amides

$R_2B\text{-}X + LiNR'_2 \longrightarrow R_2B\text{-}NR'_2 + LiX$

Compound	R	X	R'	R(x) Temp. (°C)
7	F	F	$SiMe_3$[a]	0[b]
8	Cl	Cl	$SiMe_3$	0[c]
9	F	F	Ph[a]	0[d]
10	Cl	Cl	Ph	-78[b]
11	F	F	*i*-Pr_2[a]	0[b]
12	F	F	$H,COCH_3$[a]	0[b]
13	Cl	Cl	$H,COCH_3$	0[b]
14	F	F	H,COPh[a]	0[e]
15	Cl	Cl	H,COPh	0[b]
16		Cl	H, *t*-butyl	0[f]
17	NMe_2	Cl	H, *t*-butyl	0[a]

a) Ratio B:N = 2:1
b) solvent : Hexane
c) solvent : Ether
d) solvent : Benzene
e) solvent : THF
f) solvent : Toulene

After characterization of compounds 7-17 with both ^{11}B and ^{1}H NMR each was then individually reacted with pinacolone and diethyl ketone and

monitored using ^1H NMR. The results of those reactions are summarized in Table 7.

Table 7: Reactions of boron amides with ketones

$R_2B\text{-}NR'_2$ + Ketone $\xrightarrow{R.T.}$

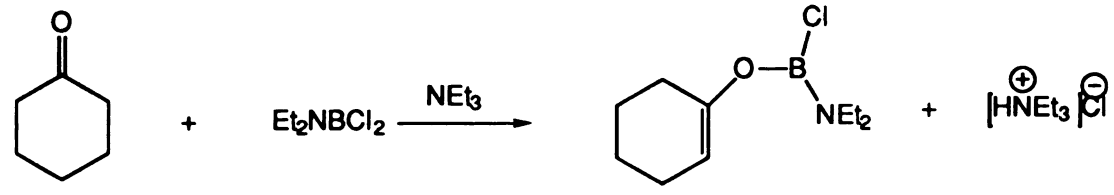
Compound	pinacolone	diethyl ketone	Time
7[c]	no reaction	no reaction	9 hrs[a]
8[c]	no reaction	no reaction	10hrs[a]
9[c]	self-condensation		overnight[b]
10[c]	self-condensation		10hrs[b]
11[c]	self-condensation		overnight[b]
12[c]	no reaction	no reaction	18hrs[a]
13[c]	no reaction	no reaction	overnight[a]
14[d]	no reaction	no reaction	overnight[a]
15[c]	no reaction	no reaction	overnight[a]
16[e]	self-condensation		overnight[a]
17[c]	no reaction	no reaction	overnight[a]

a) At room temperature
b) In a 50°C water bath
c) in Benzene
d) in THF
e) in Toluene

Evidence of any reaction was determined by a change in the proton NMR spectra. Both the disappearances of the α - hydrogen peaks (1.76 ppm for pinacolone and 2.0 ppm for diethyl ketone) and the appearance of enolate peaks (approx. 4.0-5.0 ppm) indicated that enolization had occurred. No evidence of any such change in the ^1H NMR spectra for compounds 7, 8, 12-15, and 17 was observed.

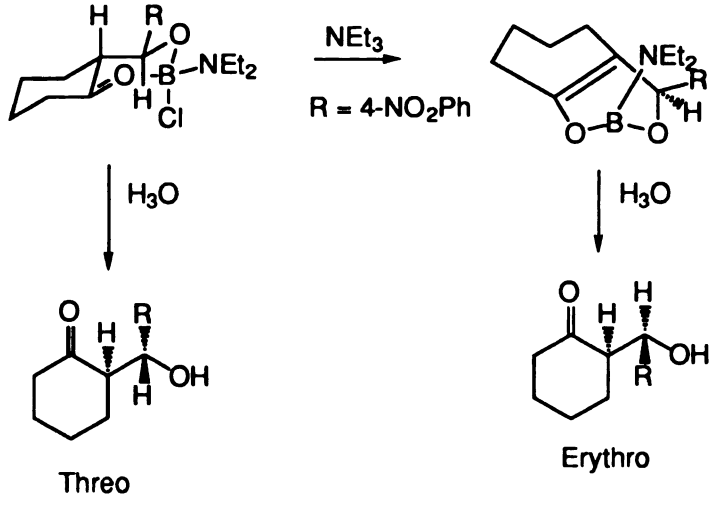
However, compounds 9-11 underwent self-condensation. Self-condensation was also observed by Sugasawa, who used Cl_2B-NEt_2 – diethylaminodichloroborane[45]. In his report, Sugasawa explained that the vinyloxyaminochloroborane assisted in the self-condensation reaction of the ketones. The carbonyl compounds used in Sugasawas study included cyclohexanone, propanal, and cyclopentanone.

A typical reaction involved the combination of the ketone, diethylaminodichloroborane, and triethylamine in a 1:1:2 ratio, respectively[45]. The mixture was stirred in dichloromethane at 4-8 ^0C, for 20 hours. The product obtained was the boron enolate, a vinyloxyaminochloroborane, Eq. 49. If the reaction was allowed to occur at a higher temperature, the self-condensation product would result[45]. This would explain why boron amides 9-11 and 16 all gave the self-condensation products, the reaction temperature for these reactions was at, or above, room temperature.



(49)

Sugasawa also reported that the use of triethylamine is necessary, Eq. 49, to help prevent self-condensation. The triethylamine also plays a role in the diastereoselection of the subsequent aldol condensation reaction[45].



(50)

When triethylamine was present the ratio of threo to erythro products was 2.4:1, without the triethylamine, the diastereoselection increased to 5:1 (threo to erythro)[45]. The two proposed transition states, Eq. 50, show that in the presence of triethylamine, the protonation adjacent to the carbonyl that would lead to the erythro product is enhanced by the NEt_2 group, which helps block the upper face that results in the threo isomer.

EXPERIMENTAL

The solvents used - hexane and diethyl ether - were dried over calcium hydride, distilled and stored in an inert N_2 atmosphere prior to use. All ^{31}P, ^{11}B, ^{13}C, ^{1}H NMR data was obtained using the either the Varian 300 MHz or Gemini 300 MHz NMR. The external references for ^{31}P, ^{11}B, spectra were H_3PO_4 and BF_3OEt_2, respectively. Unless otherwise noted the internal reference for the ^{13}C and ^{1}H data was $CDCl_3$ with TMS. All reagents and reaction products were handled in an inert atmosphere of N_2. NMR samples were sealed in 5mm NMR tubes, capped with a rubber septum and secured with Teflon tape. The butyl lithium used below was purchased from Aldrich as a 1.6 M solution in hexane.

Synthesis of disilylalted ethanolamine systems[47]: In a 250 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.047 mmoles of N-alkylethanolamine was dissolved in THF. At -78° C, 0.09 mmoles of butyl lithium was added via syringe. The pale yellow solution was allowed to stir for 10 minutes then was warmed to room temperature and then stirred for an additional 10 minutes. Then solution was cooled to -30° C and 0.09 mmoles of TMSCl was slowly added via syringe. After stirring for 15 minutes at room temperature the colorless solution was vacuum distilled using a vigreux column. The solution is stored under inert atmosphere in a round bottom flask with a small piece of calcium hydride until needed.

Synthesis of the 1-Aza-2-Bora-3-oxacyclopentane systems[47]: A 100 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, was charged with 2.5 mmol of a BCl_3 solution. At -78° C, 2.5 mmol of the disilylated ethanolamine derivative was added using a syringe. An immediate precipitate was formed. After stirring for 15 minutes at room temperature the solvents were removed under reduced pressure to give a pale yellow soild product - a 1,3,2-oxazaborolidine.

Synthesis of difluoro-bis(trimethylsilyl)amino borane (7)[30]: In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1

mmol of 1,1,1,3,3,3-hexamethyldisilazane was dissolved in 4 mL of hexane. At 0°C, 1 mmol butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of BF_3OEt_2 was dissolved in 2 mL of ether. At 0°C, the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 17.0 ppm
^{1}H : (C_6H_6, D_2O, external) - 0.003 ppm

Synthesis of bis(trimethylsilyl)aminodichloroborane (8)[30]: In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of 1,1,1,3,3,3-hexamethyldisilazane was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol hexane solution of BCl_3 was dissolved in 2 mL of additional hexane. Next, at 0°C, the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 36.56 ppm
^{1}H : (C_6H_6, D_2O, external) - 0.015 ppm

Synthesis of diphenylaminodichloroborane[45] (9): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.162 g (1 mmol) of diphenyl amine was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition

proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of BF_3OEt_2 was dissolved in 2 mL of ether. Then at 0°C the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 1.015, 23.780 ppm

Synthesis of diphenylaminodichloroborane[45] (10): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.162 g (1 mmol) of diphenylamine was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of a hexane solution of BCl_3 was dissolved in 2 mL of additional hexane. At -78°C, the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR was analysis performed.

^{11}B : (C_6H_6, D_2O, external) - 32.25 ppm

Synthesis of diisopropylaminodifluoroborane[45] (11): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of diisopropyl amine was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of BF_3OEt_2 was dissolved in 2 mL of

ether. At 0°C, the lithium salt of the amine was added to this flask, after several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 0.444, 17.394, 24.403 ppm

Synthesis of N-(difluoroboro)acetamide (12): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.05967 g (1 mmol) of acetamide was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of BF_3OEt_2 was dissolved in 2 mL of ether. At 0°C, the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 16.97, 0.412, 0.88 ppm

Synthesis of N-(dichloroboro)acteamide (13): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.5967 g (1 mmol) of acetamide was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of a hexane solution of BCl_3 was dissolved in 2 mL of additional hexane. At 0°C, the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - 18.51 ppm

Synthesis of N-(difluoroboro)benzamide (14): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.1211 g (1mmol) of benzamide was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of BF_3OEt_2 was dissolved in 2 mL of ether. At 0°C the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (C_6H_6, D_2O, external) - -1.221 ppm

Synthesis of N-(dichloroboro)benzamide (15): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.1211 g (1 mmol) of benzamide was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of a hexane solution of BCl_3 was dissolved in 2 mL of additional hexane. At 0°C the lithium salt of the amine was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. After filtration, the solvents were evaporated under reduced pressure, and NMR was analysis performed.

^{11}B : (C_6H_6, D_2O, external) - 15.17 ppm

Synthesis of 1-methyl-3-(*t*-butylamino)-1,3,2 oxazaborolidine (16): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.262 mL (1 mmol) of *t*-butyl amine was dissolved in 4 mL of hexane. At 0°C, 1.56 mL (1 mmol) of butyl lithium was added. A salt precipitate was formed

as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1mmol of N-methyl-1,3,2 oxazaborolidine was dissolved in 5 mL of toluene and the lithium salt of the amide was added to this flask. After several minutes the solution became cloudy. The mixture was allowed to stir for 1 hour at room temperature. The resulting mixture was filtered, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (THF, D_2O, external) - 27.923, 24.641, 8.705 ppm

Synthesis of bis(dimethylamino)-*t*-butylaminoborane (17): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.262 mL (1 mmol) of t-butyl amine was dissolved in 4 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. A salt precipitate was formed as the addition proceeded. The solution was allowed to stir at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 5 mmol of BCL_3 was dissloved in 2 mL of hexane. At -78°C, the litium salt of deiethyl amine was added. After several minutes the solution became cloudy. The mixture was allowed to stir for 15 minutes at -78°C and for then for 1 hour at room temperature. The resulting mixture was filterd and the solvents were evaporated under reduced pressure. The solid was then suspended in hexane and the lithium salt of t-butyl amine was introduced at -78°C. This mixture stirred for 45 minutes at -78°C then at room temperature for 1.5 hours. After filtration, the solvents were evaporated under reduced pressure, and NMR analysis was performed.

^{11}B : (Toluene, D_2O, external) - 45.413, 18.235, -17.513 ppm

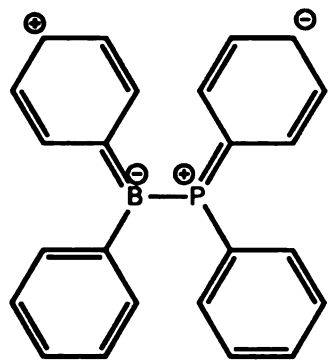
CHAPTER 3: BORON PHOSPHIDES

Background

The lack of any significant success with boron amides led us to next examine the reactions of boron phosphides with carbonyl acids. We postulated that a longer boron - phosphorus bond may enable the boron phosphides to act as better bases than boron amides, toward carbonyls.

Unlike many boron amides, boron phosphides of the type $R_2B\text{-}PR'_2$, have little or no double bond character between the boron and phosphorus, if R is a heteroatom. In fact, compounds with the formula, $(R_2N)_2B\text{-}PR'_2$, are monomeric, which indicates double bond character, but the double bond is between the nitrogen and the boron[47]. In these compounds competition exisists between nitrogen and phosphorus for the electron donation into the empty p orbital on boron. Nitrogen is more effective in the donation of its lone pair so, pi bonding exists, but it is between nitrogen and boron, and not between boron and phosphorus. A shortened boron - nitrogen bond has been measured in several boron phosphides[47]. The pi bonding between boron and nitrogen would allow phosphorus to be both basic and nucleophilic.

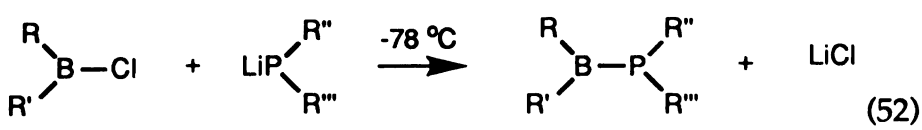
Teteraalkyl boron phoshpides (R and R' = hydrocarbons) exhibit considerable double bond character between boron and phosphorus[48]. In fact, tetraalkyl boron phosphides form trimers, tetramers and in some cases are polymers[48]. Tetraalkyl boron phosphides can be monomeric if the R group is sterically demanding, and many examples of monomeric, tetraalkyl boron phosphides can be found in the literature[49-53]. Work done by Coates and Livingstone showed the boron phosphide $Ph_2B\text{-}PPh_2$ is a monomer[50]. This compound, shown in Eq. 51, is a monomer because of conjugation between the boron and the aryl groups, not because of a double bond with phosphorus.



(51)

Control over the extent of the double bond character between boron and phosphorus, in boron phosphides, has been accomplished by careful selection of ligands for boron and phosphorus. Electron withdrawing substituents on boron enhance the double bond character[49]. Also, placement of either electropositive substituents or bulky groups on phosphorus, which would force phosphorus to become more planar, increase the extent of pi bonding[54]. Measurement of the length of the boron - phosphorus bond, the degree of pyramidicity at phosphorus, and phosphorus barrier to inversion all indicate the degree of pi bonding between boron and phosphorus[54]. In summary, a short boron - phosphorus bond, a low degree of pyramidicity at phosphorus and, a low barrier to inversion of phosphorus imply conjugation between boron and phosphorus[47,54].

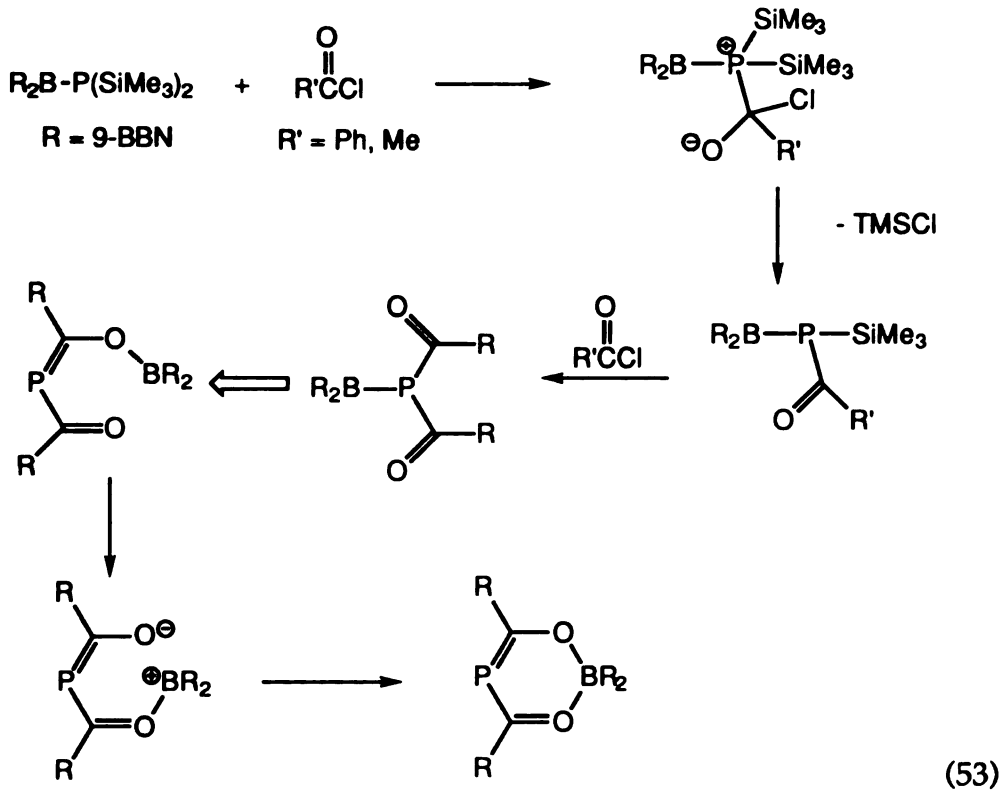
Boron phosphides are most often synthesized through a salt elimination reaction between a phosphorus anion and the appropriate boron chloride, shown in Eq. 52[47].



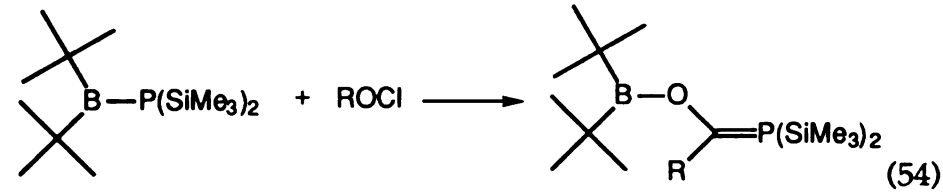
(52)

The chemistry of boron phosphides is not well documented. The major focus in this area of chemistry is synthesis and characterization, including the type of bond between boron and phosphorus and the existance as monomers or aggregates.

In 1994, Noth showed that a monomeric boron phosphide reacted with an acyl chloride, (Eq. 53), to give several different reaction products[49].



The products obtained for this reaction depend on borons substituents for example, when bulky tertiary butyl groups are put on boron, as in Eq. 54, the reaction will stop at 1:1 stoichiometry[49].



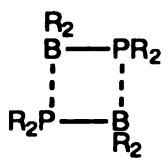
This reaction gave some insight to the reactivity of boron phosphides and with this information we began our studies with boron phosphides.

Tetraalkyl boron phosphides, $R_2B\text{-}PR'_2$, (when R = Me or Et and R' = t-butyl or $SiMe_3$) are commercially used as wide band gap semiconductors and as thermal coatings after pyrolytic polymerization[55].

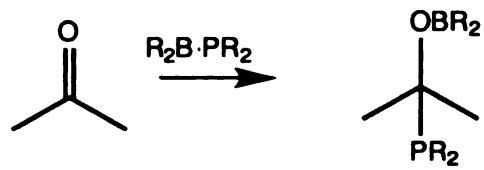
Results

Our work with boron phosphides and their 1:1 reactions with carbonyl compounds yielded several observations. First, the boron phosphides we synthesized exist as monomer and dimers in solution, Eq. 55, which indicates little double bond character between the boron and phosphorus. Second, phosphorus exhibits a strong tendancy to add to the carbonyl carbon, as illustrated in Eq. 55. The addition to the carbonyl represented the most challenging aspect of this research. In order to quantitatively enolize carbonyl compounds the addition reaction had to be stopped.

Monomer/dimer



Addition by phosphorus

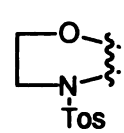


(55)

Compounds A-E in Table 8, below, show the boron phosphides that were synthesized in our laboratory, before this work.

Table 8: The first Boron Phosphides tested with carbonyl acids

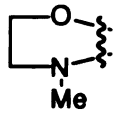
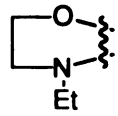
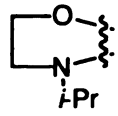
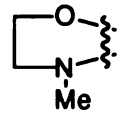
$R_2B\text{-}X + LiPR'_2 \longrightarrow R_2B\text{-}PR'_2 + LiX$

Compound	R	X	R'
A	cyclohexane	Cl	*t*-butyl
B	cyclohexane	Cl	Ph
C		Cl	Ph
D	$(i\text{-}Pr_2N)_2$	Cl	Ph
E	o- $C_6H_4O_2$	Cl	Ph

Of the above boron phosphides, A was able to enolize ketones however, the addition product is also present. Boron phosphide B gave the boron enolate only for the bulky diisopropyl ketone, and the reaction of E to give enolates is very slow. The remaining boron phosphides, in table 8, gave no evidence of enolization. In order to form enolates, the ligands on both boron and phosphorus needed modification. We want to make boron more electron deficient and, at the same time, make the phosphorus more basic. To this end, the boron phosphides in Table 9 were synthesized by a salt elimination reaction between a lithium dialkylphosphide salt and the corresponding boron chloride species.

Table 9: Synthesis of Boron Phosphides

$R_2B\text{-}X + LiPR'_2 \longrightarrow R_2B\text{-}PR'_2 + LiX$

Compound	R	X	R'	R(x) Temp. (°C)
18	DIP	Cl	Ph	-78[a]
19		Cl	Ph	-78[b]
20		Cl	Ph	-78[b]
21		Cl	Ph	-78[b]
22		Cl	$SiMe_3$	-78[b]
23	Cl	Cl	Ph	-78[a]
24	F	F	Ph[d]	-78[a]
25	Cl	Cl	$SiMe_3$	-78[a]
26	F	F	$SiMe_3$[d]	-78[a]
27	o- $C_6H_4O_2$	Cl	$SiMe_3$	-78[c]

a) solvent : Hexane
b) solvent : Toluene
c) solvent : 1:1 Hexane : Benzene
d) Ratio B:P = 2:1

Each boron phosphide was characterized by ^{31}P, ^{11}B and ^{1}H NMR. The reactions with diethyl ketone and pinacolone were monitored using both ^{31}P and ^{1}H NMR. Table 10, below, outlines the results of those reactions.

Table 10: Reactions of boron phosphides with ketones

$R_2B\text{-}PR'_2$ + Ketone ⟶

Compound	pinacolone	diethyl ketone	Time
18[d]	no reaction	no reaction	24 hrs.[a]
19[e]	80% addition	>90% addition	approx. 15 min.[b]
20[e]	75% addition	31% addition	approx. 15 min.[b]
21[e]	8.0% addition	35% addition	10hrs.[b]
22[e]	enolization	enolization	1.5 hrs.[c]
23[f]	no reaction	no reaction	24hrs.[a]
24[f]	no reaction	no reaction	24hrs.[a]
25[f]	no reaction	no reaction	24hrs.[a]
26[f]	no reaction	no reaction	24hrs.[a]
27[e]	no reaction	no reaction	24hrs.[a]

a) At room temperature.
b) Ketone added at -78°C and slowly warmed to room temperature while in spectrometer.
c) Ketone added at -20°C and slowly warmed to room temperature while in spectrometer.
e) in Hexane
d) in Toluene
f) in Benzene

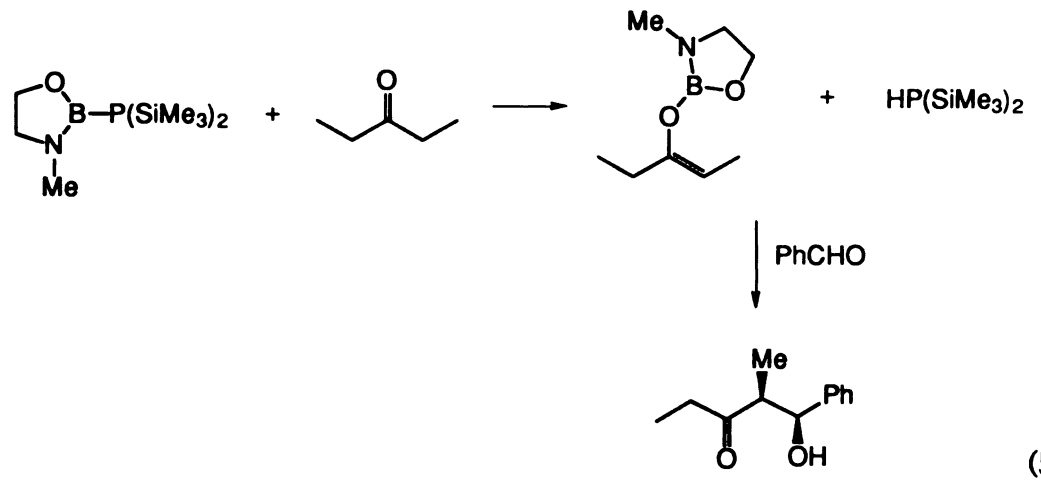
Discussion

For compounds 18-21, 23, and 24 the boron phosphide peak (^{31}P) is between -250 and -255 ppm, while the ^{31}P peak for diphenyl phosphine ($HPPh_2$) is located at -40 ppm. A successful enolization would involve a decrease in the (^{31}P) boron phosphide peak and a corresponding increase in the secondary phosphine peak. The computer integrator was used to detect fluctuations in those peaks.

Compounds 19-21 showed a decrease in the boron phosphide peak and a corresponding increase in the diphenyl phosphine peak, which indicated enolization. However, the enolization reaction was in competition with addition of phosphorus to the ketone. The appearance of a new phosphorus resonance at around 12 ppm was the addition product. The data in table 10 show for compounds 19-21, the addition reaction is fast and the products are in significant yield.

The boron phosphide (^{31}P) resonance for compounds 22, and 25-27 is found between -255 and -265 ppm, while the resonance for bis(trimethylsilyl)phosphine ($HP(SiMe_3)_2$) is located at -240 ppm. The ^{31}P NMR was monitored during both reactions of compound 22 with pinacolone and diethylketone. These reactions showed a disappearance of the boron phosphide peak along with a corresponding increase in the secondary phosphine resonance, again indications of successful enolization. In contrast to compounds 19-21, there was no new phosphorus resonance. Upon completion of the reaction (boron phosphide peak less than 10%, based on integration values) the ^1H NMR was observed to confirm the presence of enolate peaks (between 4.0 - 5.0 ppm). This is the first known example of a boron phosphide that will enolize carbonyls, in a nearly quantitative fashion, like pinacolone and diethyl ketone. The major drawback to this base is the time required to form the enolate, longer reaction times decrease the overall stereoselectivity.

The geometry of the enolate obtained with the reaction of compound 22 and diethyl ketone was determined. The geometry assignment of the enolate derived from diethyl ketone was taken from Brown's procedure[9]. This involved a 1:1 reaction between the enolate, of diethyl ketone, and benzaldehyde. The ^1H NMR of the aldol condensation product gave resonances for the *syn* or erythro isomer which indicated that the enolate geometry was Z, Eq. 56.



(56)

The results of this research showed that ligand modification from phenyl to trimethylsilyl suppressed the addition reaction. However, when the addition reaction is suppressed, the enolization also dramatically slows down. The phenyl group on phosphorus did not lower the nucleophilicity of phosphorus enough to prevent addition, which would explain the predominance of the addition product seen with the boron phophides that had the phenyl ligand. However, the trimethylsilyl ligand did reduce the nucleophilicity at phosphorus and suppressed the addition. Unfortunately, the trimethylsilyl ligand also slowed down enolization. Slower reaction time allows for equilibration of the ketone, and increases the chance for self-condensation of the unenolized ketone.

EXPERIMENTAL

The solvents used - hexane, toulene, THF, and benzene - were dried over calcium hydride, distilled and stored in an inert N_2 atmosphere prior to use. All ^{31}P, ^{11}B, ^{13}C, ^{1}H NMR data was obtained using the either the Varian 300 MHz or Gemini 300 MHz NMR. The external references for ^{31}P, ^{11}B, spectra were H_3PO_4 and BF_3OEt_2, respectively. Unless otherwise noted the internal reference for the ^{13}C and ^{1}H data was $CDCl_3$ with TMS. All reagents and reaction products were handled in an inert atmosphere of N_2. NMR samples were sealed in 5mm NMR tubes, capped with a rubber septum and secured with Teflon tape. The butyl lithium used below was purchased from Aldrich as a 1.6M solution in hexane.

Synthesis of disilylalted ethanolamine systems[46]: In a 250 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.047 mmoles of N-alkylethanolamine was dissolved in THF. At -78° C, 0.09 mmoles of butyl lithium was added via syringe. The pale yellow solution was allowed to stir for 10 minutes then was warmed to room temperature and then stirred for an additional 10 minutes. Then solution was cooled to -30° C and 0.09 mmoles of TMSCl was slowly added via syringe. After stirring for 15 minutes at room temperature the colorless solution was vacuum distilled using a vigreux column. The solution is stored under inert atmosphere in a round bottom flask with a small piece of calcium hydride until needed.

Synthesis of the 1-Aza-2-Bora-3-oxacyclopentane systems[46]: A 100 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, was charged with 2.5 mmol of a BCl_3 solution. At -78° C, 2.5 mmol of the disilylated ethanolamine derivative was added using a syringe. An immediate precipitate was formed. After stirring for 15 minutes at room temperature the solvents were removed under reduced pressure to give a pale yellow soild product - a 1,3,2-oxazaborolidine.

Synthesis of Lithium bis(trimethylsiyl)phosphide-bis(tetrahydrofuran)[56]: In a 100 mL round bottom flask equipped with a magnetic stirrer and N_2

inlet/outlet line, a THF solution Tris(trimethylsilyl)phosphine[55] (30 mmoles), at 0° C, an ether solution of methyl lithium (11 ml of a 2.69M solution) was added slowly over twenty minutes, while stirring. The resulting pale yellow solution was stirred for twenty minutes at 0° C, then at room temperature for 8 hours. The solvents were removed under reduced pressure and the yellow residue was suspended in 30ml of pentane. THF was added to the solution until dissolution was achieved (aprrox. 10 ml). At -78° C, yellow crystals precipitated out and the solvents were removed with a syringe. ^{31}P data gave a single peak at -298ppm. The product is stored in a round bottom flask, in a freezer.

Synthesis of B-diphenylphosphinodiisopinocampheylborane (18): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 0.20 mL of a 0.5 M solution in hexane of DIP chloride was dissolved in an additional 1.0 mL of hexane. At 0°C, 1.5 mmoles lithium diphenyl phosphine (in a THF solution) was added with a syringe. A salt precipitate was formed upon completion of addition. The solution was allowed to stir at 0°C for 30 minutes, then at room temperature for 1 hour. The solvents were removed under reduced pressure and NMR analysis was performed.

^{31}P : (Hexane, D_2O, external) - 5.372 ppm
^{11}B : (Hexane, D_2O, external) - 88.00, 89.017 ppm (doublet)

Synthesis of 1-methyl-3-diphenylphosphino-1,3,2-oxazaborolidine (19): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of N-methyl-1,3,2-oxazaborolidine is dissolved in 5 mL of toluene and 2.5 mmol of lithium diphenyl phosphine (in a THF solution) was added with a syringe at -78°C. The solution was stirred at -78°C for 30 minutes then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (C_6H_6, D_2O, external) - 65.0 ppm

Synthesis of 1-ethyl-3-diphenylphosphino-1,3,2-oxazaborolidine (20): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1mmol of N-ethyl-1,3,2-oxazaborolidine was dissolved in 5 mL of toluene and then 1 mmol of a THF solution of lithium diphenyl phosphine was added via syringe, at -78°C. The solution was stirred at -78°C for 30 minutes then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (C_6H_6, D_2O, external) - -63.69 ppm
^{11}B : (C_6H_6, D_2O, external) - 33.65 ppm

Synthesis of 1-isopropyl-3-diphenylphosphino-1,3,2-oxazaborolidine (21): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1mmol of N-isopropyl-1,3,2-oxazaborolidine was dissolved in 5 mL of toluene and then 1 mmol of a THF solution of lithium diphenyl phosphine was added via syringe, at -78°C. The solution was stirred at -78°C for 30 minutes then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (Toluene, D_2O, external) - -66.385 ppm
^{11}B : (Toluene, D_2O, external) - 31.38 ppm

Synthesis of N-methyl-3-bis(trimethylsilylphophino)-1,3,2-oxazaborolidine (22): In a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 1 mmol of N-methyl-1,3,2-oxazaborolidine was dissolved in 5 mL of toluene . At -78°C, 1 mmol of a THF solution of lithium bis(dimethylsilyl)phosphide-bis-THF was added. A salt precipitate was formed upon completion of addition. The solution was allowed to stir at -78°C for 30 minutes, then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (Toluene, THF, D_2O, external) - -269.28 ppm
^{11}B : (Toluene, THF, D_2O, external) - 25.64, 6.549 ppm

Synthesis of dichloro-diphenylphosphinoborane (23): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 2 mmol of diphenyl phosphine was dissolved in 1.0 mL of hexane. At 0°C, 1 mmol of butyl lithium was added. The solution stirred at 0°C for 15 minutes then at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 2 mmoles of a hexane solution of BCl_3 was dissolved in 2 mL of additional hexane at -78°C. The lithium phosphide was added at -78°C and the solution was stirred at -78°C for 30 minutes then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (C_6H_6, D_2O, external) - 37.462, 36.972 ppm
^{11}B : (C_6H_6, D_2O, external) - 17.41, 7.46 ppm

Synthesis of difluoro-diphenylphosphinoborane (24): In a 10 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 2 mmoles diphenyl phosphine was dissolved in 2 mL of hexane. At 0°C, 2 mmoles butyl lithium was added. The solution stirred at 0°C for 15 minutes then at room temperature for 15 minutes.

In a separate 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 4 mmoles of BF_3OEt_2 was dissolved in 2 mL of ether at -78°C. The lithium phosphide was added at -78°C and the solution was stirred at -78°C for 30 minutes then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (C_6H_6, D_2O, external) - -12.680, 37.97 ppm
^{11}B : (C_6H_6, D_2O, external) - 0.127 ppm

Synthesis of dichloro-bis(trimethylsilylphosphino)borane (25): In a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 2 mmoles of a hexane solution of BCl_3 was dissolved in an additional 2 mL of hexane at -78°C. To this solution was added 1 mmol of a THF solution of

lithium bis(dimethylsilyl)phosphide-bis-THF, at -78°C. The solution stirred at -78°C for 30 minutes, then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (C_6H_6, D_2O, external) - -40.0 ppm
^{11}B : (C_6H_6, D_2O, external) - 17.63, -3.04 ppm

Synthesis of difluoro-bis(trimethylsilyl)phosphinoborane (26): In a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 2 mmoles of BF_3OEt_2 was dissolved in 2 mL of THF at -78°C. To this solution was added 1 mmol of a THF solution of lithium bis(dimethylsilyl)phosphide-bis-THF, at -78°C. The solution was stirred at -78°C for 30 minutes then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (C_6H_6, D_2O, external) - -234.0, -250.0 ppm
^{11}B : (C_6H_6, D_2O, external) - 17.71, 0.206, -1.11 ppm

Synthesis of B-bis(trimethylsilylphophino)cathecolborane (27): To a 25 mL round bottom flask equipped with a magnetic stirrer and N_2 inlet/outlet line, 2 mmoles of a 1:1 benzene : hexane solution of cathechol boron chloride was added. At -78°C, 2 mmoles of a THF solution of lithium bis(dimethylsilyl)-phosphide-bis-THF was added. The solution was stirred at -78°C for 30 minutes, then at room temperature for 1 hour. After filtration, the solvents were evaporated under reduced pressure and NMR analysis was performed.

^{31}P : (Hexane, D_2O, external) - -253.81 ppm
^{11}B : (Hexane, D_2O, external) - 38.68, 20.819, 18.95 ppm

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