Pergamon

Tetrahedron 55 (1999) 1197–1248

TETRAHEDRON

Tetrahedron report number 481

RECENT DEVELOPMENTS IN THE CHEMISTRY OF AMINE- AND PHOSPHINE-BORANES

Bertrand Carboni * and Laurence Monnier

Synthèse et électrosynthèse organiques, UMR CNRS 6510, Bat 10, Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes Cedex, France.

Received 10 November 1998

Contents

Fax : (33) 02 99 28 69 55 E-mail : bertrand.carboni@univ-rennes1.fr

PII: S0040-4020(98)01103-X

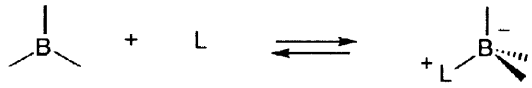
1. INTRODUCTION

The chemistry of organoboranes shows peculiar characteristics resulting from the electronic structure of the boron atom (three valence electrons and four atomic orbitals). Trisubstituted derivatives exist as electron-deficient trigonal entities and usually act as Lewis acids. They have a strong tendency to react with nucleophiles to give more or less stable species possessing a tetrahedral boron atom.[1] Many pertinent reviews and books have been devoted to the chemistry of these tetrasubstituted four coordinated derivatives. Most of them deal with the negatively charged organoborates that are key intermediates in the great majority of the ionic organoborane reactions.[2] Only a few reports or chapters in more general books are specifically concerned with neutral species [3] and, to the best of our knowledge, none of them has been published since the mid-1980s, except a survey of cyclic boron-containing systems [4] and an account of the synthesis and the reactions of some phosphine-boranes.[5] The purpose of this review is to focus on recent advances in the preparation of neutral amine- and phosphine boranes adducts (Figure 1) and their subsequent synthetic applications. No attempt has been made to cover extensively boron heterocycles containing intramolecular N-B or N-P coordinations which were previously reviewed in 1995.[4] Only some representative examples are given when necessary to illustrate new aspects of their chemistry.

Figure 1. Neutral amine- and phosphine adducts.

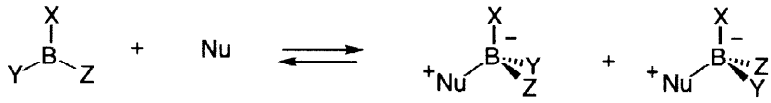
2. GENERAL CONSIDERATIONS

The exact nature of the boron-nitrogen or boron-phosphorus bond in neutral amine- and phosphine adducts has not been established univocally and may vary between two extremes. Incomplete sharing of the electron pair results in a weak bond whereas complete sharing involves a charge transfer to the boron atom resulting in a very strong bond. The stability of amine- and phosphine-boranes is therefore greatly affected by the nature of the groups directly attached both to the boron and the nitrogen or the phosphorus atoms. Some addition compounds are only stable at low temperature while others can be distilled without decomposition even at atmospheric pressure. In many cases, an equilibrium is established depending upon base and acid strengths, conditions of pressure, stoichiometry and temperature (Scheme 1).



Scheme 1

It is worth noting that ate complexes containing a stereogenic boron are created when the four substituents are different (Scheme 2).[6,7] A number of such compounds having a single configuration at boron are known in the literature.[7] Some of them have been directly obtained as single isomers, the others have been resolved by classical methods or by using the phenomenon of crystallization-induced asymmetric transformation. Interconversion of the two stereoisomers occurs if the complex is insufficiently stabilized. Thus, if the stereochemical information is readily stored at boron and can be used in asymmetric synthesis, it can also be readily erased.



Scheme 2

The stability of selected systems has been studied in order to establish relatively general principles. Polar effects have been underscored in the series Me_3NBF_3, $Me_3NBF_2CH_3$, Me_3NBFMe_2, Me_3NBMe_3. Trifluoroborane-trimethylamine is the most stable, the three highly electronegative fluorine atoms increasing the Lewis acidity compared to the situation where the boron was bound to electron releasing alkyl groups.[8] However, such expectations only based on electronegativity are not always verified and it is known that the Lewis acidities of boron halides increase in the order $BF_3 < BCl_3 < BBr_3$. This behaviour has been often attributed to back-donation of charge from the $p\pi$ orbitals of halogens to that of boron, although recent computational analysis of the bonding in boron trifluoride and boron trichloride complexes with ammonia suggested that the key factor was the ability of the borane to accept an extra charge.[9]

Steric strains also directly affect the stability of the Lewis acid-base adducts. For trimethylborane-amine complexes, it can be seen from the values of the enthalpies of dissociation that the order of stability $NH_3 < Me_3N < MeNH_2 < Me_2NH$ almost fits with simple electronegative arguments. When the size of the acid changes, electronic effects can be often negated and, with tri-*t*-butylborane, complete domination of steric factors was observed, $(t\text{-Bu})_3BNEt_3 < (t\text{-Bu})_3BNHEt_2 < (t\text{-Bu})_3BNH_2Et < (t\text{-Bu})_3BNH_3$.[10] In the field of

arylboranes, while Ph_3B has been known to give 1:1 adducts with tertiary amines, Ar_3B (Ar = 2,6-$(MeO)_2C_6H_3$) only form isolable adducts with ammonia and some primary amines, but not with tertiary, secondary or *sec*-alkyl amines.[11]

Similar studies have been carried out with phosphorus derivatives. For example, PH_3 coordinates to fluorine substituted triarylboranes $B(C_6H_xF_{5-x})_3$ to form 1:1 complexes.[12] The most stable adduct is $(C_6F_5)_3BPH_3$ where the P-B bond length (2.046 ± 0.002 Å, compared with the sum of covalent radii 1.90 Å) suggests a weak coordination. Accordingly, this complex releases gazous phosphine when heated at 50°C. (2,6-F_2-$C_6H_3)_3B$ forms a weaker adduct and $(C_6H_5)_3B$ does not give any complex at all.

Determination of the kinetic parameters for dissociation of the N-B coordination bonds in intramolecular boronate-and borane-amine complexes (Figure 2) reveals that the barrier height is affected by various factors, including boron and nitrogen substituents and solvents. This barrier is reduced when *N*-methyl are replaced by *N*-ethyl groups. The strength of the B-N bond is also modified by the Lewis acidity of the boron moiety, which is known to be weaker in a boronate than in a trialkylborane.[13] Phosphine-boranes with the P-B bond integrated into a five-, six- or seven-membered ring have been recently prepared by hydroboration of alkenyldiphenylphosphine using 9-borabicyclononane.[14]

Figure 2. 2-(N,N-dialkylaminomethyl)phenylboranes.

Numerous boron heterocycles derived from boronic and borinic esters have been prepared, thus exploiting the stabilization of the intramolecular boron-nitrogen coordination (Figure 3).[4,15] In some cases, such as 2-pyridylthio derivatives, they can even be treated with hydrochloric acid without decomposition.

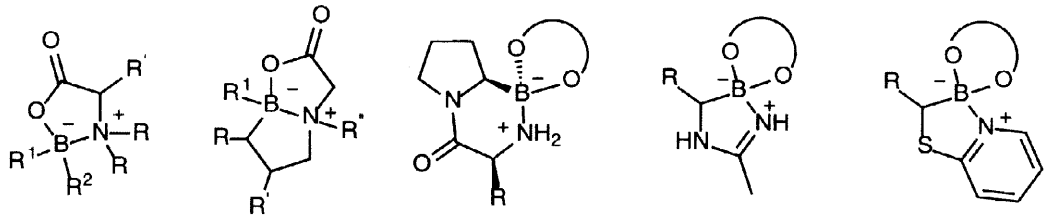


Figure 3. Some boron heterocycles with intramolecular boron-nitrogen chelation

Many theoretical and structural studies have been devoted to donor-acceptor complexes. For example, H_3NBF_3, which was the first coordination compound of any element, synthetized in 1809 by Gay-Lussac,[16] has been subjected to extensive examination. The experimental techniques employed varied from gas phase electron diffraction, X-ray diffraction, microvawe, ESCA, UPS spectroscopy to vibrational spectroscopy in the gas, liquid, solid states and in cryogenic matrixes.[17] A number of *ab initio* molecular orbital studies were also carried out. [18] This topics with no immediate applications to organic synthesis is not developed in this review. However, it is worth noting the importance of intermolecular interaction in several amine-borane complexes resulting from unconventional B-H···H-N hydrogen bond.[19]

The development of the chemistry of amine- and phosphine-borane adducts is intimately coupled with the application of spectroscopic methods.[20] Although the final structural proof rests on X-ray analysis (B-N in the range 1.55-1.75 Å and B-P in the range 1.90-2.10 Å),[21] NMR spectroscopy have been found to give reliable and very helpful informations in the assignment of structures [20,22] and in the study of chemical behaviour.[23] The intramolecular complex formation has been also studied in the gas phase by UV photoelectron spectroscopy.[24]

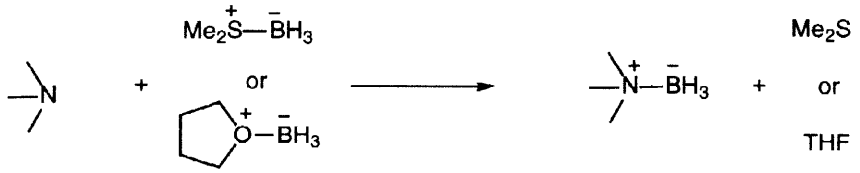
3. SYNTHESIS OF AMINE- AND PHOSPHINE-BORANES

The most obvious synthesis of amine and phosphine-borane complexes involved the simple mixing of the Lewis base and the organoborane or exchange reactions. Other methods were based on the modification of pre-existing complexes. We chose to examine the approaches dealing with the reactivity of the amine or phosphine moieties of these complexes in Section 4.4, since, in most cases, borane complexation was then used as a temporary protection or activation of the Lewis base.

3.1. Creation of a new boron-heteroatom bond

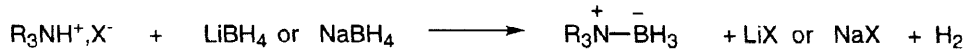
3.1.1. Amine and phosphine-BH_3

Me_3NBH_3 was first synthesized in 1937 by reaction of diborane and trimethylamine.[25] Since this initial discovery, a large number of complexes have been prepared from a wide range of amines. $THFBH_3$ or Me_2SBH_3, which are easier to handle, are now preferred instead of diborane (Scheme 3).[26] Amine exchange reactions have been also reported.[27]



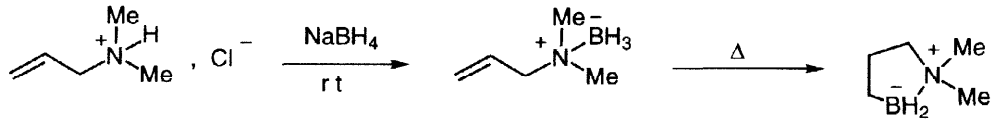
Scheme 3

Lithium or sodium borohydride are also valuable sources of borane when starting from amine salts (Scheme 4).[28] For the synthesis of H_3BNH_3, best results were obtained from ammonium carbonate and sodium borohydride in THF.[29]



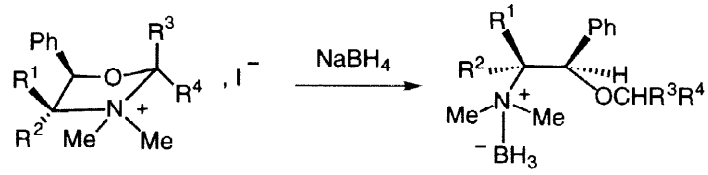
Scheme 4

Dimethylallylamine hydrochloride reacts at room temperature with sodium borohydride to afford the corresponding borane complex, while, at higher temperature, hydroboration occurs giving an azaborolidine (Scheme 5).[30]



Scheme 5

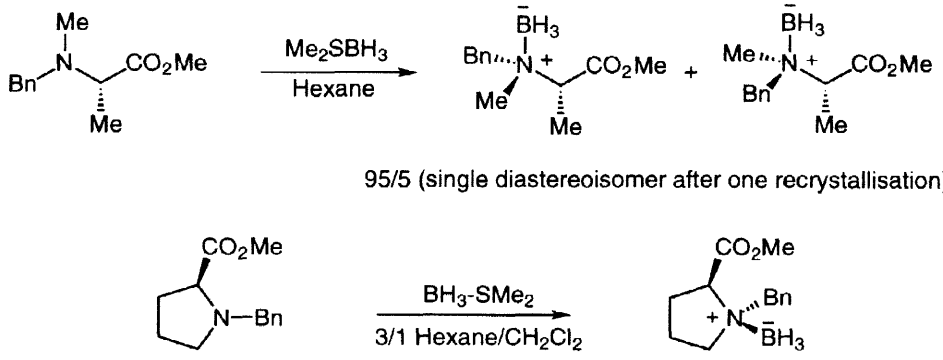
Regioselective reductive ring opening of oxazolidinium methiodides can be achieved in the presence of sodium borohydride in dimethoxyethane (Scheme 6). [31].



Scheme 6

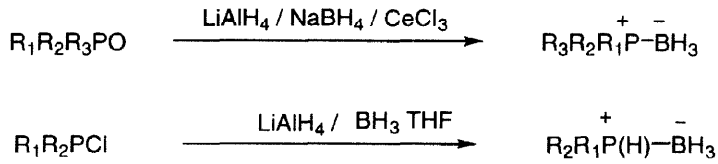
When the amine have three different substituents and a stereogenic carbon, borane complexation can afford a mixture of diastereoisomeric adducts, which can be separated by simple selective crystallization or column chromatography.[32] In the case of methyl (*S*)-*N*-benzyl-*N*-methylalaninate, it was possible to obtain selectively one isomer using the

phenomenon of crystallisation-induced asymmetric transformation (Scheme 7).[33] (*S*)-*N*-benzylproline methyl ester gave a single diastereoisomer with BH_3 and CO_2Me *cis* to each other.[34]



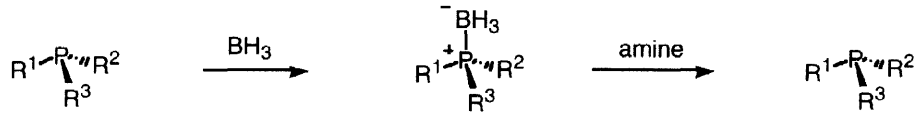
Scheme 7

As with their amino analogues, phosphine-borane adducts usually have been synthesized from borane dimethyl sulfide or borane tetrahydrofuran complexes. Amine-boranes can be also used for exchange reactions provided that amine is removed by distillation.[35] Corrosive and air-sensitive phosphines were best generated *in situ* from phosphine oxides or chlorophosphines (Scheme 8).[36,37]



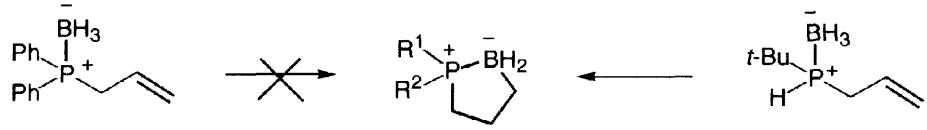
Scheme 8

The boronation of P-chiral phosphines occurred with complete preservation of the stereochemical integrity at phosphorus. When required, chiral non-racemic phosphine-boranes can be obtained in high enantiomeric purity by recristallization. Liberation of the enantiomerically pure phosphines was achieved from the corresponding boranes complexes with retention of configuration (see Section 4.4) (Scheme 9).



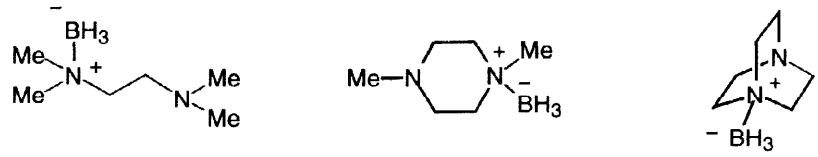
Scheme 9

A large number of primary, secondary and tertiary phosphines, phosphites, oxazaphospholidines, aza- and diazaphospholes and monochlorophosphines give stable adducts with BH_3.[38] Chemoselective borane addition to phosphines occured in the presence of other functional groups such as alkyne, ester, nitrile,[39] and phosphonate groups.[40] Alkenyl, allyl and 3-butenyldiphenylphosphines are also readily converted into their monoborane adducts. No cyclic product can be obtained even on prolonged thermal treatment, while the allyl-*t*-butylphosphine derivative gives internal hydroboration at 30°C (Scheme 10).[38,41,42] The formation of dihydrophosphinine-borane complex was accompanied by reductive side-reactions giving rise to saturated derivatives. [43]



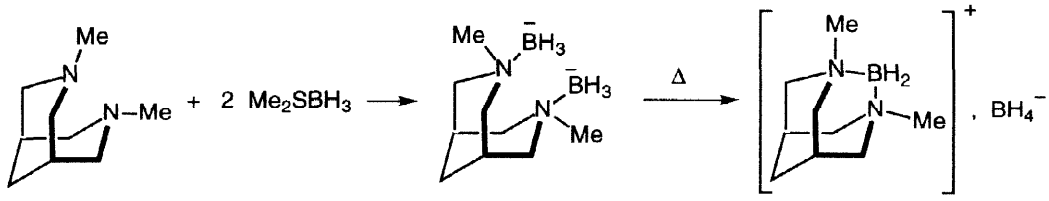
Scheme 10

Mono- and bis-BH_3 adducts of diamines have also received attention and it has been reported that tetramethylethylenediamine, *N,N'*-dimethylpiperazine and 1,4-diazabicyclo-[2.2.2]octane each form a monoadduct that can be isolated and characterized (Scheme 11).[44]



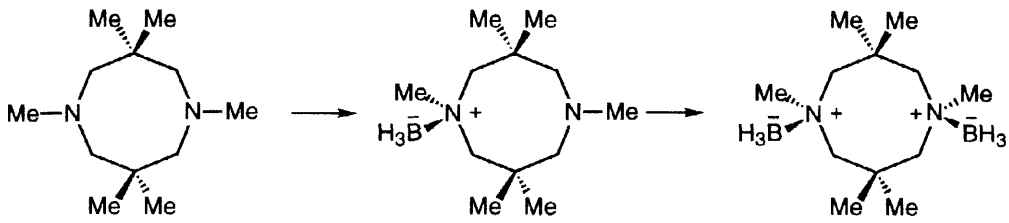
Scheme 11

Bis-chelation was observed with 3,7-dimethyl-3,7-diazabicyclo[3,3,1]nonane, which reacted with two equivalents of borane-dimethylsulfide to give a high melting point solid.[45] Heating this compound at 100°C in the solid state led to a new product, which is a member of a class of boron-containing cations of the type $BH_2L_2^+$, first examined by Miller and Muetterties (Scheme 12). [46]



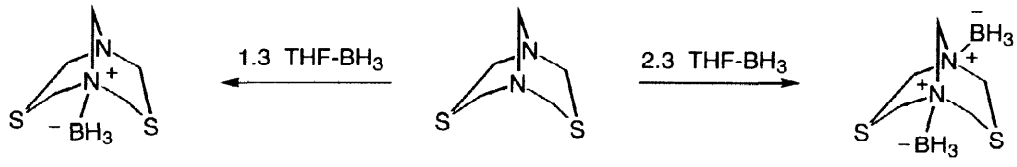
Scheme 12

For 1,3,3,5,7,7-hexamethyl-1,5-diazacyclooctane, the monoborane adduct was present, but the bis-adduct was the major product. Its structure was determined by X-ray crystallography to be a twist-boat-boat with the BH_3 groups *cis* (Scheme 13).



Scheme 13

Although there are four donor sites in 1,5-dithia-3,7-diazabicyclo-[3.3.1]nonane only mono- and di-*N*-coordinations were observed depending on the amount of borane (Scheme 14). [47] Evaporation of the solvent caused partial decomplexation. This fact can be attributed to the very open angles around the nitrogen atoms that does not favour a strong coordination. The N-B bond is weaker in the bisadduct due to the presence of an important electron withdrawing effect resulting from the coordination of the other nitrogen atom. This was also observed with imidazolidines.[48]

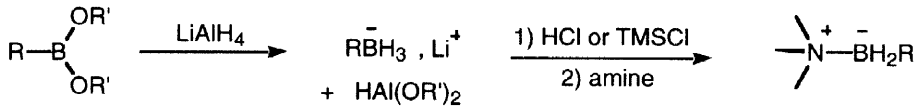


Scheme 14

A series of phosphine-BH_3 derived from bis(diphenylphosphino)alkanes have been also synthesized.[49] Only bis(borane) adducts were isolated, with the exception of 1,2-bis((*S*,*S*)-2,4-dimethylphosphetano)benzene, which was shown to form the monoborane derivative.[50] Analogous partially or fully borylated adducts were obtained from polyphosphines.[51]

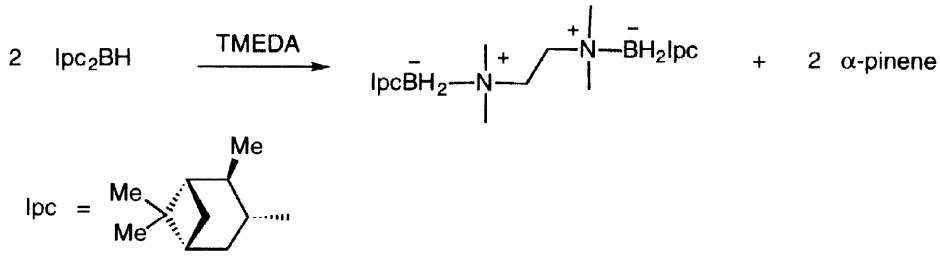
3.1.2. Amine- and phosphine-H_2BR

Monoorganylborane complexes have been prepared by addition of the amine to the corresponding borane, first generated from boroxines,[52] 2-alkyl-1,3,2-benzodioxaboroles [53] or boronic esters (Scheme 15).[54]



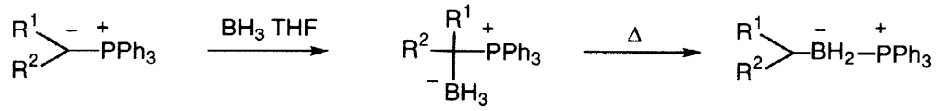
Scheme 15

Monoalkylborane-amine complexes were also readily available by dehydroboration of thexylmonoalkylboranes.[55] Similarly, *N,N,N',N'*-tetramethylethylenediamine displaces α-pinene to produce the solid 1/2 adduct of the base and monoisopinocampheylborane (Scheme 16).[56].



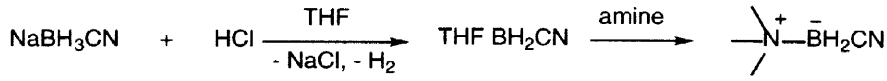
Scheme 16

In a different approach, alkylidenetriphenylphosphoranes add BH_3 to give a stable phosphonium salts, which rearrange on heating to afford monoalkylborane-triphenylphosphine adducts (Scheme 17).[57]



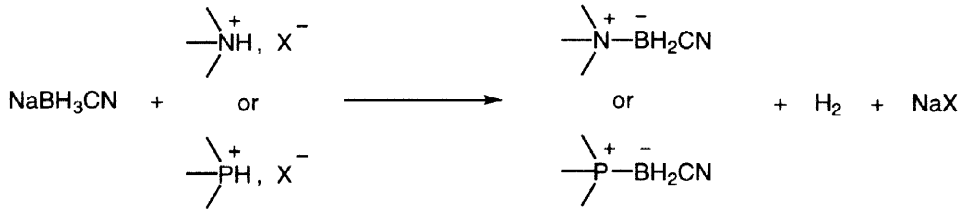
Scheme 17

Amine-cyanoborane complexes were first prepared from sodium cyanoborohydride. Addition of hydrochloric acid in THF was followed by an exchange reaction to afford the amine adduct (Scheme 18).[58]



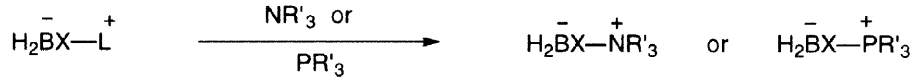
Scheme 18

This method was later improved by employing ammonium or phosphonium salts to introduce simultaneously the amine and the acid. A number of amine and phosphine-cyanoboranes were prepared by using this efficient and practical route (Scheme 19).[59]



Scheme 19

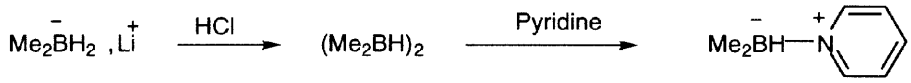
A variety of monosubstituted borane adducts have been also obtained by amine or phosphine exchange reactions from an appropriate substrate (Scheme 20).[60,61]



Scheme 20

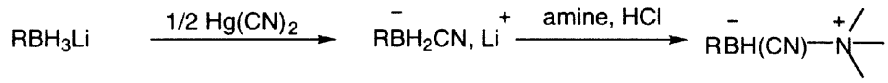
3.1.3. Amine- and phosphine-HBRR'

Except in a few cases, dialkylboranes readily disproportionate. Therefore, as their monoalkyl congeners, they were mostly prepared *in situ* from R_2BH_2Li and stabilized by complexation (Scheme 21).[62]



Scheme 21

Trimethylamine- and pyridine- monoalkylcyanoboranes have been synthesised from the corresponding borohydride and the amine hydrochloride (Scheme 22).[63]

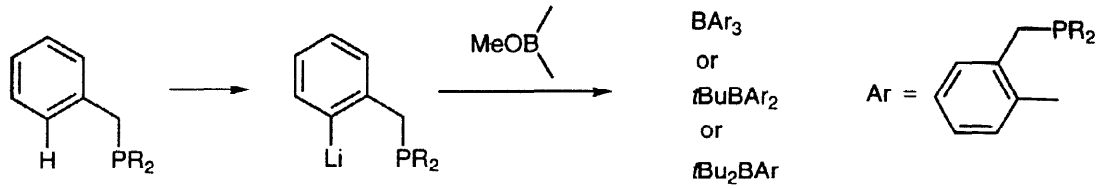


Scheme 22

As monohalogenoboranes, dihalogenoboranes easily add amines or phosphines. In the case of difluoroborane derivatives, the initial formation of the 1/1 adducts was followed by redistribution reactions.[64]

3.1.4. Amine- and phosphine-BR_3

As previously described, the addition compounds were readily obtained from the corresponding amine or phosphine and the trisubstituted boranes (trialkylboranes,[65] trihalogenoboranes,[66] boroxines,[67] triarylboron compounds [68]). Ortholithiation of (diphenylphosphinomethyl)benzene (ArH) has been used to prepare the sterically crowded cyclic phosphine-boranes BAr_3, tBuBAr_2 and tBu$_2$BAr from the lithiated ligand LiAr and B(OMe)$_3$, tBuB(OMe)$_2$ and tBu$_2$BOMe, respectively (Scheme 23).[69] Intramolecular chelation was observed for tBuBAr_2 and tBu$_2$BAr, while the steric bulk in BAr_3 led to the formation of oligomers in solution.



Scheme 23

The reactivity of diborane compounds $B_2(1,2\text{-}E_2C_6H_4)_2$ (E=O or S) has also been studied with respect to their ability to coordinate Lewis bases. Mono- and bis adducts of 4-methylpyridine, phenyldimethylphosphine and triethylphosphine have been isolated (Figure 4).[70]

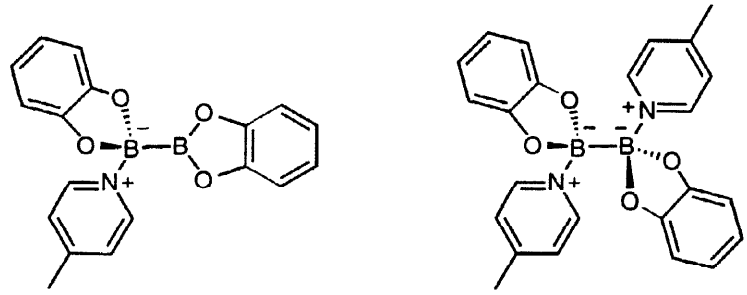
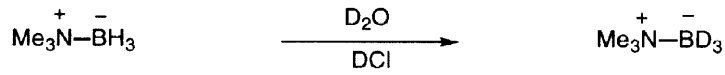


Figure 4 . Mono- and bis adducts of diborane compounds

Finally, the transformation of perfluoroalkylderivatives of tricoordinate boron into tetracoordinate species has also been reported. Trifluoromethyl boron compounds behave in an entirely specific fashion and a recent overview presented the preparation and the reactivity of trifluoromethyl-substituted borane-amine adducts.[71]

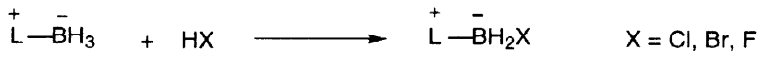
3.2. Modification of a preexisting complex

The boron hydrogens of borane-trimethylamine undergo a rapid exchange with deuterium much faster than hydrolysis when this complex is stirred with acidic deuterium oxide (Scheme 24).[72]



Scheme 24

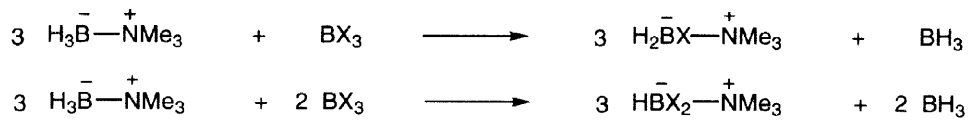
Monohalogenated amine- and phosphine borane complexes were obtained by treatment of the parent derivative with hydrogen halide (Scheme 25).[73, 74, 75, 76, 77]



L = amine or phosphine

Scheme 25

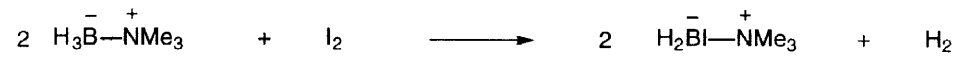
Boron halides can also be used as halogenating agents, mono- or dihalogeno derivatives being then produced depending upon stoichiometry. This redistribution reaction apparently occurred without cleavage of the boron-nitrogen bond (Scheme 26).[73,76,78,79,80]

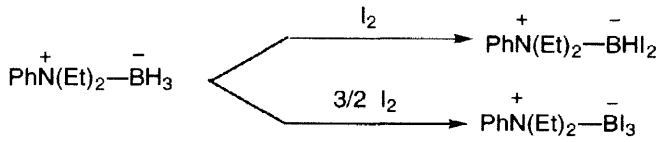


X = Br, Cl

Scheme 26

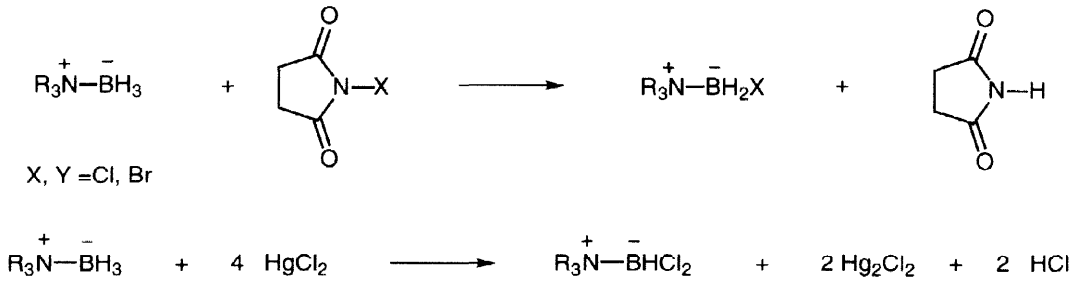
Direct action of halogen also yielded amine- and phosphine-haloboranes. Chlorine reacted vigorously with trimethylamine-borane in benzene solution while bromination and iodination were not so fast.[73,75,77] With a ratio complex/iodine = 2/1, the amine-monoiodoborane was isolated. Di- and triiodoborane adducts have been generated provided different ratios were used (Scheme 27).[81]





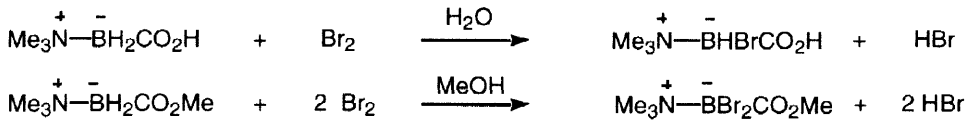
Scheme 27

Several other reagents such as *N*-halosuccinimides,[82,79] mercuric chloride,[83] hypochlorous acid,[84] or halocarbons [85] have been also successfully investigated for the preparation of mono- or polyhaloborane complexes (Scheme 28).



Scheme 28

Amine-carboxyboranes were readily decarbonylated with bromide in dichloromethane to produce amine-dibromoboranes, while in protic solvents such as water, only substitution takes place giving bromocarboxyboranes complexes (Scheme 29).[86]



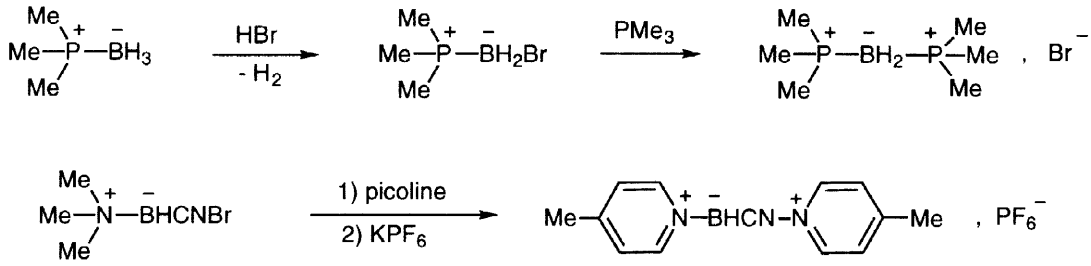
Scheme 29

Exchange reactions of halogens with various anionic nucleophiles have been investigated as efficient routes to new complexes.[87,88] For example, trimethylamine-monoiodoborane and sodium cyanide led to the corresponding cyanoborane, [89] which can be also conveniently prepared by treatment of borane complexes with mercuric cyanide [90] (Scheme 30).

Scheme 30

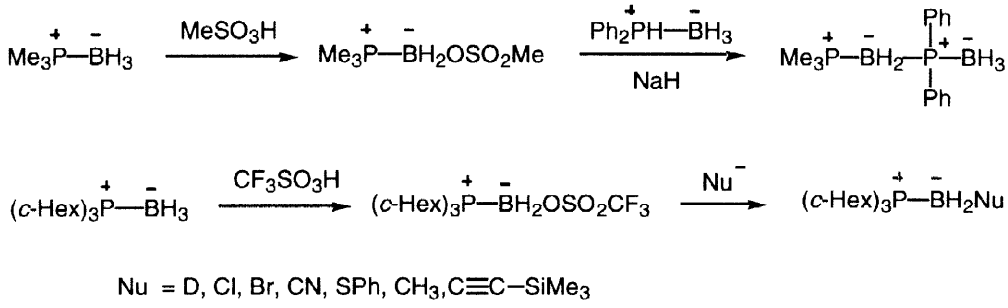
Boron trichloride adducts reacted with pseudohalide salts MX (X=NCO, NCS) to afford completely substituted products. According to the stoichiometry, either mixed species or tetrapseudohaloborate anions were obtained.[91]

The introduction of a second trialkylphosphine moiety at the boron atom of phosphine borane complexes led to symmetrical cations which have been the source of a coordination chemistry.[92] Bis-amine cations have been synthesized likewise from bromocyanohydroboranes while dibromocyanoboranes did not react with amines even under harsher conditions (Scheme 31).[93] A boronium ion analogue of the tropane ring system has been prepared from homopiperazine and bromoborane-dimethylsulfide.[94]



Scheme 31

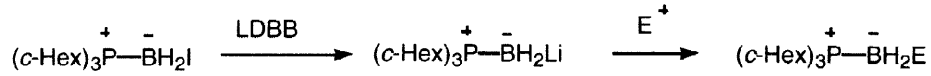
Phosphine-boranes reacted with methanesulfonic or trifluoromethanesulfonic acid to give the corresponding sulfonates. Various substitution products were obtained by addition of nucleophiles to these highly reactive species (Scheme 32).[95]



Nu = D, Cl, Br, CN, SPh, $CH_3C{\equiv}C{-}SiMe_3$

Scheme 32

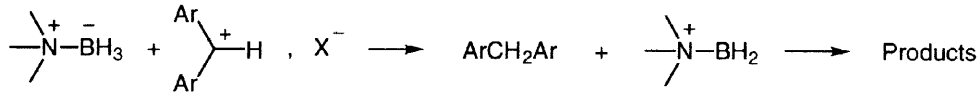
The generation of tricoordinate boron anions has been achieved from tricyclohexylphosphine-monoiodoborane and lithium 4,4'-di-*tert*-butylbiphenylide (LDBB). The addition of a variety of electrophiles afforded new phosphine-boranes possessing a substituent at the boron atom (Scheme 33).[96]



E = D, $SiMe_3$, RX, aldehyde, ketone, epoxide, ester, disulfide, ...

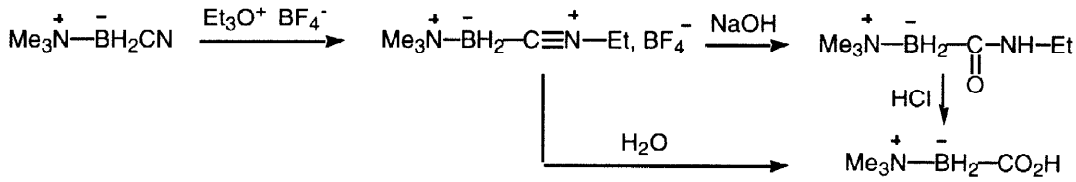
Scheme 33

The kinetics and mechanism of hydride abstractions from trialkylamine boranes with benzydryl cations have been determined photometrically (Scheme 34).[97] Borenium ions, generated from 2,3-benzaborolidines and trityl salts, are exceptionally potent electrophiles.[98]



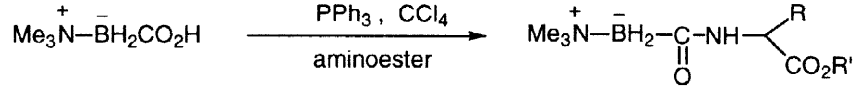
Scheme 34

A number of boron analogues of amino acid betaines (see Section 5.1) have been synthesized from a cyanoborane precursor by addition of triethyloxonium tetrafluoroborate. Basic hydrolysis gave the corresponding amide while the acid can be directly obtained from the nitrilium salt and water (Scheme 35).[99] Other alkylating agents, such as *t*-butyl chloride in the presence of antimony pentachloride, have also been employed.[100].



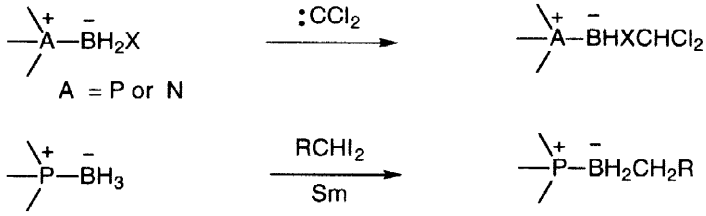
Scheme 35

Esters derivatives have been prepared by a variety of routes including the direct treatment of a nitrilium salt with an alcohol [101] and the esterification of the corresponding boron amino acid.[102] A number of boron-containing di- and tripeptides were synthesized by condensation reactions in the presence of triphenylphosphine and carbon tetrachloride (Scheme 36).[103]



Scheme 36

Dichlorocarbene has been found to insert into the boron-hydrogen bond of triarylphosphine-borane adducts.[104] Other various functionalized amine- and phosphine borane complexes were later prepared by this method [105] and, more recently, methylene insertion has been reported with samarium carbenoids (Scheme 37).[106].



Scheme 37

4. Reactivity

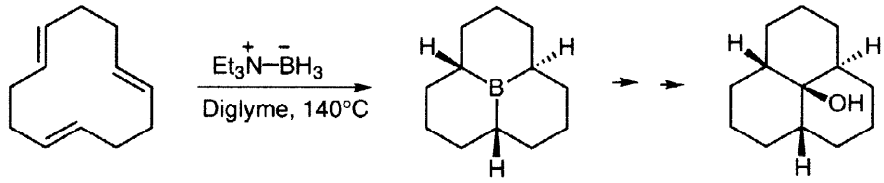
4.1. Hydrolysis

Most of borane-aliphatic amine complexes are quite stable in water and alcohols at near neutrality and room temperature while aryl amine derivatives are less stable and usually react with protic media and moist air.[107] As a general rule, the reactivity of the donor base-borane adducts is highly sensitive to structural variations both in the donor moiety and in the coordination sphere of boron. The kinetics of solvolysis in acidic media have been the subject of numerous investigations. [108]

Phosphine-borane complexes appear to be more resistant to hydrolysis than their corresponding amino analogues. For example, triphenylphosphine-borane is a crystalline solid which is unchanged after six months on the open bench and it was reported to resist 3M HCl at 150°C for 3h.[109].

4.2. Borane complexes as hydroborating agents

Amine- and phosphine-borane complexes are notably more stable than the usual hydroborating reagents such as borane-tetrahydrofuran or borane-dimethylsulphide. But, if they are easily handled, they concomitantly show a lower reactivity toward alkenes and alkynes.[107,110] The hydroboration reaction proceeds *via* a prior dissociation mechanism and the ease of addition greatly varies with the strength of the complex.[111,112] When it is necessary to heat, the slow generation of borane can then be an advantage, as in the synthesis of polycyclic organoboranes (Scheme 38).[113]



Scheme 38

Relatively drastic conditions can also cause undesired substantial isomerisations, [114] which can be suppressed by co-addition of alkylating agents, Lewis acids or elemental sulfur.[115]

More reactive adducts might be expected with relatively hindered alkylamines or less basic arylamines. Indeed, borane-dialkylphenylamine complexes hydroborate alk-1-enes without heating,[112,116] and selective hydroboration of monosubstitued alkene over disubstituted olefin has been achieved using *N,N*-diethylaniline-diiodoborane at room temperature. [117] New hydroborating agents have been prepared from silylamine-boranes.[118]

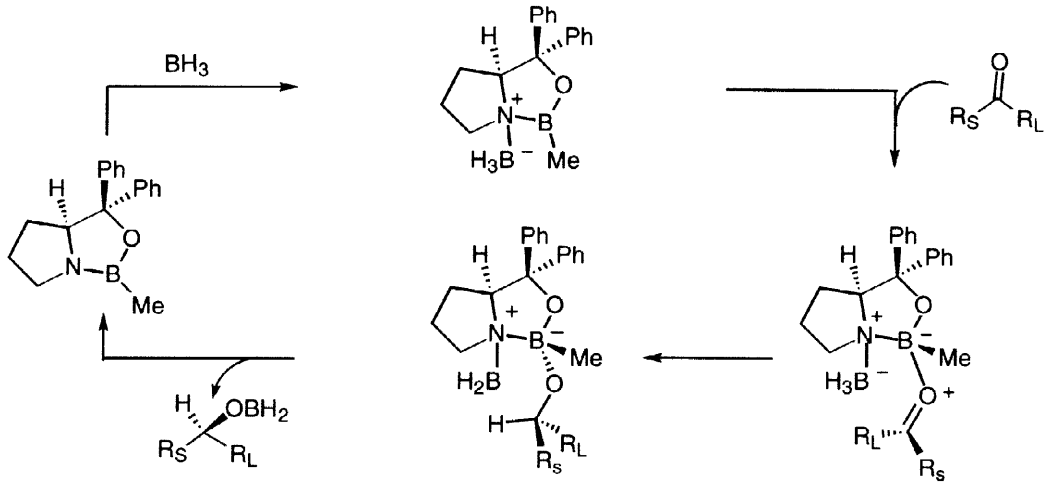
Borane-diethylaniline complex has been also used to promote the formation of alkenyl boronic esters from alk-1-ynes [119] and to prepare dialkylketones from alkenes in the presence of cobalt chloride and carbon monoxide.[120]

4.3. Borane complexes as reducing agents

Although amine boranes have been known for many years, some of them being commercially available, their use as reducing agents has only been really recognized since the late 1970's.[107,110] They often required acidic or relatively harsh conditions to show a satisfactory reactivity. Recent investigations with more reactive complexes have demonstrated a variety of useful and unique reducing abilities, which nicely complements those of other organoborane reagents.[112,121]

Chiral amine-borane complexes have been reported to reduce aromatic ketones in the presence of Lewis acid with modest enantioselectively (e.e. $\leq$ 57%).[122] By contrast, following the pioneering work of the group of Itsuno,[123] considerable improvements were introduced by Corey and co-workers by simple modifications such as the use of the oxazaborolidine derived from (*S*)-2-(diphenylhydroxymethyl)pyrrolidine as a catalyst in the presence of borane tetrahydrofuran.[124] The mecanism of the reduction was assumed to involve an amine-borane complex, X-ray structure of which was recently determined (Scheme 39).[125] In the postulated

transition state, the carbonyl oxygen coordinates the boron atom of the oxazaborolidine ring *cis* to the BH_3 and intramolecular hydride transfer occurs selectively to a single face of the ketone.



Scheme 39

For the enzyme-like behaviour of the oxazaborolidine, which brings together the reductant and the carbonyl substrate, these boron heterocycles have been named 'chemzymes'. Numerous syntheses have been carried out taking advantage of this major advance in the enantioselective reduction of prochiral ketones to secondary alcohols.[126] Terpenic azaborocyclohexanes [127] and oxazaphospholidines [128] complexed with BH_3 have also been reported more recently as promising enantioselective reducing agents (Figure 5).

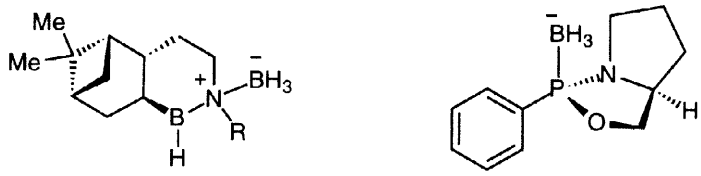
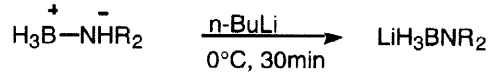


Figure 5. Azaborocyclohexane- and oxazaphospholidine-borane complexes

Lithium aminoborohydrides are a new class of powerful reducing agents comparable in power with lithium aluminium hydride.[129] These non-pyrophoric and thermally stable species were easily prepared in large scale from almost any amine-borane complexes, thus allowing control of the steric and electronic environment of these reagents (Scheme 40).

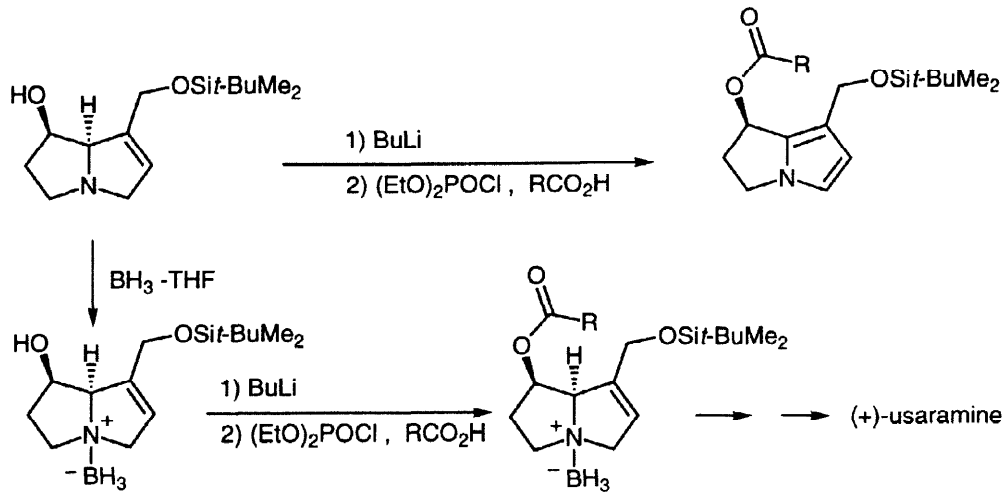


Scheme 40

A number of other reductive processes involving *N,N*-diethylaniline-halogenoboranes have been also described : reductive dimerization of sulfonyl chlorides to disulfides, deoxygenation of sulfoxides,[130] reductions of amides, iodination of alcohols, reductive iodinations of ketones and carboxylic acids, [131] cleavage of ethers, geminal diacetates,[132] and lactones [133], hydroiodic acid addition to alkenes and alkynes.[134]

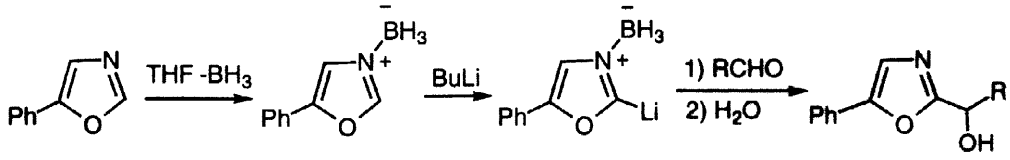
4.4. BH_3 as a protecting or an activating group of amines and phosphines

Borane complexation of amines appears to be a useful method for preventing undesired reactions. For example, anhydrovinblastine-BH_3 has the advantage of being highly stable, while the base is known to be oxidized quickly and spontaneously by air oxygen into leurosine.[135] The formation of a considerable amount of pyrrole in the synthesis of (+)-usaramine was suppressed when the pyrrolizidine intermediate was first treated with borane-THF (Scheme 41).[136] In the case of dihydroconessine, selective protection of the dimethylamino group prevented reactions of cyanogen bromide and perbenzoic acid with the pyrrolidine moiety.[137]



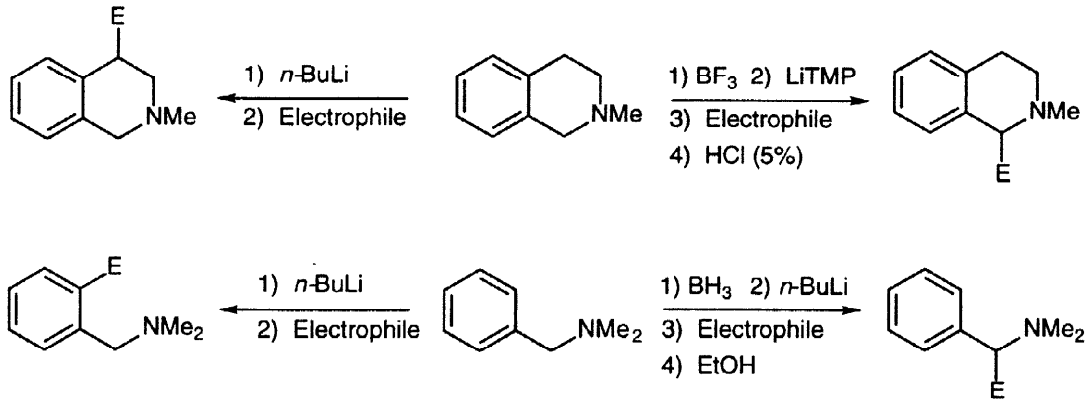
Scheme 41

Attempts to trap 2-lithiooxazoles with electrophiles contend with complications due to electrocyclic ring opening process. This troublesome anionic reaction is completely suppressed using a borane derivative (Scheme 42).[138] Direct access to lithiated aziridine-borane complexes has been also reported.[139]

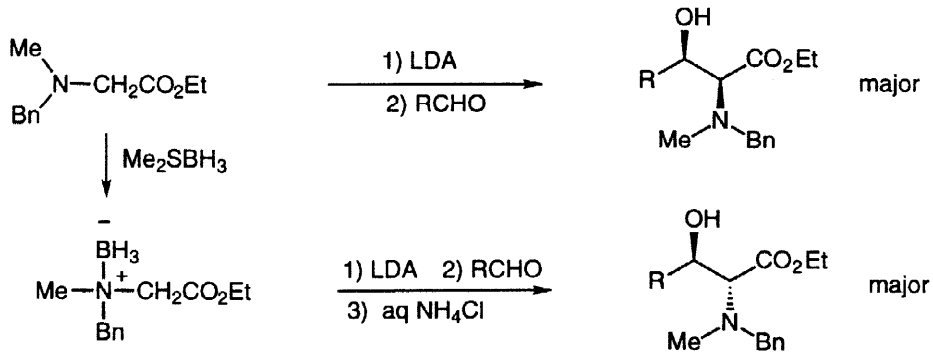


Scheme 42

Boron complexation has also found valuable synthetic applications in the activation of tertiary amines.[140] α-Deprotonation is promoted and a number of α-amino carbanions can then be efficiently generated and trapped by various electrophiles, mostly with a modification of the regiochemical course of the reaction (Scheme 43).[141] Lewis acid addition also selectively affected the *anti/syn* ratio in aldol reactions of ethyl *N*-benzyl-*N*-methylglycinate (Scheme 44).[142]



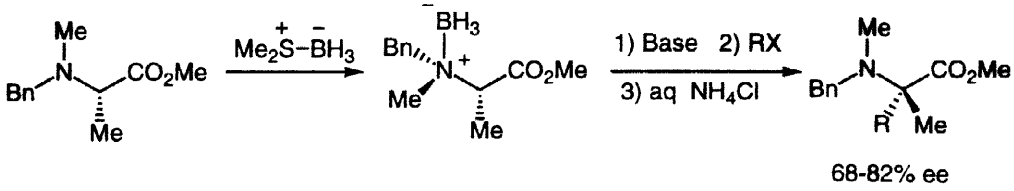
Scheme 43



Scheme 44

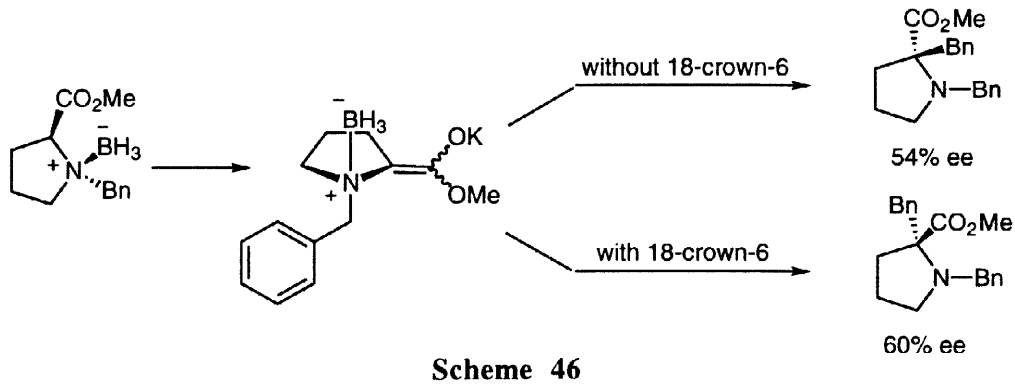
A pertinent review of this topic appeared very recently [143] and we have only selected some representative examples with regard to asymmetric synthesis. Alkylation of alanine

derivatives possessing a temporary stereogenic nitrogen atom afforded, after aqueous workup, disubstituted amino esters in enantomeric purities up to 82% (Scheme 45).[144]



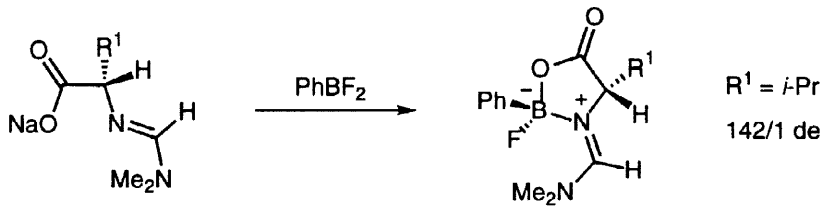
Scheme 45

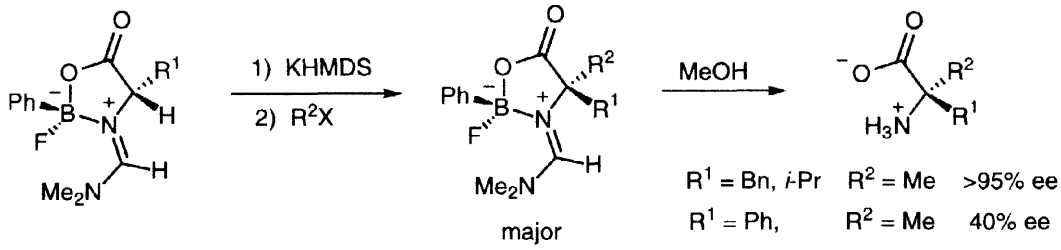
Inversion of the diastereoselectivity was observed in the reaction of potassium enolate of (*S*)-*N*-benzylproline methyl ester-BH_3 adduct in the presence *versus* in the absence of a crown ether (Scheme 46). [145]



Scheme 46

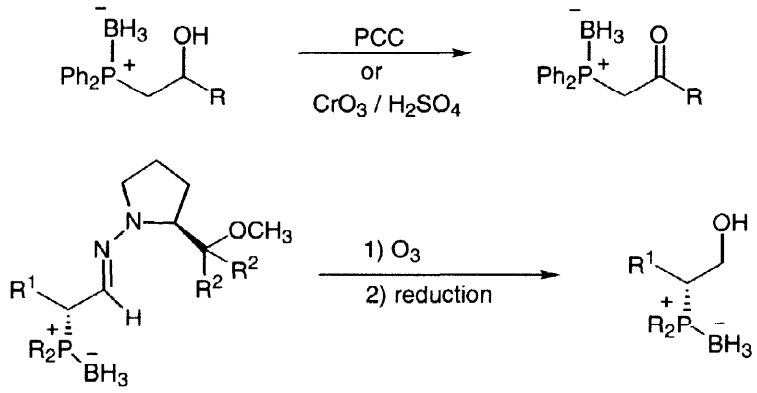
Another interesting approach has been reported in the deprotonation of oxazaborolidinones, which can also serve as chiral equivalents of aminoacid enolates. Crystallization of a mixture of phenyldifluoroborane and α-amidino carboxylates under conditions of second-order asymmetric transformation results in nearly complete conversion of the less soluble isomer. This technique affords relatively stable complexes having a single configuration at the stereogenic boron. Reaction of the corresponding potassium enolates with electrophiles allowed the synthesis of chiral α,α-dialkyl amino acids with high levels of optical purity (Scheme 47).[146]





Scheme 47

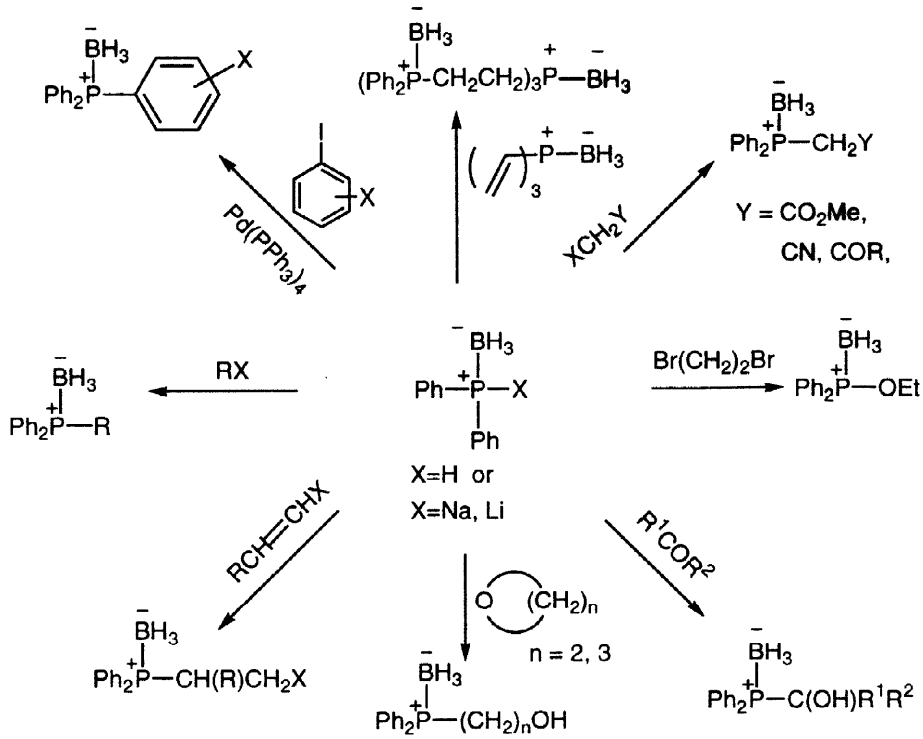
As for their nitrogen analogues, BH_3 can serve as protective group of phosphines during purification procedures [147] or during chemical manipulations such as alcohol [148] or hydrazone oxidation,[149] alkylation,[150] organozincs additions [151] or Wittig reactions [146] (Scheme 48). The electrosynthesis of a polypyrrole film bearing a diphosphine substituent protected from oxidation by borane complexation recently has been described.[152]



Scheme 48

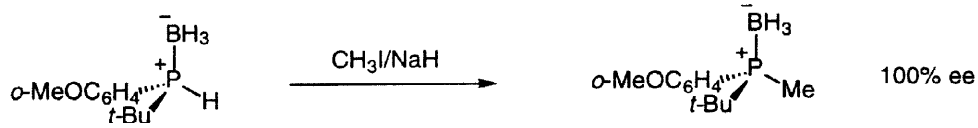
It is noteworthy that the addition of borane occurs with retention of configuration at the phosphorus atom.[153] The deboronation is also stereospecific and can be done with various reagents (Et_2NH [154], morpholine,[155] DABCO [156], HBF_4).[157] Quaternary phosphonium salts have been directly prepared from the corresponding borane complex by treatment with an alkylating agent in the presence of oct-1-ene.[158]

Besides a simple role of protection, complexation of phosphines with BH_3 has attracted the interest of several research groups because of the peculiar chemical properties of the resulting adducts. Secondary phosphine-boranes were easily deprotonated to give the corresponding anion, which have also been generated from triphenylphosphine-BH_3.[159] Treatment with a variety of electrophiles afforded new functionalized complexes in good yields (Scheme 49).

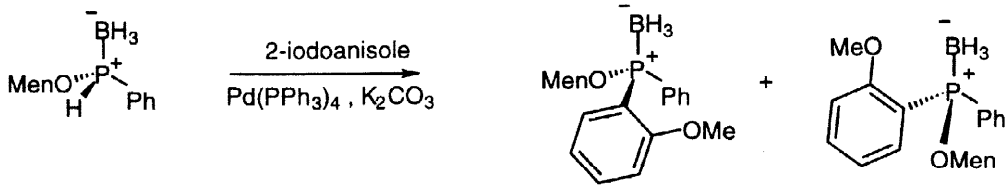


Scheme 49

In the synthesis of *P*-substituted-*o*-anisylcyclohexyl-(or *t*-butyl)phosphine-borane, the alkylation reaction occurred with retention of configuration (Scheme 50).[160] In contrast, the specificity of the palladium-catalyzed arylation reaction depended largely on the solvent and the base used (Scheme 51).[161]

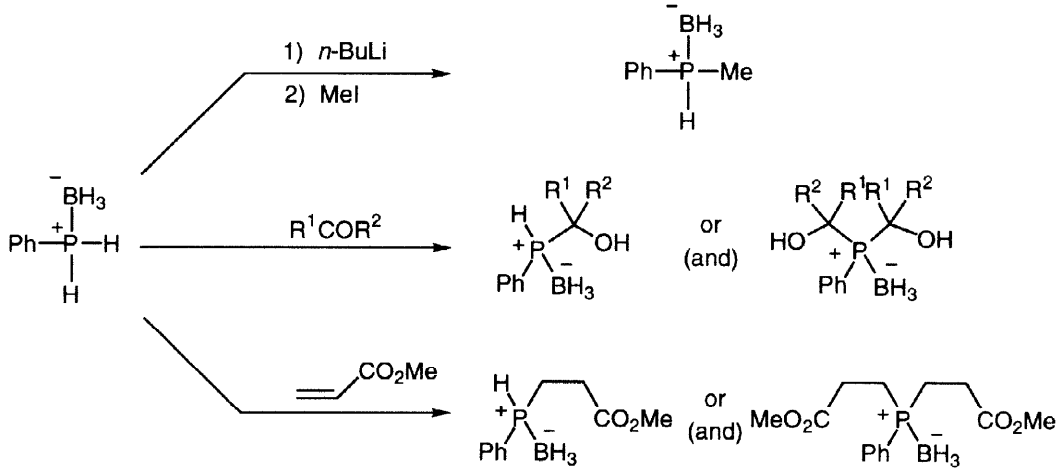


Scheme 50



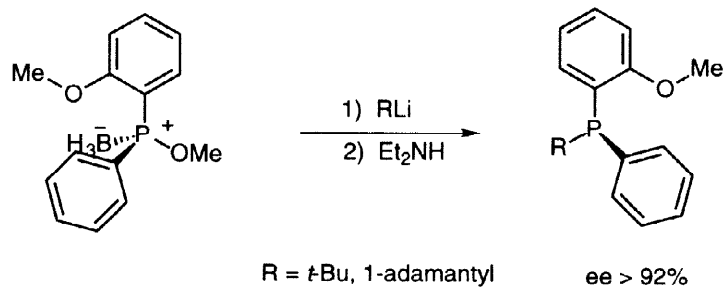
Scheme 51

P-H activation has been also applied in the case of primary phosphines. After treatment with *n*-butyllithium, alkylation with methyl iodide proceeded in high yield while hydrophosphination of carbonyl derivatives was carried out under neutral conditions.[162] Reactions with α,β-unsaturated esters afforded in reasonable yields either the mono- or the bis-adducts (Scheme 52).[163]



Scheme 52

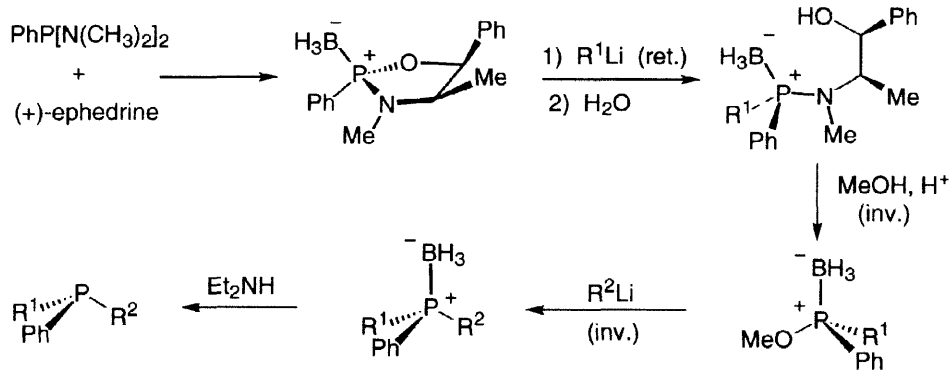
The reactions of optically active menthyloxymethylphenylphosphine-borane with organolithium compounds afforded the corresponding substitution products with high stereoselectivity and inversion of configuration.[164] In this way, bulky residues were introduced to give tertiary phosphines in greater than 92% ee (Scheme 53).[165]



Scheme 53

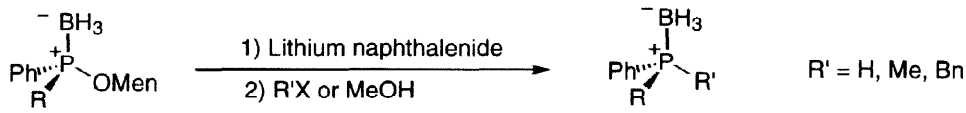
A successfull sequential double displacement was based on the use of pure diastereomeric crystalline oxazaphospholidines as precursors to chiral non-racemic phosphines. At low temperature, alkyl and aryl lithium reagents afforded the corresponding phosphinamides by stereoselective P-O bond cleavage, with retention of configuration at the phosphorus atom.

Acid methanolysis, followed by reactions with different organolithium compounds, yielded products in high enantiomeric excess that have been further increased by recrystallisation (Scheme 54).[166] The regio- and stereochemistry of nucleophilic attack at the *P*-chiral center of a dioxaphospholane-borane complex has also been studied by the same group.[167]



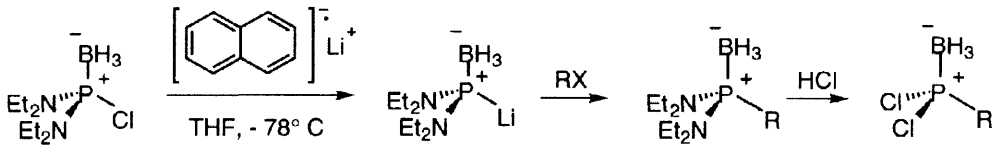
Scheme 54

Diastereoisomerically pure phosphine-boranes possessing a menthyloxy group were reduced by lithium naphtalenide with cleavage of the P-O bond. The subsequent reaction with electrophiles afforded the corresponding tertiary phosphine-boranes with good to excellent enantiomeric excess (Scheme 55).[168]



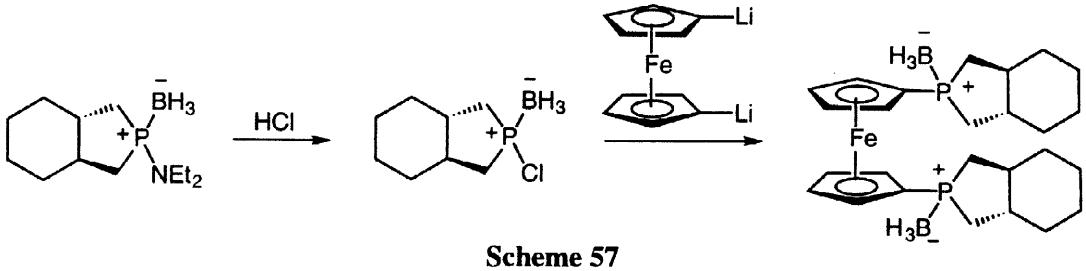
Scheme 55

In a related approach, lithiated bis-(diethylamino)phosphine-borane complex undergoes nucleophilic substitution with various organic halides in good yields. Interestingly, the amino groups can be readily replaced by chloride to afford dichlorophosphine-borane complexes (Scheme 56).[169]

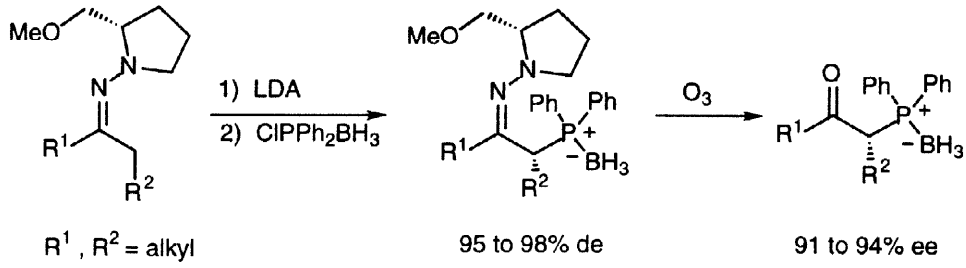


Scheme 56

These intermediates and their monochloro analogues, which can also be prepared by direct complexation of the corresponding phosphines with BH_3, were found to be excellent precursors for further chemistry.[170] They have been converted into triorganophosphines by addition of organometallics (Scheme 57)[169,171,172] or used in the synthesis of α-phosphanyl ketones and 2-phosphanyl alcohols (Scheme 58).[173]

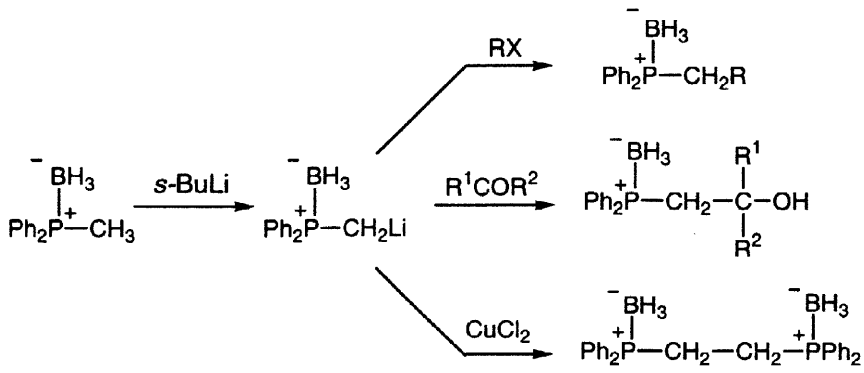


Scheme 57



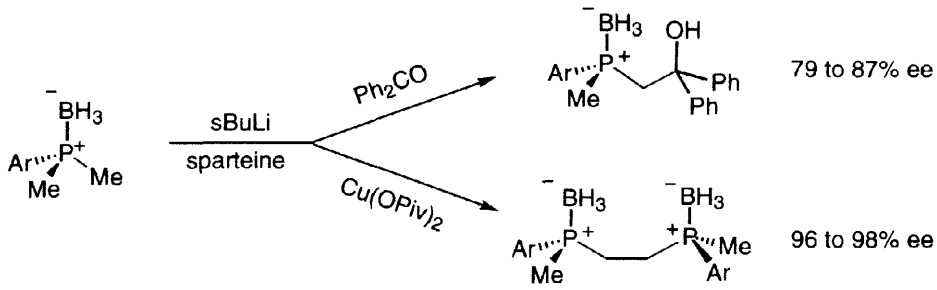
Scheme 58

As with the P-H bond, borane complexation activates the adjacent methyl group to deprotonation. The resulting carbanions reacted with alkyl halides and carbonyl compounds and underwent copper-promoted oxidative coupling to give diphosphines (Scheme 59).[170,174] Borane adducts of (3-anisyl)- and (3-fluorophenyl)diphenylposphine can be readily deprotonated at the heteroadjacent *para* position.[175]



Scheme 59

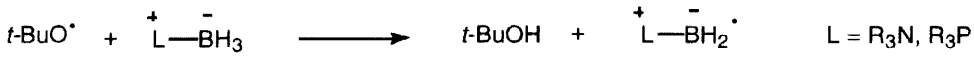
Enantioselective deprotonation has been achieved in the presence of sparteine as a route to C_2-symmetric *P*-chiral diphosphines (Scheme 60).[176]



Scheme 60

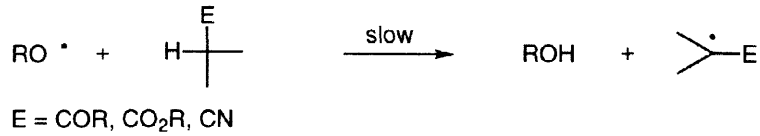
4.5. Amine- and phosphine-borane complexes in radical reactions.

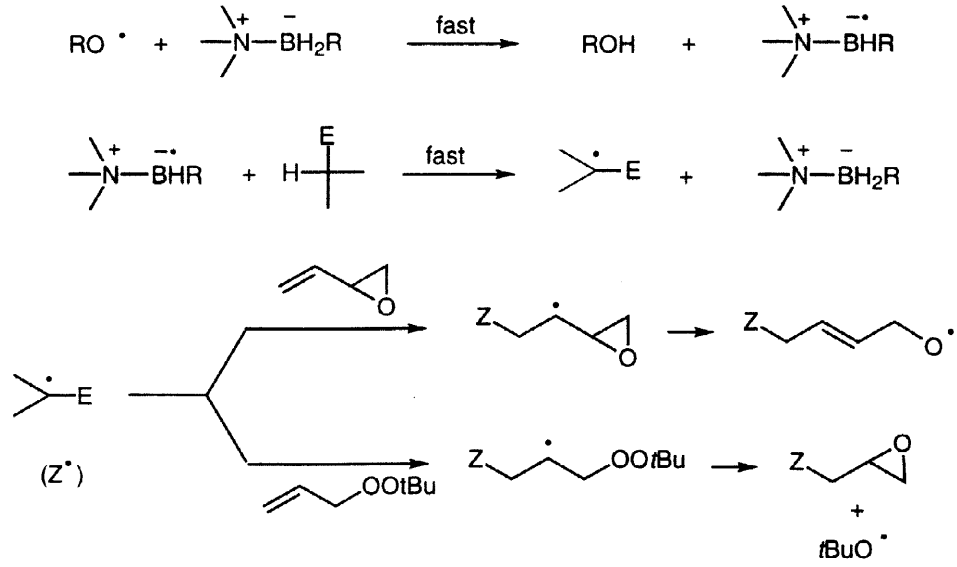
Amine- and phosphine-borane complexes have also found valuable applications in radical chemistry. Roberts's group has extensively studied the generation and the reactivity of amine- and phosphine-boryl radicals, mainly by ESR spectroscopy (Scheme 61).[177]



Scheme 61

They rapidly abstract halogen from simple alkyl bromides.[178] Addition to fullerene C_{60} was also recently reported.[179] Amine-borane complexes can function as polarity-reversal catalysts in hydrogen-atom abstraction reactions. The single-step abstraction by *t*-butoxyl radical is replaced by a two-step catalytic cycle. The electron-rich hydrogen atom is first abstracted from the amine-alkylborane to give a nucleophilic amine-boryl radical, which subsequently captures with high regioselectivity the hydrogen α to a carbonyl group.[180] α-Alkoxycarbonylalkyl radicals formed in this reaction add to vinylic epoxides and to allylic *tert*-butyl peroxides (Scheme 62). [181] The adducts radicals evolve into allyoxyl and *tert*-butoxyl radicals leading to chain reactions for the synthesis of allylic alcohols and 2,3-epoxypropanated products.





Scheme 62

Optically active amine-borane complexes have been used for kinetic resolution of racemic carbonyl-containing compounds under conditions of polarity-reversal catalysis.[182] It is also worth noting that primary aminyl-borane are able to transfer a β-hydrogen atom to simple alkenes to form alkyl radicals.[183] Phophine-boranes have been found to be good selective reagents for the deoxygenation of alcohol xanthate's.[184]

5. Miscellaneous Applications

5.1. Boron analogues of biomolecules

Boron analogues of biologically important molecules constitute an exciting class of organoboranes because of their potential medicinal value.[185] Of particular interest have been amine-carboxyboranes, which are isoelectronic and isostructural with their naturally occurring carbon counterparts (Figure 6).[186]

Figure 6. Amino acid derivatives and their boron analogues.

The replacement of a carbon by a boron atom has a profound effect on the pK_a. For example, H_3NBH_2COOH has a carboxyl group pKa of 8.3 compared to 2.4 for glycine.

Similarly, the pK_a for the ammonium deprotonation is >11 while, for glycine, it is 9.7.[187] Thus, while the compounds are similar in size and geometry, they have very different electronic and hydrogen bonding properties and, therefore, different biological responses. Indeed, a diverse array of aminoacid analogues, including precursors and derivatives (such as peptides), have been synthesized and have expressed a promising therapeutic potential, as antiproliferative, antiinflammatory, analgesic, and hypolipidemic agents.[188,189]

Another class of boron analogues of biomolecules are nucleosides and nucleic acid derivatives. Hydrolytically stable nucleosides cyanoboranes were prepared by an exchange reaction of silylated nucleosides with triphenylphosphine-cyanoborane (Figure 7).[190] 2'-Deoxycytidine-N^3-cyanoborane was shown to possess antineoplastic activity in murine and human cell cultures.[191]

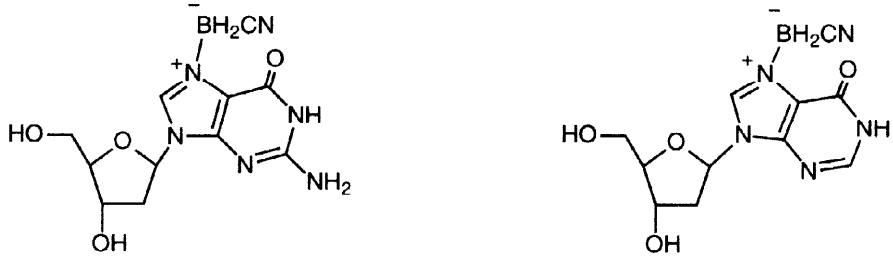
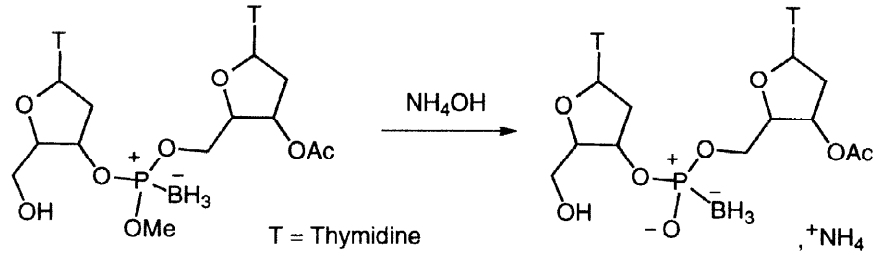


Figure 7. Nucleosides cyanoboranes

The "boronophosphates" oligonucleotides were prepared by treatment of a phosphite-borane with base (Scheme 63).[192] The internucleotide boronophosphate group is remarkably stable to basic and acidic hydrolysis and also quite stable to nucleases. This is of considerable importance for a possible use in antisense therapy and in boron neutron capture therapy (BNCT).[193]



Scheme 63

Related to these species are nucleoside triphosphates that are substrates for DNA polymerases and can be enzymatically incorporated into DNA during the polymerase chain reaction (Figure 8).[194]

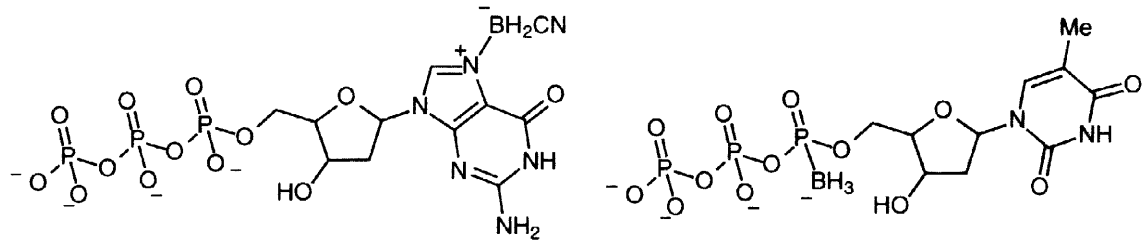
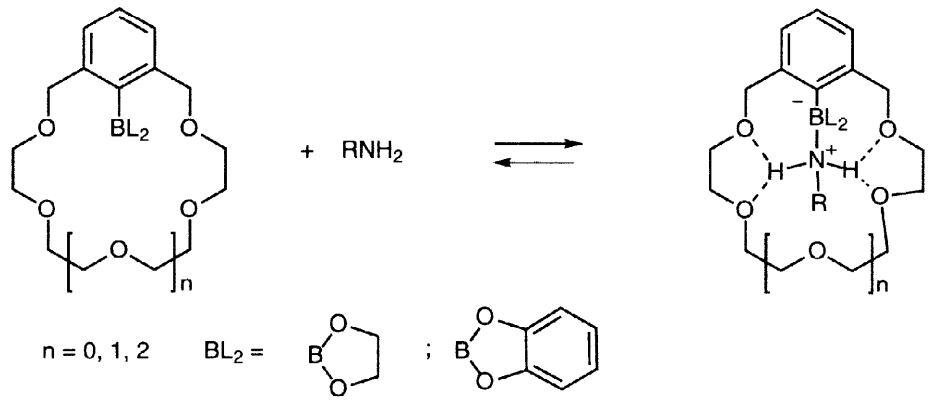


Figure 8. Boronated nucleoside triphosphates

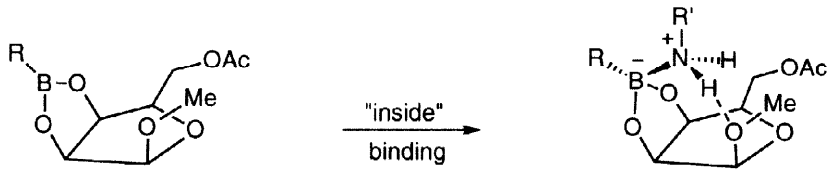
In a different area, it is also worth noting the design and the synthesis of saccharide-photoinduced electron transfer sensors based on the intramolecular interaction of a boronic acid unit and a tertiary amine.[195]

5.2. Molecular recognition with boron-containing host molecules

Host molecules containing a Lewis acid metal centre and donor sites selectively bind primary amines *via* three-point binding (Scheme 64). The presence of a reversible boron-nitrogen bond permit the simultaneous formation of hydrogen bonds with the donor positions situated spatially nearby.[196] Boronated lyxofuranosides serve also as heterotopic host molecules, multi-point binding occurring at the "inside" position due to synergistic effects (Scheme 65).[197]

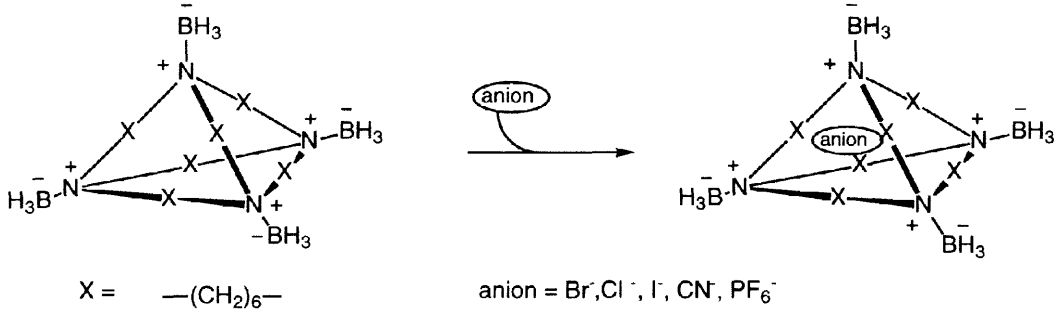


Scheme 64



Scheme 65

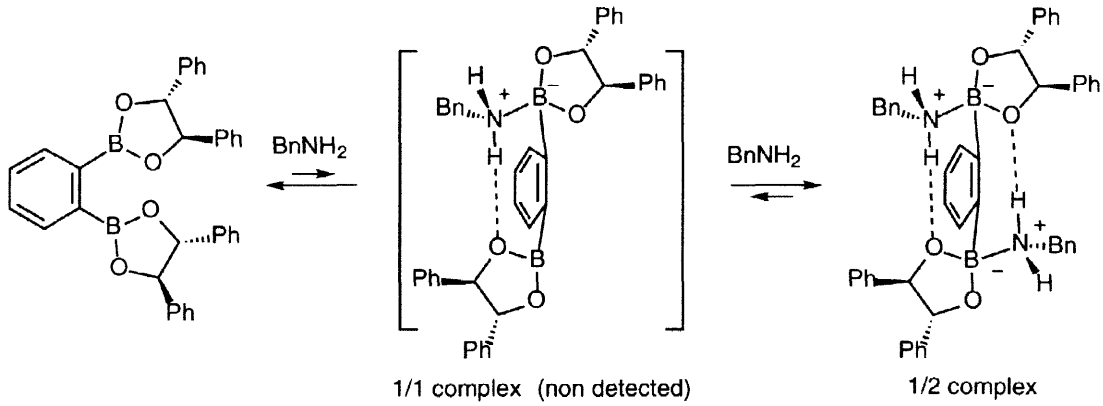
The addition of borane to a macrotricyclic tetramine produced a tetraadduct containing all four boron-nitrogen bonds in fixed orientation with their positive ends pointing towards the centre of the cavity (Scheme 66). The formation of host-guest inclusion complexes, which arose essentially from ion-dipole interactions, was confirmed ^{1}H NMR and by electrospray mass spectroscopy.[198]



Scheme 66

A new type of neutral paraquat receptor was described the structure of which incorporated two dative B-N dipoles fixed in convergent orientations that are complementary with the two cationic centres of paraquat.[199]

A chiral diboronic ester with two Lewis acid centers showed exceptionally strong binding with benzylamine. The formation of a 1/2 complex can be explained in terms of an allosteric effect. The first amine molecule coordinates with one of the two boron atoms. At the same time, one NH proton interacts with one of the two oxygen atoms in the other dioxaborolane ring to form a hydrogen bond. As a result, the two boronic esters are conformationally fixed to provide a preferable binding to the second amine molecule (Scheme 67).[200]



Scheme 67

Similarly, the Lewis acid, prepared from phenylboronic acid and (+)-tartaric acid, selects 1,6-diaminohexane over 1,2-diaminoethane by using two boron centres and two carbonyl oxygens (Figure 9). In the interaction with 1,2-diamino-1,2-diphenylethane, it chooses a different complexation pattern by recognizing the chiralitiy of the amine.[201]

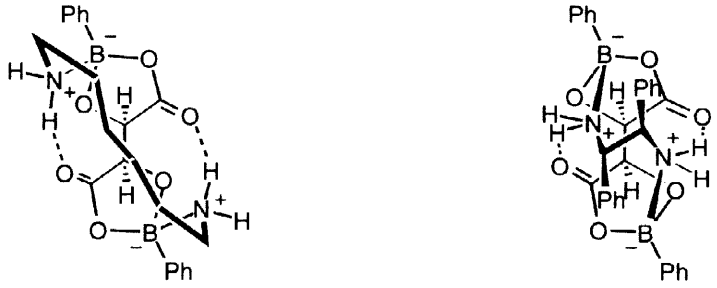
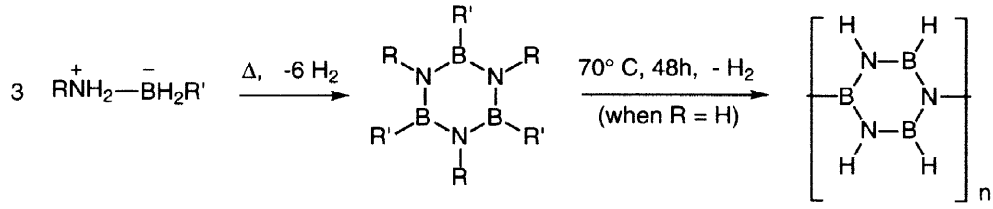


Figure 9. 1/1 Complexes of diamines and a chiral dioxaborolanone.

5.3. Borane complexes in material science

Thermolysis of amine-borane complexes produces borazines. The parent compound (R=H) readily dehydropolymerizes at moderate temperatures to afford polyborazylene $(B_3N_3H_4)_n$, which is a good precursor of boron nitride (Scheme 68).[202] The pyrolysis of pyridine-borane adducts in argon yields borocarbonitrides with graphite like, turbostatic structure.[203,204]

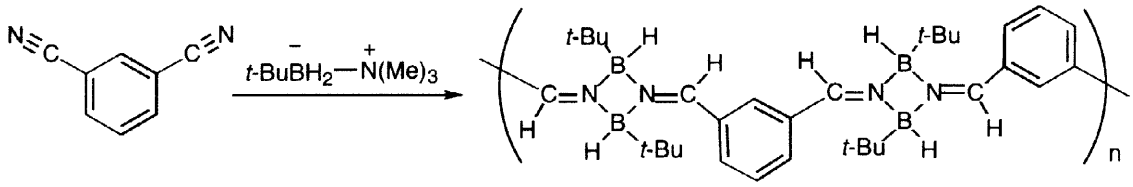


Scheme 68

Preceramic precursors containing Al-N-B linkages were produced from the reactions of Me_3NAlH_3 with NH_3BH_3 in 1:1 and 1:2 ratios in toluene solutions followed by treatment with liquid ammonia. Both precursors were transformed into intimate ceramic mixtures of AlN and BN *via* pyrolysis under NH_3 at 1000°C.[205] The synthesis of a boron-substituted polyaromatic mesophase was studied by copyrolysis of a filtered coal tar pitch with pyridine-borane under an argon atmosphere. These mesophases are potential precursors for the

production of boron-substituted sintered carbons.[206] Modification of SiC precursors with an amine-borane complex was recently reported. [207]

Hydroboration polymerisation of dicyano compounds with *t*-butylborane-trimethylamine complex produced boron-containing polymers. This reaction includes the dimerization of iminoborane to form the cycloborazane unit as the key step (Scheme 69).[208] Borane-amine complexes were also reported to be effective reagents with regard for cross-linking of elastomers.[209].



Scheme 69

A series of neutral pyridyl adducts involving strong Lewis acids BF_3 and $C6H6)_3$ has ben prepared and their secondorder nonlinear optical coefficints have been examined.[210]

6. Concluding remarks

Amine- and phosphine-borane complexes have stimulated research interest from chemists for nearly a century. However, it is only in the last three decades that a better understanding of their basic reactions has led to a wide range of new synthetic applications. Oxazaborolidines have proven to be very efficient catalysts in the enantioselective reduction of prochiral ketones and significant advances have been made in the preparation of chiral non-racemic phosphines by using borane both as a protecting and an activating group. Promising results were also reported in various areas, such as boron analogues of aminoacids and nucleotides, boron-containing host molecules and in materials sciences. The chemistry of amine- and phosphine-borane complexes will certainly find many other opportunities for further expansion into stereocontrolled transformations and other useful applications.

ADDENDUM

Several new results have been described in the literature since the original manuscript was submitted. We have not modified the initial text and the representative examples previously

chosen to illustrate the chemistry of amine- and phosphine-boranes. References from the end of 1997 to the middle of 1998 have been simply added and collated under the different topics.

Acknowledgments : We are grateful to the Conseil Régional de Bretagne for a doctoral fellowship (LM).

References and notes

1 For general reviews and books, see: (a) Pelter, A.; Smith, K.; Brown, H.C. *'Boranes Reagents'*, Katritzky, A.R.; Meth-Cohn, O.; Rees, C.W. Eds., Academic Press, New York, 1988. (b) *'Current Topics in the Chemistry of Boron'*, Kabalka, G. Ed., The Royal Society of Chemistry, Cambridge, 1994. (c) Matteson, D.S. *'Stereodirected Synthesis with Organoboranes'*, Springer, Berlin, 1995. (d) Vaultier, M.; Carboni, B. in *'Comprehensive Organometallic Chemistry II'*, Abel, E.V.; Stone, F.G.A.; Wilkinson, G. Eds., Pergamon Press, Oxford, 1995, Vol 11, p 191. (e) *'Advances in Boron Chemistry'*, Siebert, W. Ed., The Royal Society of Chemistry, Cambridge, 1997.

2 (a) Negishi, E.I. *J. Chem. Ed.* **1975**, *52*, 159. (b) Negishi, E.I. *J. Organomet. Chem.* **1976**, *108*, 281. (c) Cragg, G.M.L.; Koch, K.R. *Chem. Soc. Rev.* **1977**, *6*, 393. (d) Suzuki, A. *Acc. Chem. Res.* **1982**, *15*, 178. (e) Koster, R. in *'Organobor Verbindungen, Houben Weyl Methoden der Organischen Chemie'*, Köster, R. Ed., Thieme, Stuttgart, 1982, Vol. XIII 3b, p 749. (f) Odom, J.D. in *'Comprehensive Organometallic Chemistry'*, Wilkinson, G.; Stone, F.G.A.; Abel, E.W. Eds., Pergamon Press, Oxford, 1982, Vol. 1, p 296. (g) Negishi, E. in *'Comprehensive Organometallic Chemistry'*, Wilkinson, G.; Stone, F.G.A.; Abel, E.W. Eds., Pergamon Press, Oxford, 1982, Vol. 7, p 255, 265, 303, 323 and 337. (h) Suzuki, A. *Topics in Current Chemistry* **1983**, *112*, 67. (i) Mikhailov, B.M.; Bubnov, Y.N. in *'Organoboron Compounds in Organic Synthesis'*, Harwood Academic Publishers GmbH, Glasgow, 1984, p 433, 549 and 677. (j) Negishi, E.I.; Idacovage, M.J. *Org. React.* **1985**, *33*, 1. (k) ref 1a, p 280. (l) ref 1d p 220.

3 (a) Gerrard, W. *'The Organic Chemistry of Boron'*, Academic Press, London, 1961, p 161 and 187.(b) Niedenzu, K.; Dawson, J.W. in *'The Chemistry of Boron and its Compounds'*, Mutterties, E.L. Ed., Wiley, New York, 1967, p 377 and 617. (c) Nöth, H. *'Progress in Boron Chemistry'*, Steinberg, H.; Brotherton, R.J. Eds., 1970, p 211. (d) Lane, C.F. *Aldrichimica Acta* **1973**, *6*, 51. (e) Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287. (f) Köster, R. in *'Organobor Verbindungen, Houben Weyl Methoden der Organischen Chemie'*, Köster, R. Ed.; Thieme, Stuttgart, 1982, Vol.XIII 3b, p 423. (g) Odom, J.D. in *'Comprehensive Organometallic Chemistry'*, Wilkinson, G.; Stone, F.G.A.; Abel, E.W. Eds., Pergamon Press, Oxford, 1982, Vol. 1, p 298. (h) Hutchins, R.O.; Learn, K.; Nazer, B.; Pytlewski, D. *Org. Prep. Proced. Int.* **1984**, *16*, 335.

4 Housecroft, C.E. in *'Comprehensive Organometallic Chemistry II'*, Abel, E.W.; Stone, F.G.A.; Wilkinson, G., Eds., Pergamon, 1995, Vol.1, 129.

5 Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655.

Commun. **1989**, 900. Mohler, L.K.; Czarnik, A.W. *J. Am. Chem. Soc.* **1993**, *115*, 7037. Sutton, C.H.; Baize, M.W.; Todd, L.J. *Inorg. Chem.* **1994**, *33*, 4221. Györi, B; Kovács, Z.; Emri, J.; Berente, Z. *J. Organomet. Chem.* **1994**, *484*, 225. Györi, B.; Kovács, Z.; Emri, J.; Lázár I. *Inorg. Chim. Acta* **1994**, *218*, 21. Györi, B.; Berente, Z.; Emri, J.; Lázár, I. *Synthesis* **1995**, 191.

7 Györi, B. Emri, J. *J. Organomet. Chem.* **1982**, *238*, 159. Farfán, N.; Contreras, R. *Heterocycles* **1985**, *23*, 2989. Mancilla, T.; Contreras, R. *J. Organomet. Chem.* **1987**, *321*, 191. Brown, H.C.; Gupta, A.K. *J. Organomet. Chem.* **1988**, *341*, 73. Farfán, N.; Mancilla, T.; Castillo, D.; Uribe, G.; Carrillo, L.; Joseph-Nathan, P.; Contreras, R. *J. Organomet. Chem.* **1990**, *381*, 1.Vedejs, E.; Fields, S.C.; Schrimpf, M.R. *Pure Appl. Chem.* **1993**, *65*, 723. Snow, R.J.; Bachovchin, W.W.; Barton, R.W.; Campbell, S.J.; Coutts, S.J.; Freeman, D.M.; Gutheil, W.G.; Kelly, T.A.; Kennedy, C.A.; Krolikowski, D.A.; Leonard, S.F.; Pargellis, C.A.; Tong, L.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 10860. Vedejs, E.; Fields, S.C.; Lin, S.; Schrimpf, M.R. *J. Org. Chem.* **1995**, *60*, 3028. Ollivault, M.; Monnier, L.; Carboni, B. *Tetrahedron: Asymmetry* **1997**, *8*, 1955. For the synthesis of an enantiomerically pure planar-borabenzene complex, see: Tweddell, J.; Hoic, D. A.; Fu, G. C. *J. Org. Chem.* **1997**, *62*, 8286. For a direct observation of stereotopic group recognition in solution and solid state, see : Huskens, J.; Goddard, R.; Reetz, M. *J. Am. Chem. Soc.* **1998**, *120*, 6617.

8 Burg, A.B.; Green, A.A. *J. Am. Chem. Soc.* **1943**, *65*, 1838.

9 Brinck, T.; Murray, J.S.; Politzer, P. *Inorg. Chem.* **1993**, 32, 2622.

10 Brown, H.C. in '*Borane in Organic Chemistry*', Cornell University Press, **1972**, New York, p 53. See also : Flores-Segura, H.; Torres, L.A. *Struct. Chem.* **1997**, *8*, 227.

11 Wada, M.; Kanzaki, M.; Ogura, H.; Hayase, S.; Erabi, T. *J. Organomet. Chem.* **1995**, *485*, 127.

12 Bradley, D.C.; Hursthouse, M.B.; Motevalli, M.; Zheng, D.H. *J. Chem. Soc., Chem. Commun.* **1991**, *101*, 7. Bradley, D.C.; Harding, I.S.; Keefe, A.D.; Motevalli, M.; Zheng, D.H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931.

13 Burgemeister, T.; Grobe-Einster, R.; Grotstollen, R.; Mannschreck, A.; Wulf, G. *Chem. Ber.* **1981**, *114*, 3403. Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1168. Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1554. Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1832. Toyota, S.; Oki, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2215. Toyota, S.; Futawaka, T.; Ikeda, H.; Oki, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2499. Similar phosphorus derivatives have been also prepared : Müller, G.; Lachmann, J. *Z. Naturforsch.* **1993**, *48b*, 1248.

14 Schmidbaur, H.; Sigl, M.; Schier, A. R. *J. Organomet. Chem.* **1997**, *529*, 323. Sigl, M.; Schier, A.; Schmidbaur, H. *Chem. Ber./Recueil* **1997**, *130*, 951. See also : Gaumont, A.C.; Bourumeau, K.; Denis, J.M.; Guenot, P. *J. Organomet. Chem.* **1994**, *484*, 9.

15 For some supplementary examples, see: Arbuzov, B.A.; Nikonov, G.N. *Rev. Hetero. Chem.* **1990**, *3*, 1. Biedrzycki, M.; Scouten, W.H.; Biedrzycka, Z. *J. Organomet. Chem.* **1992**, *431*, 255. Farfán, N.; Silva, D.; Santillan, R. *Heteroatom Chem.* **1993**, *4*, 533. Mohler, L.K.; Czarnik, A.W. *J. Am. Chem. Soc.* **1993**, *115*, 7037. Vedejs, E.; Fields, S.C.; Schrimpf, M.R. *Pure Appl. Chem.* **1993**, *65*, 723. Snow, R.J.; Bachovchin, W.W.; Barton, R.W.; Campbell, S.J.; Coutts, S.J.; Freeman, D.M.; Gutheil, W.G.; Kelly, T.A.; Kennedy, C.A.; Krolikowski, D.A.; Leonard, S.F.; Pargellis, C.A.; Tong, L.; Adams, J. *J. Am. Chem. Soc.* **1994**, *116*, 10860. Kliegel, W.; Riebe, U.; Rettig, S.J.; Trotter, J. *Can. J. Chem.* **1995**, *73*, 835.Vedejs, E.; Fields, S.C.; Lin, S.; Schrimpf, M.R. *J. Org. Chem.* **1995**, *60*, 3028. Wrackmeyer, B.; Maisel, H.E.; Milius, W. *Z. Naturforsch.* **1995**, *50b*, 809. Balueva, A.S.;

Mustakimov, E.R.; Nikonov, G.N., Pisarevskii, A.P.; Struhkov, Y.T.; Litvinov, I.A.; Musin, R.R. *Russ. Chem. Bull.* **1996**, *45*, 1965. Ollivault, M.; Monnier, L.; Carboni, B. *Tetrahedron: Asymmetry* **1997**, *8*, 1955. Ashe, A. J.; Kampf, J. W.; Waas, J. R. *Organometallics*, **1997**, *16*, 163. Höpfl, H.; Farfán, N.; Castillo, D.; Santillan, R.; Contreras, R.; MartinezMartinez, F. J.; Galvan, M.; Alvarez, R.; Fernandez, L.; Halut, S.; Daran, J. C. *J. Organomet. Chem.* **1997**, *544*, 175. Höpfl, H.; Farfán, N. *J. Organomet. Chem.* **1997**, *547*, 71. Cruz, A.; MaciasMendoza, D.; BarraganRodriguez, E.; Tlahuext, H.; Noth, H.; Contreras, R. *Tetrahedron: Asymmetry* **1997**, *8*, 3903. AndradeLopez, N.; CartasRosado, R.; GarciaBaez, E.; Contreras, R.; Tlahuext, H. *Heteroatom Chem.* **1998**, *9*, 399. For a soluble polymer approach to the purification of β-amino alcohols using borinate complexes, see: Kim, M.; Janda, K.D. *J. Org. Chem.* **1998**, *62*, 889.

16 Gay-Lussac, J.L.; Thenard, J.L. *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, *2*, 210.

17 Nxumalo, L.M.; Andrzejak, M.; Ford, T.A. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 377 and references therein.

18 Bühl, M.; Steinke, T.; von Ragué Schleyer, P. Boese, R. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1160. Brinck, T.; Murray, J.S.; Politzer, P. *Inorg. Chem.* **1993**, *32*, 2622. Jonas, V.; Frenking G. *J. Chem. Soc.,Chem. Commun.* **1994**, 1489. Jonas, V.; Frenking, G.; Reetz, M.T. *J. Am. Chem. Soc.* **1994**, *116*, 8741. Fujiang, D.; Fowler, P.W.; Legon, A.C. *J. Chem. Soc.,Chem. Commun.* **1995**, 113. Nxumalo, L.M.; Andrzejak, M.; Ford, T.A. *Vibrational Spectroscopy* **1996**, *12*, 221. Durig, J.R.; Shen, Z. *J. Mol. Stuct. (Theochem)* **1997**, *397*, 179. Rablen, P.R. *J. Am. Chem. Soc.* **1997**, *119*, 8350 and references therein. Anane, H.; Boutalib, A.; Tomas, F. *J. Phys. Chem. A* **1997**, *101*, 7879. Höpfl, H.; Galvan, M.; Farfan, N.; Santillan, R. *J. Mol. Stuct. (Theochem)* **1998**, *427*, 1.

19 Crabtree, R.H.; Siegbahn, P.E.; Eisenstein, O.; Rheingold, A.L.; Koetzle, T.F. *Acc. Chem. Res.* **1996**, *29*, 348.

20 Wrackmeyer, B.; Köster, R. in *'Houben Weyl, Methoden der Organischen Chemie'*, Köster, R. Ed., Thieme, Stuttgart, 1984, Vol XIIIc, p 519.

21 Bruce, M.I. in *'Comprehensive Organometallic Chemistry II'*, Abel, E.W.; Stone, F.G.A.; Wilkinson, G., Eds., Pergamon, 1995, vol.13, p 107. The synthesis of new phosphine- and amine-boranes complexes is often accompanied with the corresponding X-ray data. For some specific recent references on X-ray analysis of amine- or phosphine-borane adducts, see: Ferguson, G.; Kaitner, B.; Myers, M.; Spalding, T.R. *Acta Cryst.*, **1990**, *C46*, 125. Blumenthal, A.; Bissinger, P.; Schmidbaur, H. *J. Organomet. Chem.* **1993**, *462*, 107. Nagawa, Y.; Goto, M.; Honda, K.; Nakanishi, H. *Analytical Sciences* **1994**, *10*, 525. Wrackmeyer, B.; Maisel, H.E.; Milius, W. *Z. Naturforsch.* **1995**, *50b*, 809. Day, M.W.; Mohr, B.; Grubbs, R.H. *Acta Cryst.* **1996**, *C52*, 3106. Bradley, D.C.; Harding, I.S.; Keefe, A.D.; Motevalli, M.; Zheng, D.H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931. Robinson, P.D.; Groziak, M.P.; Yi, L. *Acta Cryst.*, **1996**, *C52*, 2826. Lube, M. S.; Wells, R. L.; White, P. S. Inorg. Chem. **1996**, *35*, 5007. Mancilla, T.; Höpfl, H.; Bravo, G.; Carrillo, L. *Main Group Metal Chemistry* **1997**, *20*, 31. Qiao, S.; Hoic, D.A.; Fu, G.C. *Organometallics* **1997**, 16, 1501. Maderna, A.; Pritzkow, H.; Siebert, W.; Sommerfeld, T.; Cederbaum, L. S. *Z. Naturforsch.* **1997**, *52b*, 1315. Brown, D. S.; Carmalt, C. J.; Cowley, A. H.; Decken, A.; Isom, H. S. *Heteroatom Chem.* **1998**, *9*, 79. Schlengermann, R.; Sieler, J.; Hey Hawkins, E. *Main Group Chem.* **1997**, *2*, 141.

22 Nöth, H.; Wrackmeyer, B. in *'NMR Basic Principles and Progress'*, Diehl, P.; Fluck, E.; Kosfeld, R. Eds., Springer Verlag, Berlin, 1978. Hermanek, S. *Chem. Rev.* **1992**, *92*, 325. Szántay Jr, C.; Balázs,

M.; Bölcskei, H.; Szántay, C. *Tetrahedron* **1991**, *47*, 1265. Flores-Parra, A.; Fárfan, N.; Hernández-Bautista, A. I.; Fernández-Sánchez, L.; Contreras, R. *Tetrahedron* **1991**, *47*, 6903. Deng, R.M.K.; Dillon, K.B. *Polyhedron*, **1992**, *11*, 397. Wrackmeyer, B.; Kupce, E.; Koster, R.; Seidel, G. *Magn. Res. Chem.* **1992**, *30*, 393. Ariza-Castolo, A.; Paz-Sandoval, M. A.; Contreras, R. *Magn. Res. Chem.* **1992**, *30*, 520. Penner, G.H.; Daleman, S.I.; Custodio, A.R. *Can. J. Chem.*, **1992**, *70*, 2420. Padilla-Martinez, I. I.; Ariza-Castolo, A.; Contreras, R. *Magn. Res. Chem.* **1993**, *31*, 189. Farfán, N.; Silva, D.; Santillan, R. *Heteroatom Chem.* **1993**, *4*, 533. Power, W.P. *J. Am. Chem. Soc.* **1995**, *117*, 1800. Penner, G.H.; Zhao, B.; Jeffrey, K.R. *Z. Naturforsch.* **1995**, *50a*, 81. Martinez-Aguilera, L.M.R.; Cadenas-Pliego, G.; Flores-Parra, A.; Contreras, R. *Tetrahedron: Asymmetry* **1995**, *6*, 1585. Livant, P.; Majors, A.W.; Webb, T.R. *J. Org. Chem.* **1996**, *61*, 3061. Höpfl, H.; Farfán, N.; Castillo, D.; Santillan, R.; Contreras, R.; MartinezMartinez, F. J.; Galvan, M.; Alvarez, R.; Fernandez, L.; Halut, S.; Daran, J. C. *J. Organomet. Chem.* **1997**, *544*, 175.

23 Li, H.; Hardin, C.; Shaw, B. R. *J. Am. Chem. Soc.* **1996**, *118*, 6606.

24 Lee, K.J.; Livant, P.; McKee, M.L.; Worley, S.D. *J. Am. Chem. Soc.* **1985**, *107* 5901. Wiesmann, R.F.; Rademacher, P. *Chem. Ber.* **1994**, *127*, 1105.

25 Burg, A.B.; Schlesinger, H.I. *J. Am. Chem. Soc.* **1937**, *59*, 780.

26 Such a vast number of amine-boranes have been prepared that no attempt was made to list them. Tables cataloguing these compounds can be found in ref. 3. More recent compounds are described all along the review. For example, see: Zaidlewicz, M.; Brown, H.C. *'Advances in Boron Chemistry'*, Siebert, W. Ed., The Royal Society of Chemistry, Cambridge, **1997**, 171.

27 Brown, H.C.; Schlesinger, H.I.; Cardon, *J. Am. Chem. Soc.* **1942**, *64*, 325. S.Z. Baldwin, R.A.; Washburn, R.M. *J. Org. Chem.* **1961**, *26*, 3549. Mark Midland, M.M.; Kazubski, A. *J. Org. Chem.* **1992**, *57*, 2953.

28 Schaeffer, G.W.; Anderson, E.R. *J. Am. Chem. Soc.* **1949**, *71*, 2143. For the use of a tetraethylammonium salt, see: Spielvogel B.F., Ahmed, F.U.; McPhail, A.T. *J. Am. Chem. Soc.* **1986**, *108*, 3824. For a crown-ether catalyzed reaction, see: Kampel, V.; Warshawsky, A. *J. Organomet. Chem.* **1994**, *469*, 15. For the generation of borane from sodium borohydride and iodine in the presence of the amine, see: Nainan, K.C.; Ryschkewitsch, G.E. *Inorg. Chem.* **1969**, *8*, 2671.

29 Hu, M.G.; Van Paasschen, J.M.; Geanangel, R.A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2147.

30 Polivka, Z.; Ferles, M. *Coll. Czech. Chem. Commun.*. **1969**, *34*, 3009. Baboulene, M.; Torregrosa, J.L.; Speziale, V.; Lattes, A. *Bull. Soc. Chim. Fr.* **1980**, 565. Goeller, B.; Dicko, A.; Baboulene, M. *Main Group Met.Chem.* **1997**, *20*, 795. For a detailed review of the hydroboration reactions of ω-amino alkenes, see: Mikhailov, B.M.; Bubnov, Y.N. in *'Organoboron Compounds in Organic Synthesis'*, Harwood Academic Publishers GmbH, Glasgow, 1984, p 127. A new surfactant family whose hydrophilic head contains an intramolecular borane-amine complex has been recently reported : Le Tourmelin, J.B.; Baboulene, M. *Langmuir*, **1996**, *12*, 2128.

31 Andrés, C.; Delgado, M.; Pedrosa, R. *Synth. Commun.*. **1992**, *22*, 829.

32 Fiaud, J.C.; Kagan, H.B. *Bull. Soc. Chim. Fr.* **1969**, 2742. Picot, A.; Lusinchi, X.; *Bull. Soc. Chim. Fr.* **1977**, 1227.

33 Ferey, V., Toupet, L., Le Gall, T., Mioskowski, C. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 430.

34 Ferey, V.; Vedrenne, P.; Toupet, L.; Le Gall, T.; Mioskowski, C. *J. Org. Chem.* **1996**, *61*, 7244.

35 Baldwin, R.A.; Washburn, R.M. *J. Org. Chem.* **1961**, *26*, 3549.

36 Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato K. *J. Am. Chem. Soc.* **1985**, *107*, 5301. Imamoto, T.; Oshiki,T.; Onozawa, T.; Kusumoto, T.; Sato K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

37 Gaumont, A.C.; Bourumeau, K.; Denis, J.M.; Guenot, P. *J. Organomet. Chem.* **1994**, *484*, 9.

38 As for their amino analogues, a vast number of phosphine-borane complexes have been descibed and no attempt was made to list them. Tables cataloguing these compounds can be found in ref. 3. More recent complexes are described throughout the review.

39 Langer, F.; Püntener, K.; Stürmer, R.; Knochel, P. *Tetrahedron: Asymmetry* **1997**, *8*, 715.

40 Köckritz, A.; Weigt, A.; Kant, M. *Phosphorus Sulfur and Silicon* **1996**, *117*, 287.

41 Shay, R.H.; Diel, B.N.; Schubert, D.M.; Norman, A.D. *Inorg. Chem.* **1988**, *27*, 2378.

42 Schmidbaur, H.; Sigl, M.; Schier, A. R. *J. Organomet. Chem.* **1997**, *529*, 323.

43 Keglevich, G.; Újszászy, K.; Szöllösy, A.; Ludányi, K.; Töke, L. *J. Organomet. Chem.* **1996**, *516*, 139.

44 Gatti, A.R.; Wartik, T. *Inorg. Chem.* **1966**, *5*, 329. Gatti, A.R.; Wartik, T. *Inorg. Chem.* **1966**, *5*, 2075. VanPaasschen, J.M.; Geanangel, R.A. *Can. J. Chem.* **1975**, *53*, 723.

45 Livant, P.; Majors, A.W.; Webb, T.R. *J. Org. Chem.* **1996**, *61*, 3061.

46 Miller, N.E.; Muetterties, E.L. *J. Am. Chem. Soc.* **1964**, *86*, 1033. For reviews on these boronium ions, see: Shitov, O.P.; Ioffe, S.L.; Tartakovskii, V.A.; Novikov, S. *Ups. Khim.* **1970**, *39*, 1913 (*Engl. Trans. : Russ. Chem. Rev.* **1970**, *39*, 906). Ryschkewistch, G.E. in *'Boron Hydride Chemistry'*, Mutterties, E.L., Ed.; Academic Press, New York, 1975, p 223.

47 Cadenas-Pliego, G.; Contreras, R.; Flores-Parra, A.; Daran, J.C.; Halut, S. *Phosphorus, Sulfur and Silicon* **1993**, *84*, 9.

48 Ariza-Castalo, A.; Contreras, R. in *'Current Topics in the Chemistry of Boron'* Kabalka, G.W., Ed.; Royal Society of Chemistry, Cambridge, 1994, p 91.

49 Nainan, K.C.; Ryschkewitsch, G.E. *Inorg. Chem.* **1969**, *8*, 2671. Beres, J.; Dodds, A., Novabito, A.J.; Adams, R.M. *Inorg. Chem. Acta* **1971**, *10*, 2072. Martin, D.R.; Merkel, C.M.; Ruiz, J.P.; Mondal, J.U. *Inorg. Chem. Acta* **1985**, *100*, 293. Martin, D.R.; Merkel, C.M.; Ruiz, J.P. *Inorg. Chem. Acta* **1986**, *115*, L29. Schmidbaur H.; Stutzer A.; Bissinger P.; Schier A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1519. Börner, A.; Ward, J.; Ruth, W.; Holz, J.; Kless, A.; Heller, D., Kagan, H. *Tetrahedron* **1994**, *50* 10419. Seitz, T.; Muth, A.; Huttner, G. *Chem. Ber.* **1994**, *127*, 1837. Longeau, A.; Langer, F.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 2209. Longeau, A.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 6099. Langer, F.; Püntener, K.; Stürmer, R.; Knochel, P. *Tetrahedron: Asymmetry* **1997**, *8*, 715. Longeau, A.; Durand, S.; Spiegel, A.; Knochel, P. *Tetrahedron: Asymmetry* **1997**, *8*, 987.

50 Marinetti, A.; Kruger, V.; Buzin, F.X. *Tetrahedron Lett.* **1997**, *38*, 2947.

51 Schmidbaur, H.; Wimmer, T.; Grohmann, A.; Steigelmann, O.; Müller, G. *Chem. Ber.* **1989**, *122*, 1607. Schmidbaur, H.; Wimmer, T.; Lachman, J.; Müller, G. *Chem. Ber.* **1991**, *124*, 275. Schmidbaur, H.; Stützer, A.; Herdtweck, E. *Chem. Ber.* **1991**, *124*, 1095. Schmidbaur, H.; Stützer, A.; Bissinger,

P.; Schier, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1519. Seitz, T.; Huttner, G.; Büchner, M. *Z. Naturforsch.* **1994**, *49b*, 1813. Baudler, M.; Block, C. *Z. Anorg. Allg. Chem.* **1996**, *622*, 2035, 2042 and 2519. Antelmann, B.; Winterhalter, U.; Huttner, G.; Janssen, B. C.; Vogelgesang, J. *J. Organomet. Chem.* **1997**, *546*, 407.

52 Hawthorne, M.F. *J. Am. Chem. Soc.* **1961**, *83*, 831.

53 Brown, H.C.; Gupta, S.K. *J. Am. Chem. Soc.* **1971**, *93*, 4062.

54 Singaram, B.; Cole, T.E.; Brown, H.C. *Organometallics* **1984**, *3*, 774. Cole, T.E.; Bakshi, R.K.; Singaram, B.; Sbreknik, M.; Brown, H.C. *Organometallics* **1986**, *5*, 2303.

55 Negishi, E.I.; Brown, H.C. *Synthesis* **1974**, 77.

56 Brown, H.C.; Schwier, J.R.; Singaram, B. *J. Org. Chem.* **1978**, *43*, 4395. Brown, H.C., Mandal, A.K., Yoon, N.M., Singaram, B., Schwier, J.R., Jadhav, P.K. *J. Org. Chem.* **1982**, *47*, 5069. Brown, H.C.; Cole, T.E.; Srebnik, M.; Kim, K.W. *J. Org. Chem.* **1986**, *51*, 4925.

57 Bestmann, H.J.; Röder, T.; Sühs, K. *Chem. Ber.* **1988**, *121*, 1509.

58 Uppal, S.S.; Kelly, H.C. *J. Chem. Soc., Chem. Commun.* **1970**, 1619.

59 Wisian-Neilson, P.; Das, M.K.; Spielvogel B.F *Inorg. Chem.* **1978**, *17*, 2327. Das, M.K.; Roy, S. *Synth. React. Inorg. Met-Org. Chem.* **1985**, *15*, 53. Burnham, B.; Chen, S.Y.; Rajendran, K.G.; Sood, A.; Spielvogel, B.F.; Yousef, J.A.; Burnham, B.; Hall, I.H. in *'Current Topics in the Chemistry of Boron'* Kabalka, G.W., Ed., Royal Society of Chemistry, Cambridge, 1994, p 189.

60 Das, M.K.; Mukherjee, P. *J. Chem. Res. (S)* **1987**, 368. Sood, C.K.; Sood, A.; Spielvogel, B.F.; Yousef, J.A.; Burnham, B.; Hall, I.H. *J. Pharm. Sci.* **1991**, *80*, 1133. Sood, A.; Sood, C.K.; Spielvogel, B.F.; Hall, I.H. *Tetrahedron* **1991**, *47*, 6915. Mittakanti, M.; Morse, K.W. *Inorg. Chem.* **1991**, *30*, 2434. For the synthesis of 2'-deoxynucleoside-cyanoboranes, see for example : Sood, A.; Spielvogel, B.F.; Shaw, B.R. *J. Am. Chem. Soc.* **1989**, *111*, 9234. Sood, A.; Spielvogel, B.F.; Shaw, B.R.; Carlton, L.D.; Burnham, B.S.; Hall, I.H.; Hall, E.S. *Anticancer Res.* **1992**, *12*, 335. Sood, A.; Shaw, B.R.; Spielvogel, B.F.; Hall, E.S.; Chi, L.K.; Hall, I.H. *Pharmazie*, **1992**, *47*, 833. Tomasz, J.; Shaw, B.R.; Porter, K.; Spielvogel, B.F.; Sood, A. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1373. Chen, Y.Q.; Qu, F.C.; Zhang, Y.B. *Tetrahedron Lett.* **1995**, *36*, 745.

61 Nöth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 2251.

62 Brown, H.C.; Cole, T.E.; Srebnik, M.; Kim, K.W. *J. Org. Chem.* **1986**, *51*, 4925. For a direct preparation of dialkylborane-complexes from the corresponding stable precursors, see: Brown, H.C.; Singaram, B. *Inorg. Chem.* **1979**, *18*, 53.

63 Mills, W.J.; Sutton, C.H.; Libby, E.; Todd, L.J. *Inorg. Chem.* **1990**, *29*, 302.

64 Tuchagues, J.P.; Laurent, J.P.; Mongeot, H.; Dazord, J.; Cueilleron, J. *J. Organomet. Chem.* **1973**, *54*, 69.

65 Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3070.

66 Drake, J.E.; Rapp, B. *J. Chem. Soc. Dalton Trans.* **1972**, 2341. VanPaasschen, J.M.; Geanangel, R.A. *Can. J. Chem.* **1975**, *53*, 723. Denniston, M.L.; Martin, D.R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1461. Bula, M.J.; Hartman, S.; Raman, C.V. *Can. J. Chem.* **1975**, *53*, 326. Brown, H.C.; Singaram, B. *Inorg. Chem.* **1979**, *18*, 53.

67 Snyder, H.R.; Konecky, M.S.; Lennarz, W.J. *J. Am. Chem. Soc.* **1958**, *80*, 3611. Beckett, M.A.; Strickland, G.C.; Varma, K.S.; Hibbs, D.E.; Hursthouse, M.B.; Abdul Malik, K.M. *Polyhedron* **1995**, *14*, 2623.

68 Bradley, D.C.; Harding, I.S.; Keefe, A.D.; Motevalli, M.; Zheng, D.H. *J. Chem. Soc., Dalton Trans.* **1996**, 3931.

69 Muller, G.; Lachmann, J. *Z. Naturforsch.* **1993**, *48b*, 1248. For related compounds, see: Braunschweig, H.; Dirk, R.; Englert, U. *Z. Anorg. All. Chem.* **1997**, *623*, 1093.

70 Clegg, W.; Dai, C.; Lawlor, F.J.; Marder, T.B.; Nguyen, P.; Norman, N.C.; Pickett, N.L.; Power, W.P.; Scott, A.J. *J. Chem. Soc., Dalton Trans.* **1997**, 839.

71 Pawelke, G.; Bürger, H. *Applied Organomet. Chem.* **1996**, *10*, 147.

72 Davis, R.E.; Brown, A.E.; Hopmann, R.; Kibby, C.L. *J. Am. Chem. Soc.* **1963**, *85*, 487.

73 Nöth, H.; Beyer, H. *Chem. Ber.* **1960**, *93*, 2251.

74 VanPaaschen, J.M.; Geanangel R.A. *J. Am. Chem. Soc.* **1972**, *94*, 2680.

75 Sisler, H.; Mathur, M.A. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1745.

76 Brown, M.P.; Heseltine, R.W.; Smith, P.A.; Walker, P.J. *J. Chem. Soc. (A)* **1970**, 410.

77 Frisch, M.A.; Heal, H.G.; Mackle, H.; Madden, I.O. *J. Chem. Soc.* **1965**, 899.

78 Ratajczak, S. *Bull. Soc. Chim. Fr.* **1960**, 487.

79 Jugie, G.; Laussac, J.P.; Laurent, J.P. *Bull. Soc. Chim. Fr.* **1970**, 2542.

80 Faulks, J.N.G.; Greenwood, N.N.; Morris, J.H. *J. Inorg. Nucl. Chem.* **1967**, *29*, 329.

81 Reddy, C.K.; Periasamy, M. *Tetrahedron Lett.* **1990**, *31*, 1919. Narayana, C.; Padmanabhan, S.; Kabalka, G.W. *Tetrahedron Lett.* **1990**, *31*, 6977. Reddy, C.K.; Periasamy, M. *Tetrahedron* **1992**, *48*, 8329. Das, M. K.; Saha, U.; Banerjee, R. *Ind. J. Chem. Sect. A* **1996**, *35*, 513.

82 Douglass, J.E. *J. Org. Chem.* **1966**, *31*, 962.

83 Wiggins, J.W.; Ryschkewitsch, G.E. *Inorg. Chim. Acta* **1970**, *4*, 33. Beachley, O.T.; Washburn, B. *Inorg. Chem.* **1975**, *14*, 120.

84 Bell, K.E.; Kelly, C.R.; Minter, D.E.; Kelly, H.C. *Inorg. Chim. Acta* **1993**, *211*, 187.

85 Ryschkewitsch, G.E.; Miller, V.R. *J. Am. Chem. Soc.* **1973**, *95*, 2836.

86 Györi, B.; Kovács, Z.; Emri, J.; Berente, Z. *J. Organomet. Chem.* **1994**, *484*, 225. Györi, B.; Kovács, Z.; Emri, J.; Lázár, I. *Inorg. Chim. Acta* **1994**, *218*, 21.

87 Bratt, P.J.; Brown, M.P.; Seddon, K.R. *J. Chem. Soc., Dalton Trans.* **1974**, 2161.

88 Schmidbaur, H.; Weiss, E. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 283.

89 Mills, W.J.; Todd, L.J.; Huffman, J.C. *J. Chem. Soc., Chem. Commun.* **1989**, 900.

90 Emri, J.; Györi, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1303.

91 Atchekzaï, J.; Ouassas, A.; R'kha, C.; Bonnetot, B.; Mongeot, H.; Frange, B. *Synth. React. Inorg. Met-Org. Chem.* **1991**, *21*, 1133. Atchekzaï, J.; Bonnetot, B.; Mongeot, H.; Boufi, S.; Frange, B. *Can. J. Chem.* **1992**, *70*, 2520.

92 Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287. Schmidbaur, H.; Wimmer, T.; Reber, G.; Müller, G. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1071. Sigl, M.; Schier, A.; Schmidbaur, H. *Chem. Ber./Recueil* **1997**, *130*, 1411 and references therein.

93 Györi, B.; Kovács, Z.; Emri, J.; Lázár, I. *Inorg. Chim. Acta* **1994**, *218*, 21. Emri, J.; Kovacs, Z.; Györi, B.; Lázár, I. *Inorg. Chim. Acta* **1994**, *223*, 155.

94 Davis Jr, J.H.; Madura, J.D. *Tetrahedron Lett.* **1996**, *37*, 2729.

95 Imamoto, T.; Oshiki, T. *Tetrahedron Lett.* **1989**, *30*, 383. Imamoto, T.; Asakura, K.; Tsuruta, H.; Kishikawa, K.; Yamaguchi, K. *Tetrahedron Lett.* **1996**, *37*, 503. Imamoto, T.; Hirakawa, E.; Yamanoi, Y.; Inoue, T.; Yamagushi, K.; Seki, H. *J. Org. Chem.* **1995**, *60*, 7697.

96 Imamoto, T. ; Hikosaka, T. *J. Org. Chem.* , **1994**, *59*, 6753. Blumenthal, A. ; Bissinger, P. ; Schmidbaur, H. *J. Organomet. Chem.* **1993**, *462*, 107.

97 Funke, M.A., Mayr, M., *Chem. Eur. J.* **1997**, *3*, 1214.

98 Vedejs, E.; Nguyen, T.; Powell, D.R.; Schrimpf, M.R. *Chem. Commun.* **1996**, 2721.

99 Spielvogel, B.F.; Wojnowich, L.; Das, M.K.; McPhail, A.T.; Hargrave, K.D. *J. Am. Chem. Soc.* **1976**, *98*, 5702. Spielvogel, B.F. in *'Advances in Boron and the Boranes'*, Liebman, J.F.; Greenberg, A.; Williams, R.E., Eds., VCH, New-York, 1988, p 329. Das, M.K.; Mukherjee, P. *J. Chem. Res. (S)* **1985**, 66. Mills, W.J.; Sutton, C.H.; Baize, M.W.; Todd, L.J. *Inorg. Chem.* **1991**, *30*, 1046. Sood, A.; Spielvogel, B.F. *Main Group Metal Chemistry* **1989**, *12*, 143. For the corresponding phosphorus derivatives, see: Wisian-Neilson, P.; Wilkins, M.A.; Weigel, F.C.; Foret, C.J.; Martin, D.R. *J. Inorg. Nucl. Chem.* **1981**, *43*, 457. Sood, A.; Sood, C.K.; Hall, I.H.; Spielvogel, B.F. *Tetrahedron* **1991**, *47*, 6915. Berente, Z.; Györi, B. *Chem. Commun.* **1997**, 1799.

100 Lázár, I.; Emri, J.; Györi, B.; Kovács, Z. *Polyhedron* **1994**, *13*, 2599.

101 Hall, I.H.; Starnes, C.O.; McPhail, A.T.; Wisian-Neilson, P.; Das, M.K.; Harchelroad Jr., P.; Spielvogel, B.F. *J. Pharm. Sci.* **1980**, *69*, 1025.

102 Spielvogel, B.F.; Ahmed, F.U.; McPhail, A.T. *Synthesis*, **1986**, 833. Mittakanti, M.; Feakes, D.A.; Morse, K.W. *Synthesis* **1992**, 380. Györi, B.; Kovács, Z.; Emri, J. ; Berente, Z. *J. Organomet. Chem.* **1994**, *484*, 225. Spielvogel, B.F.; Ahmed, F.U.; Silvey, G.L.; Wisian-Neilson, P.; McPhail, A.T. *Inorg. Chem.* **1984**, *23*, 4322. Györi, B.; Berente, Z.; Emri, J.; Lázár, I. *Synthesis*, **1995**, 191. For other derivatives of amine-carboxyborane, see: Das, M.K.; Mukherjee, P. *J. Chem. Res. (S)*, **1987**, 368. Sutton, C.H.; Baize, M.W.; Todd, L.J. *Inorg. Chem.* , **1994**, *33* , 4221.

103 Sood, A.; Sood, C.K.; Spielvogel, B.F.; Hall, I.H. *Eur. J. Med. Chem.* **1990**, *25*, 301. Hall, I.H.; Hall, E.S.; Miller III, M.C.; Sood, A.; Spielvogel, B.F. *Amino Acids.* **1993**, *4*, 287.

104 Bedel, C.; Foucaud, A. *Tetrahedron Lett.* **1993**, *34*, 311.

105 Monnier, L. Ph. D. Thesis, University of Rennes 1, 1997. Keglevich, G.; Újszászy, K.; Szöllôsy, A.; Ludányi, K.; Tõke, L. *J. Organomet. Chem.* **1996**, *516*, 139.

106 Imamoto, T.; Yamanoi, Y. *Chem. Lett.* **1996**, 705.

107 Lane, C.F. *Aldrichimica Acta* **1973**, *6*, 51.

108 Das, M.K.; Bandyopadhyay, S.N.; Bhattacharyya, S.; Banerjee, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2929. Bell, K.E.; Kelly, H.C. *Inorg. Chem.* **1992**, *31*, 2665. Bell, K.E.; Kelly, H.C. *Inorg. Chem.* **1996**, *35*, 7225. Murariev, D.; Warshawsky, A. *React. Funct. Polymer* **1996**, *29*, 185.

109 Frisch, M.A.; Heal, H.G.; Mackle, H.; Madden, I.O. *J. Chem. Soc.* **1965**, 899.

110 Hutchins, R.O.; Learn, K.; Nazer B., Pytlewski, D. *Org. Prep. Proced. Int.* **1984**, *16*, 335.

111 Brown, H.C.; Chandrasekharan, J. *J. Am. Chem. Soc.* **1984**, *106*, 1863. It is worth noting that the use of chiral amine-borane complexes with prochiral olefins gave, after oxidation, the corresponding alcohols in low enantiomeric excess. It indicates that the Lewis base was present in the hydroboration transition state. Narayana, C.; Periasamy, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1857. Andres, C.; Delgado, M.; Pedrosa, R. *Anal. Quimica.* **1993**, *89*, 630.

112 Zaidlewicz, M.; Brown, H.C. *'Advances in Boron Chemistry'*, Siebert, W. Ed., The Royal Society of Chemistry, Cambridge, **1997**, 171.

113 Rotermund, G.W.; Koster, R. *Justus Liebigs Ann. Chem.* **1965**, *686*, 153.

114 Ashby, E.C. *J. Am. Chem. Soc.* 1959, *81*, 4791. Baker, C.S.L. *J. Organomet. Chem.* **1969**, *19*, 287.

115 Pelter, A.; Rosser, R.; Mills, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1014. Brown, H.C.; Murray, K.J.; Murray, L.J.; Snover, J.A.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4233. Bestmann, H.J.; Sühs, K.; Röder, T. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 1038.

116 Brown, H.C.; Murray, L.T. *Inorg. Chem.* **1984**, *23*, 2746. Narayana, C.; Periasamy, M. *J. Organomet. Chem.* **1987**, *323*, 145. Zaidlewicz, M.; Brown, H.C. *'Advances in Boron Chemistry'*, Siebert, W. Ed., The Royal Society of Chemistry, Cambridge, **1997**, 171. Brown, H.C.; Kanth, B.J.V.; Zaidlewicz, M. *J. Org. Chem* **1998**, *63*, 5154.

117 Reddy, C.K.; Periasamy, M. *Tetrahedron* **1992**, *48*, 8329.

118 Soderquist, J.A.; Medina, J.R.; Huertas, R. *Tetrahedron Lett.* **1998**, *39*, 6119 and 6123.

119 Suseela, Y.; Bhanu Prasad, A.S.; Periasamy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 446.

120 Rao, M.L.; Periasamy, M. *Tetrahedron Lett.* **1995**, *36*, 9069.

121 Reddy, C.K.; Periasamy, M. *Tetrahedron* **1992**, *48*, 8329. Das, M.K.; Maiti, P.K.; Bhaumik, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 810. Chen, J.; Wayman, K.A.; Belshe, M.A.; DiMare, M. *J. Org. Chem.* **1994**, *59*, 523. Boman, M.D.; Guch, I.C.; DiMare, M. *J. Org. Chem.* **1995**, *60*, 5995. Salunke, A.M.; Burkhard, E.R. *Tetrahedron Lett.* **1997**, *38*, 1519.

122 Fiaud, J.C.; Kagan, H.B. *Bull. Soc. Chim. Fr.* **1969**, 2742. Grundon, M.F.; McCleery, D.G.; Wilson, J.W. *J. Chem. Soc., Perkin Trans. 1* **1981**, 231. Eleveld, M.B.; Hogeveen, H. Elevald *Tetrahedron Lett.* **1986**, *27*, 635. Kanth, J.V.B.; Periasamy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1145. Andres, C.; Delgado, M.; Pedrosa, R. *Ann. Quimica* **1993**, *89*, 629. Periasamy, M.; Kanth, J.V.B.; Reddy, C.K. *J. Chem. Soc., Perkin Trans. 1* **1995**, 427. Yamaguchi, Y.; Takada, A.; Okamoto, Y. *J. Het. Chem.* **1997**, *34*, 1737.

123 Hirao, A.; Itsuno, S.; Nakahama, S.; Yamazaki, N. *J. Chem. Soc., Chem. Commun.* **1981**, 315. Itsuno, S.; Ito, K.; Nakahama, S. *J. Chem. Soc., Chem. Commun.* **1983**, 469. Itsuno, S.; Nakano,

M.; Miyazaki, K.; Masuda, H.; Ito, K.; Hirao, A.; Nakahama, S. *J. Chem. Soc., Perkin Trans 1* **1985**, 2039.

124 Corey, E.J.; Bakshi, R.K.; Shibata, S. *J. Am. Chem. Soc.* **1987**, *109*, 5551.

125 Corey, E.J.; Azimioara, M.; Sarshar, S. *Tetrahedron Lett.* **1992**, *33*, 3429.

126 For some recent reviews, see: Matteson, D.S. '*Stereodirected Synthesis with Organoboranes*', Springer, Berlin, 1995, 353. Vaultier, M.; Carboni, B. in'*Comprehensive Organometallic Chemistry II*', Abel E.V.; Stone, F.G.A.; Wilkinson, G. Eds., Pergamon Press, Oxford, 1995, Vol 11, **191**. Deloux, L.; Srebnik, M. *Chem. Rev.* **1993**, *93*, 763. Wallbaum, S.; Martens, J. *Tetrahedron: Asymmetry* **1992**, *3*, 1475. Singh, V.K. *Synthesis* **1992**, 605. Corey, E.J.. Helal, C.H. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1987.For some recent references, see: Taraba, M.; Palecek, J. *Chem. List* **1997**, *91*, 9. Prasad, K.R.K.; Joshi, N.N. *Tetrahedron: Asymmetry* **1997**, *8*, 173. Reiners, I.; Martens, J. *Tetrahedron: Asymmetry* **1997**, *8*, 277. Almqvist, F.; Torstensson, L.; Gudmundsson, A.; Frejd, T. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 376. Simpson, A.F.; Szeto, P.; Lathbury, D.C.; Gallagher, T. *Tetrahedron: Asymmetry* **1997**, *8*, 673. Lang, A.; Noth, H.; Schmidt, M. *Chem. Ber. Recueil.* **1997**; *130*, 241. Salunkhe, A. M.; Burkhardt, E.R. *Tetrahedron Lett.* **1997**, *38*, 1523. Bellucci, C.M.; Bergamini, A.; Cozzi, P.G.; Papa, A.; Tagliavini, E.; UmaniRonchi, A. *Tetrahedron: Asymmetry* **1997**, *8*, 895. LeToumelin, J.B.; Baboulene, M. *Tetrahedron: Asymmetry* **1997**, *8*, 1259. Shimizu, M.; Tsukamoto, K.; Fujisawa, T. *Tetrahedron Lett.* **1997**, *38*, 5193. Kanoh, N.; Ishihara, J.; Murai, A. *Synlett* **1997**, 737. Mahsui, K.; Shiori, T. *Synlett* **1997**, 273. Felder, M.; Giffels, G.; Wandrey, C. *Tetrahedron: Asymmetry* **1997**, *8*, 1975. Ostendorf, M.; Romagnoli, R.; Pereiro, I.C.; Roos, E.C.; Moolenaar, M.J.; Speckamp, W.N.; Hiemstra, H. *Tetrahedron: Asymmetry*, **1997**, *8*, 1773. Woltersdorf, M.; Kranich, R.; Schmalz, H.G. *Tetrahedron* **1997**, *53*, 7219. Lewis, P.T.; Davis, C.J.; Saraiva, M.C.; Treleaven, W.D.; McCarley, T.D.; Strongin, R.M. *J. Org. Chem.* **1997**, *62*, 6110. Hull, K.G.; Visnick, M.; Tautz, W.; Sheffron, A. *Tetrahedron* **1997**, *53*, 12405. Reiners, I.; Groger, H.; Martens, J. *J. Prakt. Chem., Chem. Zeit.* **1997**, 339, 541. Speicher, A.; Eicher, T. *J. Prakt. Chem., Chem. Zeit.* **1997**, *339*, 594. Li, X.S.; Xie, R.G. *Tetrahedron: Asymmetry* **1997**, *8*, 2283. Higashijima, S.; Itoh, H.; Senda, Y.; Nakano, S. *Tetrahedron: Asymmetry* **1997**, *8*, 3107. Corey, E. J.; GuzmanPerez, A.; Lazerwith, S. E. *J. Am. Chem. Soc.* **1997**, *119*, 11769. Jones, G. B.; Heaton, S. B.; Chapman, B. J.; Guzel, M. *Tetrahedron: Asymmetry* **1997**, *8*, 3625. Calmes, M.; Escale, F.; Paolini, F. *Tetrahedron: Asymmetry* **1997**, *8*, 3691. Shen, Z. X.; Zhang, Y. W.; Lu, J.; Xu, X. N.; Lu, C. R. *Chin. J. Chem.* **1997**, *15*, 459. Brodfuehrer, P. R.; Smith, P.; Dillon, J. L.; Vemishetti, P. *Org. Proc. Res. Develop.* **1997**, *1*, 176. Schmidt, R.; Jockel, H.; Schmalz, H. G.; Jope, H. *J. Chem. Soc. Perkin Trans. 2* **1997**, 2725. Schmalz, H. G.; Jope, H. *Tetrahedron* **1998**, *54*, 3457. Pinho, P.; Guijarro, D.; Andersson, P. G. *Tetrahedron* **1998**, *54*, 7897. Zhou, Y. G.; Hou, X. L.; Dai, L. X. *Chin. J. Chem.* **1998**, *16*, 284. Bringmann, G.; Breuning, M. *Synlett* **1998**, 634. Masui, M.; Shioiri, T. *Tetrahedron Lett.* **1998**, *39*, 5195. Tamiaki, H.; Kouraba, M.; Takeda, K.; Kondo, S.; Tanikaga, R. *Tetrahedron : Asymmetry* **1998**, *9*, 2101. Fujisawa, T.; Onogawa, Y.; Shimizu, M. *Tetrahedron Lett.* **1998**, *39*, 6019. Bach, J.; Garcia, J. *Tetrahedron Lett.* **1998**, *39*, 6761. Bach, J.; Galobardes, M.; Garcia, J.; Romea, P.; Tey, C.; Urpi, F.; Vilarrasa, J. *Tetrahedron Lett.* **1998**, *39*, 6765. Cho, B. T.; Chun, Y. S. *J. Org. Chem.* **1998**, *63*, 5280. For polymer-bound oxazaborolidine catalysts, see: Giffels, G.; Beliczey, J.; Felder, M.; Kragl, U. *Tetrahedron: Asymmetry* **1998**, *9*, 691 and references therein.

127 Midland, M.M.; Kazubski A. *J. Org. Chem.* **1992**, *57*, 2953.

128 Brunel, J.M.; Pardignon, O.; Faure, B.; Buono, G. *J. Chem. Soc., Chem. Commun.* **1992**, 287. Buono, G.; Brunel, J.M.; Faure, B.; Pardignon, O. *Phosphorus, Sulfur, and Silicon* **1993**, *75*, 43. Brunel, J.M.; Buono, G. *Synlett* **1996**, 177. Chiodi, O.; Fotiadu, F.; Sylvestre, M.; Buono, G. *Tetrahedron Lett.* **1996**, *37*, 39. Brunel, J.M.; Chiodi, O.; Faure, B.; Fotiadu, F.; Buono, G. *J. Organomet. Chem.* **1997**, *529*, 285. For closely related systems with phosphinamides, see: Burns, B.; Merifield, E.; Mahon, M.F.; Molloy, K.C.; Wills, M. *J. Chem. Soc. Perkin Trans. 1*, **1993**, 2243. Burns, B.; King, N.P.; Studley, J.R.; Tye, H.; Wills, M. *Tetrahedron: Asymmetry* **1994**, *5*, 801. Gamble, M.P.; Studley, J.R.; Wills, M. *Tetrahedron: Asymmetry* **1996**, *7*, 3071. Burns, B.; Gamble, M.P.; Simm, A.R.C.; Studley, J.R.; Alcock, N.W.; Wills, M. *Tetrahedron: Asymmetry* **1997**, *8*, 73.

129 Fisher, G.B.; Harrison, J.; Fuller, J.C.; Goralski, C.T.; Singaram, B. *Tetrahedron Lett.* **1992**, *33*, 4533. Fuller, J.C.; Stangeland, E.L.; Goralski, C.T.; Singaram B. *Tetrahedron Lett.* **1993**, *34*, 257. Fisher, G.B.; Fuller, J.C.; Harrison, J.; Goralski, C.T.; Singaram, B. *Tetrahedron Lett.* **1993**, *34*, 1091. Fisher, G.B.; Fuller, J.C.; Harrison, J.; Alvarez, S.G.; Burkhardt, E.R.; Goralski, C.T.; Singaram, B. *J. Org. Chem.* **1994**, *59*, 6378. Harrison, J.; Fuller, J.C.; Goralski, C.T.; Singaram, B. *Tetrahedron Lett.* **1994**, *35*, 5201. Fuller, J.C.; Belisle, C.M.; Goralski, C.T.; Singaram, B. *Tetrahedron Lett.* **1994**, *35*, 5389. Harrison, J.; Alvarez, S.G.; Godjoian, G.; Singaram, B. *J. Org. Chem.* **1994**, *59*, 7193. Alvarez, S.G.; Fisher, G.B.; Singaram, B. *Tetrahedron Lett.* **1995**, *36*, 2567. Collins, C.J.; Fisher, G.B.; Reem, A.; Goralski, C.T.; Singaram, B. *Tetrahedron Lett.* **1997**, *38*, 529. See also : Myers, A.G.; Yang, B.H.; Kopecky, D.J. *Tetrahedron Lett.* **1996**, *37*, 3623.

130 Narayana, C.; Padmanabhan, S.; Kabalka, G.W. *Synlett* **1991**, 125.

131 Reddy, C.K.; Periasamy, M. *Tetrahedron* **1992**, *48*, 8329.

132 Narayana, C.; Padmanabhan, S.; Kabalka, G.W. *Tetrahedron Lett.* **1990**, *31*, 6977. For the regioselective reductive opening of 4,6-O-benzylidene acetals of glucose or glucosamine derivatives by BH_3-Me_2NH-BF_3-OEt_2, see: Oikawa, M.; Liu, W.C.; Nakai, Y.; Koshida, S.; Fukase, K.; Kusumoto, S. *Synlett* **1996**, 1179.

133 Narayana, C.; Reddy, N.K.; Kabalka, G.W. *Tetrahedron Lett.* **1991**, *32*, 6855.

134 Reddy, C.K.; Periasamy, M. *Tetrahedron Lett.* **1990**, *31*, 1919.

135 Balázs, M.; Szántay Jr, C.; Bölcskei, H.; Szántay, C. *Tetrahedron Lett.* **1993**, *34*, 4397.

136 White, J.D.; Amedio, J.C.; Gut, S.; Ohira, S. Jayasinghe, L.R. *J. Org. Chem.* **1992**, *57*, 2270.

137 Picot, A.; Lusinchi, X. *Bull. Soc. Chim. Fr.* **1977**, 1227.

138 Vedejs, E.; Monahan, S.D. *J. Org. Chem.* **1996**, *61*, 5192.

139 Vedejs, E.; Kendall, J.T. *J. Am. Chem.Soc.* **1997**, *119*, 6941.

140 For a study of the α-CH acidity and reactivity of borane-base complexes in the gas phase, see: Ren, J.; Workman, D.B.; Squires, R.R. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2230.

141 Kessar, S.V.; Singh, P.; Vohra, R.; Kaur, N.P.; Singh, K.N. *J. Chem. Soc.,Chem. Commun.*, **1991**, 568. Kessar, S.V.; Singh, P.; Singh, K.N., Dutt, M. *J. Chem. Soc.,Chem. Commun.*, **1991**, 570. Kessar, S.V.; Vohra, R.; Kaur, N.P.; Singh, K.N.; Singh, P.*J. Chem. Soc., Chem. Commun.* **1994**, 1327. Ebden, M.R.; Simpkins, N.S.; Fox, D.N.A. *Tetrahedron Lett.* **1995**, *36*, 8697. Katritzky, A. R.; Fang, Y. F.; Belyakov, S. A. *Org. Prep. Proced. Int.* **1998**, *30*, 325. For regioselective *N*-alkylation of

2-aminobenzylamine *via* chelation with 9-BBN, see: Bar-Haim, G.; Kol, M. *Tetrahedron Lett.* **1998**, *39*, 2643.

142 Ferey, V.; Le Gall, T.; Mioskowski, C. *J. Chem. Soc., Chem. Commun.* **1995**, 487.

143 Kessar, S.V.; Singh, P. *Chem. Rev.* **1997**, *97*, 721.

144 Ferey, V.; Toupet, L.; Le Gall, T.; Mioskowski, C. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 430.

145 Ferey, V.; Vedrenne, P.; Toupet, L.; Le Gall, T.; Mioskowski, C. *J. Org. Chem.* **1996**, *61*, 7244.

146 Vedejs, E.; Fields, S.C.; Schrimpf, M.R. *J. Am. Chem. Soc.* **1993**, *115*, 11612. Vedejs, E.; Fields, S.C.; Schrimpf, M.R. *Pure Appl. Chem.* **1993**, *65*, 723. Vedejs, E.; Fields, S.C.; Lin, S.; Schrimpf, M.R. *J. Org. Chem.* **1995**, *60*, 3028.

147 Lopusinski, A.; Bernet, B.; Linden, A.; Vasella, A. *Helv. Chim. Acta* **1993**, *76*, 94. Börner, A.; Ward, J.; Ruth, W.; Holz, J.; Kless, A.; Heller, D., Kagan, H. *Tetrahedron*, **1994**, *50* 10419. Chen, Z.; Jiang, Q.; Zhu, G.; Xiao, D.; Cao, P.; Guo, C.; Zhang, X. *J. Org. Chem.* **1997**, *62*, 4521.

148 Pellon, P. *Tetrahedron Lett.* **1992**, *33*, 4451.

149 Enders, D.; Berg, T.; Raabe, G.; Runsink, J. *Helv. Chim. Acta* **1996**,*79*, 118. Enders, D.; Berg, T. *Synlett* **1996**, 796. Enders, D.; Berg, T.; Raabe, G.; Runsink, J. *Liebigs Ann./Recueil* **1997**, 345.

150 Seitz, T.; Muth, A.; Huttner, G. *Chem. Ber.* **1994**, *127*, 1837. Seitz, T.; Huttner, G.; Büchner, M. Z. *Naturforsch.* **1994**, *49b*, 1813. Soulier, E.; Clement, J. C.; Yaouanc, J. J.; desAbbayes, H. *Tetrahedron Lett.* **1998**, *39*, 4291.

151 Lutz, C.; Graf, C.D.; Knochel, P. *Tetrahedron*, **1998**, *54*, 10317.

152 Stéphan, O.; Riegel, N., Jugé, S. *J. Electroanal. Chem.* **1997**, *421*, 5.

153 Corey, E.J.; Chen, Z.; Tanoury, G.J. *J. Am. Chem. Soc.* **1993**, *115*, 11000. Sheehan, S.K.; Jiang, M.; McKinstry, L.; Livinghouse, T.; Garton, D. *Tetrahedron*, **1994**, *50*, 6155. Bader, A.; Pabel, M.; Willis, A.C.; Wild, S.B. *Inorg. Chem.* **1996**, *35*, 3874. Vedejs, E.; Donde, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9293.

154 Imamoto, T. *Pure Appl. Chem.* **1993**, *65*, 655. Jugé, S.; Stephan, M.; Merdès, R., Genêt, J.P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531. Ramsden, J.A.; Brown, J.M.; Hursthouse, M.B.; Karalulov, A.I., *Tetrahedron: Asymmetry* **1994**, *5*, 2033. Langer, F.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 4591. Muci, A.R.; Campos, K.R.; Evans, D.A. *J. Am. Chem. Soc.* **1995**, *117*, 9075. Brown, J.M.; Laing, J.C.P. *J. Organomet. Chem.* **1997**, *529*, 435.

155 Imamoto, T.; Matsuo, M.; Nomomura, T.; Kishikawa, K.; Yanagawa, M. *Heteroatom Chem.* **1993**, *4*, 475. Brenchley, G.; Fedouloff, M.; Mahon, M.F.; Molloy, K.C.; Wills, M. *Tetrahedron*, **1995**, *50*, 10581. Longeau, A.; Durand, S.; Spiegel, A.; Knochel, P. *Tetrahedron: Asymmetry* **1997**, *8*, 987.

156 Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523. Brenchley, G.; Fedouloff, M.; Mahon, M.F.; Molloy, K.C.; Wills, M. *Tetrahedron*, **1995**, *50*, 10581. M. Morimoto, T.; Ando, N.; Achiwa, K. *Synlett* **1996**, 1211. Marinetti, A.; Kruger, V.; Buzin, F.X. *Tetrahedron Lett.* **1997**, *38*, 2947.

157 McKinstry, L.; Livinghouse, T. *Tetrahedron Lett.* **1994**, *35*, 9319. McKinstry, L.; Livinghouse, T. *Tetrahedron*, **1995**, *51*, 7655. Chen, Z.; Jiang, Q.; Zhu, G.; Xiao, D.; Cao, P.; Guo, C.; Zhang, X. *J. Org. Chem.* **1997**, *62*, 4521.

158 Pelter A., Rosser R., Mills, S. *J. Chem. Soc., Chem. Commun.* **1981**, 1014. Uziel, J.; Riegel, N. ; Aka, B. ; Figuière, P. ; Jugé, S. *Tetrahedron Lett.* **1997**, *38*, 3405.

159 Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. Brisset, H. ; Gourdel, Y.; Pellon, P.; Le Corre, *Tetrahedron Lett.* **1993**, *34*, 4523. Gourdel, Y.; Pellon, P.; Toupet, L.; Le Corre, M. *Tetrahedron Lett.* **1994**, *35*, 1197. McKinstry, L.; Livinghouse, T. *Tetrahedron* **1995**, *51*, 7655. Pellon, P.; Le Goaster, C.; Toupet, L. *Tetrahedron Lett.* **1996**, *37*, 4713. Yamago, S., Yanagawa, M., Mukai, H.; Nakamura E. *Tetrahedron* **1996**, *52*, 5091. For the *in situ* generation of $PhPRLiBH_3$ from Ph_2PRBH_3, see: Pellon, P. *Tetrahedron Lett.* **1992**, *33*, 4451. Pellon, P.; Le Goaster, C.; Marchand, G.; Toupet, L. *Heteroatom Chem.* **1997**, *8*, 123.

160 Imamoto, T.; Matsuo, M.; Nomomura, T.; Kishikawa, K.; Yanagawa, M. *Heteroatom Chem.* **1993**, *4*, 475.

161 Imamoto, T.; Oshiki, T.; Onozawa, T.; Matsuo, M.; Hikosaka, T.; Yanagawa, M. *Heteroatom Chem.* **1992**, *3*, 563. Oshiki, T.; Imamoto, T. *J. Am. Chem. Soc.* **1992**, *114*, 3975.

162 Bourumeau, K.; Gaumont, A.C.; Denis, J.M. *J. Organomet. Chem.* **1997**, *529*, 205.

163 Bourumeau, K.; Gaumont, A.C.; Denis, J.M. *Tetrahedron Lett.* **1997**, *38*, 1923.

164 Oshiki, T.; Imamoto, T. *Bull. Chem. Soc. Jap.* **1990**, *63*, 3719. Imamoto, T.; Tsuruta, H. *Chem. Lett.* **1996**, 707.

165 Brown, J.M.; Laing, J.C.P. *J. Organomet. Chem.* **1997**, *529*, 435.

166 Jugé, S.; Stéphan, M.; Laffite, J.A.; Genêt, J.P. *Tetrahedron Lett.* **1990**, *31*, 6357. Jugé, S.; Genêt, J.P. US Patent, 5,043,465, 1991. Jugé, S.; Stephan, M.; Merdès, R.; Genêt, J.P., Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531. Ramsden, J.A.; Brown, J.M.; Hursthouse, M.B.; Karalulov, A.I., *Tetrahedron: Asymmetry* **1994**, *5*, 2033. Pepper, V.; Stingl, K.; Thümler, H.; Saak, W.; Haase, D.; Pohl, S.; Jugé, S.; Martens, J. *Liebigs Ann.* **1995**, 2123. Kaloun, E.B.; Merdes, R.; Genêt, J.P.; Uziel, J.; Jugé, S. *J. Organomet. Chem.* **1997**, *529*, 455.

167 Uziel, J.; Stephan, M.; Kaloun, E.B.; Genêt, J.P.; Jugé, S. *Bull. Soc. Chim. Fr.* **1997**, *134*, 379.

168 Oshiki, T.; Hikosaka, T.; Imamoto, T. *Tetrahedron Lett.* **1991**, *32*, 3371. Imamoto, T.; Matsuo, M.; Nomomura, T.; Kishikawa, K.; Yanagawa, M. *Heteroatom Chem.* **1993**, *4*, 475. Imamoto, T.; Yoshizawa, T.; Hirose, K.; Wada, Y.; Masuda, H.; Yamaguchi, Y.; Seki, H. *Heteroatom Chem.* **1995**, *6* , 99.

169 Longeau, A.; Knochel, P. *Tetrahedron Lett.* **1996**, *37*, 6099. Longeau, A.; Durand, S.; Spiegel, A.; Knochel, P. *Tetrahedron Lett.* **1997**, *38*, 987.

170 Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287.

171 Longeau A., Langer F., Knochel P. *Tetrahedron Lett.* **1996**, *37*, 2209.

172 Kaloun, E.B.; Merdes, R.; Genêt, J.P.; Uziel, J.; Jugé, S. *J. Organomet. Chem.* **1997**, *529*, 455.

173 Enders, D.; Berg, T.; Raabe, G.; Runsink, J. *Liebigs Ann./Recueil* **1997**, 345.

174 Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. Jugé, S.; Stephan, M.; Laffite, J.A.; Genêt, J.P. *Tetrahedron Lett.* **1990**, *31*, 6357. Schmidt, U.; Riedl, B.; Griesser, H.; Fitz, C. *Synthesis*, **1991**, 655. Corey, E.J.; Chen, Z.; Tanoury, G.J. *J. Am. Chem. Soc.* **1993**, *115*, 11000. Webb, K.M.; Miller, *J. Organomet. Chem.* **1993**, *460*, 1. Imamoto, T.;

Tsuruta, H.; Wada, Y.; Masuda, H.; Yamaguchi, K. *Tetrahedron Lett.* **1995**, *36*, 8271. For the metallation of 3,4-dimethylphosphole, see: Huy, N.H.T.; Mathey, F. *Organometallics* **1994**, *13*, 925.

175 Desponds, O.; Huynh, C.; Schlosser, M. *Synthesis* **1998**, 983.

176 Muci, A.R.; Campos, K.R.; Evans, D.A. *J. Am. Chem. Soc.* **1995**, *117*, 9075. Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635. Wolfe, B.; Livinghouse, T. *J. Am. Chem. Soc.* **1998**, *120*, 5116.

177 Baban, J.A.; Marti, V.P.J.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. II* **1985**, 1723. Green, I.G.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. II* **1986**, 1597 and references therein.

178 Paul, V.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. II* **1988**, 1183.

179 Tumanskii, B.L.; Bashilov, V.V.; Solodovnikov, S.P.; Bubnov, N.N.; Sokolov, V.I.; Kampel, V.T.; Warshawsky, A. *Russ. Chem. Rev.* **1994**, *43*, 624.

180 Kaushal, P.; Mok, P.L.H.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. II* **1990**, 1663 and references cited.

181 Dang, H.S.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. 1* **1993**, 891.

182 Dang, H.S.; Diart, V.; Roberts, B.P. *J. Chem. Soc. Perkin Trans. 1* **1994**, 1033. Dang, H.S.; Diart, V.; Roberts, B.P.; Tocher, D.A. *J. Chem. Soc. Perkin Trans. II* **1994**, 1039.

183 Kirwan, J.N.; Roberts, B.P. *J. Chem. Soc., Chem. Commun.* **1988**, 480 ; *J. Chem. Soc. Perkin Trans. II* **1989**, 539.

184 Barton, D. H. R.; Jacob, M. *Tetrahedron Lett.* **1998**, *39*, 1331.

185 Morin, C. *Tetrahedron* **1994**, *50*, 12521. See also : Medicinal Applications of Boron in '*Current Topics in the Chemistry of Boron*"' Kabalka, G.W., Ed.; Royal Society of Chemistry, Cambridge, 1994, 145.

186 For the synthesis of these compounds, see Section 3.2.

187 Spielvogel, B.F. in '*Advances in Boron and the Boranes*', Liebman, J.F.; Greenberg, A.; Williams, R.E. Eds., VCH, New-York, **1988**, 329. Spielvogel, B.F.; Sood, A.; , Shaw, B.R.; Hall, I.H. '*Current Topics in the Chemistry of Boron*', Kabalka, G.W., Ed.; Royal Society of Chemistry, Cambridge, **1994**, 193. Spielvogel B.F. *Phosphorus, Sulfur and Silicon* **1994**, *87*, 267.

188 Biological activities were often reported with the description of the synthesis.

189 For some supplementary recent references, see: Hall, I.H.; Hall, E.S; Chi, L.K.; Miller III, M.C.; Bastow, K.F.; Sood, A.; Spielvogel, B.F. *Appl. Organometal. Chem.* **1992**, *6*, 229. Hall, I.H.; Rajendran, K.G.; Chen, S.Y.; Norwood, V.N.; Morse, K.W.; Sood, A.; Spielvogel, B.F. *Appl. Organometal. Chem.* **1994**, *8*, 473. Burnham, B.S.; Chen, S.Y.; Sood, A.; Spielvogel, B.F.; Hall, I.H. *Pharmazie* **1995**, *50*, 779. Miller, M.C.; Shrewsbury, R.P.; Elkins, A.L.; Sood, A.; Spielvogel, B.F.; Hall, I.H. *J. Pharm.Sci.* **1995**, *84*, 933. Hall, I.H.; Rajendran, K.G.; Chen, S.Y.; Wong, OiT.; Sood, A.; Spielvogel, B.F. *Arch. Pharm.(Weinheim Ger.)* **1995**,*328*, 39. Rajendran, K.G.; Sood, A.; Spielvogel, B.F.; Hall, I.H.; Norwood, V.M.; Morse, K.W. *Appl. Organometal. Chem.* **1995**, *9*, 111. Chen, S.Y.; Burnham, B.S.; Spielvogel, B.F.; Sood, A.; Wyrick, S.D.; Hall, I.H. *Appl. Organometal. Chem.* **1996**, *10*, 279. Miller, M. C.; Spielvogel, B. F.; Hall, I. H. *Appl. Organometal. Chem.* **1998**, *12*, 87.

190 Sood, A.; Spielvogel, B.F.; Shaw, B.R. *J. Am. Chem. Soc.* **1989**, *111*, 9234. Burnham, B.S.; Wyrick, S.D.; Hall, I.H.; Sood, A.; Spielvogel, B.F. *J. Label. Compd. Radiopharm.* **1991**, *29*, 469.

191 Sood, A.; Spielvogel, B.F.; Shaw, B.R.; Carlton, L.D.; Burnham, B.S.; Hall, I.H. *Anti Cancer Res.* **1992**, *12*, 335.

192 Tomasz, J.; Shaw, B.R.; Porter, K.; Spielvogel, B.F.; Sood, A. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1373. Chen, Y.Q.; Qu, F.G.; Zhang, Y.B. *Tetrahedron Lett.* **1995**, *36*, 745. Zhang, J. C.; Terhorst, T.; Matteucci, M. D. *Tetrahedron Lett.* **1997**, *38*, 4957. Higson, A. P.; Sierzchala, A.; Brummel, H.; Zhao, Z. Y.; Caruthers, M. H. *Tetrahedron Lett.* **1998**, *39*, 3899. Jin, Y.; Just, G. *Tetrahedron Lett.* **1998**, *39*, 6429.

193 Hawthorne, M.F. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 950. Goudgaon, N.M.; Fulcrand El-Kattan, G.; Schinazi, R.F. *Nucleosides and Nucleotides*, **1994**, *13*, 849.

194 Tomasz, J.; Shaw, B.R.; Porter, K.; Spielvogel, B.F.; Sood A. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1373. Porter, K.; Bridley, D.; Huang, F.; Sood, A.; Spielvogel, B.F.; Shaw, B.R. *Genome Sequencing and Analysis Conference V*, Abstracts, Hilton Head Island, SC, **1993**. Krzyzanowska, B.K.; He, K.; Hasan, A.; Shaw, B.R. *Tetrahedron* **1998**, *54*, 5119.

195 For a recent review on saccharide sensing with molecular receptors based on related boronic acids, see: James, T.D.; Sandanayake, K.R.A.; Shinkai, S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1911.

196 Reetz, M.F.; Niemeyer, C.M.; Hermes, M.; Goddard, R. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1017.

197 Reetz, M.F.; Huff, J.; Goddard, R. *Tetrahedron Lett.* **1994**, *35*, 2521.

198 Worm, K.; Schmidtchen, F.P.; Schier, A.; Schäfer, A.; Hesse, M. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 327.

199 Bien, J.T.; Eschner, M.J.; Smith, B. *J. Org. Chem.* **1995**, *60*, 4525.

200 Nozaki, K.; Yoshida, M.; Takaya, H. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2452. Nozaki, K.; Yoshida, M.; Takaya, H. *Bull. Chem. Soc. Jap.* **1996**, *69*, 2043.

201 Nozaki, K.; Tsutsumi, T.; Takaya, H. *J. Org. Chem.* **1995**, *60*, 6668.

202 Paine, R.T.; Narula, C.K. *Chem. Rev.* **1990**, *90*, 73. Fazen, P.J.; Beck, J.S.; Lynch, A.T.; Remsen, E.E.; Sneddon, L.G. *Chem. Mater.* **1990**, *2*, 96. Kim, D.P.; Economy, J. *Chem. Mater.* **1993**, *5*, 1216. Kim, D.P.; Economy J. *Ceram. Trans.* **1993**, *38*, 47. Paine, R.T.; Sneddon, L.G. *Chemtech*, **1994**, 29. Cofer, C.G.; Economy, J.; Ferber, M.K.; Lara-Curzio, E. *Ceram. Eng. Sci. Proc.* **1994**, *15(A)*, 447. Fazen, P.J.; Remsen, E.E.; Beck, J.S.; Carroll, P.J.; McGhie, A.R.; Sneddon L.G. *Chem. Mater.* **1995**, *7*, 1942. Kim, D.P.; Cofer, C.G.; Economy, J. *J. Am. Ceram. Soc.* **1995**, *78*, 1546.

203 Walkers, B.E.; Rice, R.W.; Becher, P.F.; Bender, B.A.; Coblenz, W.S. *Ceram. Bull.* **1983**, *62*, 916. Riedel, R.; Bill, J.; Passing, G. *Adv. Mater.* **1991**, *3*, 551. Bill, J.; Riedel, R.; Passing, G. *Z. Anorg. Allg.Chem.* **1992**, *610*, 83.

204 For a recent review on novel high-performance ceramics from molecular precursors, see: Baldus, H.P.; Jansen, M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 328 .

205 Dou, D.; Ketchum, D.R.; Hamilton, E.J.M.; Florian, P.A.; Vermillion, K.E.; Grandinetti, P.J.; Shore, S.G. *Chem. Mater.* **1996**, *8*, 2839.

206 Eichner, T.; Braun, M.; Huttinger, K.J. *Carbon* **1996**, *34*, 1367.

207 Hemida, A. T.; Pailler, R.; Birot, M.; Pillot, J. P.; Dunogues, J. *J. Mater. Sci.* **1997**, *32*, 3237.

208 Chujo, Y.; Tomita, I.; Murata, N.; Mauermann, H.; Saegusa, T. *Macromolecules* **1992**, *25*, 27.

209 Baker, C.S.L.; Barnard, D.; Porter, M. Rubber Chem. Technol. **1970**, *43*, 501. Schnecko H.; Steffen U. *Makromol. Chem.*, **1976**, *177*, 1725.

210 Lesley, M.J.G.; Woodward, A.; Taylor, N.J.; Marder, T.B.; Cazenobe, I.; Ledoux, I.; Zyss, J.; Thornton, A.; Bruce, D.W.; Kakkar, A.K. *Chem. Mat.* **1998**, *10*, 1355.

Biographical sketch

Bertrand Carboni

Laurence Monnier

Bertrand Carboni was born in Rennes, France, in 1954. He received his degree from "Ecole Nationale Supérieure de Chimie de Paris" in 1977 and obtained his "Thèse de Docteur-Ingénieur" in 1980 working under the supervision of Pr Robert Carrié. From 1981, he was a research scientist at Rhône-Poulenc in Vitry sur Seine working on the synthesis of new fungicides and herbicides. After three years, he returned to the University of Rennes and entered the CNRS. He earned a Ph.D. under the direction of Professor Robert Carrié and Dr Michel Vaultier in 1986 on the chemistry of azides. From 1989 to 1990, he conducted postdoctoral studies in Professor Bernd Giese's group at Basel on stereoselective radical reactions. He was promoted to the position of "Directeur de Recherche" in 1996. His research interests concern the use of organoboranes in organic synthesis and biology, the design of new polyamine derivatives as antiproliferative agents and, more recently, solid-phase organic synthesis.

Laurence Monnier was born in Loudéac, France, in 1969. She obtained her Ph.D under the direction of Dr Bertrand Carboni in 1997 on the synthesis of boron analogues of biologically active compounds. Her research interests concern the preparation of new amine- and phosphine-borane complexes by insertion reactions of dichlorocarbene into boron-hydrogen bonds and the development of new routes to a-aminoboronic acid