THE CYCLIC COORDINATION OF BORON COMPOUNDS
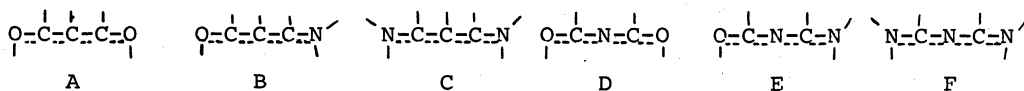
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Abstract

The methods of synthesis, structure and reactivities of the cyclic boron compounds having the double inner coordination of R_2B groups with terminal heteroatoms in the five- and three-membered chains are discussed. β-Diketonates, β-ketoiminates, β-diiminates, diacetamidates, acylamidinates, imidoylamidinates of boron, cyclic amidinoboranes and the cyclic coordination diboron compounds are described.

INTRODUCTION

The specificity of boron is its ability to produce various complexes whose investigations have been quite important in describing the modern coordination chemistry problems, providing an interface for all chemical areas. Among the different types of boron complexes special attention may be drawn to the cyclic systems, in which the double inner coordination with the boron atom is realized via the heteroatoms located at the ends of the five-membered chain. β-Diketonates are typical chelates of such type. Recently a variety of oxygen-nitrogen and nitrogen analogs of boron β-diketonates have been described. They include β-ketoiminates, β-diiminates, diacylamidates, acylamidinates and imidoylamidinates of boron. All these chelates have one common feature: five-membered chains with a delocalized system of bonds (A-F) joined to the R_2B boryl group via the two donor-acceptor bonds taking part in their formation.

$$O{=}C{=}C{=}C{=}O \qquad O{=}C{=}C{=}C{=}N \qquad N{=}C{=}C{=}C{=}N \qquad O{=}C{=}N{=}C{=}O \qquad O{=}C{=}N{=}C{=}N \qquad N{=}C{=}N{=}C{=}N$$

| A | B | C | D | E | F |

There also exist the four-membered cyclic coordination boron compounds with delocalized system of bonds $>N{=}C{=}N<$ obtained from the trivalent boron compounds and symmetric disubstituted amidines. The six-membered chelates with two boron atoms in the cycle are known. They result from the 1,4-coordinative addition of aminoboranes to the boron compounds having a coordinatively unsaturated heteroatom in position 2 of the functional group. Some of such types of boron chelates may be used in organic synthesis.

Boron β-diketonates

In 1905 Diltey was the first to study the reaction of boron compounds with β-diketones. He prepared the complex (1) by action of acetylacetone on BCl_3 /1/.


1
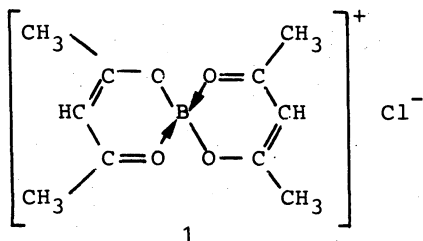
Unlike BCl_3, boron trifluoride and acetylacetone afford difluoroboryl-
acetylacetonate (2) /2/.

$$BF_3 + CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3 \longrightarrow$$


2
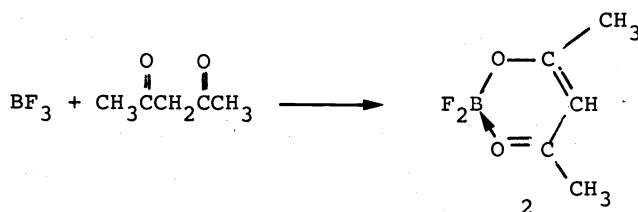
Analogously acetylacetone reacts with 1,3,2-benzodioxaborol deriva-
tives giving chelate (3) /3,4/.

3
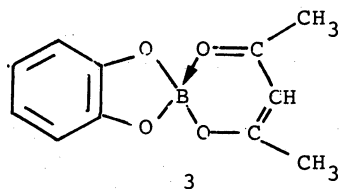
It was then found that trialkylboranes may react with acetylacetone
and other β-diketones yielding dialkylboryl-β-diketonates. Unlike
alcohols reacting with trialkylboranes at 160°C /5,6/ the reaction
with acetylacetone (after a short induction period) proceeds sponta-
neously with vigorous heating of the mixture /7/.

$$R_3B + CH_3COCH_2COCH_3 \longrightarrow \qquad\qquad + RH$$


$$R = C_3H_7, C_4H_9$$
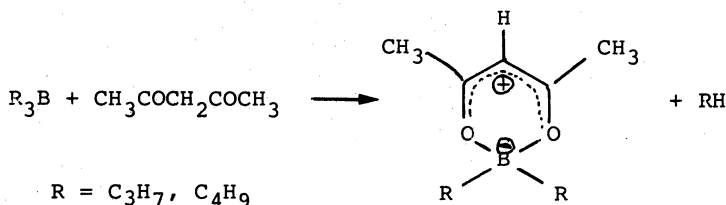
Dialkylboryl-acetylacetonates are produced smoothly also by action of
acetylacetone on the esters of dialkylborinic and dialkylthioborinic
acids /7/. Boron β-dicarbonyl chelates are prepared from acetoacetic
ester and trialkylboranes /8,9/ or from dialkyl(diaryl)chloroboranes
/10/. Triarylboranes /11/, esters of diarylboronic acids /12/ and di-
phenylchloroborane /13/ react smooth with β-diketonates to form di-
arylboryl-β-diketonates. Various B-alkylboracyclanes (borolanes,
borinanes, 1-boraindanes etc.) reacting with acetylacetone are con-
verted into acetylacetonates: depending on the structure of initial
compound the cleavage may involve cyclic alone or both cyclic and
outer B-C bonds /11/, e.g.:
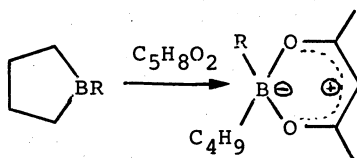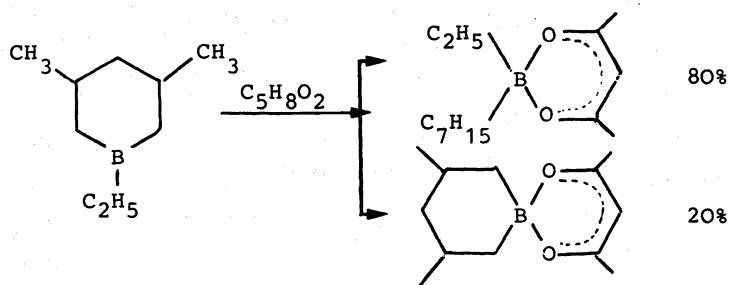
In this view it is interesting to note that in boracyclopentane and boracyclopentene o-carborane derivatives, action of acetylacetone cleaves the B-C bond remote from the carborane nucleus /14/.
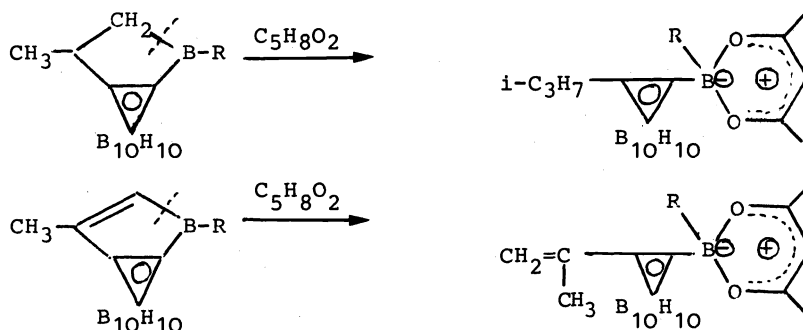

According to the data of PMR spectra both methyl groups in acetylaceto-nates of boron are magnetically equivalent (δ = 2.00 ppm); this is evidence of their symmetric structure and thus of an equivalence of both B-O bonds /9/. An X-Ray study of difluoroboryl-benzoylacetonate demonstrated that the lengths of both B-O bonds are equal to 1,488 Å, also equivalent are the lengths of bonds O(I)-C(4), O(2)-C(2) (1,304Å) and C(2)-C(3), C(3)-C(4) (1.389Å) /15/.
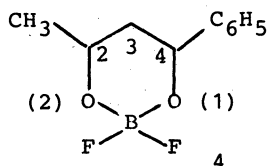

Symmetry of the ring electron cloud along the B-C(3) axis may be attained when both oxygen atoms in β-diketonates are in a trigonal valent state and together with the trigonal carbon atoms produce a 5-center π-system of six π-electrons, three of which being contributed by two oxygen atoms. Evidence of a trigonal valent state (sp^2) for the oxygen atoms in boron β-diketonates is obtained from the interatomic distances in compound (4), where D (C-O)=1.304Å, compared to those in resorcine and fluoroglucine with tetrahedral oxygens D (C-O)=1.36Å. When an electron transfers entirely to the boron, the β-diketonate would have structure (5). Structure (6) with semicordinated oxygen - boron bonds /16,17/ corresponds more exactly to the properties of boron β-diketonates.
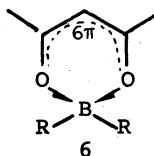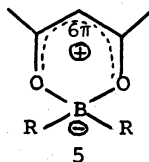
β-Diketonates are stable in water and hydrolyse on refluxing with aqueous alkali /9/. They may take part in electrophilic substitution reactions on the chelate ring e.g. bromination /9/. The action of per- chloric acid on diphenylborylbenzoylacetophenonate affords a crystalli- ne solid to which the structure of salt (7) was assigned /18/.
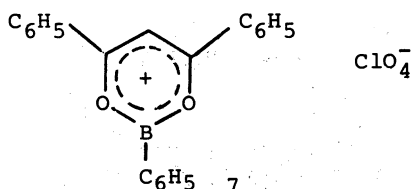

Action of acetic and trimethylacetic acids on β-diketonates results in a nucleophilic substitution at the boron atom with conservation of the chelate ring /19/.
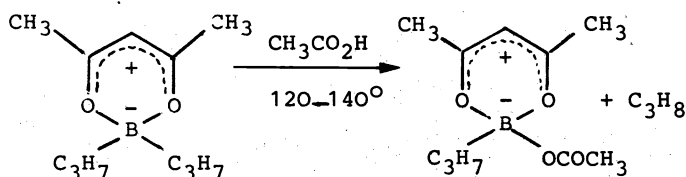

Boron β-ketoiminates
Nitrogen analogs of boron β-diketonates in which the boryl group is coordinatively bound to the oxygen and nitrogen atoms were obtained by various methods. Diphenylboryl-acetylacetoniminates are prepared from acetylacetone, ammonia and phenylboronic acid anhydride /20/. The dibutyl analog was obtained from tributylborane and 2-imino-4- pentanone /8,9/. A series of β-ketoiminates of boron /8/ was genera- ted by addition of vinyloxyboranes to nitriles /21/.
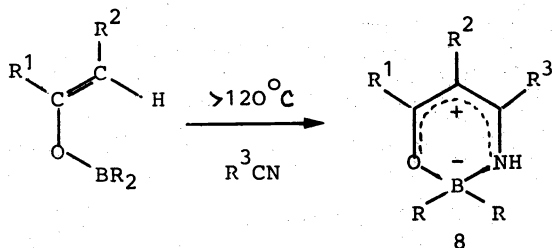
Compounds (8) are heat and hydrolysis resistent.

Boron β-diiminates
Nitrogen analogs of boron β-diketonates, β-diiminates, are prepared smoothly by addition of enaminoboranes to nitriles. The first enamino- boranes (9) were obtained from dialkylthioborinates and cyclohexanone imines reacting in tautomeric enamine form /22-25/.
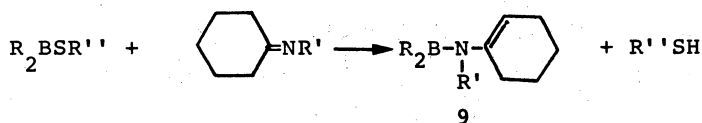

$R = C_3H_7, C_4H_9; R' = i-C_4H_9, C_6H_5$

Ketiminoboranes also enter the reaction with thioborinates /26-28/.
The reaction of alkylarylketimines with dialkylthioborinates affords
iminoboranes existing as a mixture of tautomeric imino- (10) and
enamino structures (11) /26,28/.
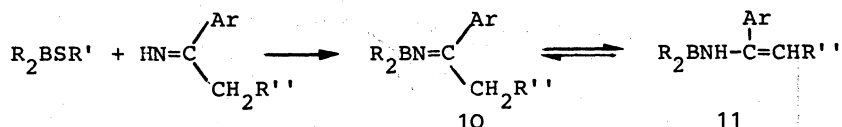
Investigation of the chemical properties of enaminoboranes obtained
from cyclohexanone imines showed that they may react with nitriles
giving intracomplexes (12) /23,24/.
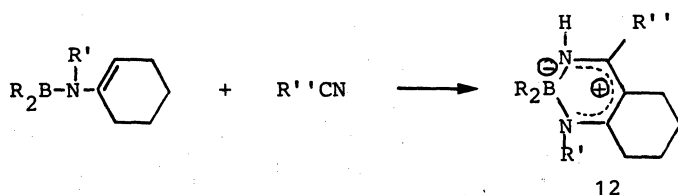
The reaction of 1-cyclohexenyl-2-butyl-1,2-azaborolidine with benzo-
nitrile afforded tricyclic boron β-diiminate (13), a dark-red liquid
/25/.
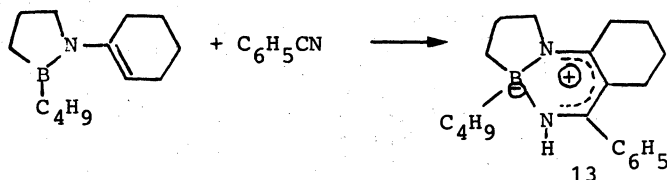
The nitriles may react not only with enamines containing cyclohexenyl
radicals but also with boron acyclic enamines. The equilibrium mixtures
of desmotropic compounds (14) and (15) react with nitriles at 100-130°C
leading to boron β-diiminates (16). This procedure afforded dibutyl-
boryl(α-benzimidoyl-propiophenoiminate) (16a), dibutylboryl(α-benzi-
midoylbutyrophenoniminate) (16b) and dibutylboryl(α-acetimidoylpropio-
phenoniminate) (16c) /28/.
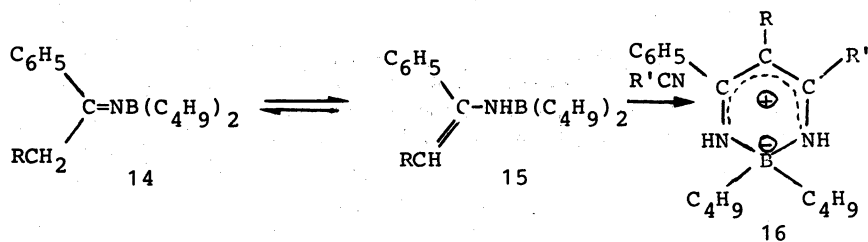
16a: R=CH₃, R'=C₆H₅;   16b: R=C₂H₅, R'=C₆H₅

16c: R=R'=CH₃

Compound 16a is a red crystalline solid (m.p. 45-48°), compounds 16b
and 16c are viscous orange-red liquids stable in air. The structure
of β-diiminates (16) was established on the basis of UV, IR, PMR and
NMR ^{11}B spectra. The ^{11}B NMR spectra of compounds 16a-c contain the
signals from ^{11}B nuclei in the high field region (δ = +1.9 - +4.3 ppm).
The IR spectra show characteristic absorptions for the NH groups
(3390-3396 cm^{-1}). The PMR spectra of compounds 16a and 16b exhibit a
signal from the NH protons (5.05 and 5.00 ppm). The proton equivalence
of the NH groups of compounds 16a and 16b is manifested in a symmetric
distribution of electronic density in boron β-diiminates , which could
be attained by inclusion of both nitrogen atoms having a trigonal va-
lent state into the common five-center system of π-orbitals occupied
by six π-electrons: three electrons from the three carbon atoms and
two electrons from the two nitrogen atoms. The structure of β-di-
iminates may be described by formula (17) with semicoordinative B-N
bonds produced by a boron electron and three electrons from the two
nitrogen atoms.

17
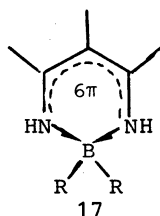
In discussing the reaction mechanism of organoboron enamines with ni-
triles one should start from the specific ability of trivalent boron
compounds to react coordinatively with the nitrogen-containing li-
gands, in particular with nitriles (18). A subsequent generation of a
chemical bond between the nitrile carbon atom and the enamine β-
carbon atom occurs via transfer of nitrogen of the nitrilic group
from a linear divalent into the trigonal trivalent state, the B-N
coordination bond transforming into the B-N covalent one. There also
occurs a simultaneous rearrangement of the system into compounds with
two azomethine bonds (19) where an imine nitrogen plays the role of li-
gand. Further migration of hydrogen from C(4) to N(2) leads to the β-
diiminate (16) with a delocalized five-center system and equivalent B-
N bonds /28/.

18   19   16
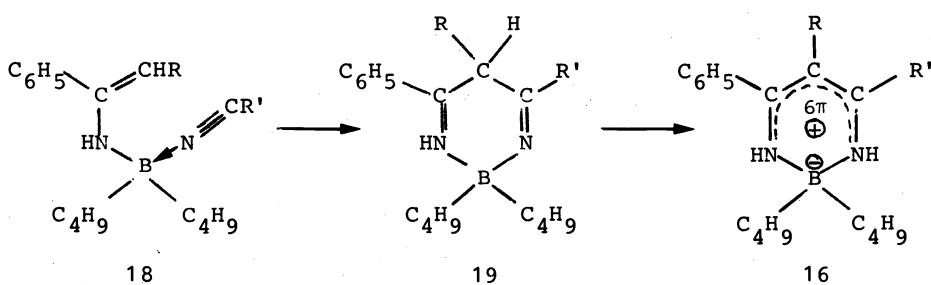
In the synthesis of boron β-diiminates with a vinyl group at C(4) the
initial compounds are allyldialkylboranes /29/. The latter compounds
may add to nitriles giving rise (at 50°) to 1-substituted (butadien-1,
3-yl-1)aminodialkylboranes (20), which dimerize on storage. The di-
mers (21) split on heating into monomers which, in the presence of
nucleophilic agents (traces of water, alcohols, amines), convert into
dienylaminoboranes (22). Compounds (22) add to nitriles giving β-di-
iminates (23).

$R' = CH_3$, C_6H_5, $CH_2=CH-$,
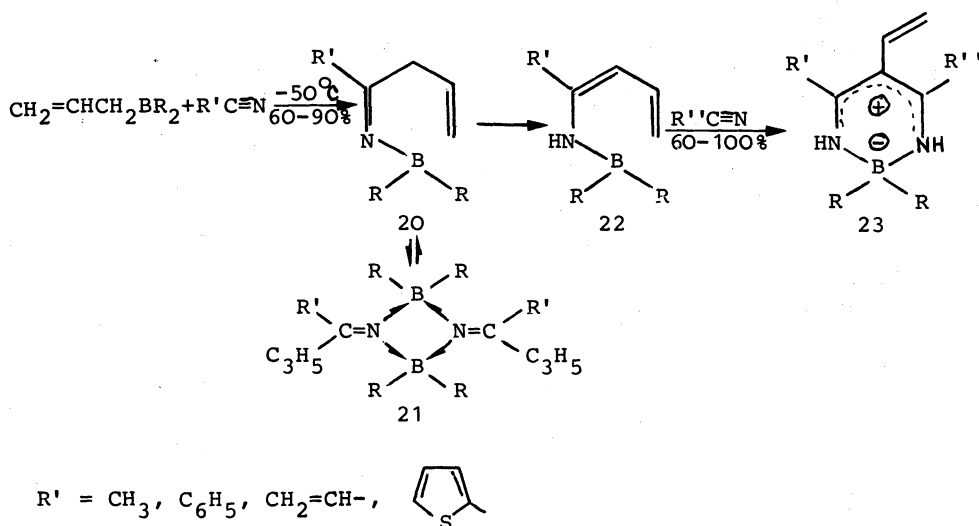
The boron β-diiminates (24) when heated with butanol in the presence of HCl with subsequent treatment of the mixture with sodium bicarbonate yield 9-alkyl-1,2,3,4-tetrahydroacridines or their 7-substituted derivatives (25) /30,31/.

X = H, CH_3, Cl

R'= CH_3, C_3H_7
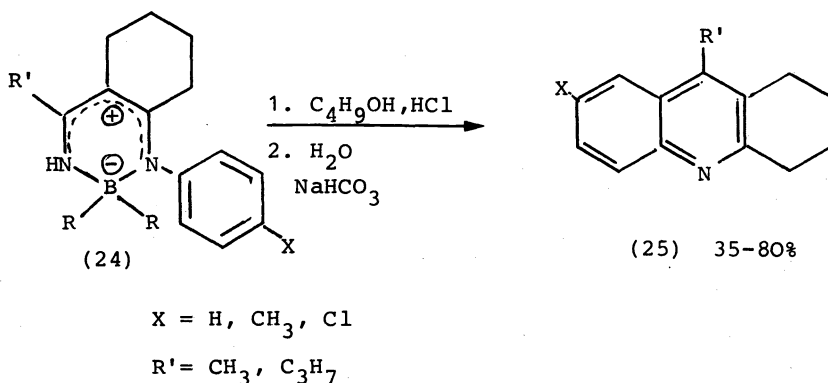
Boron diacylamidates

Since diacetamide structurally resembles acetylacetone one may expect formation of its respective chelates, heteroanalogs of acetylacetonates. Actually, dialkylboryldiacetamidates (26) were prepared by heating diacetamide with dialkylthioborinates or with trialkylboranes /32/.

R = C_2H_5, C_4H_9, C_6H_{11}
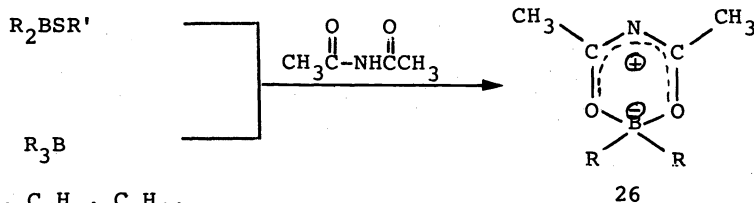
Dialkylboryldiacetamidates (26) are colourless or yellow liquids distilling in vacuo without decomposition, and are unstable in the presence of moisture and oxygen. The IR spectra of compounds (26) contain no absorption bands in the NH stretching region or between 1600–1750 cm^{-1}, specific to acetamide, but display intensive bands at 1595 cm^{-1} and 1476 cm^{-1}. The inner coordinative bonds are confirmed by the ^{11}B NMR spectra (for compound (26), R=C_2H_5, the chemical shift·

is -13.1 ppm). The single CH_3 group signals observed in the PMR spec-
tra of compounds (26) (for dibutylboryldiacetamidate δ = 2.10 ppm),
are evidence of their symmetric structure. In these compounds the ni-
trogen and oxygen atoms are in a trigonal valent state, causing an
equilization of the C-N and O-B bonds. The action of water or methanol
on compounds (26) results in their hydrolysis to diacetamide and di-
alkylborinic acid or its methyl ester. The lower stability of β-di-
acetamidates with respect to β-diketonates is revealed by their trans-
formation into β-diketonates under action of acetylacetone.

$$+ CH_3CONHCOCH_3$$
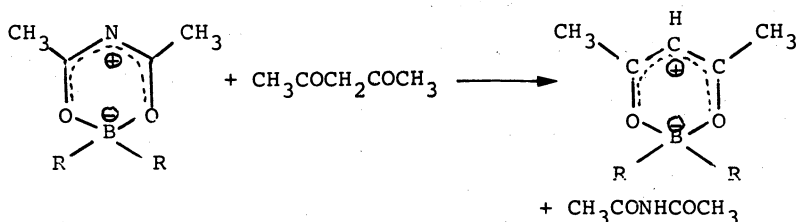
Boron acylamidinates
Acylaminodialkylboranes (27) generated from primary amides and di-
alkylthioborinates /33,34/ or trialkylboranes in tetrahydrofuran /13,
14/ add to nitriles producing the cyclic coordination compounds of
dialkylborylacylamidinates (28) /33,35,36/.
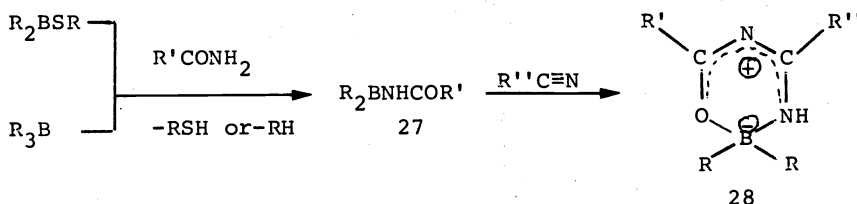
The chelates (28) are most conveniently prepared from trialkylboranes,
amides and nitriles by refluxing the mixtures of reagents in THF or
some other solvent. Addition of acylaminodialkylboranes (27) to nitri-
les may follow two mechanisms. It is most probable that compounds(27)
reacting in their tautomeric form (29) at first yield the nitrile
adducts (30) which then undergo transformations similar to those ob-
served in the reactions of enaminoboranes with nitriles.
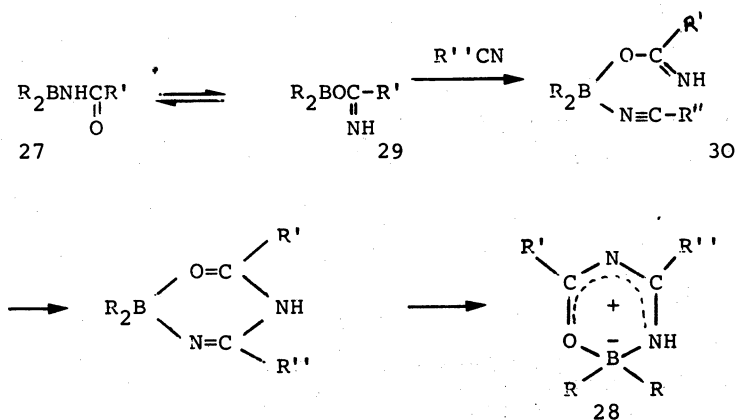
On the other hand, addition of dialkylborylacylaminoboranes to nitri-
les may be discussed as "amidoboration" of nitriles, similar to thio-
boronation of acetonitrile /37/:

$$R_2BNHCR' + R''C{\equiv}N \longrightarrow R_2B{\cdots}NHCR' \longrightarrow R_2B \underset{N=C}{\overset{O=C}{<}} \longrightarrow 28$$
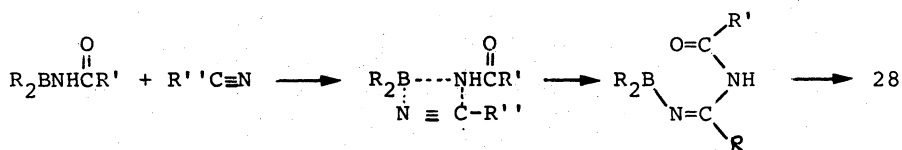
The chelates (28) may be prepared from N-acylamidines and trialkylboranes, dialkylboronates or dialkylborinates /36/.

$$\left.\begin{array}{l} R_3B \\ R_2BOR \\ \\ R_2BSR \end{array}\right\} \xrightarrow[\text{-RH, -ROH or -RSH}]{R'CONH-C(NH)R''} 28$$
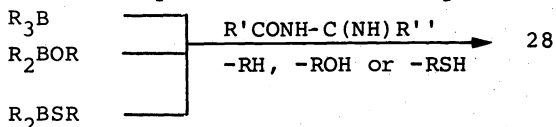
$R = C_2H_5, C_3H_7, C_4H_9, C_6H_5$

$R' = CH_3, C_3H_7, (CH_3)_3C, C_6H_5CH_2, C_6H_5$

$R'' = CH_3, C_2H_5, (CH_3)_3C, C_6H_5$

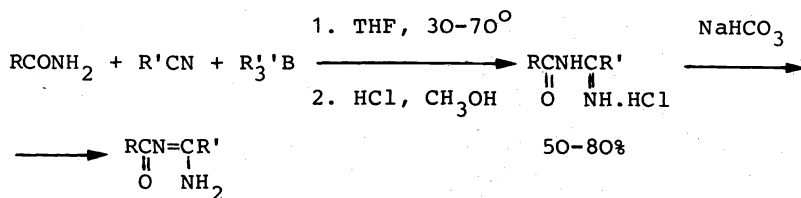The ^{11}B NMR spectra of all chelates (28) show the signals specific for the boron coordination compounds ($\delta = -2.7 - -6.4$ ppm from $(C_2H_5)_2O{\cdot}BF_3$). The PMR and IR spectra of the chelates correspond completely to their assigned structures. Dialkylborylacylamidinates (28) in an ethereal HCl solution produce unstable 1:1 adducts which are probably the boronium salts with N-acylamidines as ligands (31).
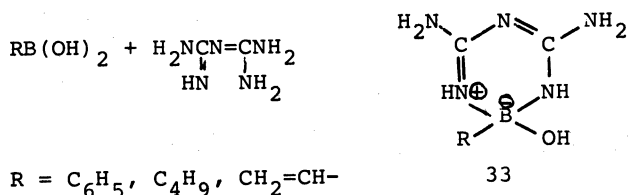
$$\xrightarrow{HCl} \qquad 31$$
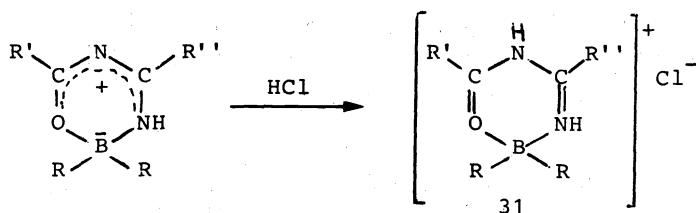
Treatment of dialkylborylacylamidinates (28) with an ethereal HCl solution and methanol gives N-acylamidines /35,38/. N-Acylamidine hydrochlorides may be obtained in one step by refluxing a tetrahydrofuran solution of the mixture of amide, nitrile and trialkylborane, followed by treatment of the reaction mixture with an ethereal HCl solution and methanol.

$$RCONH_2 + R'CN + R_3''B \xrightarrow[\text{2. HCl, } CH_3OH]{\text{1. THF, 30-70}^\circ} \underset{O \quad NH{\cdot}HCl}{RCNHCR'} \xrightarrow{NaHCO_3}$$

$$\longrightarrow \underset{O \quad NH_2}{RCN=CR'} \qquad\qquad 50\text{-}80\%$$

Is should be noted that acyl derivatives of amidines, specifically nitrogen unsubstituted ones, have been studied rather insufficiently. Amidine acylation using the common methods is obviously less suitable for the synthesis of N-acylamidines. Although Pinner as early as 1889 obtained N-benzoylbenzamidine from benzamidine hydrochloride and benzoic anhydride in the presence of NaOH (3%), this method has not been extended to other acylamidines /40/.

Boron imidoylamidinates

The cyclic boron coordination compounds with the system of -N-C-N-C-N-
bonds (32,33) were first prepared by the action of biguanide on diethyl-
aminodiphenylborane or organoboron acids /41/.

$$(C_6H_5)_2BN(C_6H_5)_2 \ + \ H_2NCN=CNH_2 \longrightarrow$$

$$\underset{HN \quad NH_2}{\overset{\parallel \quad |}{}}$$

32

$$RB(OH)_2 \ + \ H_2NCN=CNH_2$$

$$\underset{HN \quad NH_2}{\overset{\parallel \quad |}{}}$$

33

R = C_6H_5, C_4H_9, CH_2=CH-
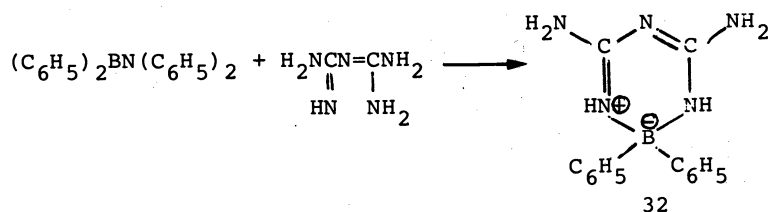
An asymmetric structure with inequivalent (covalent and coordinative)
B-N bonds was assigned to these compounds. Further investigations de-
veloped different methods of synthesis of such chelates with hydrocar-
bon radicals at the carbon atoms and with imidoylamidines playing the
role of chelating agents. A simple synthesis of dialkylborylimidoyl-
amidinates involves heating of trialkylboranes with the respective
nitriles and amidines /42/. The first reaction step produces a trial-
kylborane - amidine complex (34); heating the latter leads to imidoyl-
aminodialkylborane (35) with elimination of alkane.

$$R_3B \ + \ R'C{\overset{\nearrow NH}{\underset{\searrow NH_2}{}}} \longrightarrow R_3B \leftarrow NH{=}\underset{NH_2}{\overset{|}{C}}{-}R' \ \xrightarrow{100\text{-}150^{\circ}C} \ R_2BNH\underset{NH}{\overset{\parallel}{C}}R'$$

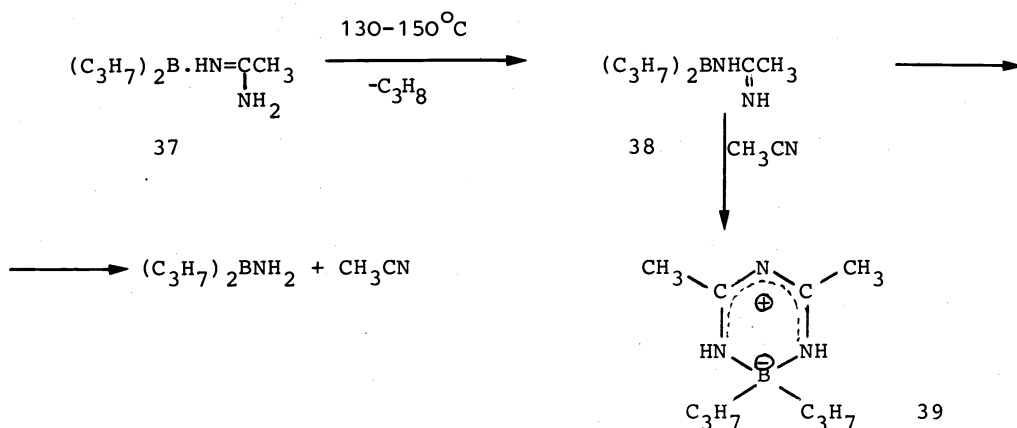**34**   **35**
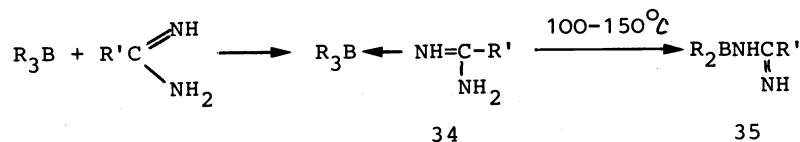
Compound (35) adds to nitrile to produce the respective dialkylboryl-
imidoylamidinate (36). The reaction mechanism may be similar to that
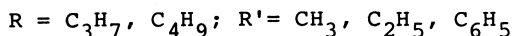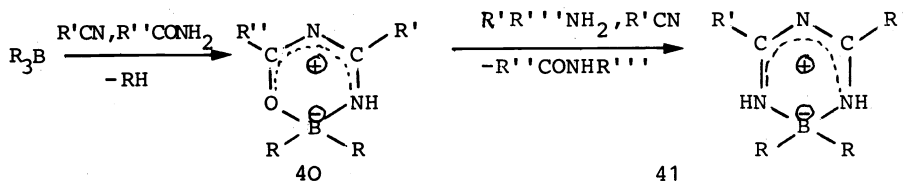for the enaminoborane reaction with nitriles.

$$R_2B{-}NH{-}\underset{NH}{\overset{\parallel}{C}}{-}R' \ + \ R''C{\equiv}N \longrightarrow$$

35

36; 66-80%
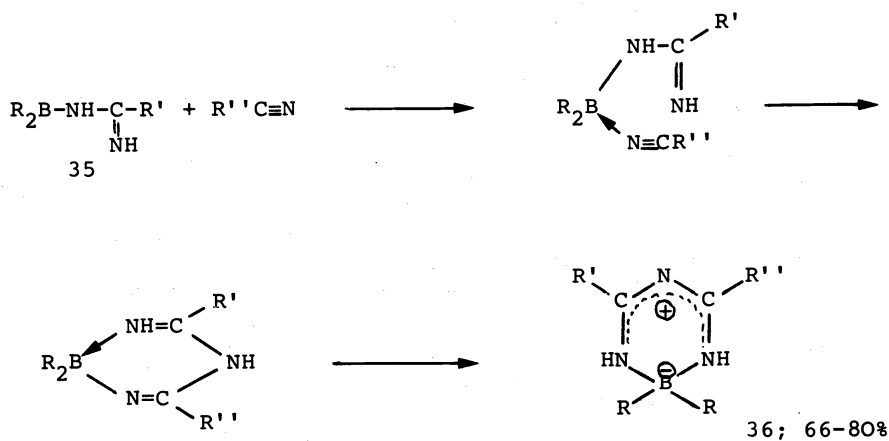
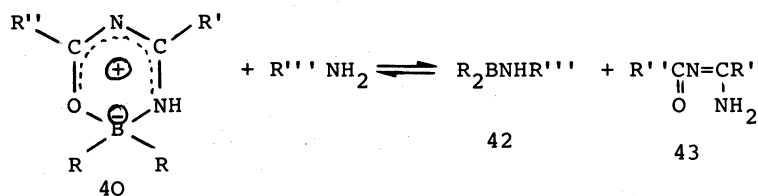R = C_3H_7, C_4H_9; R'= CH_3, C_6H_5; R''= CH_3, C_6H_5

A variation of this method is the synthesis of boron imidoylamidinates using esters of thioorganoboron acids /42/. Following this method one may obtain the chelates with both alkyl and acyl radicals at the boron atom. It should be pointed out that trialkylborane amidine complexes convert to chelates in rather low yield on heating. Thus the complex of tripropylborane with acetamidine (37) at 130-150°C gives dipropyl-borylacetimidoylacetamidinate (39). As the first step complex (37) gives acetimidoylaminodipropylborane (38) (via propane elimination) which then cleaves into aminodipropylborane and acetonitrile. The latter reacts with (38) to yield (39) /43/.
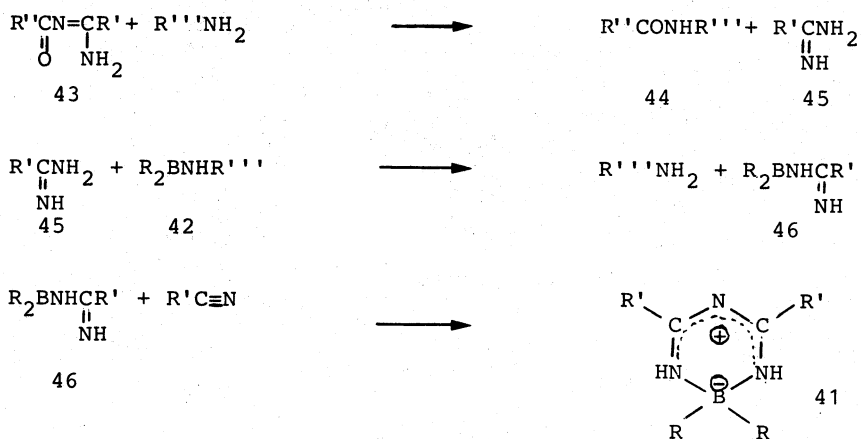
$(C_3H_7)_2B \cdot HN=\underset{\underset{NH_2}{|}}{C}CH_3$ $\xrightarrow[-C_3H_8]{130-150°C}$ $(C_3H_7)_2B\underset{\underset{NH}{|}}{N}H\overset{\overset{O}{||}}{C}CH_3$ $\longrightarrow$

       37   38 $\downarrow$ CH$_3$CN

$\longrightarrow$ $(C_3H_7)_2BNH_2 + CH_3CN$

    39

Dialkylborylimidoylamidinates may be prepared without the use of amidines from trialkylboranes, amides and nitriles /44/. Thus an equimolar mixture of trialkylborane and primary amide was heated at 80-100°C with a two- or three-fold nitrile excess. Then without isolating the intermediate dialkylborylacylamidinates (40) the mixture was treated with ammonia or propylamine. The yields of chelates are 40-50%.

R_3B $\xrightarrow[-RH]{R'CN, R''CONH_2}$ $\xrightarrow[-R''CONHR''']{R'R'''NH_2, R'CN}$

                     40   41

   $R = C_3H_7, C_4H_9$; $R' = CH_3, C_2H_5, C_6H_5$

The reaction shown in the scheme is based on the ability of dialkyl-borylacylamidinates (40) to undergo cleavage with nitrogen bases. Ammonia or primary amine reacts with chelate (40) to give aminoborane (42) and N-acylamidine (43). (43) is then cleaved by amine into the respective amide (44) and amidine (45). The generated amidine (45) and aminoborane (42) afford imidoylaminoborane (46). The latter adds further to the nitrile giving dialkylborylimidoylamidinate (41).

$+ R'''NH_2 \rightleftharpoons R_2BNHR''' + R''\underset{\underset{O}{||}}{C}N=\underset{\underset{NH_2}{|}}{C}R'$

     40   42   43

R''CN=CR' + R'''NH$_2$ $\longrightarrow$ R''CONHR''' + R'CNH$_2$

(structures 43, 44, 45)

R'CNH$_2$ + R$_2$BNHR''' $\longrightarrow$ R'''NH$_2$ + R$_2$BNHCR'

(structures 45, 42, 46)

R$_2$BNHCR' + R'C≡N $\longrightarrow$ (chelate structure 41)

It can be seen from these schemes that the basic course of the process
discussed involves the nitrile transformation into imidoylamidine
which in the last reaction step is fixed as ligand in the chelate (41).
The amides play an auxiliary function and return (in the form of the
respective N-substituted compounds in the case of primary amines).
The proposed synthesis of chelates (41), in spite of the lower yield
with respect to the method based on amidines, has an advantage: the
chelates could be prepared without preliminary synthesis of amidines,
a troublesome procedure in the case of aliphatic amidines. The struc-
ture of dialkylborylimidoylamidinates (41) was established by means
of IR, PMR and ^{11}B NMR spectroscopic methods. The ^{11}B NMR spectra show
the signals in the high field region (1 - 4 ppm), and the positions do
not change with increasing temperature to 180°C. The PMR spectra of
dialkylborylacetimidoylacetamidinates (41, R'=CH$_3$) exhibit a singlet
for the methyl groups (δ = 2.01 ppm) and a singlet for the nitrogen
protons (δ = 6.0 - 6.6 ppm) confirming an equivalence of CH$_3$ groups
and hydrogen atoms and thus a symmetric structure for the dialkyl-
borylimidoylamidinates (41). The molecular symmetry is explained by
the fact that all three nitrogen atoms as well as ring carbon atoms
are in the trigonal valent state, producing in general a five-center
π-system localizing six π-electrons. The comparatively low dipole
moments of dialkylborylimidoylamidinates (1.88 D for 41, R'= C$_6$H$_5$) are
in agreement with structure (47) having semicoordinative bonds.

(structure 47)
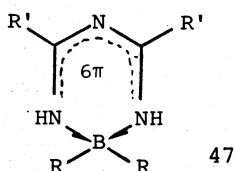
Dialkylborylimidoylamidinates are stable in air and do not hydrolyze
upon refluxing with water or alkalies, and with strong acids (HCl,
HClO$_4$) they produce adducts /19,42/ which are boronium salts (48).

(structure 48)
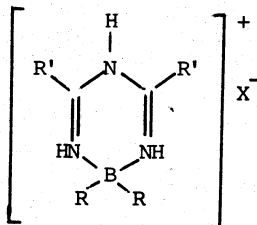
X = Cl, ClO$_4$ 48

At 120-130°C, dibutylborylbenzimidoylbenzamidinate reacts with acetic acid with substitution of the boron alkyl radical for an acetoxy group /19/.

49   50
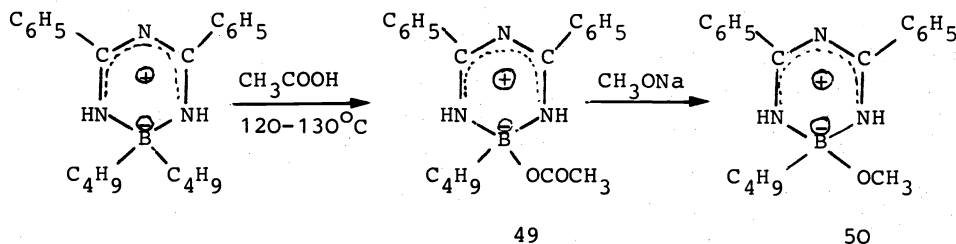
In the compound (49) generated, the acetoxylic group is replaced by a methoxy group in the presence of sodium methylate, giving (50).

Amidinoboranes

Among the different types of boron amidine derivatives /42,43,45-50/, of specific interest are dialkylborylamidines (51) produced from the symmetrical amidines and trialkylboranes or dialkylthioborinates /51/.
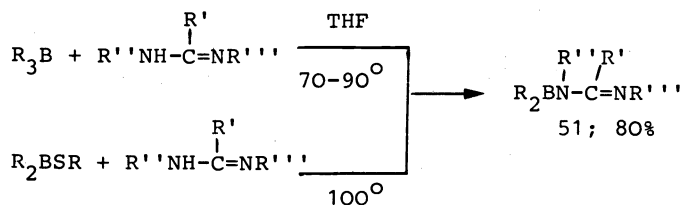

51a: R = C_3H_7,   R' = C_6H_5,   R'' = R''' = CH_3

51b: R = C_7H_9,   R' = C_6H_5,   R'' = R''' = CH_3

51c: R = iso-C_4H_9,   R' = C_6H_5,   R'' = R''' = CH_3

51d: R = iso-C_3H_7,   R' = C_6H_5,   R'' = R''' = CH_3

51e: R = iso-C_4H_9,   R' = C_6H_5,   R'' = CH_3, R''' = C_6H_5

51f: R = C_4H_9,   R' = C_6H_5,   R'' = R''' = iso-C_3H_7

51g: R = C_4H_9,   R' = CH_3,   R'' = R''' = $CH_2C_6H_5$

According to the data of ^{11}B NMR and PMR spectra, compounds (51d - g) are the intracoordinated cyclic compounds (52) while compounds 51a - c exist in the form of an equilibrium mixture of the open (51) and cyclic structures (52). The ^{11}B NMR spectra of coumpounds (51a - c) have two signals in the high (δ = -8 - -10 ppm) and low (δ = -50 ppm) fields. The PMR spectra show three signals from methyl groups. The ^{11}B NMR spectra of compounds (51d - g) contain one signal (δ = -8 - -12 ppm) and the PMR spectrum of 51d shows the signal from CH_3-groups.


52
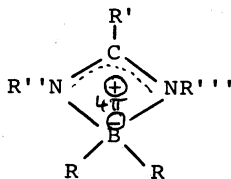
An equivalence of R-N and thus B-N bonds is attained by inclusion of both trigonal nitrogen atoms into the common three-center orbital occupied by four electrons: one from carbon and three electrons from two nitrogen atoms. Three electrons of the nitrogen atoms and an electron of one boron produce two B-N bonds (52). The structure (53) with semi-coordinative B-N bonds corresponds more exactly to the cyclic amidino-boranes. A four-membered structure of an amidinoborane is naturally unusually strained and thus the bonds C-N and B-N are actually of banana-like pattern (54).
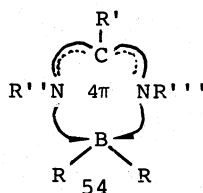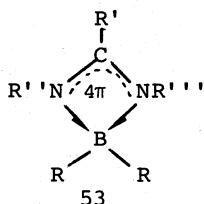

## The six-membered cyclic coordination diboron compounds

In some chemical reactions 1,2-azaborolidines have been found to display behaviour different from the acyclic aminoboranes /52,53/. The reaction of 2-alkyl-1,2-azaborolidines with acid anhydrides proceeds specifically /54/. These reagents   (3:1) produce along with intracomplex acyloxy (γ-aminopropyl)alkylboranes (55) also the six membered cyclic coordination diboron compounds (56) formed by two different organoboron compounds.
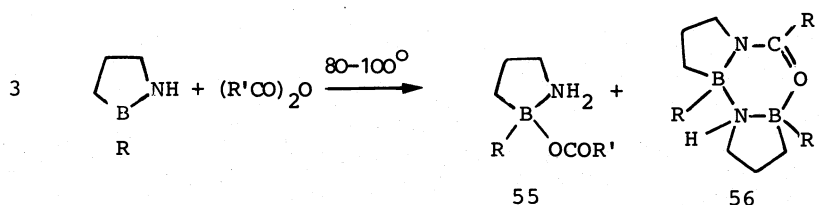

Such complexation may be named 1,4-coordinative interaction, unlike 1,2-coordination taking place on the dimerization of organoboron compounds, e.g. aminoboranes. Formation of such boron complexes is of a general character and could be represented by the following scheme:
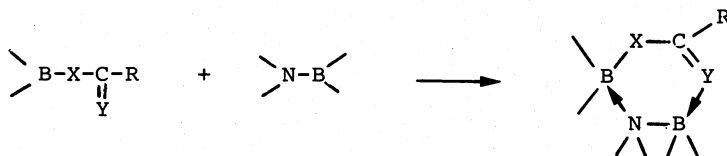

1,4-Coordination is realized between 2-alkyl-1,2-azaborolidines or aminodialkylboranes and acetoxydialkylboranes.
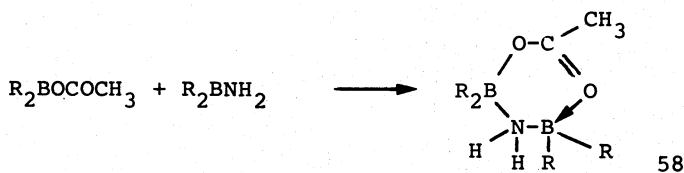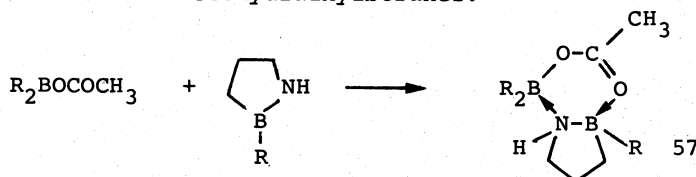
In compounds (56-58) charge redistribution may occur and depending on the substituents they may have more or less symmetric structure. Thus the ^{11}B NMR spectrum of compound (59) contains one signal (δ = -3.3 ppm from $(C_2H_5)_2O.BF_3$). In the PMR spectrum all 4 ethyl groups at the boron are equivalent (the CH_2 multiplet centered at 0.36 ppm and the CH_3 multiplet at 0.77 ppm).

59
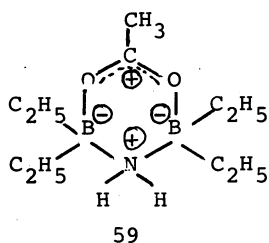
1,4-Coordination compounds result from acetaminodialkylboranes and aminoboranes (60) /55/ and from amidine-trialkylboranes and aminoboranes (61) /43/.

$$R_2BNHCOCH_3 + R_2BNH_2 \longrightarrow$$

60

$$R_3B.NH=C-CH_3 + 2\ R_2BNH_2 \longrightarrow$$
$$\qquad\quad |$$
$$\qquad NH_2$$

61
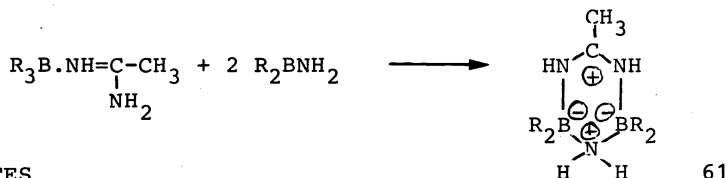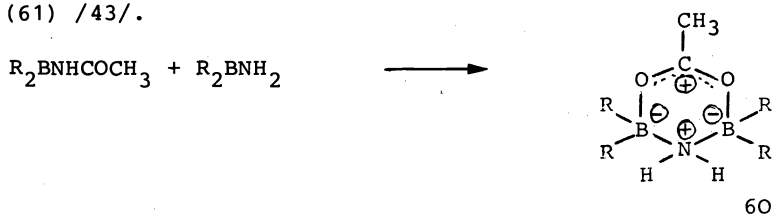
REFERENCES

1. W. Dilthey, Ann.Chem.344,300(1905).
2. G.T. Morgan and R.H. Tunstall, J.Chem.Soc.125,1963(1924).
3. H. Schäfer and O. Braun, Naturwissenschaften 39,280(1952).
4. A.T. Balaban, O.N. Bantea and M. Mocanu, Tetrahedron Lett.1964,2049.
5. B.M. Mikhailov, V.A. Vaver and Yu.N. Bubnov, Dokl.Acad.Nauk SSSR 126,575(1959).
6. B.M. Mikhailov and Yu.N. Bubnov, Izvest.Acad.Nauk SSSR, Otd.Khim. Nauk,1960,1872.
7. B.M. Mikhailov and Yu.N. Bubnov, Izvest.Acad.Nauk SSSR, Otd.Khim. Nauk,1960,1883.
8. M.F. Hawthorne and M. Reintjes, J.Am.Chem.Soc.86,5016(1964).
9. M.F. Hawthorne and M. Reintjes, J.Org.Chem.30,3851(1965).
10. W. Gerrard, M.F. Lappert and R. Shafferson, Chem. and Ind.(London), 1958,722.
11. R. Köster and G.W. Rotermund, Ann.689,40(1965).
12. I. Bally, A. Arsene, M. Bacesku-Roman and A.T. Balaban, Tetrahedron Lett.1965,3929.
13. L.H. Toporcer, R.E. Dessy and S.I.E. Green, Inorg.Chem.4,1949(1965).
14. B.M.Mikhailov and E.A. Shagova, Zh.Obshch.Khim.45,1052(1975).
15. A.W. Hanson and E.W. Macaulay, Acta Cryst.B28,1961(1972).
16. B.M. Mikhailov, Chemistry of Boron Hydrides,Publ."Science",Moscow, 1967.
17. B.M. Mikhailov, Progress in Boron Chemistry, Vol.3,p.313,Pergamon Press,1970.
18. A.T.Balaban, A. Arsene, J.Bally, A.Barabas, M. Parashiv, M. Roman and E. Romas, Rev.Roum.Chim.15,635(1970).
19. B.M. Mikhailov, V.A. Dorokhov and V.I.Seredenko, Zh.Obshch.Khim. 43,862(1973).
20. M.J.S. Dewar and R.C. Dougherty, Tetrahedron Letters,1964,987.
21. R. Köster and W. Fenzl, Angew.Chem.80,756(1968).
22. V.A. Dorokhov and B.M. Mikhailov, Izvest.Acad.Nauk,Ser.Khim.1966, 364.

23. V.A. Dorokhov and B.M. Mikhailov, Dokl.Acad.Nauk SSSR 187,1300,
    (1969).
24. V.A. Dorokhov, O.G. Boldyreva, B.M. Zolotorev, O.S. Chizhov and
    B.M. Mikhailov, in press.
25. V.A. Dorokhov, O.G. Boldyreva, V.S. Bogdanov and B.M. Mikhailov,
    Zh.Obshch.Khim.42,1558(1972).
26. B.M. Mikhailov, G.S. Ter-Sarkisjan, N.N. Govorov and N.A. Nikolaeva,
    Izvest.Acad.Nauk,Ser.Khim.1974,2389.
27. B.M. Mikhailov, G.S. Ter-Sarkisjan, N.N. Govorov and N.A. Nikolaeva,
    Izvest.Acad.Nauk,Ser.Khim.1976.
28. B.M. Mikhailov, G.S. Ter-Sarkisjan and N.N. Govorov, Izvest.Acad.
    Nauk,Ser.Khim.1976.
29. Yu.N. Bubnov, A.V. Tsyban and B.M. Mikhailov, Izvest.Acad.Nauk,
    Ser.Khim. in press.
30. B.M. Mikhailov, V.A. Dorokhov and O.G. Boldyreva, Izvest.Acad.
    Nauk,Ser.Khim.1973,2643.
31. V.A. Dorokhov, O.G. Boldyreva and B.M. Mikhailov, in press.
32. V.A. Dorokhov, L.I. Lavrinovich and B.M. Mikhailov, Dokl.Acad.
    Nauk SSSR 195,1100(1970).
33. B.M. Mikhailov and V.A. Dorokhov, Izvest.Acad.Nauk SSSR,Ser.Khim.
    1970,1446.
34. V.A. Dorokhov, L.I. Lavrinovich, I.P. Yakovlev and B.M. Mikhailov,
    Zh.Obshch.Khim.41,2501(1971).
35. B.M. Mikhailov and V.A. Dorokhov, Izvest.Acad.Nauk SSSR,Ser.Khim.
    1971,201.
36. V.A. Dorokhov, L.I. Lavrinovich, M.N. Bochkareva and V.S. Bogdanov,
    Zh.Obshch.Khim.43,1115(1973).
37. B.M. Mikhailov, V.A. Dorokhov and I.P. Yakovlev, Izvest.Acad.Nauk
    SSSR,Ser.Khim.1966,332.
38. B.M. Mikhailov, V.A. Dorokhov and L.I. Lavrinovich, Zh.Obshch.
    Khim.42,1553(1972).
39. A. Pinner, Ber.22,1606(1889).
40. A. Pinner, Ber.22,1600(1889).
41. I.E. Milks, G.W. Kennerly and J.H. Polevy, J.Am.Chem.Soc.84,2529
    (1962).
42. B.M. Mikhailov, V.A. Dorokhov and V.I. Seredenko, Dokl.Acad.Nauk
    SSSR 199,1328(1971).
43. V.A. Dorokhov and B.M. Mikhailov, Zh.Obshch.Khim.41,2702(1971).
44. B.M. Mikhailov, V.A. Dorokhov and L.I. Lavrinovich, Zh.Obshch.
    Khim.44,1888(1974).
45. V.A. Dorokhov, V.I. Seredenko and B.M. Mikhailov, Izvest.Acad.
    Nauk SSSR,Ser.Khim. in press.
46. V.A. Dorokhov, V.I. Seredenko and B.M. Mikhailov, Zh.Obshch.Khim.
    46,(1976).
47. V.A. Dorokhov, V.I. Seredenko and B.M. Mikhailov, Zh.Obshch.Khim.
    45,1772(1975).
48. B.M. Mikhailov and V.A. Dorokhov, Izvest.Acad.Nauk SSSR,Ser.Khim.
    1973,2649.
49. B.M. Mikhailov, V.A. Dorokhov, V.I. Seredenko and I.P. Yakovlev,
    Izvest.Acad.Nauk SSSR,Ser.Khim.1974,1665.
50. V.A. Dorokhov, V.I. Seredenko and B.M. Mikhailov, Izvest.Acad.
    Nauk SSSR,Ser,Khim. in press.
51. B.M. Mikhailov, V.A. Dorokhov and L.I. Lavrinovich, Izvest.Acad.
    Nauk SSSR,Ser.Khim. in press.
52. B.M. Mikhailov, V.A. Dorokhov and N.V. Mostovoj, Zh.Obshch.Khim.,
    Problems of Organic Synthesis 1965,233.
53. N.V. Mostovoj, V.A. Dorokhov and B.M. Mikhailov, Izvest.Acad.
    Nauk SSSR,Ser.Khim.1966,90.
54. V.A. Dorokhov and B.M. Mikhailov, Izvest.Acad.Nauk SSSR, Ser.Khim.
    1970,1804.
55. B.M. Mikhailov, V.A. Dorokhov, V.S. Bogdanov, I.P. Yakovlev and
    A.D. Naumov, Dokl.Acad.Nauk SSSR,194,595(1970).