THE CYCLIC COORDINATION OF BORON COMPOUNDS

B. M. Mikhailov

The N.D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Moscow, USSR

Abstract

The methods of synthesis, structure and reactivities of the cyclic boron compounds having the double inner coordination of R₂B groups with terminal heteroatoms in the five- and three-membered chains are discussed. β-Diketonates, β-ketoiminates, β-dilinates, 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-dilinates, 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 R₂B boryl group via the two donor-acceptor bonds taking part in their formation.

There also exist the four-membered cyclic coordination boron compounds with delocalized system of bonds 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 BCl₃ /1/.

\[
\text{CH}_3\quad \text{O} \quad \text{B} \quad \text{O} \quad \text{C} \quad \text{CH}_3 \\
\text{HC} \quad \text{B} \quad \text{O} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{O} \quad \text{B} \quad \text{O} \quad \text{C} \quad \text{CH}_3
\]

Cl⁻
Unlike BCl₃, boron trifluoride and acetylacetone afford difluoroboryl-acetylacetone (2) /2/.

\[
\text{BF}_3 + \text{CH}_3\text{CCH}_2\text{CCH}_3 \rightarrow \text{F}_2\text{B} = \text{C} = \text{C} = \text{C} = \text{O}
\]

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

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

\[
R_3\text{B} + \text{CH}_3\text{COCH}_2\text{COCH}_3 \rightarrow \text{2} \text{CH}_3 + RH
\]

\(R = \text{C}_3\text{H}_7, \text{C}_4\text{H}_9\)

Dialkylboryl-acetylacetonates are produced smoothly also by action of acetylacetone on the esters of dialkyborinic and dialkythioborinic acids /7/. Boron \(\beta\)-dicarboxylyl chelates are prepared from acetoacetic ester and trialkylboranes /8,9/ or from dialkyl(diaryl)chloroboranes /10/. Triarylboranes /11/, esters of diarylboronic acids /12/ and diphenylchloroborane /13/ react smoothly with \(\beta\)-diketonates to form diarylboryl-\(\beta\)-diketonates. Various \(\beta\)-alkylboracyclanes (borolanes, borinanes, 1-boraindanes etc.) reacting with acetylacetone are converted 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.:
The cyclic coordination of boron compounds

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 acetylacetonates of boron are magnetically equivalent ($\delta = 2.00$ 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(1)-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 $\beta$-diketonates are in a trigonal valent state and together with the trigonal carbon atoms produce a 5-center $\pi$-system of six $\pi$-electrons, three of which being contributed by two oxygen atoms. Evidence of a trigonal valent state (sp$^2$) for the oxygen atoms in boron $\beta$-diketonates is obtained from the interatomic distances in compound (4), where D (C-O)=1.304Å, compared to those in resorcin and fluoroglucose with tetrahedral oxygens D (C-O)=1.36Å. When an electron transfers entirely to the boron, the $\beta$-diketonate would have structure (5). Structure (6) with semicordinated oxygen - boron bonds /16,17/ corresponds more exactly to the properties of boron $\beta$-diketonates.
beta-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 perchloric acid on diphenylborylbenzoylacetononate affords a crystalline solid to which the structure of salt (7) was assigned /18/.

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

Boron beta-ketoiminates
Nitrogen analogs of boron beta-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 beta-ketoiminates of boron /8/ was generated by addition of vinylxyboranes to nitriles /21/.

Compounds (8) are heat and hydrolysis resistant.

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

\[
R^1_{\text{B}}= \text{R}^2 + \text{NR}^1 \rightarrow R^1_{\text{B}}=\text{NR}^1 + \text{R}^2'\text{SH}
\]

\[
R = \text{C}_3\text{H}_7, \text{C}_4\text{H}_9; \text{R}' = \text{i-C}_4\text{H}_9, \text{C}_6\text{H}_5
\]
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) \(/26,28/\).

\[
\text{R}_2\text{BSR} + \text{HN} = \text{C} - \text{C} = \text{CHR}'' \rightarrow \text{R}_2\text{BN} = \text{C} - \text{CHR}'' \rightleftharpoons \text{R}_2\text{BNC} = \text{CHR}''
\]

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 benzocyanide afforded tricyclic boron \(\beta\)-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 \(\beta\)-diiminates (16). This procedure afforded dibutylboryl(\(\alpha\)-benzimidoyl-propiophenoiminate) (16a), dibutylboryl(\(\alpha\)-benzimidoylbutyrophenoniminate) (16b) and dibutylboryl(\(\alpha\)-acetimidoylpropio-phenoniminate) (16c) \(/28/\).

\[
\text{C}_6\text{H}_5\text{CN} + \text{RCH}_2 \rightarrow \text{C}_6\text{H}_5\text{N}\text{BC}_4\text{H}_9
\]

16a: \(R=\text{CH}_3\), \(R'=\text{C}_6\text{H}_5\); 16b: \(R=\text{C}_2\text{H}_5\), \(R'=\text{C}_6\text{H}_5\)
16c: \(R=R'=\text{CH}_3\)
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-diminates (16) was established on the basis of UV, IR, PMR and NMR 11B spectra. The 11B NMR spectra of compounds 16a-c contain the signals from 11B 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-diminates, which could be attained by inclusion of both nitrogen atoms having a trigonal valent state into the common five-center system of σ-orbitals occupied by six σ-electrons: three electrons from the three carbon atoms and two electrons from the two nitrogen atoms. The structure of β-diminates may be described by formula (17) with semicoordinative B-N bonds produced by a boron electron and three electrons from the two nitrogen atoms.

In discussing the reaction mechanism of organoboran enamines with nitriles one should start from the specific ability of trivalent boron compounds to react coordinatively with the nitrogen-containing ligands, 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 ligand. 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/.

In the synthesis of boron β-diminates 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 dimers (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-diiminates (23).
The cyclic coordination of boron compounds

The boron \( \alpha \)-diimimates (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/.

Boron diaclylamidates

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

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 $-13.1 \text{ ppm}$. The single CH group signals observed in the PMR spectra of compounds (26) (for dibutylboryldiacetamidate $\delta = 2.10 \text{ ppm}$), are evidence of their symmetric structure. In these compounds the nitrogen 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 dialkylborinic acid or its methyl ester. The lower stability of $\beta$-diacetamidates with respect to $\beta$-diketonates is revealed by their transformation into $\beta$-diketonates under action of acetylacetone.

**Boron acylaminidinates**

Acylaminodialkylboranes (27) generated from primary amides and dialkylthioborinates /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 nitriles 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 observed in the reactions of enaminoboranes with nitriles.

On the other hand, addition of dialkylborylacylaminoboranes to nitriles may be discussed as "amidoboration" of nitriles, similar to thioboronation of acetonitrile /37/:
The cyclic coordination of boron compounds

The chelates (28) may be prepared from N-acylamidines and trialkylboranes, dialkylboronates or dialkylborinates /36/.

\[ R_3B \xrightarrow{R'CONH-C(NH)R''} 28 \]

\[ R_2BOR \xrightarrow{RCONH-C(NH)R''} 28 \]

\[ R_2BSR \xrightarrow{RCONH-C(NH)R''} 28 \]

\[ R = C_2H_5, C_3H_7, C_4H_9, C_6H_5 \]

\[ R' = CH_3, C_2H_5, (CH_3)_3C, C_6H_5CH_2, C_6H_5 \]

\[ R'' = CH_3, C_2H_5, (CH_3)_3C, C_6H_5 \]

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 \((C_2H_5)_2OBF_3\)). 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).

\[ \text{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.

\[ RCONH_2 + R'C-CN + R_3'B \xrightarrow{1. \text{THF, 30-70°C}} \xrightarrow{2. \text{HCl, CH}_3\text{OH}} \text{RCNHCR}'' \xrightarrow{\text{NaHCO}_3 \xrightarrow{\text{O} \text{NH}_2}} \]

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 acylaminides /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 diethylaminodiphenylborane or organoboron acids /41/.

\[
(C_6H_5)_2BN(C_6H_5)_2 + H_2NCN=CNH_2 \rightarrow \begin{array}{c}
\text{(32)} \\
\end{array}
\]

\[
RB(OH)_2 + H_2NCN=CNH_2 \rightarrow \begin{array}{c}
\text{(33)} \\
\end{array}
\]

\[
R = C_6H_5, C_4H_9, CH_2=CH-
\]

An asymmetric structure with inequivalent (covalent and coordinative) B-N bonds was assigned to these compounds. Further investigations developed different methods of synthesis of such chelates with hydrocarbon radicals at the carbon atoms and with imidoylamidines playing the role of chelating agents. A simple synthesis of dialkylborylimidoylamidinates involves heating of trialkylboranes with the respective nitriles and amidines /42/. The first reaction step produces a trialkylborane - amide complex (34); heating the latter leads to imidoylaminodialkylborane (35) with elimination of alkane.

\[
R_3B + R'\text{C=N}NH_2 \rightarrow R_3B\text{NH=CSR'} + \text{NH}_2 \rightarrow R_2BNHCR' \text{ with } 100-150^\circ C
\]

\[
\text{(34)} \quad \text{(35)}
\]

Compound (35) adds to nitrile to produce the respective dialkylborylimidoylamidinate (36). The reaction mechanism may be similar to that for the enaminoborane reaction with nitriles.

\[
R_2B-NH-CR' + R''\text{C=NR} \rightarrow \begin{array}{c}
\text{(36) 66-80%} \\
\end{array}
\]

\[
R = C_3H_7, C_4H_9; R' = \text{CH}_3, C_6H_5; R'' = \text{CH}_3, C_6H_5
\]
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 dipropylboracacetimidoylamidinate (39). As the first step complex (37) gives acetimidoylamidopropylborane (38) (via propane elimination) which then cleaves into aminodipropylborane and acetonitrile. The latter reacts with (38) to yield (39) /43/.

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 dialkylborylamidinates (40) the mixture was treated with ammonia or propylamine. The yields of chelates are 40-50%.

The reaction shown in the scheme is based on the ability of dialkyloborylamidinates (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 imidoylamino borane (46). The latter adds further to the nitrile giving dialkyloborylimidoylamidinate (41).
It can be seen from these schemes that the basic course of the process discussed involves the nitrile transformation into imidoylamine 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 amides. The structure of dialkylborylimidoylaminates (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 ($\delta = 2.01$ ppm) and a singlet for the nitrogen protons ($\delta = 6.0 - 6.6$ ppm) confirming an equivalence of CH$_3$ groups and hydrogen atoms and thus a symmetric structure for the dialkylborylimidoylaminates (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 $\pi$-system localizing six $\pi$-electrons. The comparatively low dipole moments of dialkylborylimidoylaminates (1.88 D for 41, R'=C$_6$H$_5$) are in agreement with structure (47) having semicoordinative bonds.

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

\[
\begin{align*}
\text{C}_6\text{H}_5\text{N} & \text{C}_6\text{H}_5 \\
\text{C}_4\text{H}_9 & \text{C}_4\text{H}_9 \\
\text{CH}_3\text{COOH} & \text{120-130°C} \\
\text{C}_6\text{H}_5\text{N} & \text{C}_6\text{H}_5 \\
\text{C}_4\text{H}_9 & \text{OCOCH}_3 \\
\text{CH}_3\text{ONa} & \\
\text{C}_6\text{H}_5\text{N} & \text{C}_6\text{H}_5 \\
\text{C}_4\text{H}_9 & \text{OCOCH}_3 \\
\end{align*}
\]

49

50

In the compound (49) generated, the acetoxylic group is replaced by a methoxy group in the presence of sodium methyle, 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 dialkythioborinates /51/.

\[
\begin{align*}
\text{R}_1 & \text{B} + \text{R''NH-C=NR'''} \\
\text{THF} & \text{70-90°C} \\
\text{R}_1\text{BSR} + \text{R''NH-C=NR'''} & \text{100°C} \\
\text{R''R'} & \\
\text{R}_2\text{BN-C=NR'''} & \\
\text{51; 80%} \\
\end{align*}
\]

51a: \( \text{R} = \text{C}_3\text{H}_7 \), \( \text{R'} = \text{C}_6\text{H}_5 \), \( \text{R''} = \text{R'''} = \text{CH}_3 \)

51b: \( \text{R} = \text{C}_7\text{H}_9 \), \( \text{R'} = \text{C}_6\text{H}_5 \), \( \text{R''} = \text{R'''} = \text{CH}_3 \)

51c: \( \text{R} = \text{iso-C}_4\text{H}_9 \), \( \text{R'} = \text{C}_6\text{H}_5 \), \( \text{R''} = \text{R'''} = \text{CH}_3 \)

51d: \( \text{R} = \text{iso-C}_3\text{H}_7 \), \( \text{R'} = \text{C}_6\text{H}_5 \), \( \text{R''} = \text{R'''} = \text{CH}_3 \)

51e: \( \text{R} = \text{iso-C}_4\text{H}_9 \), \( \text{R'} = \text{C}_6\text{H}_5 \), \( \text{R''} = \text{CH}_3 \), \( \text{R'''} = \text{C}_6\text{H}_5 \)

51f: \( \text{R} = \text{C}_4\text{H}_9 \), \( \text{R'} = \text{C}_6\text{H}_5 \), \( \text{R''} = \text{R'''} = \text{iso-C}_3\text{H}_7 \)

51g: \( \text{R} = \text{C}_4\text{H}_9 \), \( \text{R'} = \text{CH}_3 \), \( \text{R''} = \text{R'''} = \text{CH}_2\text{C}_6\text{H}_5 \)

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 compounds (51a - c) have two signals in the high (\( \delta = -8 - -10 \) ppm) and low (\( \delta = -50 \) ppm) fields. The PMR spectra show three signals from methyl groups. The $^{11}$B NMR spectra of compounds (51d - g) contain one signal (\( \delta = -8 - -12 \) ppm) and the PMR spectrum of 51d shows the signal from CH$_3$-groups.
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 amidinoboranes. 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 (\( \text{NC}-\text{aminopropyl} \))alkylboranes (55) also the six membered cyclic coordination diboron compounds (56) formed by two different organoboron compounds.

\[
\begin{align*}
3 \quad & \quad \text{NH} + (R''CO)_2 \quad \xrightarrow{80-100^\circ} \\
& \quad \text{NH}_2 + 55 \quad \xrightarrow{} \quad \text{COR'} + 56
\end{align*}
\]

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 ($\delta = -3.3$ ppm from (C$_2$H$_5$)$_2$OB). 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).

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

$$R_2BHCOCH_3 + R_2BHNH_2$$

$$\rightarrow$$

$$R_3BNH=CH_3 + 2 R_2BHNH_2$$

REFERENCES


