

Reviews

Boron-containing small rings: synthesis, properties, and application prospects

U. M. Dzhemilev, L. I. Khusainova, K. S. Ryazanov, and L. O. Khaifzova*

*Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347) 284 2750. E-mail: leilakh@mail.ru*

The studies published over the last 15 years on the synthesis, physicochemical properties, and application prospects of saturated and unsaturated three- and four-membered boron-containing carbocycles with one boron atom — boriranes, borirenes, boretananes, and 1,2-dihydroboretanes — are summarized and systematized. Original methods for the synthesis of boriran(en)es based on photochemical isomerization of organoboranes, double hydroboration of acetylenes with imidazol-2-ylideneboranes, and [2+1]-cycloaddition of borylenes (:B—R) to unsaturated compounds are considered. A new method for the synthesis of substituted boriranes by Cp₂TiCl₂-catalyzed cycloboration of olefins with boron halides in the presence of metallic Mg is presented. The not numerous data on the synthesis of four-membered boracyclanes (boretanes and 1,2-dihydroboretanes) based on thermal isomerization of cyclopropylboranes, [2+2]-cycloaddition of methyleneboranes to nitriles, 1,1-diethoxyethylene, or alkynes, as well as transmetalation of 1,8-dilithium naphthalene and titanacyclobutenes with boron halides, are summarized.

Key words: boriranes, borirenes, boretananes, 1,2-dihydroboretanes, photoirradiation, photoisomerization, olefins, acetylenes, catalysis, cycloboration.

Introduction

The fundamental and applied research in the field of small carbo- and heterocarbocycles — cyclopropanes, oxiranes, aziridines, phosphiranes, thiiranes and siliranes — is widely described in the world literature. These classes of compounds are used for the development and production of unique materials, highly energetic fuels, pharmaceuticals, virus inactivation agents in the production of vaccines, bioregulators used in agriculture, efficient lubricants, and other valuable compounds. Among known classes of

small heterocyclic compounds, the structures containing boron atoms are of most theoretical and practical interest. The persistent attention to these fairly rare and difficult-to-obtain compounds is dictated by specific features of the chemical behavior of small boracyclanes. These features are due to high internal energy of the strained ring, the nature of substituents capable of stabilizing the strained ring, and the property of boron atom to easily switch from the sp²- to the sp³-hybridized state owing to the vacant p-orbital.

Currently, three-membered boracyclanes are mainly prepared by the photochemical isomerization of structur-

ally diverse organoboranes and the [2+1]-cycloaddition of olefins, acetylenes, and other unsaturated compounds to borylenes generated in different ways. The synthesis of boriranes by double hydroboration of acetylenes with imidazol-2-ylideneboranes also attracted attention. Four-membered boracyclanes (boretanes and 1,2-dihydroboretanes) can be obtained by thermal isomerization of cyclopropylboranes, [2+2]-cycloaddition of methyleneboranes to alkynes, and stoichiometric transmetalation of 1,8-dilithionaphthalene or titanium-based four-membered metallacarboranes with boron dihalides (RBHal₂).

In 2014, three-membered boracyclanes were obtained by direct cycloboration of olefins and acetylenes with boron halides (BCl₃·SMe₂, BF₃·THF), in line with catalytic cycloalumination and cyclomagnesiation of unsaturated compounds with alkyl derivatives of Al and Mg catalyzed by Ti and Zr complexes (Dzhemilev reaction). The development of this method made it possible to perform efficient one-pot syntheses of not only substituted boriranes, but also five-membered organoboron compounds.^{1–3}

The recent advances in the chemistry of small boracyclanes are associated with the development of traditional and catalytic methods for their synthesis and the prospects for application of these cyclic products as photo-controlled molecular switches for molecular electronics and photonics and materials for sensors and light-emitting and electronic devices.

Apart from the theoretical and experimental studies of three-membered rings with one boron atom,⁴ there are reviews,^{5,6} where methods for the synthesis, physicochemical properties, and molecular and electronic structures of three-membered rings containing not only a boron atom, but also atoms of main group elements (Li, Si, Sn, C, N, O, S, P) and transition metals (Ni, Rh, Fe, Pd, Ir, Co, Mn, Au, Ta, *etc.*) are considered and systematized. The reviews^{7,8} addressing the chemistry of four-membered metallacarboranes containing Ir, Ti, Co, Pd, Ru, W, and other atoms describe the few existing examples of synthesis of four-membered boracyclanes.

This review presents a detailed analysis and discussion of the methods for the synthesis, physicochemical properties, and application prospects of three- and four-membered rings with one boron atom.

Boriranes and boratiranes

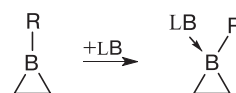
Cyclopropanes are attractive for researchers owing to the high reactivity of the strained ring and ring opening and expansion reactions. Boriranes are most reactive among three-membered heterocyclic systems, *e.g.*, oxiranes, aziridines, phosphiranes, thiiranes, and siliranes. With the exception of silicon, heteroatoms in these molecules, exert strong π -basic effects on the carbon atoms.

Examples of reverse polarity for three-membered heterocycles with π -acidic atoms are extremely rare. Boriranes are the only saturated systems with π -acidic ring atoms, due to the electron-deficient boron atom; this significantly increases their reactivity compared to other heteroanalogs.

The first mention of the possible formation of boriranes dates back to 1973;⁹ however, chemists were able to isolate them in a pure state and characterize only 10 years later.¹⁰ Free boriranes are unstable compounds sensitive to oxygen and water. They easily undergo skeletal transformations and, therefore, they are very seldom encountered. Early studies devoted to the synthesis and identification of boriranes were summarized in a review⁴ published in 1996.

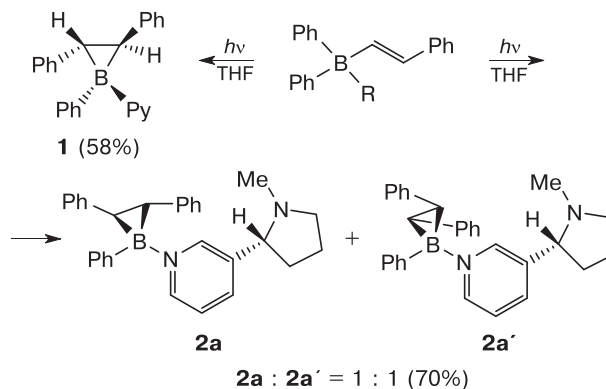
One strategy to stabilize boron heterocycles is the addition of strong Lewis bases (LB) in order to fill the vacant p_z orbital of boron and thus quench its high electrophilicity. The base-stabilized boriranes are called boratiranes (Scheme 1).

Scheme 1



These compounds were synthesized for the first time as pyridine (**1**) and (*S*)-nicotine (**2a,a'**) adducts by photoirradiation of borates in THF (Scheme 2).¹¹ Boratiranes **2a,a'** are formed as diastereomer mixtures (1 : 1). The absolute configuration of diastereomer **2a**, isolated by recrystallization from toluene, was shown by X-ray crystallographic analysis to be (2*S*,3*S*).

Scheme 2



R = Py, (*S*)-nicotine

The results of studies in the field of photochemical transformations of ammonium borate salts to the corresponding boratiranes are summarized in a review.¹²

Photochemical methods for the synthesis of boratiranes

Recently, boratiranes were prepared by UV irradiation of dimesitylboranes chelated with various biaryl groups.^{13–15} The UV irradiation-induced isomerization of *N,C*-chelated dimesitylboranes B(ppy)Mes₂ (ppy is 2-phenylpyridyl) afforded boratiranes composed of several connected rings. The photoirradiation (365 nm) of mesitylboranes **3a–f** in an inert atmosphere yielded boratirane derivatives, boratanocaradienes **4a–f** (Scheme 3). It should be noted that *N,C*-chelates play a key role in the isomerization, which implies the cleavage/formation of the B–C and C–C bonds and leads to a color change of the resulting compounds.

The products are the first example of photochromic systems switchable only on a boron center. The high interest in these systems is due to their potential use in molecular electronics and photonics.¹² However, high oxygen sensitivity of compounds of this type restricts their use in electronic devices. Indeed, in the presence of oxygen, boracyclanes **4a–f** decompose rather rapidly to give compounds **5a–f** and (MesBO)₃ (see Scheme 3).

New π -conjugated di-, tri-, and polyboranes were synthesized to study the influence of several boron photochromic centers in a molecule on the simultaneous photoisomerization.^{16,17} It was shown that isomerization of one chromophore prevents isomerization of the other one. The photoisomerization was monitored by ¹H NMR, fluorescence, and UV spectroscopy.

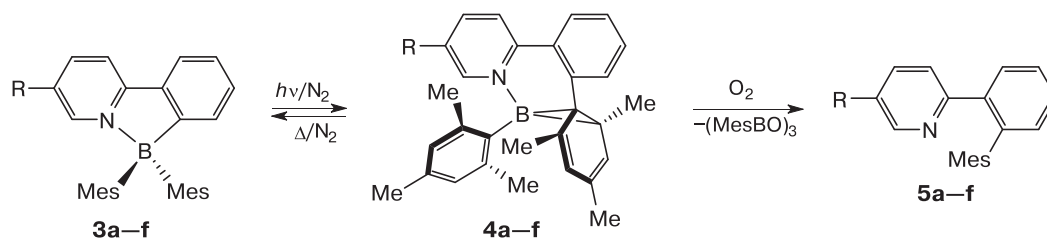
Bis-boranes **6** and **7** with two borane moieties connected by a diacetylene (**6**) or silicon (**7**) spacer were studied. It was shown that only one borane moiety undergoes photoisomerization to give monoboratiranes **8** and **9** (Scheme 4).

The UV irradiation of triborane **10** under similar conditions yielded boratirane **11**, containing only one boratirane moiety¹⁶ (Scheme 5).

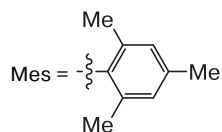
An increase in the irradiation time did not lead to a greater number of boratirane moieties. Similarly to di- and triboranes, the irradiation of hexaborane **12** led to photoisomerization of only one borane group to give compound **13** (Scheme 6).

In addition, the authors found that under UV irradiation, polyboranes isomerized faster than monoboranes. This result can be attributed to the "antenna effect",¹⁸

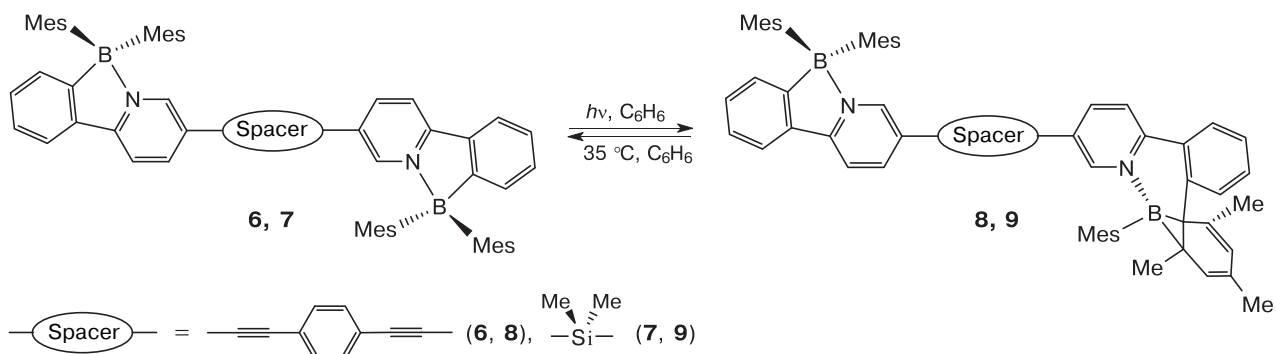
Scheme 3



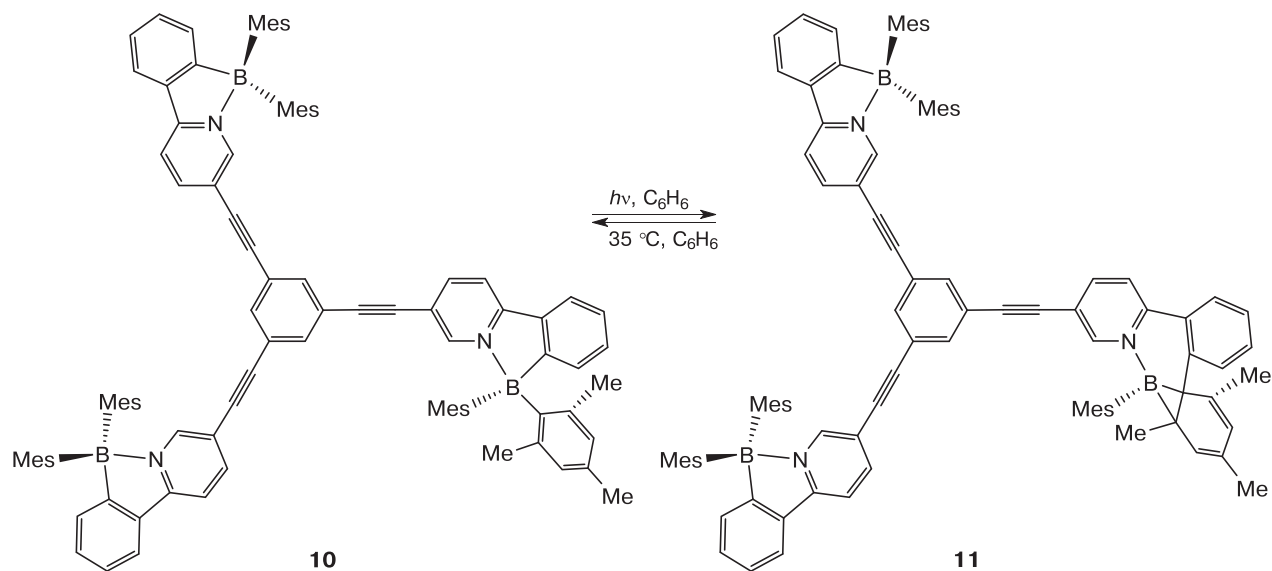
R = H (**a**), BMes₂ (**b**), TMS (**c**), CC–TMS (**d**), CC–Ph (**e**), C(O)H (**f**)



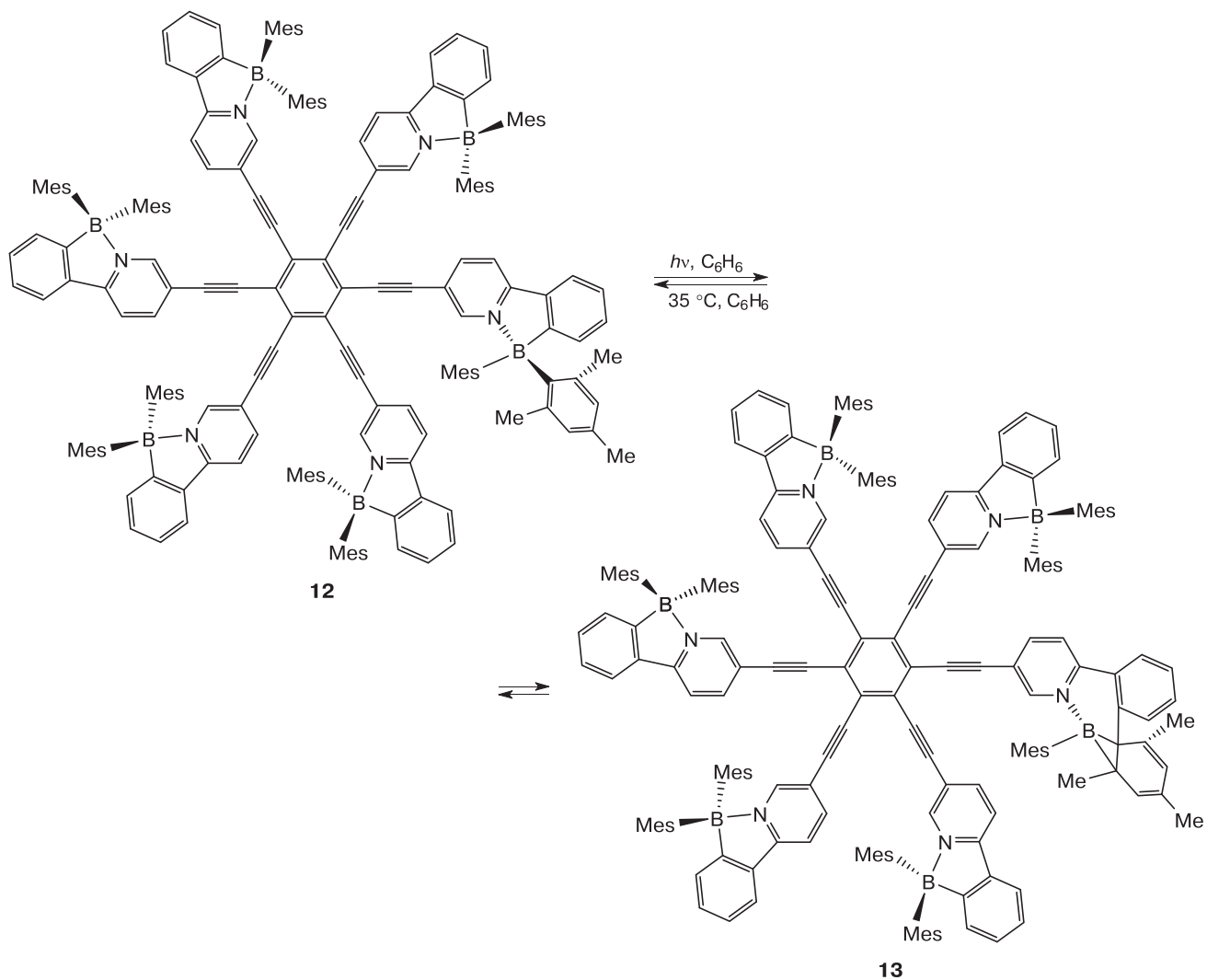
Scheme 4



Scheme 5

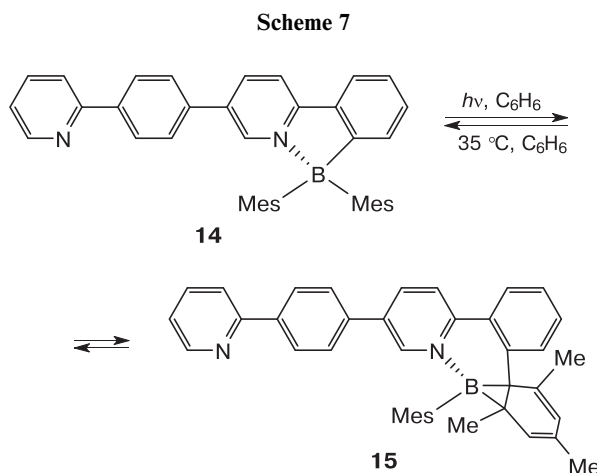


Scheme 6



owing to which multiple boron chromophores harvest more photons at the specified concentration, which accelerates photoisomerization *via* intramolecular energy transfer in one chromophore giving only one boratirane moiety.

In a study of the photochromic properties of four-coordinate boron *N,C*-chelates containing a B(ppy)Mes₂ moiety,¹⁹ new photochromic compounds containing two linearly conjugated 2-phenylpyridyl units were synthesized (Schemes 7 and 8).



Borane **14** reversibly isomerized under photoirradiation to give boratirane **15** in a high quantum yield (see Scheme 7).

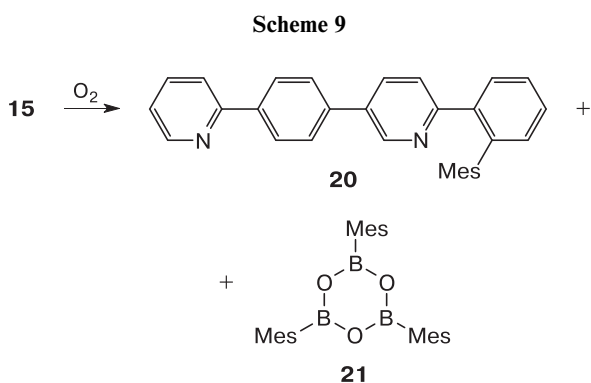
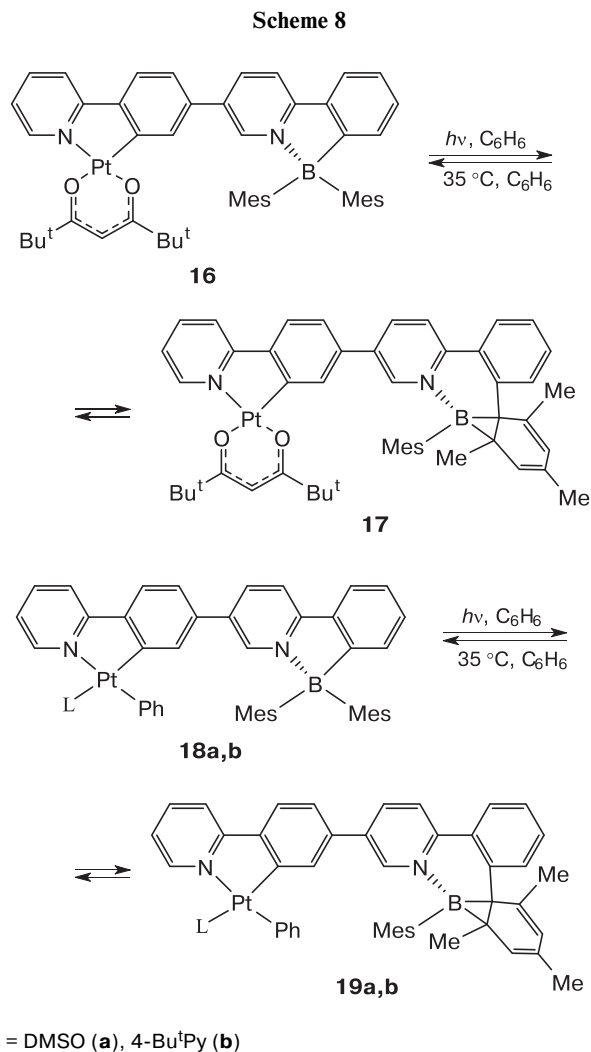
Borane **14** was converted to cyclometallated platinum(II) *N,C*-chelates **16** and **18a,b** to assess the influence of a covalently bound transition metal ion on photochromic properties of these compounds. By spectroscopic methods, it was found that the B(ppy)Mes₂ chromophore moiety reversibly photoisomerized under UV irradiation, similarly to that of compound **14**, to give boratirane adducts **17** and **19a,b**, but the quantum yield was much lower in this case (see Scheme 8).¹⁹

Boratirane **15** was converted to compound **20** and boroxine **21** as a result of the deboration in the presence of oxygen (Scheme 9).

The photochromic *N,C*-chelated organoboranes **22a–c** containing benzofuryl, benzothienyl, or *N*-phenylindolyl moieties^{20,21} isomerize to the corresponding boratiranes **23a–c** under UV light at 365 nm (Scheme 10). The isomerization is accompanied by a color change from light yellow to dark blue or green.

Stable single crystals of one of the boratiranes (namely, compound **23c**) were grown for the first time. This allowed an X-ray diffraction study of this compound, which confirmed the formation of a boratirane moiety, proposed earlier by computer calculations and NMR spectroscopy.

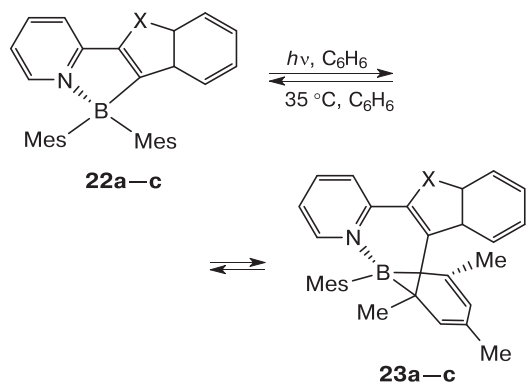
A series of *N,C*-chelated mono- and diboranes **24–28**, containing one or two thienyl groups in the molecule was synthesized.²²



It was found that only monothienyl boranes **24**, **25** undergo reversible photoisomerization to give boratiranes **29**, **30**, respectively (Scheme 11).

The isomerization of borane **25** proceeds with a significantly lower quantum yield than that of borane **24** or than the transformation of compound **3a** observed earlier.¹³ Such a behavior of these boranes is probably due to

Scheme 10

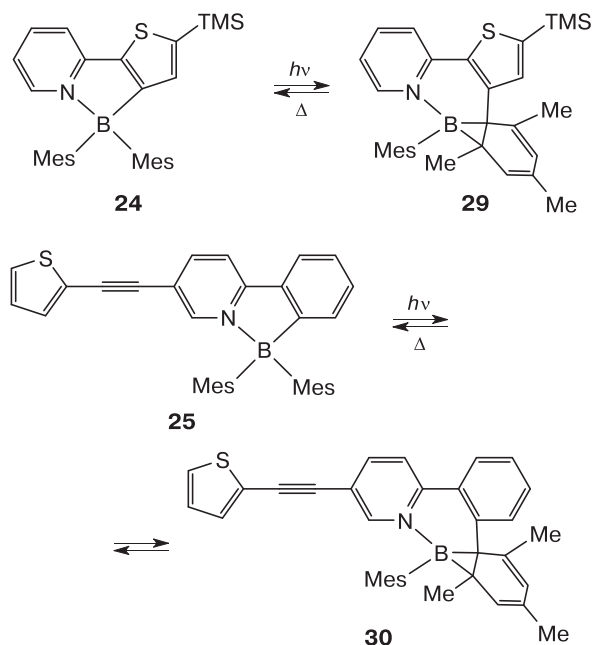
X = S (**a**), O (**b**), NPh (**c**)

a larger π -conjugation system in chelate **25** than that in compounds **24** or **3a**. According to NMR spectroscopic data, photoisomerization of boranes **24** and **25** to the corresponding boratiranes **29** and **30** is fully thermally reversible.²² It was found that *N,C*-chelated monoboranes and diboranes **26**–**28**, containing a dithienyl moiety in the molecule, are fairly stable against photoirradiation. The fluorescence data and quantum chemical calculations carried out by time-dependent density functional theory (TD-DFT) showed that the introduction of an additional dithienyl unit into the molecule gives rise to new photo-physical deactivation channels for the absorbed energy: fluorescence and charge transfer, which successfully compete with the photoisomerization.

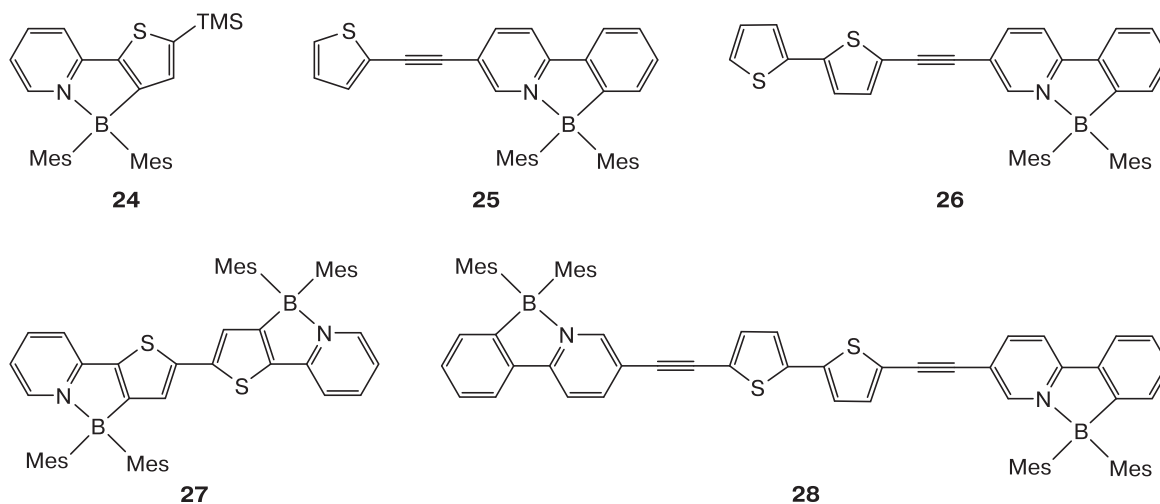
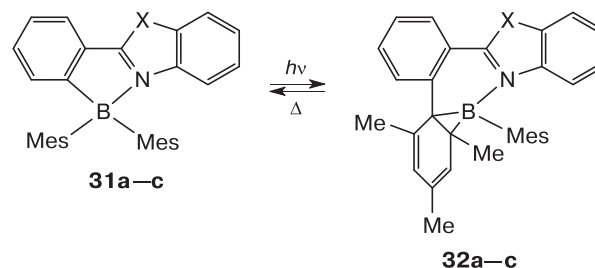
The synthesis of *N,C*-chelated dimesitylboranes **31a**–**c**, containing benzothiazolyl (**a**), benzoxazolyl (**b**), and benzoimidazolyl (**c**) moieties in the molecules was reported.²³ These compounds isomerized under UV irradiation to give corresponding boratiranes **32a**–**c** (Scheme 12).

X = S (**a**), O (**b**), NMe (**c**)

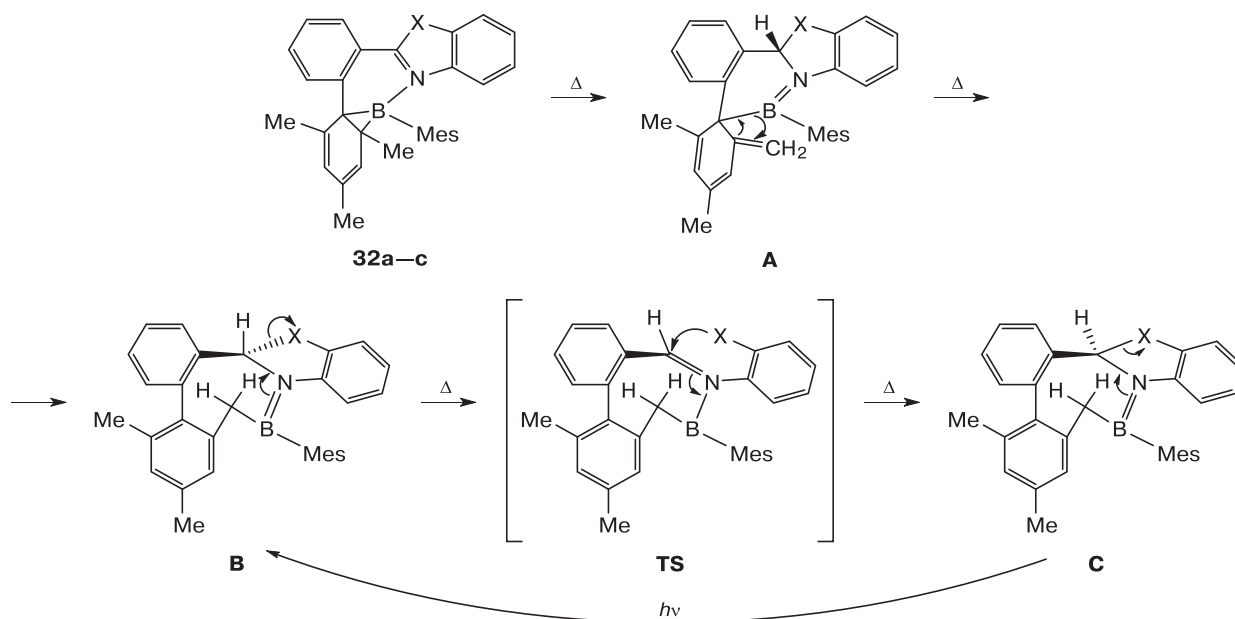
Scheme 11



Scheme 12



Scheme 13



X = S (**a**), O (**b**), NMe (**c**)

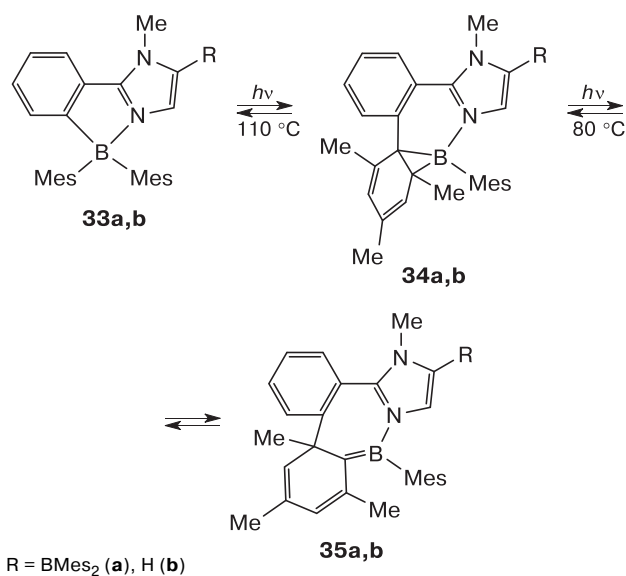
Fairly interesting results were obtained in a study of thermal transformations of boratiranes **32a–c**. Boratiranes underwent multistructural transformations on heating to give, successively, isomers **A**, **B**, and **C** (Scheme 13).

The formation of isomer **A** is facilitated by the fairly uncommon thermally induced intramolecular transfer of a proton from one methyl group of the mesityl moiety with simultaneous reduction of the azole ring. Subsequently, isomer **A** is converted to isomer **B** via the shift of the 1,3-boryl group. Notably, isomer **B** can be quantitatively converted to its diastereomer **C** by heating. The transformation of isomer **C** into isomer **B** takes place upon UV irradiation at 300 nm. The structures of isomers **B** and **C** were confirmed by NMR spectroscopy and X-ray diffraction. The mechanistic pathways of these transformations were established by DFT and TD-DFT quantum chemical calculations.²³

The photoisomerization of boranes **33a,b** resulted in the synthesis of chelated *N*-methyl-2-phenylimidazolyl boriranes **34a,b**. Further UV irradiation of these boriranes **34a,b** at 350 nm gave rise to 1,2-azaborabenzotropyliene isomers **35a,b**. This reaction is accompanied by a substantial color change. Compounds **35a,b** contain a conjugated alkylideneborane unit and can be completely converted to compounds **34a,b**, under heat treatment at 80 °C, whereas they are converted to the starting boranes under heating at 110 °C **33a,b** (Scheme 14).²⁴

The above method for the synthesis of boratiranes from dimesityl-substituted *N,C*-chelated boranes, based on dearomatization of the mesityl substituent under the action

Scheme 14

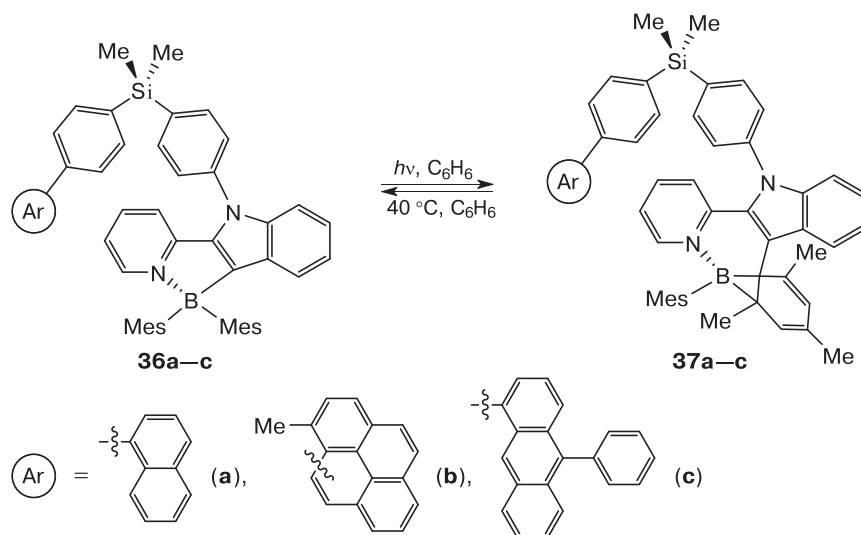


R = BMes₂ (**a**), H (**b**)

of UV irradiation, turned out to be highly efficient and was further developed. Using UV irradiation of *N,C*-chelated dimesitylboranes **36a–c** with two chromophores, it was shown that the photoisomerization yielding boratiranes **37a–c** proceeds via the triplet excited state (Scheme 15).²⁵

This conclusion is of great practical importance development of new photochromic materials based on boron complexes, because preliminary estimation of the energy of a triplet level of a substituent (naphthalene, pyrene,

Scheme 15



anthracene, *etc.*) on the boron atom allows the prediction of the efficiency of photoisomerization.

Organoboron compounds **38–40** were synthesized to study the influence of metal acetylide moieties in *N,C*-chelated organoborane molecules on the formation of boratiranes under UV irradiation.²⁶

The photochemical isomerization of boranes **38** and **39** resulted in the formation of boratiranes **41** and **42**, respectively (Scheme 16).

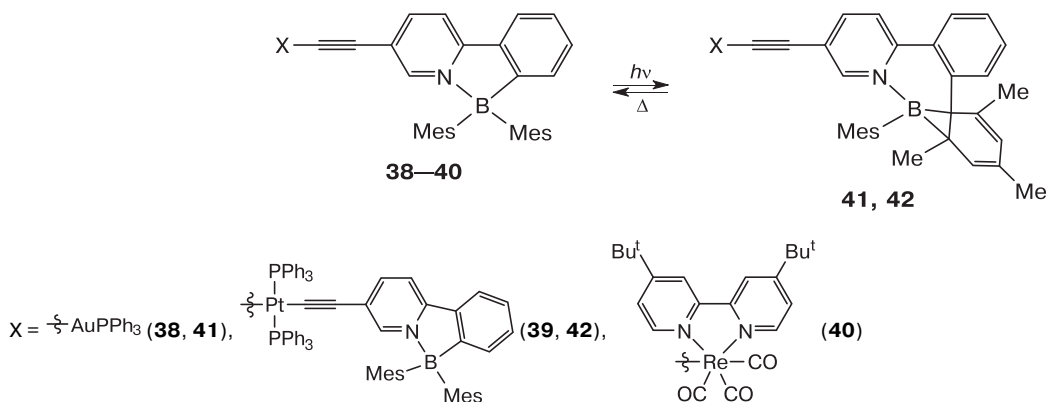
It is noteworthy that Au-containing *N,C*-chelated borane **38** was completely converted to boratirane **41** within 15 min, whereas the conversion of Pt-containing *N,C*-chelated borane **39** to boratirane **42** required 24 h. The chelated borane **40**, containing rhenium acetylide, did not exhibit photoactivity on UV irradiation and, hence, it did not isomerize to the corresponding boratirane. The key factor affecting the photoisomerization of the considered organoboron compounds is the charge transfer from

the mesityl group to the chelated part of the borane molecule. In the case of rhenium- and (to a lesser extent) platinum-containing chelate units in the borane molecules, the crucial role belongs to low-lying triplet states. These states prevent the charge transfer from the mesityl group, thus causing quenching of photoisomerization.¹⁹

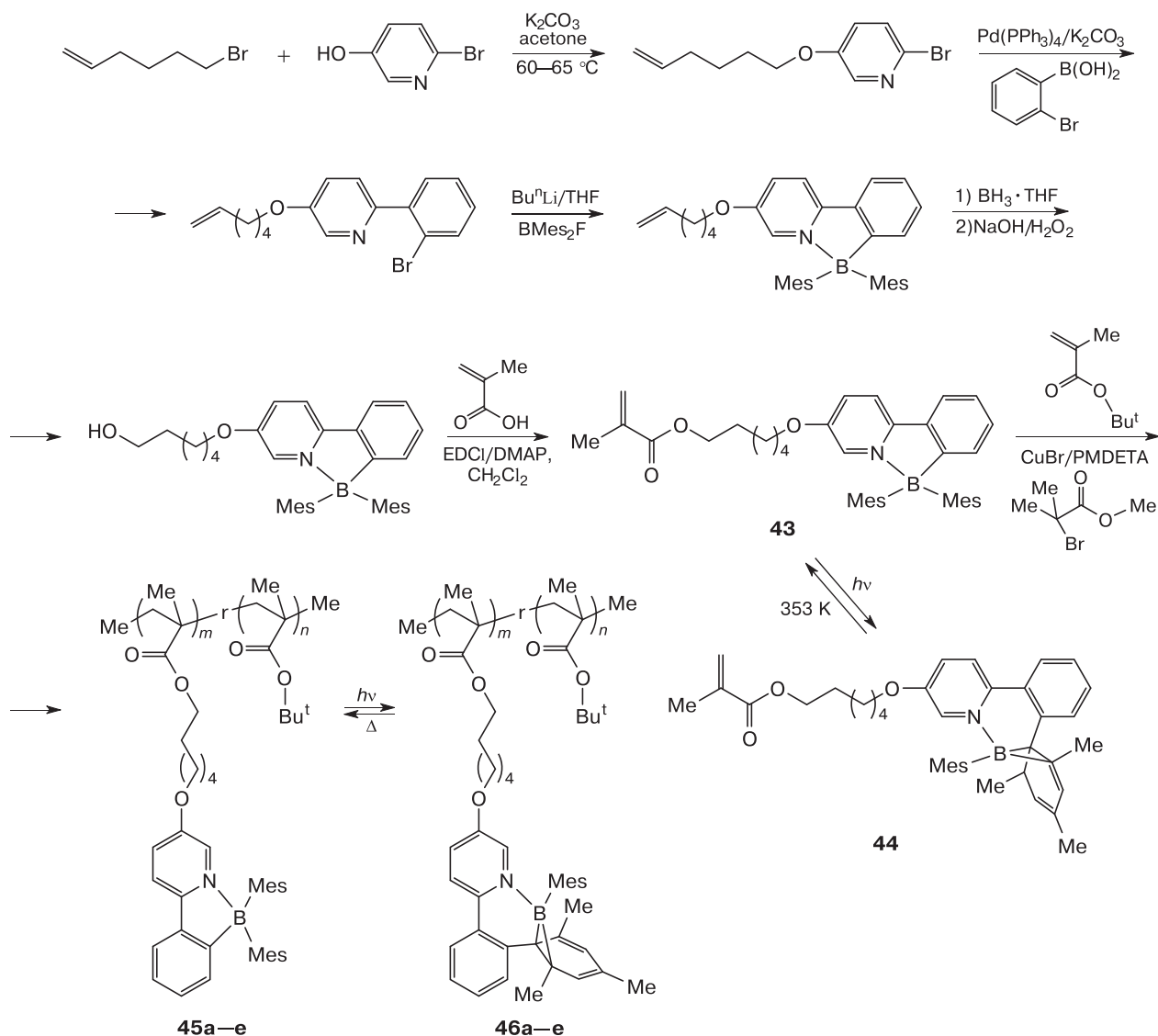
A multistep synthesis gave 6-[B(ppy)Mes₂]oxyhexyl methacrylate (BHMA) **43**, which photoisomerized to compound **44**.²⁷ In the reaction of **43** with *tert*-butyl methacrylate and methyl 2-bromo-2-methylpropionate, photochromic polymers **45a–e** were synthesized for the first time (Scheme 17).²⁷ Under UV irradiation, the borane moieties of these polymers photoisomerized to give the corresponding boratirane-containing polymers **46a–e**. These polymers showed thermally reversible photochromism, with their color changing from colorless (or light blue) to dark blue.

The new organoboron polymers can be efficiently used as photochromic switches in which the three-membered

Scheme 16



Scheme 17



$m : n = 1 : 0$ (**a**), $1 : 5$ (**b**), $1 : 10$ (**c**), $1 : 24$ (**d**), $1 : 40$ (**e**);

EDCI is 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; DMAP is 4-dimethylaminopyridine; PMDETA is *N,N,N',N',N''*-pentamethyldiethylenetriamine.

borirane ring undergoes reversible photochemical ring formation/opening reaction.

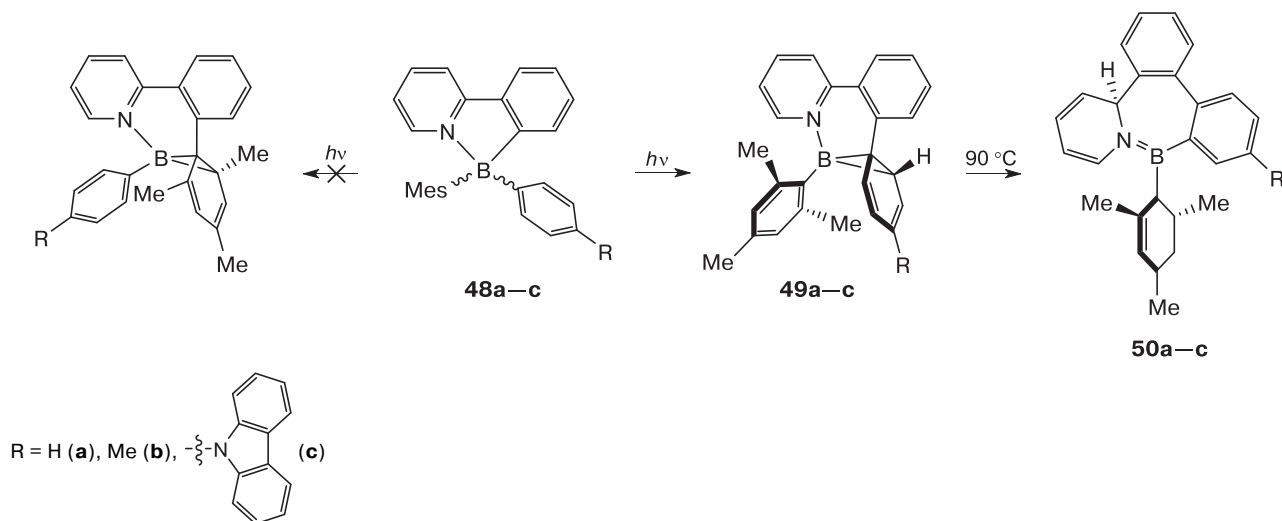
The reversible photochromic switching *via* C—C bond formation/cleavage of *N,C*-chelated organoboron compounds with a four-coordinate boron atom, $\text{B}(\text{ppy})\text{Mes}_2$, to give boratiranes is accompanied by a color change. The behavior of various diarylboranes $\text{B}(\text{ppy})\text{Ar}_2$ was studied to understand this unusual phenomenon.²⁸ It was shown that the photochromic switching to form boratirane is possible only if there are bulky mesityl groups in the molecule. Photoisomerization was not observed for compound

$\text{B}(\text{ppy})\text{Ph}_2$ **47**, which contains two boron-bound phenyl groups instead of mesityl groups.

In the authors' opinion, the B—Mes bond is markedly longer than the B—Ph bond, while the presence of electron-donating methyl groups in the aryl moiety promotes the low-energy Mes \rightarrow ppy charge transfer, which is responsible for the photochromic properties of the organoboron *N,C*-chelates.

The photoisomerization of asymmetric *N,C*-chelated organoboron compounds $\text{B}(\text{ppy})(\text{Mes})(\text{Ar})$ with two different aryl groups bound to boron, namely, boranes

Scheme 18



48a–c, was studied to elucidate the role of the structure of aryl substituents in them.²⁹ It was shown that photoisomerization involved the less substituted aryl group and gave dark-colored isomers (boratiranes) **49a–c**, which subsequently underwent thermal isomerization to be converted to air-stable *4bH*-azaborepins **50a–c** (Scheme 18).

The mechanistic aspects of these interesting and unusual photo/thermal isomerization phenomena were derived from kinetic and computational data. The mechanism of formation of *4bH*-azaborepins **50a–c** from boratiranes **49a–c** was proved using starting borane B(ppy)(Mes)(C₆D₅) enriched with deuterium (Scheme 19).²⁹ Heating of deuterated boratirane **51** resulted in the de-aromatization of the pyridyl moiety *via* direct transfer of the deuterium atom D(1) from the borirane ring to give adduct **52**.

The photoreaction of imidazole-substituted borane **53** to afford the corresponding boratirane **54** proceeded less

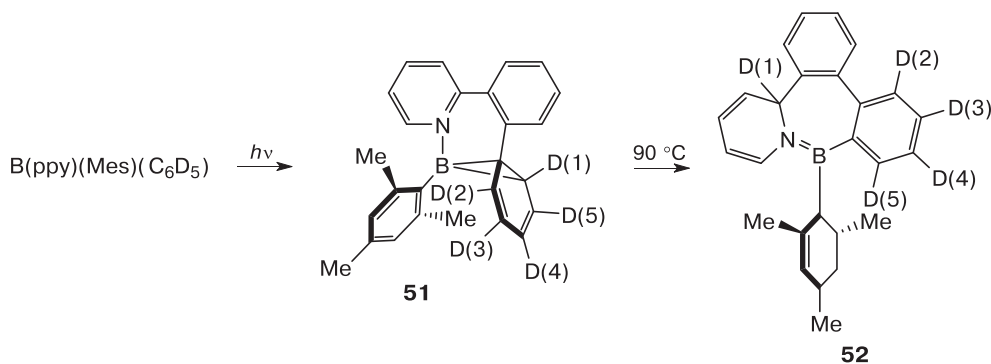
efficiently and with a lower quantum yield; meanwhile, the thermal isomerization of boratirane **54** to azaborepin **55** was faster (Scheme 20).

Apparently, the greater π -conjugation in the imidazole-containing chelating ligand and lower imidazole aromaticity compared to pyridine favor stabilization of the excited state of borane **53** and reduce the reorganization energy associated with imidazole dearomatization and, hence, promote the transformation of boratirane **54** to azaborepin **55**.

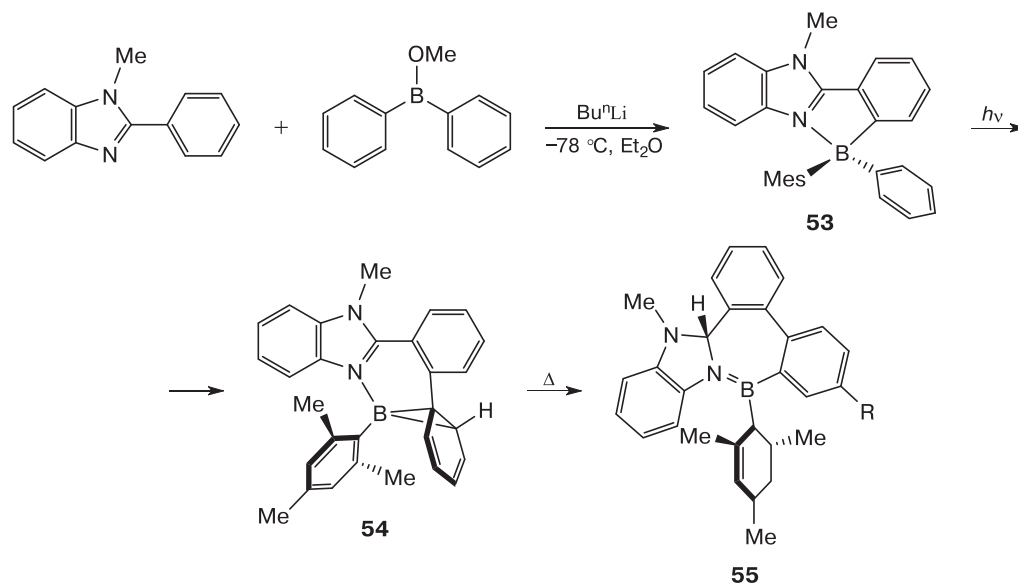
The photoisomerization of *N,C*-chelated organo-boranes **56a–c**, containing aryl substituents with electron-donating amino groups in the *para*-position, proceeding in 9 h under inert (N₂) atmosphere, was reported (Scheme 21).³⁰

It was shown that only compounds **56a,b** successfully photoisomerized (300 nm) to give boratiranes **57a,b**, whereas **56c** was unreactive, which was attributed to dif-

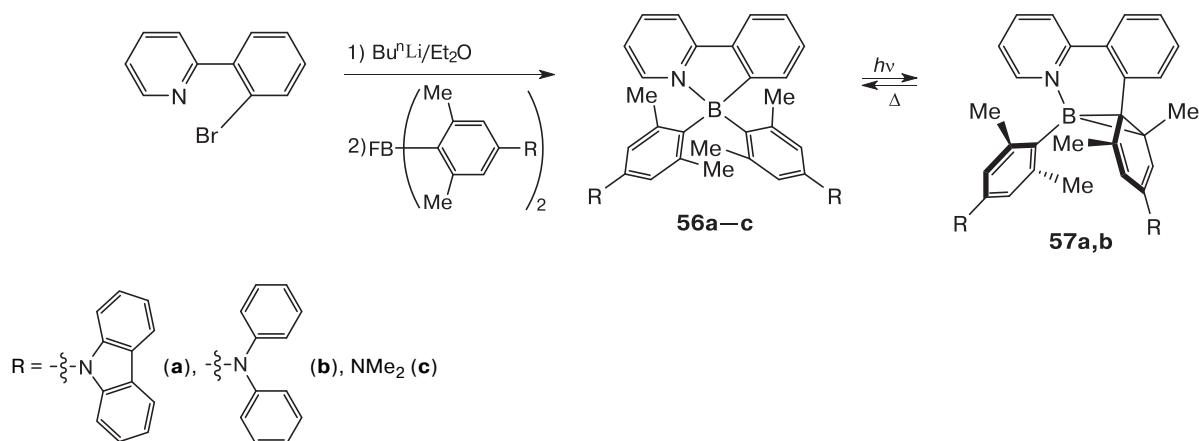
Scheme 19



Scheme 20



Scheme 21



ferences in the electron excitation mechanisms in these molecules.

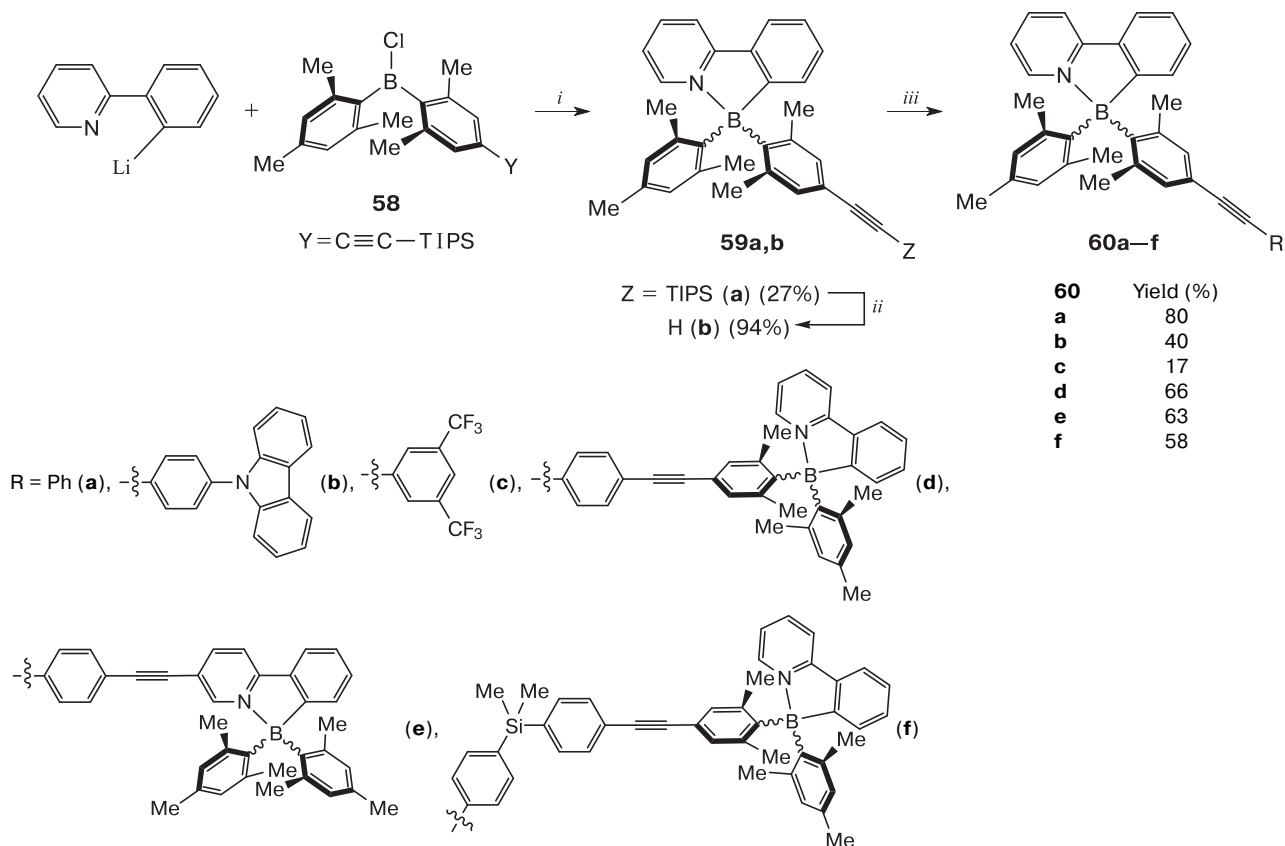
The reaction of organolithium compound with chloro(diaryl)borane **58** resulted in the synthesis of new boranes **59a,b** and **60a-f** (Scheme 22).³¹ The prepared boranes contain a *para*-ethynyl group in one of the aromatic substituents.

The photoisomerization of boranes **60a-c** proceeded regioselectively to give the corresponding boratiranes **61a-c**, which were converted into the starting boranes on

heating at $90\text{ }^\circ\text{C}$ for 1 h (Scheme 23). The structures of the starting boranes (**60a-c**) and photoreaction products (**61a-c**) were confirmed by NMR spectroscopy and mass spectrometry. Compounds **60d,e** proved to be inert to UV light.

The photoirradiation of borane **59a** resulted in the formation of boratiranes **62a** and **63a** in $\sim 6:1$ ratio, while borane **59b** was converted to **62b** and **63b** in $4:1$ ratio (Scheme 24).³¹

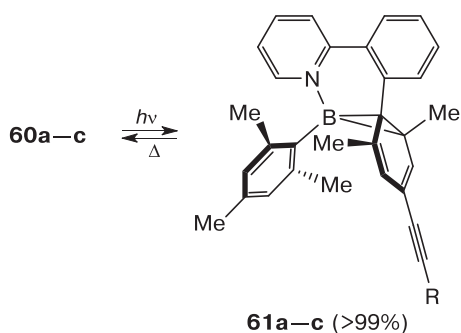
Scheme 22



R = Ph (80%) TIPS is triisopropylsilyl, TBAF is tetrabutylammonium fluoride.

Reagents and conditions: *i.* Et₂O, -78 °C; *ii.* TBAF (1.2 equiv.), THF, 0 °C, 1h; *iii.* aryl halide RHal (0.5 or 1.0 equiv.), 10 mol.% Pd(PPh₃)₄, 20 mol.% CuI, 30 equiv. NEt₃, THF, ~20 or 50 °C.

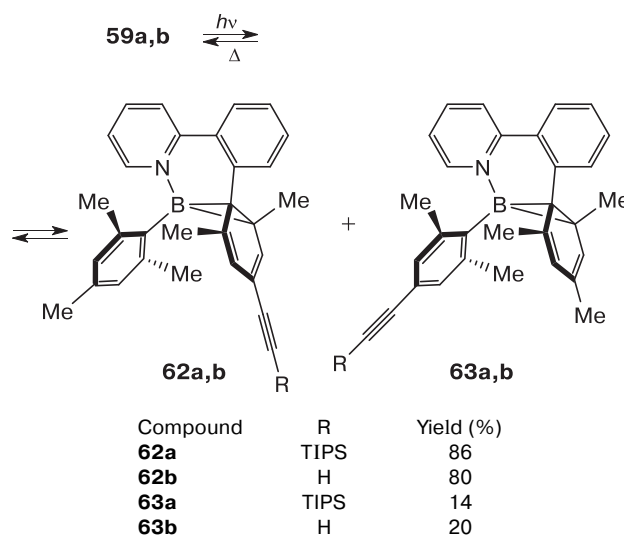
Scheme 23



R = Ph (a), C₆H₄-Cbz (Cbz is benzyloxycarbonyl) (b), 3,5-(CF₃)₂-C₆H₃ (c)

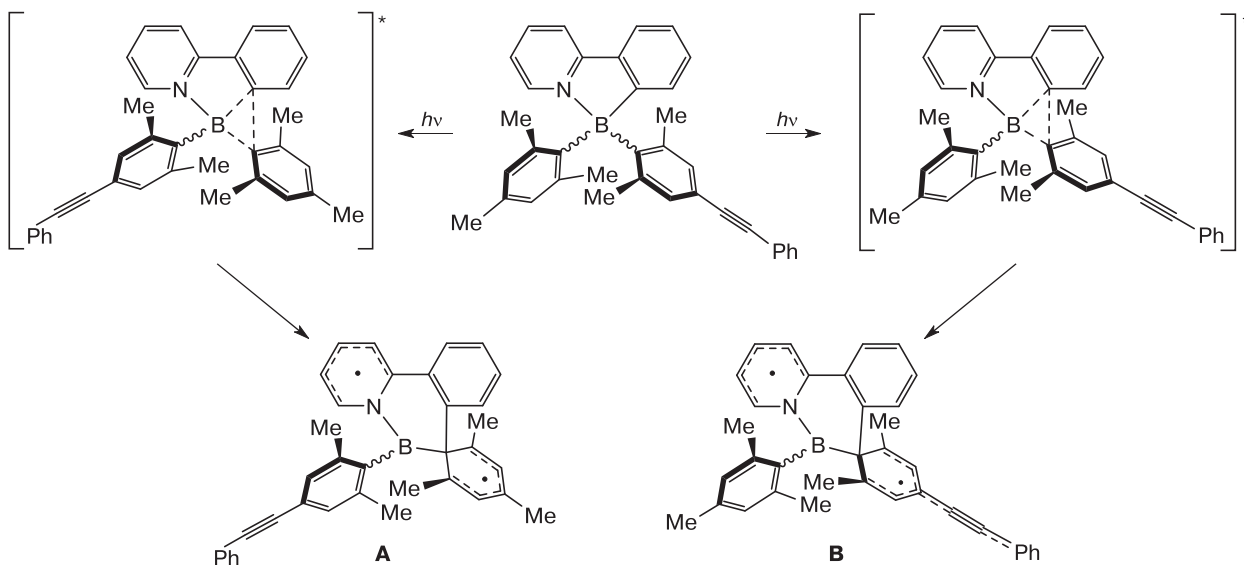
The excitation of *N,C*-chelated boron under UV irradiation leads to biradical intermediates **A** and **B** (Scheme 25), which are transformed to boratirane adducts, according to a theoretical mechanism.^{31,32} The biradical intermedi-

Scheme 24



ate **B** is the most stable due to the delocalization of electron density along the alkyne-functionalized aryl substituent.

Scheme 25



This accounts for different regioselectivities of formation of boratirane adducts.

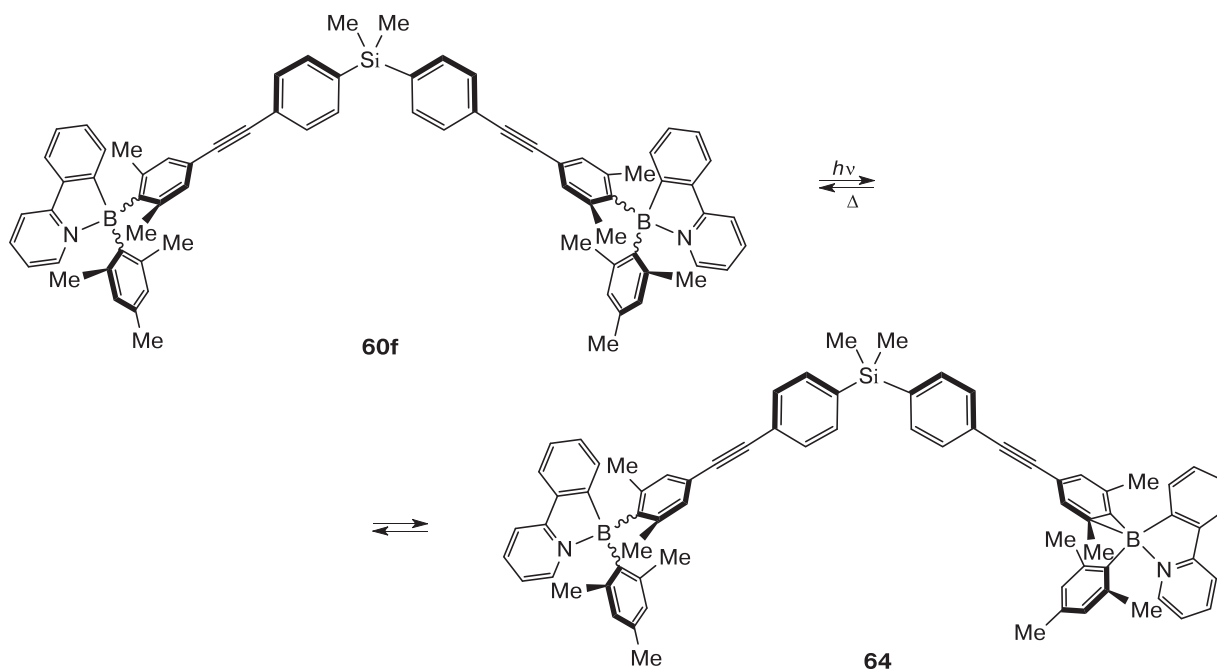
It is noteworthy that unlike 1,4-phenylene-bridged *bis*-boranes **60d,e**, which are absolutely inert to UV irradiation, *bis*-borane **60f** with a silicon bridge undergoes photoisomerization involving one boron atom, similarly to di-, tri-, and hexaboranes **6**, **7**, **10**, and **12**,^{16,17} thus giving monoboratirane **64** (Scheme 26).³¹

Scheme 27 presents the synthesis^{32,33} of a number of boranes **65a–h** with different substituents on the boron

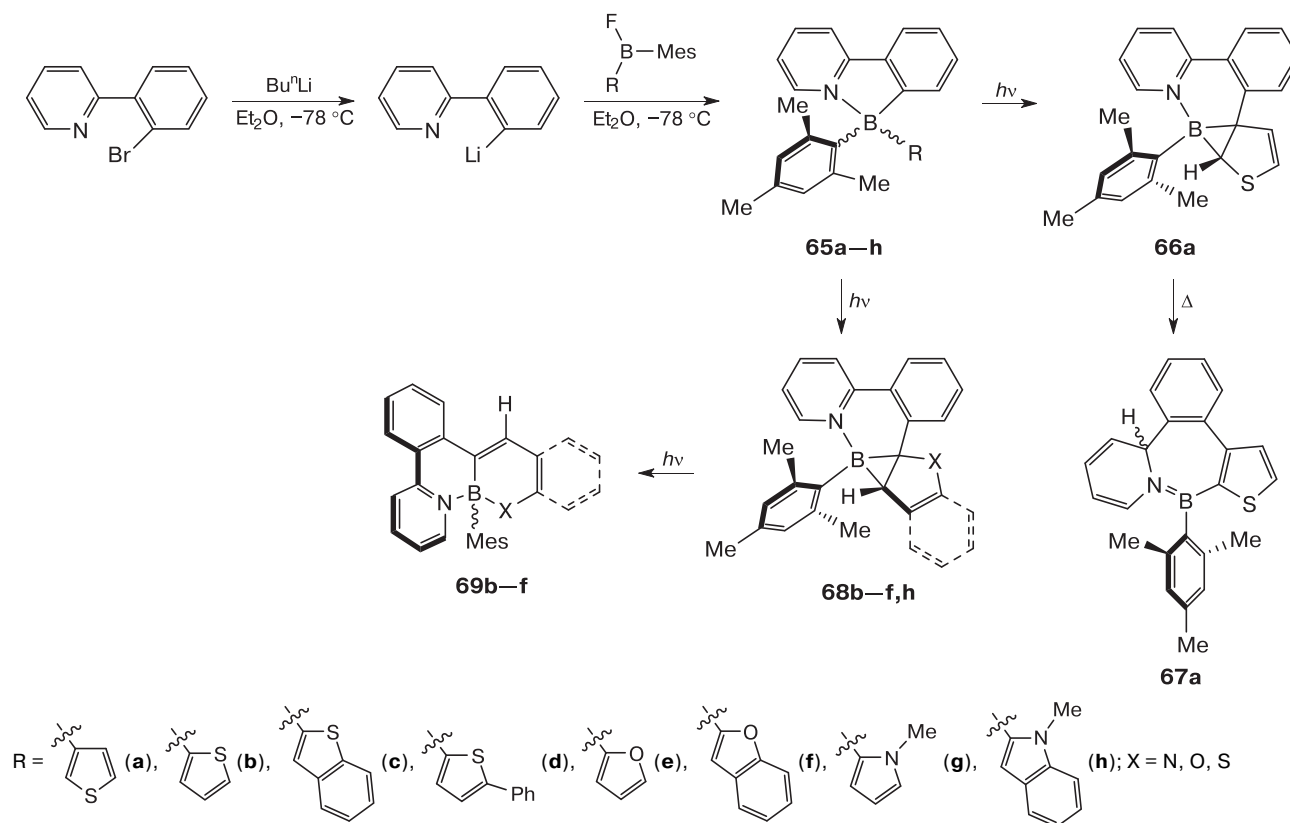
atom. In all cases, one of the substituents is mesityl, which is required in the starting molecule for photoisomerization to occur,²⁸ whereas the other one is an N,O,S-cyclic group. The boratiranes bearing a heterocyclic substituent (R) are formed regioselectively under UV irradiation of the resulting boranes. Photogenerated boratiranes **66a** and **68b–f** are formed as intermediates in these reactions and are then converted to more stable isomers **67a** and **69b–f**.

The formation of boriranes involves the heterocyclic substituents. In these boriranes, the immediate proximity

Scheme 26



Scheme 27



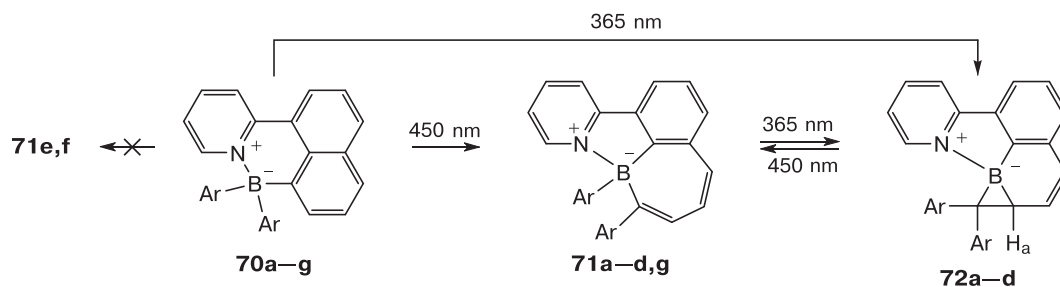
of the C(2)–X bond (X = N,O,S) and the borirane ring leads to activation of this bond and induces rearrangement of the heterocycle to give more stable isomers: 4*bH*-azaborepin **67a** and thia- and oxaborinines **69b–f**. Note that the structure of intermediate boratiranes influences their subsequent transformation. The boratiranes **68b–f** resulting from irradiation of chelated boranes with 2-thienyl or 2-furyl substituent on the boron atom, for example, are converted under subsequent irradiation to 1,2-thio- (**69b–d**) and 1,2-oxaborinines (**69e,f**), respectively. Meanwhile, boratirane **66a**, formed from borane with a 3-thienyl substituent, is converted to 4*bH*-azaborepin **67a** during heating. Acyclic borane derivatives **65h,g** show the low-

est reactivity in these reactions; compound **65g** is completely inert. Borane **65h** with an indole substituent on the boron atom is regioselectively converted to borirane during UV-irradiation for 16 h; however, more prolonged irradiation led to its decomposition.

The results of studying the phototransformation of diarylboraheterocycles B(npy)Ar₂ **70a–g**, containing 2-naphthylpyridyl moiety (npy = 2-(naphthalene-1-yl)-pyridine) in place of the 2-phenylpyridyl moiety, are depicted in Scheme 28.³⁴

It was found that heterocyclic boranes **70a–g** undergo two-step isomerization under UV irradiation in contrast to B(ppy)Ar₂ type boranes considered above (ppy = 2-phen-

Scheme 28



Ar = Ph (**a**), 4-MeOC₆H₄ (**b**), 4-MeC₆H₄ (**c**), 2,4-Me₂C₆H₃ (**d**), 3,5-(CF₃)₂C₆H₃ (**e**), C₆F₅ (**f**), Mes (**g**)

ylpyridyl). In the first step, one aryl substituent migrates to a carbon atom of the naphthyl moiety to give borepin **71**. The second step of isomerization is the first example of reversible photoisomerization between borepin **71** and borirane **72**. The aryl substituent on the boron atom influences the photoactivity of *N,C*-chelated boranes **70a–g**.

The diphenyl-substituted borane **70a** isomerized to give boratirane **72a** in a quantitative yield (72%) under UV irradiation (365 nm). This resulted in a distinct change in the color of the solution from light yellow to bright orange. The quantum yield of photoisomerization of borane **70a** to boratirane **72a** in toluene was 14%. Interestingly, irradiation at a longer wavelength (450 nm) for 4 h afforded a mixture of borepin **71a** and boratirane **72a** in 1 : 1.2 ratio.

The irradiation (365 nm) of benzene solutions of borepin **71a** isolated in a pure state or a 1 : 1.2 mixture of compounds **71a** and **72a** resulted in a quantitative transformation of borepin **71a** to boratirane **72a**. Thus, borepin can be regarded as an intermediate in the photoisomerization of borane **70a** to boratirane **72a**.

Boranes **70b,c** with electron-donating OMe or Me groups in the *para*-position of the B-aryl moiety photoisomerized at 450 nm, similarly to borane **70a**, to give borepin and boratirane in 2.8 : 1 (for **71b** : **72b**) or 1.9 : 1 ratio (for **71c** : **72c**). Boranes **70b,c** were converted to boratiranes **72b** and **72c** in quantitative yields of 94 and 100%, respectively, under UV radiation at 365 nm.

The irradiation of borane (365 nm) **70d** with the *ortho*-Me substituent in the aryl group afforded a 1 : 4.9 mixture of compounds **71d** and **72d**. The subsequent ir-

radiation at a longer wavelength (450 nm) resulted in complete conversion of boratirane **72d** to borepin **71d**. The methyl group in the *ortho*-position of the aryl substituent in **71d** was found to stabilize the borepin isomer **71b**. Borane **70g** with two *ortho*-methyl groups virtually did not isomerize to the corresponding boratirane **72g** under similar conditions, and borepin **71g** was the only photoproduct.

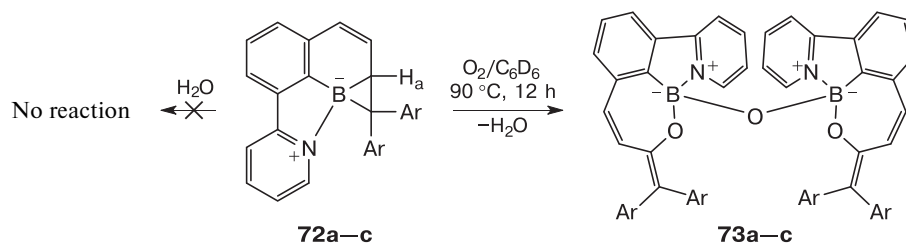
Substituted boranes **70e,f**, containing electron-withdrawing substituents on the aryl group, did not show photoactivity when irradiated at 365 nm or 450 nm. Thus, it can be concluded that the photoactivity of the considered boranes depends on both steric and electronic effects of aryl substituents attached to boron.

The structure of boratirane **72a** was established using 2D NMR spectroscopy and X-ray diffraction. The boron atom in compound **72a** is common to the boracyclohexadiene and borirane moieties, in contrast to boratanorcaradienes **4a–f** (Scheme 3). This compound is the first example of boracyclohexadienylboratirane with such type of bonding and is a rare boratanorcaradiene isomer.

Boratiranes **72a–c** are stable to water, but when kept in air for several days at 25 °C (or for 12 h with heating at 90 °C), they are converted to the corresponding dimers **73a–c** (Scheme 29).³⁴ The oxidation product **73a** obtained from boratirane **72a** (72% yield) was isolated as yellow crystals and characterized by X-ray diffraction analysis.

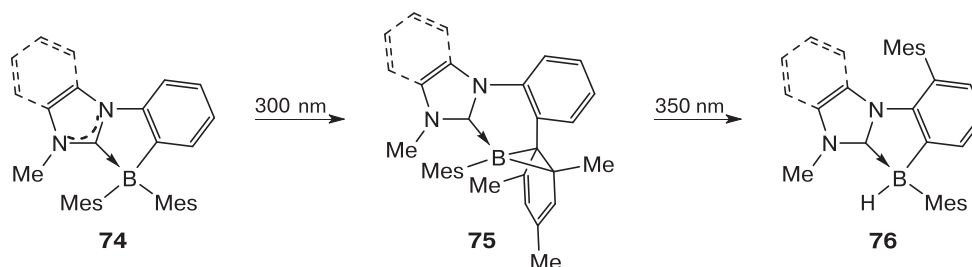
Dimesitylboranes **74** stabilized by carbenes are converted to *C,C*-chelated boratiranes **75** under UV irradiation (Scheme 30). *C,C*-Chelated boratiranes **75** are thermally stable and do not enter the reversible thermal reaction

Scheme 29



Ar = Ph (**a**), 4-OMeC₆H₄ (**b**), 4-MeC₆H₄ (**c**)

Scheme 30



even under heating to 110 °C, as opposed to previously considered *N,C*-chelated analogs.³⁵ Moreover, they are stable to oxygen and do not decompose to give deboration products and B(OMe)₃, unlike *N,C*-chelated boratiranes (see Schemes 3, 10).^{13–15,19} The subsequent photoirradiation (350 nm) of boratiranes **75** induces intramolecular rearrangement, resulting in isomeric adducts **76**.

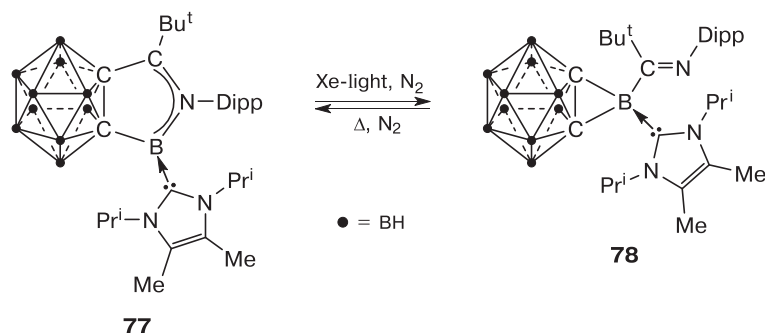
The first example of carborane-fused boratirane formed upon photoisomerization of azaborole was reported in 2017.³⁶ The irradiation of carborane-containing azaborole **77** in THF with a xenon arc lamp (400–1500 nm, 300 W) at room temperature in a nitrogen atmosphere yielded the corresponding carborane-fused boratirane **78** as colorless crystals in 82% yield (Scheme 31).

The photoisomerization of trigonal planar azaborole **77** into tetrahedral boratirane **78** is fully reversible. At ~20 °C, a pale yellow solution of boratirane **78** is very slowly converted to a dark violet solution of azaborole **77**. Note that photoisomerization is accelerated on heating. ¹H and

¹¹B NMR monitoring of these reactions demonstrated that boratirane **78** is completely converted to azaborole **77** on heating (80 °C) for 12 h. The synthesis of a similar boratirane *via* transmetalation of metallocarboranes (*e.g.*, Li₂C₂B₁₀H₁₀ or 1,2-[M]-1,2-C₂B₁₀H₁₀, where [M] is a transition metal) by treatment with R₂BHal₂ failed.

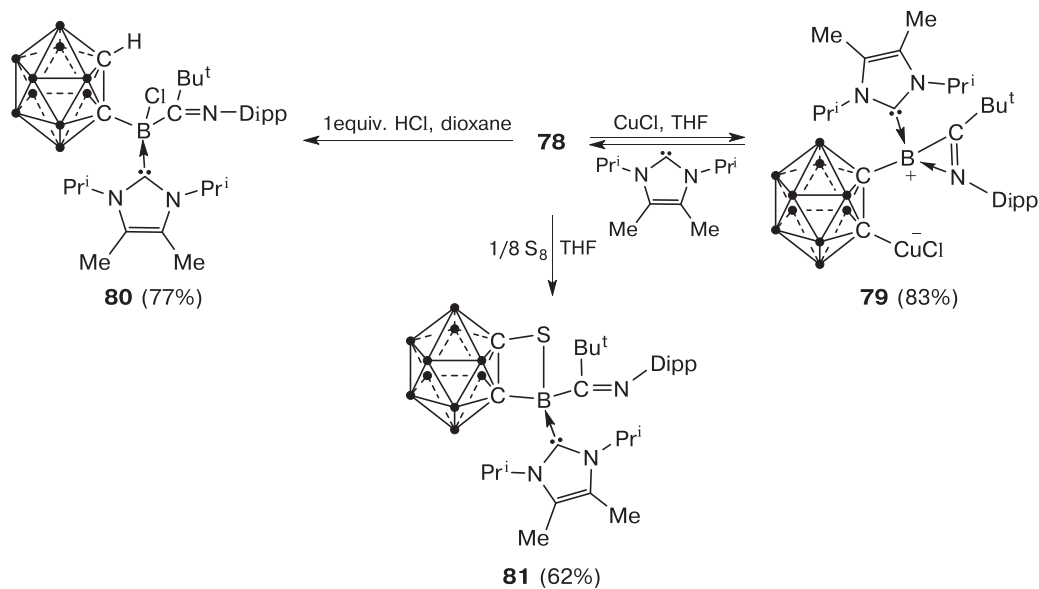
The carborane-fused boratirane **78** does not show any reactivity towards ketones, alkynes, nitriles, isonitriles, or transition metal complexes, *e.g.*, [(COD)RhCl]₂, Ni(COD)₂, and Pd(dba)₂ (COD = 1,5-cyclooctadiene, dba = dibenzylideneacetone). However, in the reaction with CuCl (1 equiv.) in a THF solution, heterolytic cleavage of the B–C bond in the borirane ring and simultaneous formation of a new BNC-three-membered ring take place giving rise to zwitter-ion **79** (Scheme 32). The addition of an equimolar amount of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene to zwitter-ion **79** results in complete conversion of **79** back to boratirane **78**. Treatment of boratirane **78** (1 equiv.) with HCl in a dioxane solution

Scheme 31

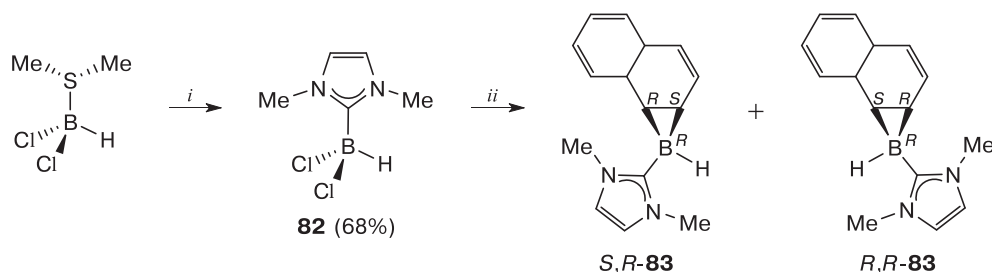


Dipp is 2,6-diisopropylphenyl.

Scheme 32



Scheme 33



Reagents and conditions: *i.* 1,3-dimethylimidazol-2-ylidene, toluene, $-78\text{ }^{\circ}\text{C}$. *ii.* 2 equiv. $\text{Na}[\text{C}_{10}\text{H}_8]$, THF, $-78\text{ }^{\circ}\text{C}$.

affords monochloroborane-carbene adduct **80** via cleavage of one B—C bond in the borirane ring.

Expansion of the three-membered ring, which was not described previously for boriranes, was noted for the first time. The reaction of boratirane **78** with elemental sulfur in THF at room temperature furnished adduct **81** in 62% yield (see Scheme 32). The molecular structure of this adduct was confirmed by X-ray crystallography. A specific feature of the obtained compound is the presence of a planar four-membered CCBS ring (the sum of the tetragon internal angles is 360°), which is formed by formal insertion of a sulfur atom into one B—C bond of the BCC borirane ring. The boron atom of the thioboretane moiety adopts a distorted tetrahedral geometry, being bound to three carbon atoms and one sulfur atom.

It is worth noting that, apart from the experimental studies cited above, there are theoretical studies^{37–43} addressing the formation, stability, and electronic structure of boriranes and boratiranes and providing detailed understanding of the mechanism of reversible photoisomerization of *N,C*-chelated organoboron compounds into boratiranes;^{44,45} these issues are beyond the scope of this review.

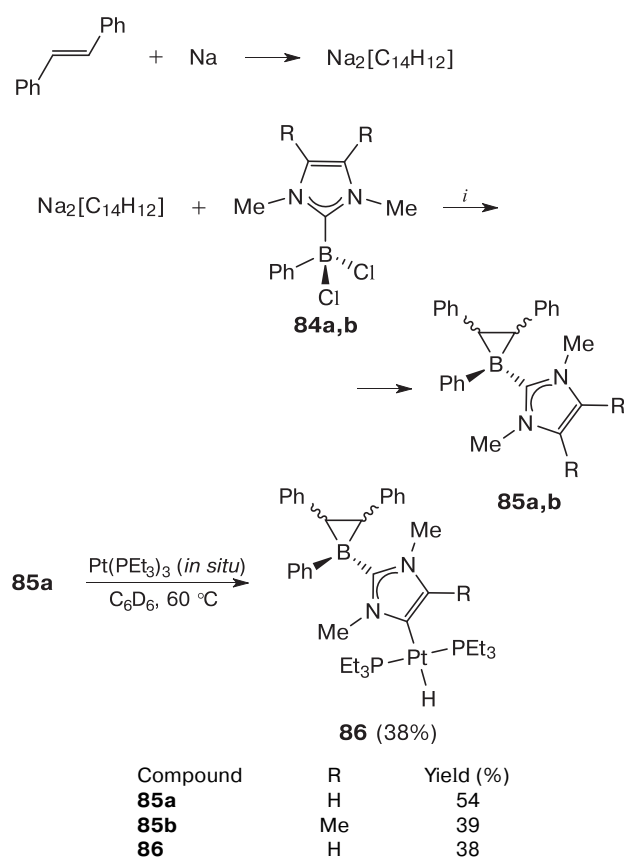
[2+1]-Cycloaddition of borylenes [RB:] to unsaturated compounds

Boratiranes stabilized by *N*-heterocyclic carbenes were synthesized by [2+1]-cycloaddition reaction of borylene [RB:] with naphthalene.⁴⁶ Borylene DMII·BH (DMII is 1,3-dimethylimidazol-2-ylidene) was generated *in situ* in the reaction of dichloroborane $\text{BHCl}_2 \cdot \text{DMII}$ (**82**) with two equivalents of sodium naphthalenide $\text{Na}[\text{C}_{10}\text{H}_8]$ in THF at $-78\text{ }^{\circ}\text{C}$. Boratirane derivative 7,8-(DMII·BH)- C_{10}H_8 (**83**) was formed as a 1 : 1 mixture of *RRS* (*R,R*-**83**) and *RSR* (*R,S*-**83**) diastereomers in a total yield of 88% (Scheme 33). The diastereomers were separated by double recrystallization from toluene at $-30\text{ }^{\circ}\text{C}$. The formation of only two possible pairs of enantiomers is due to the *syn*-selective reaction of borylene DMII·BH with naphthalene. Three stereogenic centers are generated in the three-membered ring, and the *syn*-selectivity restricts the number of possible enantiomers by two pairs (*RRS/SSR* and *RSR/SRS*).

The [2+1]-cycloaddition of the dianion of *trans*-stilbene $\text{Na}_2[\text{C}_{14}\text{C}_{12}]$ to borylenes generated from phenyl-dichloroboranes **84a,b**, stabilized by heterocyclic carbenes, led to *trans*-1,2,3-triphenylboratiranes **85a,b** (Scheme 34).^{47,48} The reaction was carried out at $-78\text{ }^{\circ}\text{C}$ (10 min), then the temperature was increased to $20\text{ }^{\circ}\text{C}$, and the mixture was additionally kept for 1.5 h.

These are the first examples of monocyclic boratiranes stabilized by heterocyclic carbenes that were produced without UV irradiation. Boratiranes were fully character-

Scheme 34



Reagents and conditions: *i.* 1) THF, $-75\text{ }^{\circ}\text{C}$, 10 min; 2) $-75 \rightarrow 25\text{ }^{\circ}\text{C}$, 1.5 h.

ized as diastereomer mixtures by NMR spectroscopy, elemental analysis, and X-ray diffraction analysis. The obtained boratiranes **85a,b** were stable in air and did not decompose even on treatment with water. They withstood heat treatment at 80 °C for several days and photolytic impact (irradiation with a mercury lamp in C₆D₆ for 1 h (**85a**) and 36 h (**85b**)). The boriranes were racemic mixtures of enantiomers and had mutually *trans*-oriented phenyl groups bound to the ring carbon atoms.

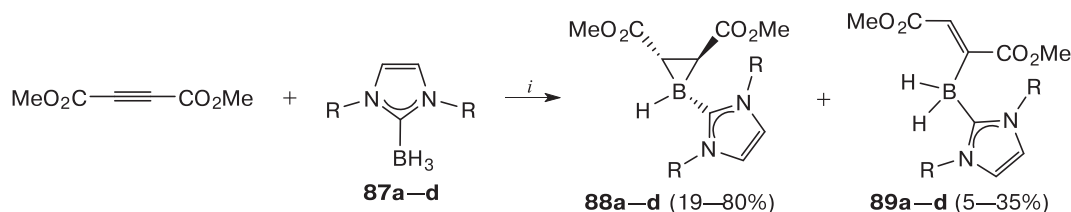
The heterocyclic carbene-stabilized boratiranes exhibit remarkable stability due to the presence of a strong Lewis base in their molecules. It is not surprising that the attempts to remove the Lewis base from compounds **85a,b** to obtain free borirane failed. The borirane ring was not destroyed even when boratirane **85a** was heated (60 °C) in benzene

with the platinum complex Pt(PEt₃)₃, generated *in situ* from Pt(PEt₃)₄, for 49 days.⁴⁷ When one C—H bond of the carbene moiety of boratirane **85a** was activated, covalently bonded complex **86** was isolated in 38% yield as colorless crystals (see Scheme 34).

Double hydroboration of acetylenes with imidazol-2-ylideneboranes

In 2017, double hydroboration of dimethyl acetylenedicarboxylate with imidazol-2-ylideneboranes **87a–d** was carried out to synthesize *trans*-dicarboxylate-substituted boriranes **88a–d** (19–80% yield) (Scheme 35).^{49,50} The synthesis was performed at different temperatures depend-

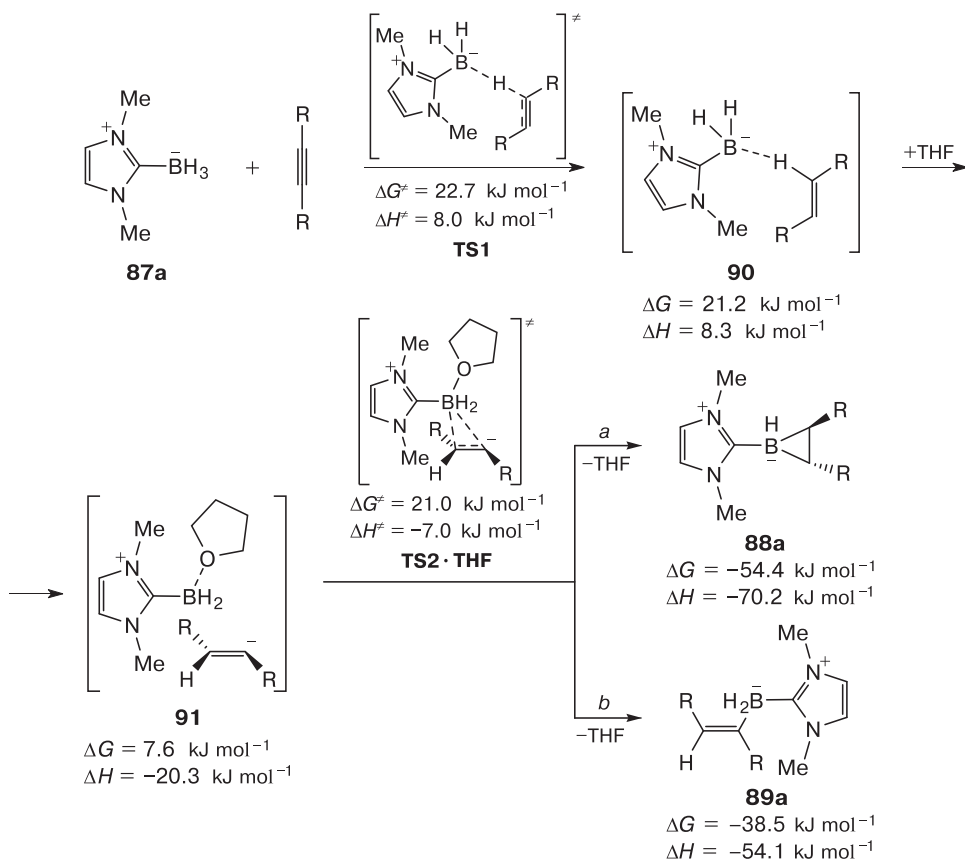
Scheme 35



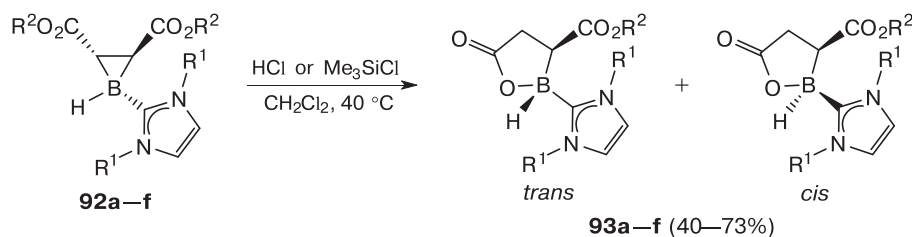
R = Me (**a**), Prⁱ (**b**), Mes (**c**), Dipp (**d**)

Reagents and conditions: *i.* THF, −78 °C...−20 °C, 18 h (**a, b**); MeCN, 80 °C, 1 h (**c**); MeCN, 80 °C, 18 h (**d**).

Scheme 36



Scheme 37



R¹ = Me, R² = Me (**a**), Bu^t (**b**); R¹ = Me(Bn), R² = Me (**c**), Bu^t (**d**); R¹ = Prⁱ, R² = Me (**e**), Bu^t (**f**)

ing on the substituent R on a nitrogen atom in the molecules of boranes **87a–d**: either with strong cooling to $-78\text{ }^\circ\text{C}$ or with heating to $80\text{ }^\circ\text{C}$.

The hydroboration of acetylenes yields alkenylboranes, according to published data.⁵¹ This was the first example of acetylene hydroboration that gave not only (*E*)-alkenylboranes **89a–d** (5–35%), but also boratiranes **88a–d** (19–80%). Compounds **88a–d** and **89a–d** thus obtained were stable and were not interconverted on long-term storage or under heating ($80\text{ }^\circ\text{C}$) in acetonitrile solution within a week.

The mechanism of formation of boratiranes **88a–d** and alkenylboranes **89a–d** in THF was proposed on the basis of quantum chemical calculations.⁴⁹ The thermodynamically most favorable pathways of the reaction between borane **87a** and dimethyl acetylenedicarboxylate are depicted in Scheme 36.

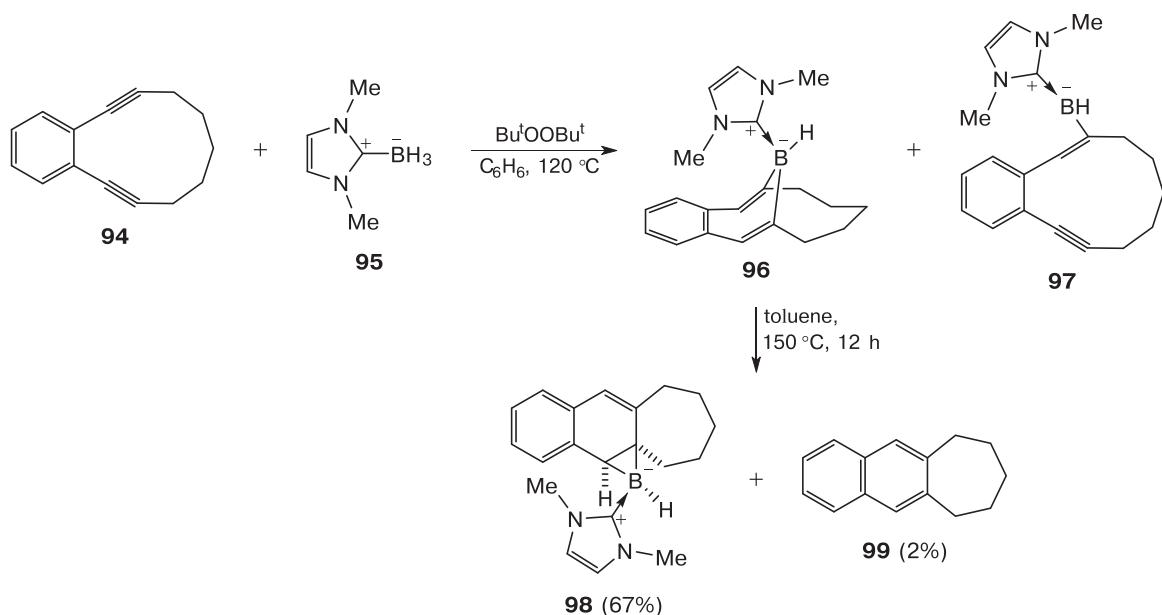
Carbene-stabilized boratiranes **92a–f** containing carboxyl groups reacted with HCl or Me₃SiCl in dichloro-

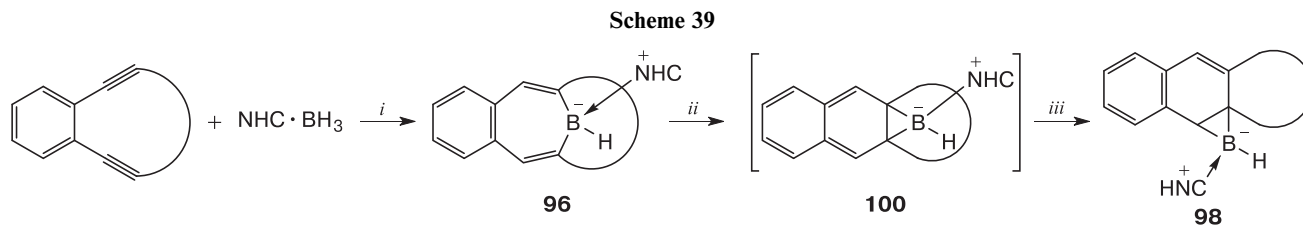
methane at $40\text{ }^\circ\text{C}$ to be converted to fairly rare compounds, boralactones **93a–f** (Scheme 37).^{52,53} It is worth noting that chemical transformations of boralactones open up a convenient route to various carboxylic acid derivatives.

The double radical *trans*-hydroboration of cyclic diyne **94** by treatment with NHC·BH₃ **95** (NHC is *N*-heterocyclic carbene) followed by thermal isomerization of the resulting borepin **96** gave annulated borirane **98** (Scheme 38).⁵⁴ Apart from borepin **96**, the radical step gives side product **97**.

The single crystals of boratirane **98** obtained by recrystallization from toluene at $30\text{ }^\circ\text{C}$ were studied by X-ray diffraction. It was found that annulated boratirane **98** is formed as a mixture of *endo/exo* isomers. The ¹¹B NMR spectrum of compound **98** exhibits, apart from the boron signal at $\delta_{\text{B}} -33.3\text{ ppm}$, one more weak signal at $\delta_{\text{B}} -30.4\text{ ppm}$, which was assigned to the *exo*-diastereomer **98** (*endo/exo* ~ 97 : 3).⁵⁴ The hypothesized *exo*-product could not be isolated and characterized. The differential

Scheme 38





i. Double *trans*-hydroboration. *ii.* 6π -electrocyclic isomerization. *iii.* 1.5-B-shift.

scanning calorimetry data indicate that the resulting boratirane **98** is highly thermally stable. The reaction mixture was found to contain minor amounts (2%) of 7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]naphthalene **99**.

The mechanism of thermal isomerization of borepin **96** to boratirane **98**, shown in Scheme 39, was proposed on the basis of DFT quantum chemical calculation.⁵⁴ These calculations show that borepin is first transformed into intermediate boranocaradiene **100** *via* thermal 6π -electrocyclic isomerization, which is followed by 1.5-shift of the boron atom to give boratirane **98**.

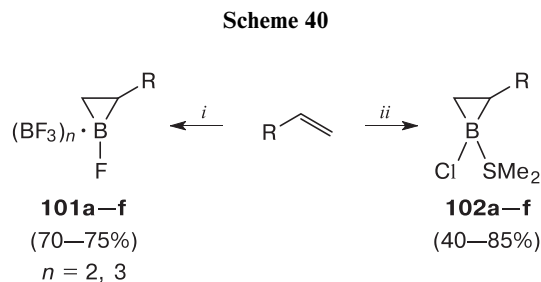
Metal complex catalysis in the synthesis of boriranes

The main approaches to the synthesis of boriranes are the photochemical isomerization of organoboranes, [2+1]-cycloaddition of borylenes (:B-R) to unsaturated compounds, and double hydroboration of acetylenes with imidazol-2-ylideneboranes.

There was no information on catalysts used in the synthesis of three-membered organoboron compounds (boriranes) until 2014. In 2014, Corresponding Member of the RAS Dzhemilev U. M. suggested the possibility of one-pot synthesis of boriranes in the presence Zr and Ti complex catalysts, according to the results of catalytic cycloalumination and cyclomagnesiation of olefins, 1,2-dienes, and acetylenes in the presence of the same metal (Zr and Ti) complexes leading to the corresponding three- and five-membered metal-carbocycles of main group metals (Al, Mg).^{55,56} Direct cycloboration of olefins was accomplished in the reactions of α -olefins with boron halides ($\text{BCl}_3 \cdot \text{SMe}_2$ or $\text{BF}_3 \cdot \text{THF}$) catalyzed by $\text{Cp}_2\text{TiCl}_2/\text{Mg}$ system in THF at 22–25 °C (Scheme 40).^{57–60} 1-Fluoro-2-alkylboratiranes (**101a–f**) and 1-chloro-2-alkyl(aryl)boratiranes (**102a–f**) were prepared in 40–85% yields under the developed conditions (α -olefin : [B] : [Mg] : [Ti] = 1 : 2 : 1 : 0.2, THF, 22–25 °C, 14 h).

The synthesized 1-fluoro-2-alkylboratiranes **101a–f** were isolated by vacuum distillation as boron trifluoride complexes.^{55,57} The number of BF_3 molecules ($n = 2$ and 3) associated with a borirane molecule was estimated by cryoscopy.

The structure of the obtained boratiranes **101a–f** and **102a–f** was confirmed by multinuclear ^1H , ^{13}C , and

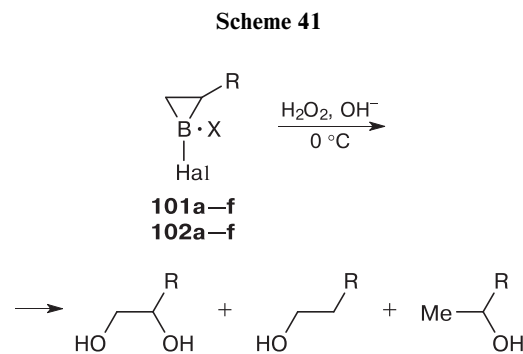


101: R = Bu (**a**), *n*-C₆H₁₃ (**b**), *n*-C₇H₁₅ (**c**), *n*-C₈H₁₇ (**d**), *n*-C₁₀H₂₁ (**e**), *n*-C₁₂H₂₅ (**f**);

102: R = Ph (**a**), Bu (**b**), *n*-C₆H₁₃ (**c**), *n*-C₈H₁₇ (**d**), CH₂OC₆H₅ (**e**), Bn (**f**)

Reagents and conditions: *i.* $\text{BF}_3 \cdot \text{THF}$, Mg, Cp_2TiCl_2 (20 mol.%), THF, 22–25 °C, 14 h. *ii.* $\text{BCl}_3 \cdot \text{SMe}_2$, Mg, Cp_2TiCl_2 (20 mol.%), THF, 22–25 °C, 14 h.

^{11}B NMR spectroscopy and chemical transformations (oxidation with $\text{H}_2\text{O}_2/\text{NaOH}$) to the corresponding diols and monoals (Scheme 41).

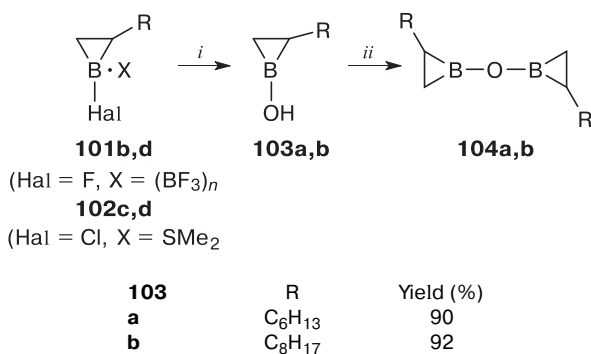


R = Bu, Alk, Ar, Hal = F, X = (BF_3)_{*n*} (**101a–f**), Hal = Cl, X = SMe_2 (**102a–f**)

Halogen-containing 2-alkyl-substituted boratiranes **101b,d** and **102c,d** reacted with water to form borinic acid derivatives, 1-hydroxyboriranes (boriran-1-ols) **103a,b** (Scheme 42).⁶¹ The obtained hydroxyboriranes **103a,b** were stable in air for several hours; however, they were found to be partly converted to anhydrides **104a,b** upon storage at 20–25 °C for 24 h.

The obtained experimental results allowed the authors to suggest that the synthesis of 1-halo-2-substituted bori-

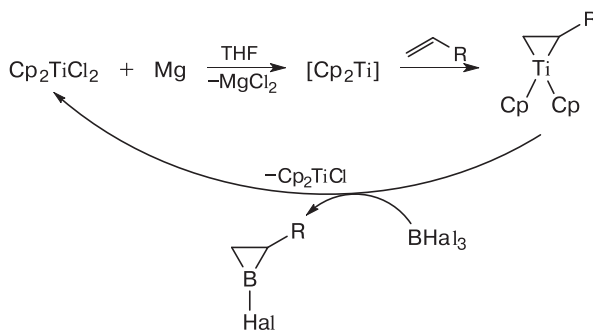
Scheme 42



Reagents and conditions: *i.* H₂O, 22–25 °C, 3 h. *ii.* 22–25 °C, 24 h.

ranes by Cp₂TiCl₂-catalyzed cycloboration of α -olefins with BHal₃ (Hal = F, Cl) proceeds *via* catalytic generation *in situ* of titanacyclopropane intermediates, which undergo transmetalation with boron halides to form boriranes (Scheme 43).^{57–60,62}

Scheme 43



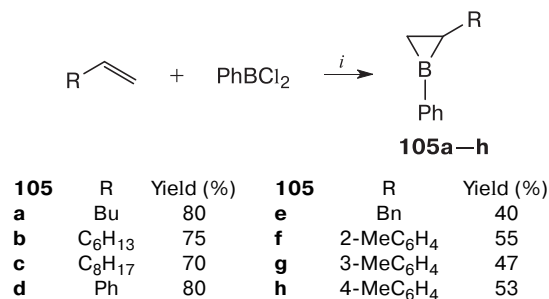
R = Alk, Ar; Hal = Cl, F

The mechanism for cycloboration of α -olefins was proposed on the basis of the results of quantum chemical DFT calculations of the thermodynamic and activation parameters of the possible pathways for the reaction of propene with BCl₃.⁶² In addition to BCl₃, aryl(alkyl)dichloroboranes RBCl₂ (R = Ar, Alk) were proposed as boron reagents for Cp₂TiCl₂-catalyzed cycloboration of α -olefins.

Further developments in the field of synthesis of substituted boriranes *via* cycloboration were to elucidate the scope of this reaction. Thus, 1-phenyl-substituted boriranes **105a–h** were prepared in 40–80% yields *via* Cp₂TiCl₂-catalyzed cycloboration of α -olefins with PhBCl₂ as a boron reagent (Scheme 44).⁶³

It was found that these boriranes easily decompose on heating above 80 °C; therefore, pyridine was added to the

Scheme 44

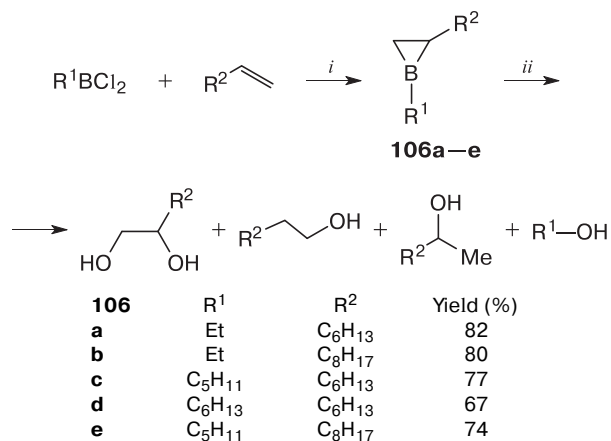


Reagents and conditions: *i.* Mg, Cp₂TiCl₂ (20 mol.%), THF, 20–25 °C, 14 h.

reaction mixture prior to vacuum sublimation to stabilize the borirane molecule. This prevented the destruction of borirane during the isolation. Meanwhile, the pyridine complex was not strong enough under sublimation conditions and underwent cleavage to form free borirane. The isolated free boriranes were solids stable for a long time under inert atmosphere.

In order to study the influence of the structure of starting dichloroboranes on the yield and selectivity of formation of three-membered organoboron compounds, the reactions of different alkyl- and arylalkyldichloroboranes RBCl₂ (R = Et, C₅H₁₁, C₆H₁₃, Ph(CH₂)₂, Naph(CH₂)₂ (Naph is naphthyl)) with α -olefins in the presence of Cp₂TiCl₂ as a catalyst were studied.^{64,65} The reactions of α -olefins with alkyldichloroboranes RBCl₂ (R = Et, C₅H₁₁, C₆H₁₃) gave 1,2-dialkylboriranes **106a–e**, which were isolated in satisfactory yields and identified by spectral methods (Scheme 45).

Scheme 45



Reagents and conditions: *i.* Mg, Cp₂TiCl₂ (20 mol.%), THF, 50–55 °C, 5 h. *ii.* H₂O₂, OH[–], 0 °C.

The oxidation of 1,2-dialkylboriranes **106a–e** with hydrogen peroxide in an alkaline medium gave the cor-

responding di- and mono-ols in 1 : 1 : 1 : 3 ratio in quantitative yields.

Unlike the Cp_2TiCl_2 -catalyzed cycloboration of α -olefins with PhBCl_2 (see Scheme 44) or $\text{BCl}_3 \cdot \text{SMe}_2$ and $\text{BF}_3 \cdot \text{THF}$ (see Scheme 40), which are conducted at 20–25 °C, the reaction with alkyl-dichloroboranes (see Scheme 45) proceeds at 50–55 °C. According to experimental results, cycloboration of α -olefins with $\text{Ph}(\text{CH}_2)_2\text{BCl}_2$ proceeds with difficulty even on heating to 50–100 °C, while dichloro[1-(2-naphthyl)ethyl]borane does not react at all. Probably, low reactivity of arylalkyl-dichloroboranes is due to an increase in the energy barrier for the intramolecular cyclization step in comparison with that calculated for BCl_3 .⁶² The barrier (or the activation energy E_a) for cycloboration at room temperature was calculated to be $\sim 20 \text{ kcal mol}^{-1}$.

Apart from alkyl- and aryl-dichloroboranes, the cycloalkyl-dichloroboranes such as cyclooctyl-dichloroborane **107** and *exo*-norbornyl-dichloroborane **108** successfully react in the Cp_2TiCl_2 -catalyzed cycloboration of α -olefins to form 2-alkyl-1-cyclooctyl(norbornyl)boriranes **109a,b** and **110a,b**, respectively (Scheme 46).⁶⁴ The oxidation of boriranes **109a,b** and **110a,b** on treatment with H_2O_2 /

NaOH affords the expected di- and mono-ols. It was shown that 1-norbornyl-2-alkylboriranes **110a,b** are very sensitive to air. Therefore, the target products isolated by distillation were identified as 1-(bicyclo[2.2.1]hept-2-yloxy)-2-alkylboriranes **111a,b**.

It was shown⁶⁶ that unlike acyclic α -olefins, cycloolefins (cycloheptene, *cis*-cyclooctene, and *cis/trans*-cyclododecene) and norbornene do not undergo the cycloboration.

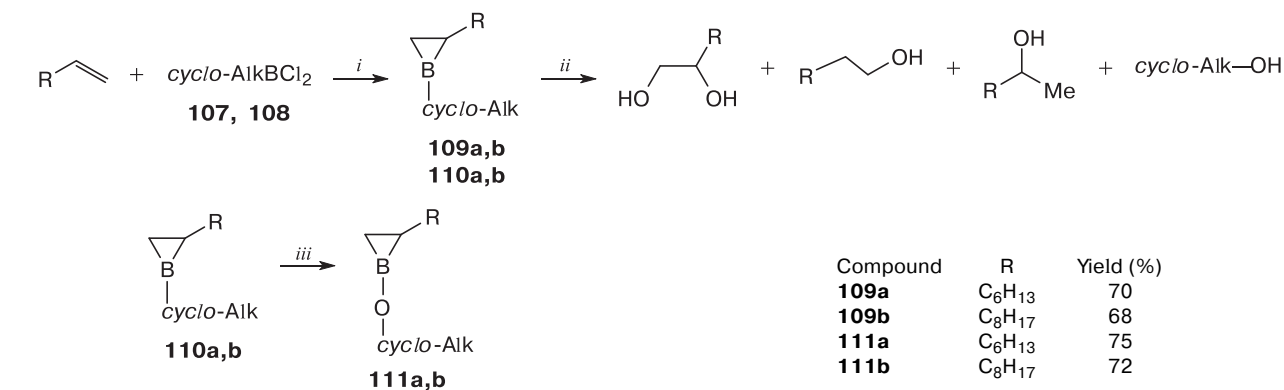
The functionally substituted dichloroboranes, e.g. $\text{Pr}^i_2\text{NBCl}_2$, give 1-alkenylboriranes **112a–d** in 69–95% yields, instead of *B*-aminoboriranes, under the developed conditions (Scheme 47).⁶⁷


Study of the scope of metal complex catalysis in the synthesis of substituted boriranes opens up broad prospects for the preparative synthesis of three-membered cyclic organoboron compounds. These studies are at their infancy; therefore, their further development and new surprising results should be expected in the future.

Borirenes and boratirenes

Boracyclopropenes (borirenes and boratirenes) are a simple example of unsaturated cyclic organoboron com-

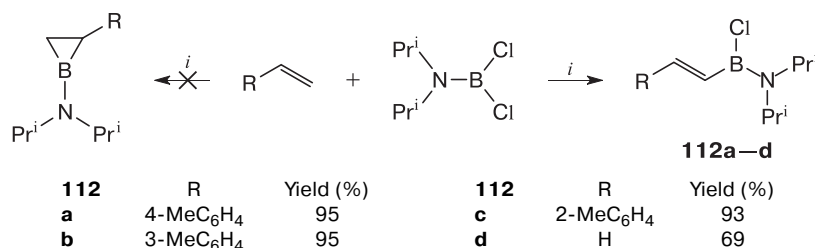
Scheme 46



cyclo-Alk — *cyclo*- C_8H_{17} (**107**, **109**),  (**108**, **110**, **111**)

Reagents and conditions: *i*. 20 mol.% Cp_2TiCl_2 , Mg, THF. *ii*. H_2O_2 , OH^- , 0 °C, 6 h. *iii*. Oxidation in air.

Scheme 47



Reagents and conditions: *i*. Mg, Cp_2TiCl_2 (20 mol.%), THF, 20–25 °C, 8 h.

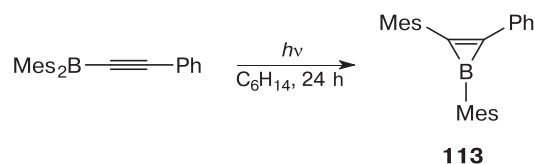
pounds. Borirenes are boron analogs of cyclopropenyl cations and represent the smallest aromatic systems. Like their saturated analogs (boriranes), borirenes have a vacant p-orbital of boron, which is capable of accepting electrons from an electron-donating molecule. However, borirenes exhibit aromatic properties unlike boriranes. Both π -electrons of the borirene ring are completely delocalized between the p-orbitals of the boron atom and two carbon atoms, which makes borirene derivatives aromatic, according to the Hückel rule.

Borirenes are a vivid example of modern chemistry, in which theoretical calculations precede the experimental research. Borirenes have been poorly studied experimentally because of problems with their isolation and crystallization. Intensive theoretical studies with the prediction of the geometry, thermodynamic stability, and reactivity of three-membered boron heterocycles began early in the 1980s.^{68,69} The first information on the synthesis of borirenes^{68–71} appeared due to the chemists' work in the field of photoinitiated transformations of boron-substituted acetylenes.

Synthesis of borirenes by photochemical isomerization

In 2005, 1,2-dimesityl-3-phenylborirene **113** was synthesized by photoisomerization of dimesitylborylphenylacetylene in a nonpolar solvent (Scheme 48).⁷²

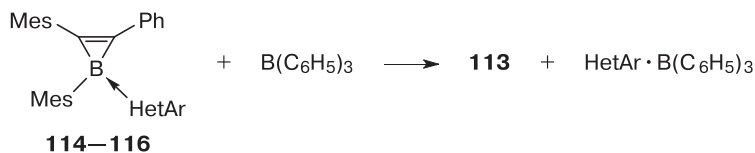
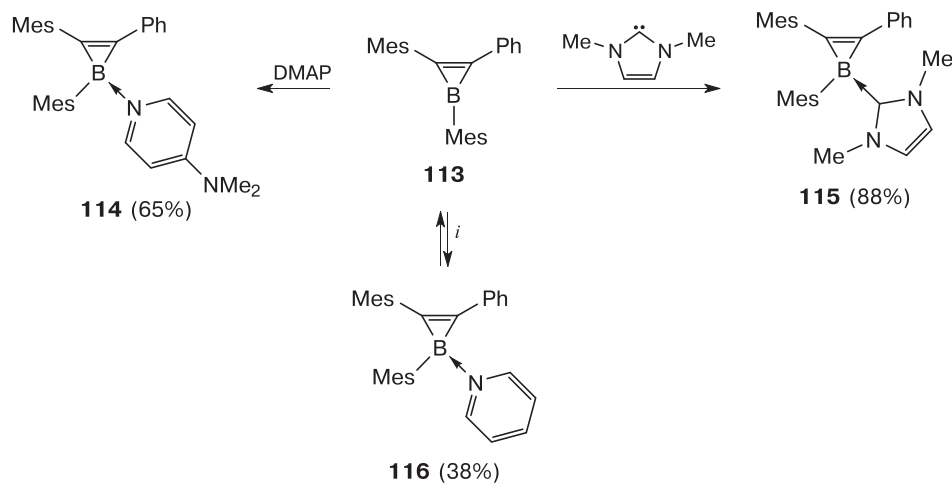
Scheme 48



It was noted that filling of the vacant p-orbital of the boron atom by addition of a Lewis base is a well-known reaction for organoboron compounds. However, the formation of such adducts of borirenes with Lewis bases disrupts any π -conjugation involving the boron atom. Thus, aromaticity or antiaromaticity disappears in the ring. This phenomenon proved to be useful, for example, for modulating the photophysical properties of boroles.^{73,74} Therefore, the reactivity of borirenes with various Lewis bases was demonstrated.⁷² Stable adducts **114** and **115** were formed in the reaction of borirene **113** with 4-dimethylaminopyridine and 1,3-dimethyl-2,3-dihydro-1*H*-imidazole. The reaction of borirene **113** with pyridine gave the corresponding pyridinate **116** (38% yield), which precipitated as a yellow-colored solid when the reaction mixture was cooled to $-40\text{ }^{\circ}\text{C}$ (Scheme 49).

It was found experimentally that these Lewis bases can be easily removed by the addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to adducts **114–116** to form the starting borirene **113** (see Scheme 49).

Scheme 49



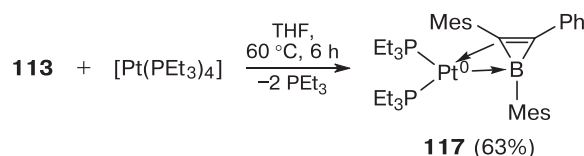
HetAr = Py, DMAP,

Reagents and conditions: *i*. Py, toluene, $\sim 20\text{ }^{\circ}\text{C}$.

The results showed that borirenes are weaker Lewis acids than $B(C_6F_5)_3$.

The reaction between 1,2-dimesityl-3-phenylborirene and tetrakis(triethylphosphine)platinum $Pt(PEt_3)_4$ in THF leads the platinum borirene complex **117**, isolated as light yellow crystals with $T_m = 151$ °C (Scheme 50).⁷⁵

Scheme 50

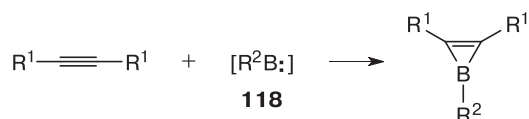


The structure of complex **117** was established by X-ray crystallography, NMR spectroscopy, and cyclic voltammetry and confirmed by DFT quantum chemical calculations. It was shown that the isolated compound **117** is a B—C coordination σ -complex containing borirene and a $Pt(PEt_3)_2$ moiety in 1 : 1 ratio.

Synthesis of borirenes by the [2+1]-cycloaddition reaction of borylenes [RB:] with acetylenes

The possibility of preparing borirenes by [2+1]-cycloaddition of borylenes ($:B-R$) **118** to acetylenes (Scheme 51) and the potential aromaticity of borirenes were first predicted in 1962⁷⁶ when three-membered boron-containing heterocycles were not yet described.

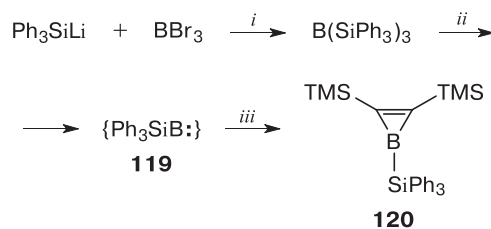
Scheme 51



The synthetic route to borirenes by the reaction of acetylenes with borylenes was proposed by Pachaly and West for the first time.⁷⁷ Triphenylsilylborylene **119** reacts with bis(trimethylsilyl)acetylene to form triphenylsilyl-2,3-bis(trimethylsilyl)borirene **120** (Scheme 52).

Note that the photochemical generation of borylene **119** took place under rather harsh conditions in these experiments, namely, on cooling the reaction mixture to -196 °C. A more convenient approach to the generation of borylenes was proposed in 2005,⁷⁸ with the aminoborylene complexes $[(CO)_5M=B=N(SiMe_3)_2]$ being used as the source of borylenes.^{72,78–81} These complexes based on group 6 transition metals ($M = Cr, Mo, W$) can be easily obtained under ambient conditions in an inert atmosphere. Thus, the transfer of the borylene $:B(N(SiMe_3)_2)$ from the coordination sphere of the metal to the triple

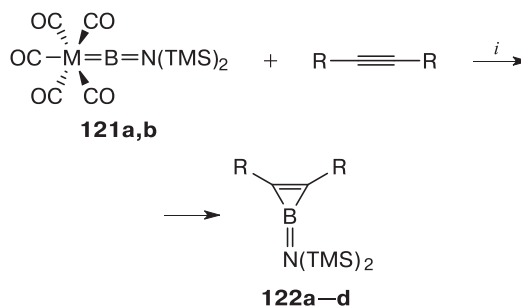
Scheme 52



Reagents and conditions. *i.* THF, heptane, -70 °C. *ii.* *hv*, -196 °C. *iii.* $TMS-C\equiv C-TMS$, 25 °C.

bond of alkyne allows the direct and selective synthesis of various substituted borirenes. Photolysis of metal borylene complexes $(CO)_5M=B=N(SiMe_3)_2$ ($M = Cr, Mo$) **121a,b** at ~ 20 °C in the presence of symmetrical acetylenes resulted in the preparation of B-aminoborirenes **122a–d** (Scheme 53)^{78,80}.

Scheme 53



$M = Cr$ (a), Mo (b)

122	R	Yield (%)	122	R	Yield (%)
a	TMS	82	c	4- $CF_3C_6H_4$	72
b	Ph	88	d	4- $OMeC_6H_4$	74

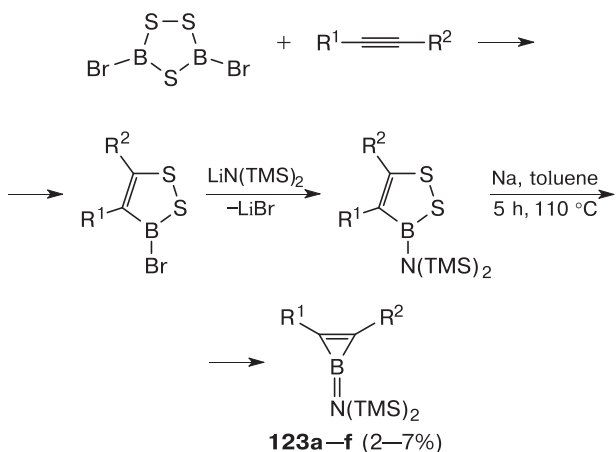
Reagents and conditions: *i.* *hv*, toluene/ C_6H_6 /THF, 2–5 h.

Borirene **122a** was isolated as pale yellow crystals by recrystallization from hexane at -60 °C and characterized by X-ray photoelectron spectroscopy. The authors⁷⁸ compared the C—C and B—C bond lengths in the borirene rings of aminoborirene **122a** and arylborirene **113**. It was concluded that the characteristic π -electron delocalization in the borirene ring is less pronounced in compound **122a** due to the presence of the amino group, which experiences π -type interaction with the vacant p-orbital of the boron atom.

The synthesis of B-aminoborirenes was carried out for the first time in 1984,⁸² but this multistep synthetic route was not further developed because of very low yields of the target products **123a–f** (2–7%) (Scheme 54).

The possibility of chemoselective borirene ring opening in B-aminoborirenes is depicted in Scheme 55.⁷⁹ The hydroboration of 1-[bis(trimethylsilyl)amino]-2,3-dieth-

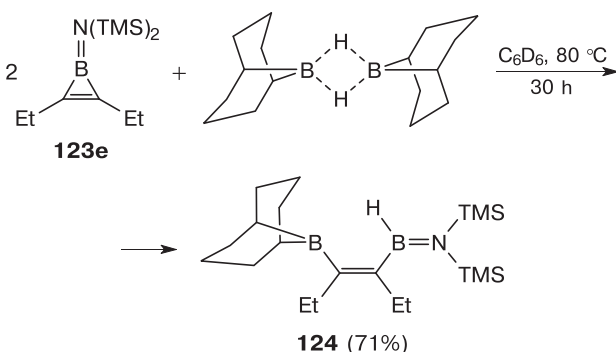
Scheme 54



R¹ = H, R² = Prⁿ (**a**); R¹ = H, R² = Buⁿ (**b**); R¹ = H, R² = Ph (**c**);
R¹ = Me, R² = Prⁿ (**d**); R¹ = R² = Et (**e**); R¹ = R² = Prⁿ (**f**)

ylborirene **123e** with 9-borabicyclo[3.3.1]nonane results in the quantitative and selective formation of *cis*-amine-(borylvinyl)borane **124**.

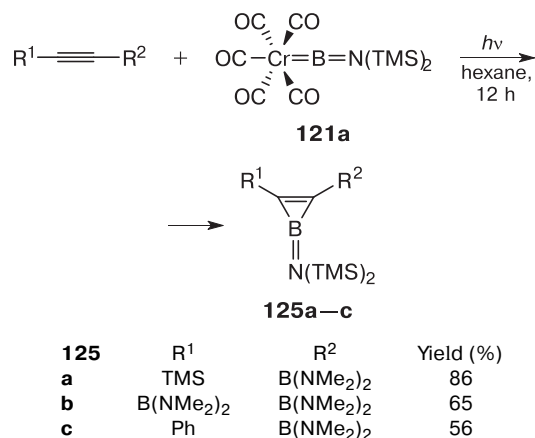
Scheme 55



The subsequent studies of borylene complexes allowed the synthesis of borirenes based on a number of unsymmetrical acetylenes with B(NMe₂)₂ moieties as substituents.⁷² Thus, the photolysis of chromium aminoborylene complex **121a** in the presence of acetylenes with various functional groups such as B(NMe₂)₂, Ph, and SiMe₃ for 12 h at room temperature gave aminoborirenes **125a–c** (Scheme 56).

Aminoborirenes **125a–c** proved to be moisture- and air-sensitive. They were isolated by fractional distillation under reduced pressure as pale yellow solid (**125a,b**) or oil (**125c**). The single crystals of these compounds suitable for X-ray diffraction were formed in pentane at a temperature of –30 °C over a week. On long-term storage under argon, monoboryl-substituted aminoborirenes **125a,c** decomposed, while monoboryl-substituted aminoborirene

Scheme 56

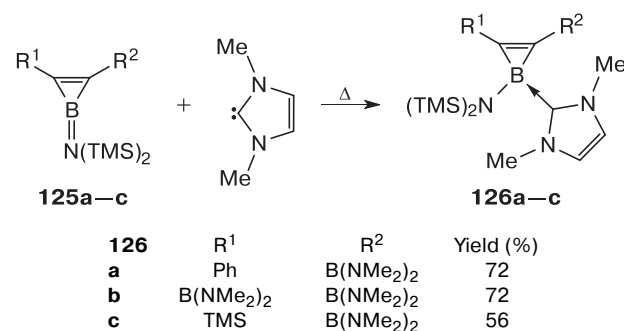


125b was more stable.⁷² It was also found that compounds **125a,b** decomposed at temperatures above 200 °C.

In accordance with X-ray diffraction data on the C–C and B–C bond lengths and the bond angles in aminoborirenes, the conjugation in the ring in borirene **125b** with two B(NMe₂)₂ substituents increases in contrast to borirene **125a**.

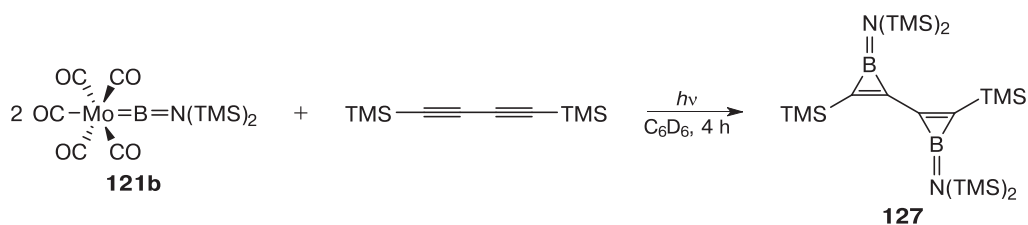
The reactivity of aminoborirenes **125a–c** towards various Lewis bases (pyridine, phosphine, and imidazole derivatives) was investigated.⁷² Compounds **125a–c** were found to be virtually unreactive towards these Lewis bases either at room temperature or on heating to 80 °C. An exception was 1,3-dimethylimidazol-2-ylidene, which reacted with aminoborirenes **125a–c** to form adducts **126a–c** (Scheme 57).

Scheme 57



It is known that boron derivatives tend to form complexes with electron-donating compounds, due to the free p-orbital of the boron atom. However, B-aminoborirenes are less prone to such quaternization, because boron and nitrogen atoms in these compounds are already bound by a covalent bond and the nitrogen lone pair forms a double bond (B=N) as a result of delocalization with the boron vacant p-orbital. Nevertheless, the stronger Lewis bases — stable carbenes, e.g., 1,3-dimethyl-2,3-dihydro-1*H*-imid-

Scheme 58



azole — form stable adducts with aminoborirenes. At the same time, quaternization of exocyclic boron atoms of aminoborirenes **126a–c** with boryl substituents is not observed even when an excess of carbene is added.

The preparation of bis-aminoborirenes **127** by the photolysis of molybdenum borylene complex $(CO)_5Mo=B=N(SiMe_3)_2$ **121b** in the presence of 1,4-bis(trimethylsilyl)buta-1,3-diyne was demonstrated (Scheme 58).⁷⁸

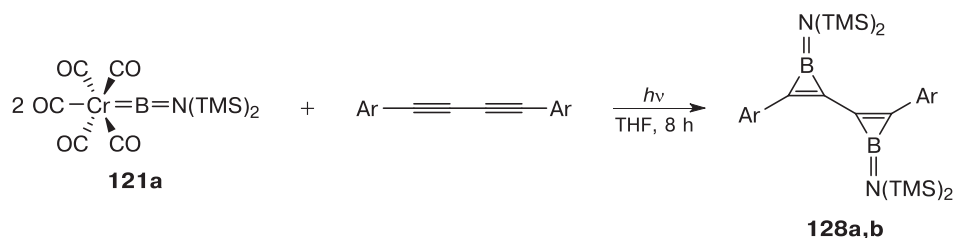
The structure of the resulting bis-aminoborirene **127** was reliably established by NMR spectroscopy (1D and 2D) and mass spectrometry.

Photolysis of chromium and molybdenum aminoborylene complexes at room temperature smoothly proceeds in the presence of aromatic diynes to give bis-aminoborirenes in high yields.⁸⁰ For example, UV irradiation

of a solution of the pale yellow borylene complex $[(CO)_5Cr=B=N(SiMe_3)_2]$ **121a** in THF with aromatic diynes such as 1,4-diphenylbuta-1,3-diyne or 1,4-bis(4-methylphenyl)buta-1,3-diyne at room temperature for 8 h resulted in the formation of bis-aminoborirenes **128a,b** (Scheme 59). The 1H and ^{11}B NMR spectroscopy data for compounds **128a,b** attest to a high symmetry of the molecule in solutions and fast rotation around the B–N bond at room temperature.

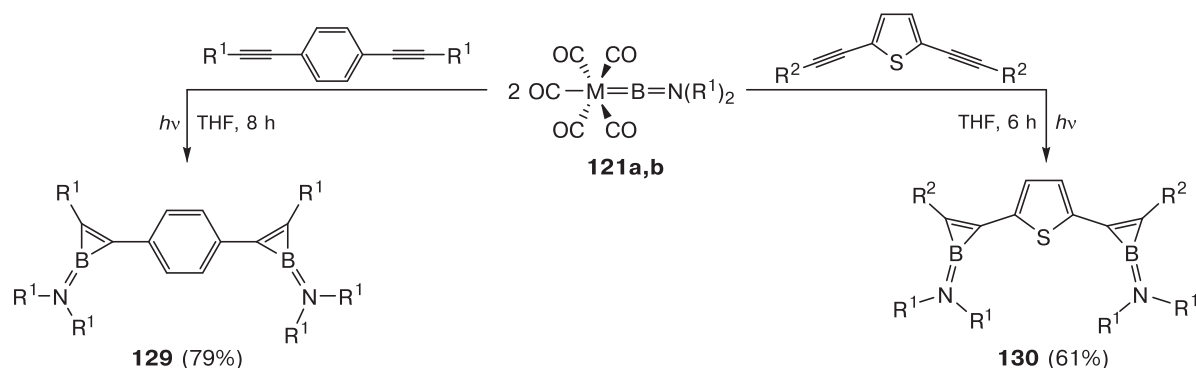
Chromium and molybdenum borylene complexes **121a,b** react in a similar way with diynes (1,4-bis(trimethylsilylethynyl)benzene or 2,5-bis(4-*N,N*-dimethylaminophenylethynyl)thiophene) in which the triple bonds are separated by a conjugated aromatic or heteroaromatic spacer (Scheme 60). The obtained bisborirenes **129** and **130** are amorphous solids, and they are sensitive to air and

Scheme 59



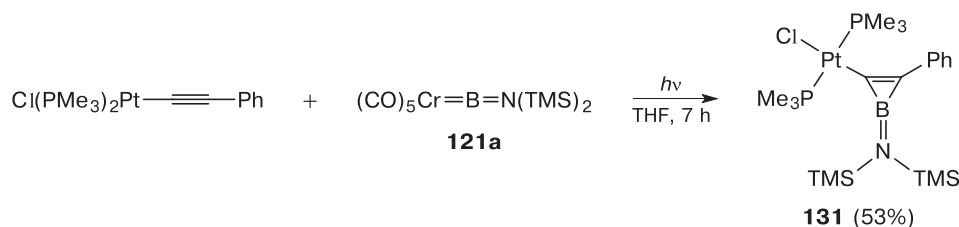
	Ar	Yield (%)
128a	H	90
128b	4-OMeC ₆ H ₄	68

Scheme 60



$R^1 = TMS$, $R^2 = 4-NMe_2C_6H_5$; M = Cr (**a**), Mo (**b**).

Scheme 61



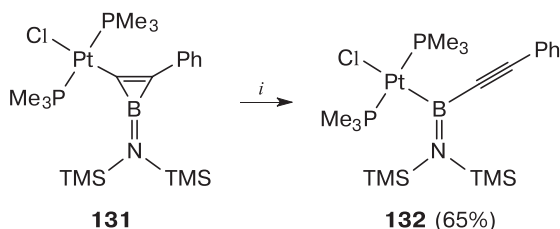
moisture. Compounds **128a,b** and **129** are the first structurally characterized *bis*-borirenes with an extended π -conjugation system including three-coordinate boron centers.

The theoretical and experimental data⁸⁰ lend further support to the description of the B=N linkage in aminoborirenes as a rather weak double bond, whose π -contribution is reduced by the incorporation of the p_z -orbital at boron into the 2π -electron aromatic ring.

The attention of researchers is attracted by boron-based π -conjugated systems due to their interesting photo-physical properties and the possibility of potential application as materials for electronics.^{83,84} For example, the transition metal borirene complex **131** was synthesized for the first time by photochemical transfer of borylene from the aminoborylene complex $[(\text{CO})_5\text{Cr}=\text{B}=\text{N}(\text{TMS})_2]$ **121a** to the σ -alkynyl platinum complex $[\text{Cl}(\text{PMe}_3)_2\text{Pt}-\text{C}\equiv\text{CPh}]$ (Scheme 61).⁸⁵ Platinum-containing alkynyls were chosen as substrates, as these complexes form an important class of organometallic compounds used in optoelectronics. The Pt-substituted aminoborirene **131** obtained in this way was isolated from the reaction mixture in ~53% yield as analytically pure crystals by filtration and subsequent crystallization from hexane at -60°C .

The irradiation of this complex in deuterated benzene in inert atmosphere for four days at room temperature gave a new acyclic boron and phosphorus organic compound **132** as a result of intramolecular photorearrangement accompanied by ring opening in borirene (Scheme 62). The Pt alkyne complex *trans*- $[\text{Cl}(\text{PMe}_3)_2\text{PtBN}(\text{SiMe}_3)_2-\text{C}\equiv\text{CPh}]$ **132** was isolated in 65% yield by recrystallization from a toluene/hexane mixture at -30°C and characterized by spectroscopy and X-ray crystallography.⁸⁶

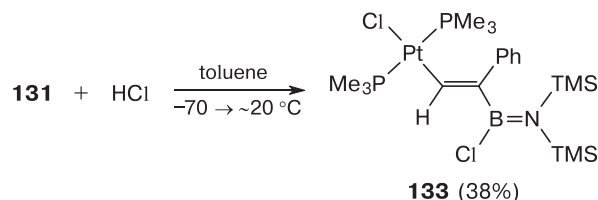
Scheme 62



Reagents and conditions: *i.* $h\nu$, C_6D_6 , 20°C , 4 days.

The treatment of borirene with Brønsted acids such as water, methanol, ethanol, acetic acid, or hydroboration reagent, for example, 9-borabicyclo[3.3.1]nonane⁷⁹ at 25°C , leads to ring opening *via* cleavage of one endocyclic B—C bond. The reactivity of Pt-substituted aminoborirene **131** towards HCl, which is a typical protic reagent, was studied (Scheme 63).⁸⁶ The reaction proceeded *via* borirene ring opening and gave the corresponding amino-(vinyl)borane **133**. The yield of the product isolated by recrystallization from hexane at -30°C as colorless crystals was 38%.

Scheme 63

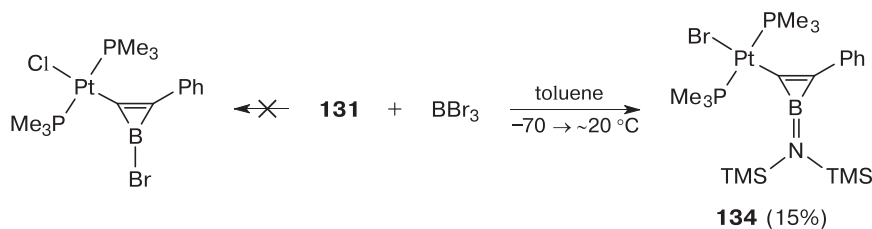


The authors assumed that the action of boron tribromide would cleave the exocyclic B=N bond to form Pt-substituted bromoborirene under the conditions used. However, the reaction between aminoborirene **131** and BBr_3 leads to the replacement of a chlorine atom by a bromine one instead of the cleavage of the B=N bond (Scheme 64). This gives platinum-containing borirene *trans*- $[\text{Br}(\text{PMe}_3)_2-\text{Pt}\{\mu-\text{BN}(\text{SiMe}_3)_2\text{C}=\text{C}\}\text{Ph}]$ **134** in 15% yield.⁸⁶

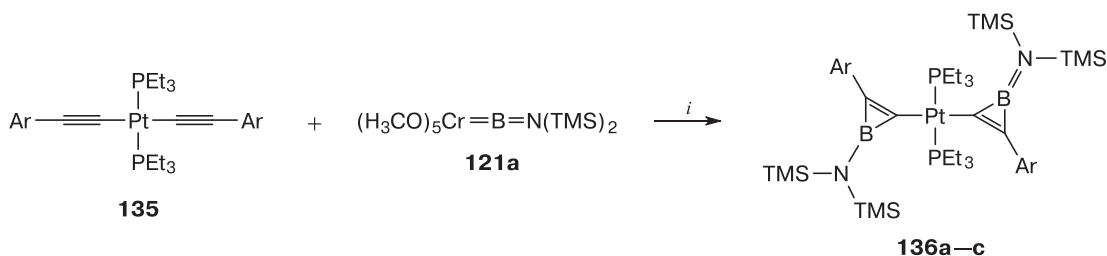
The use of *trans*-bis(alkynyl)platinum precursors as the starting monomers makes it possible to obtain organoboron hybrid molecules. These molecules have two borirene moieties separated by a platinum atom.⁸⁷ For example, the photolysis of the complex $[(\text{CO})_5\text{Cr}=\text{B}=\text{N}(\text{SiMe}_3)_2]$ **121a** and the transfer of the borylene moiety to the bis(alkynyl)platinum complex **135** in benzene or hexane for 8 h resulted in the *trans*-bis(borirene)platinum complexes **136a–c** (Scheme 65).

The reaction products **136a–c** sensitive to moisture and air were isolated as yellow crystals in satisfactory yields of 39–63% by chromatography on a specially pretreated silica gel followed by recrystallization from hexamethyldisiloxane. Platinum-containing bisborirenes **136a–c**

Scheme 64



Scheme 65



136	Ar	Yield (%)
a	Ph	39
b	4-MeOC ₆ H ₄	45
c	4-CF ₃ C ₆ H ₄	63

Reagents and conditions: *i.* Benzene or hexane, *hν*, 8 h.

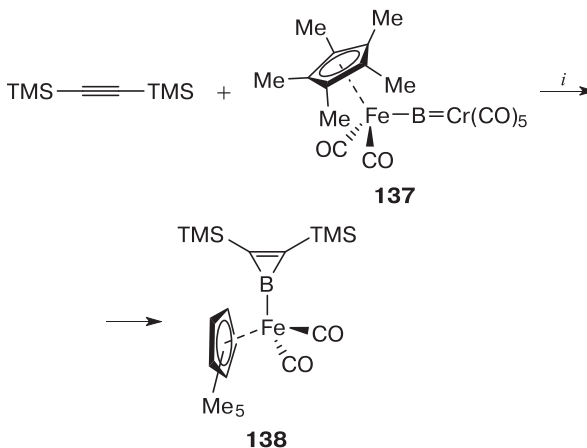
can be stored for indefinitely long time under inert atmosphere.

The ¹H, ¹³C, ²⁹Si, ³¹P, and ¹⁹⁵Pt NMR spectra of these complexes showed a double set of signals, which corresponds to different conformations (*syn* and *anti*) of the borirene moieties separated by a platinum atom. Doubling of NMR signals observed for these systems indicates that there is a rotational barrier between the platinum atom and the borirene arms at the periphery of the molecule. This results in two conformational isomers in which the borirene moieties are either held on one side of the PtX₂L₂ plane or shifted relative to this plane (*syn*- and *anti*-conformations). The hindered rotation of bonds within this molecule caused by strong electronic conjugation between the platinum core and the twin borirene aromatic system, but not by steric factors, is the reason for the coplanarity of the molecule in the solid state.⁸⁷ This interaction demonstrates novel photophysical properties of the obtained bisborirenes in comparison with monoborirenes obtained previously. *Trans*-bis(borirene) platinum complexes **136a–c**, being the first systems featuring coplanar borirene rings owing to strong π-electron interaction, can be successfully used to develop new optoelectronic devices.

The influence of exocyclic substituents at the boron atom on their properties of borirenes was studied using alternative source of borylene. Instead of the complex

[(CO)₅Cr=B=N(SiMe₃)₂] **121a**, which can be used to prepare aminoborirenes in the presence of alkynes, the borylene complex [(CO)₅Cr=BFe(CO)₂(Cp)] **137** was taken (Scheme 66).^{88–90} The reaction was conducted in a variety of solvents: hexane, benzene, or THF. The photoirradiation of complex **137** in the presence of 1,2-bis(trimethylsilyl)ethyne for 30 min led to new B-ferroborylene **138** in a quantitative yield. The structure of **138** was elucidated

Scheme 66

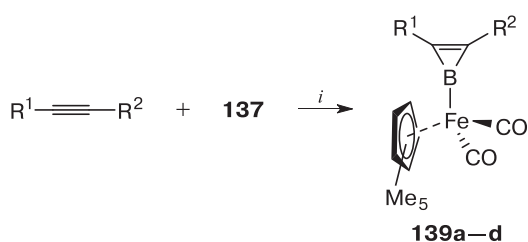


Reagents and conditions: *i.* Hexane, benzene, or THF, *hν*, 30 min.

ated through analysis of ^1H , ^{13}C , and ^{11}B NMR spectra. Ferroborene **138** slowly precipitated from the reaction mixture at $-30\text{ }^\circ\text{C}$ as yellow crystals, which made it possible to confirm its structure by X-ray diffraction analysis.

The generation of the borylene $:\text{BFe}(\text{CO})_2(\text{Cp})$ for the synthesis of B-ferroborenes was carried out by heating⁸⁸ instead of irradiation. The thermochemical reaction of alkynes (dimesitylethyne, 4,4'-(ethyne-1,2-diyl)bis(*N,N*-dimethylaniline), bis{bis(dimethylamino)boryl}ethyne, and 1-trimethylsilyl-2-bis(dimethylamino)borylethyne) with complex **137** resulted in the selective formation of B-metallated borirenes **139a–d** (Scheme 67). The reaction time depended on the nature of the starting acetylene. Initially,

Scheme 67



139	R^1	R^2	Yield (%)
a	Mes	Mes	36
b	4-NMe ₂ C ₆ H ₄	4-NMe ₂ C ₆ H ₄	24
c	B(NMe ₂) ₂	B(NMe ₂) ₂	48
d	TMS	B(NMe ₃) ₂	61

Reagents and conditions: *i.* Toluene, Δ , $120\text{ }^\circ\text{C}$, 3–5 h.

the resulting B-ferroborenes were evacuated and then recrystallized from hexane to obtain yellow-orange crystals of borirenes **139a–d** in 24–61% yields. $\text{Cr}(\text{CO})_6$ formed as a by-product was separated by sublimation.

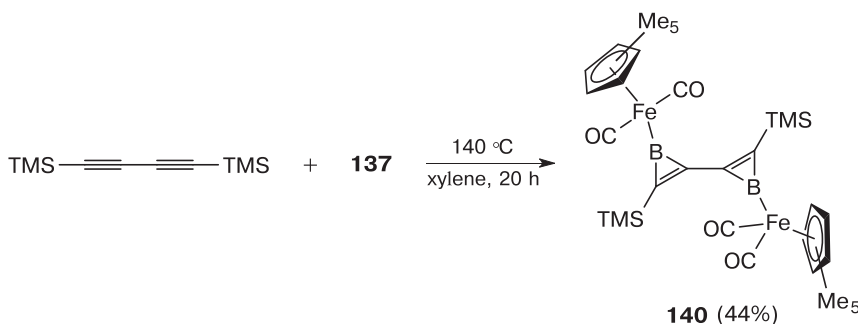
Bis(B-ferroborene) **140** was obtained in 44% yield by the reaction of 1,4-bis(trimethylsilyl)buta-1,3-diyne with a twofold excess of complex **137** carried out in xylene at $140\text{ }^\circ\text{C}$ for 20 h (Scheme 68).⁸⁹

An X-ray diffraction study of complex **140** showed that the distance between the mutually orthogonal borirene rings linked by the carbon–carbon bond is 1.413 \AA . This distance is much shorter than that between two sp^2 -hybridized carbon atoms of a typical biphenyl. This fact can be explained by delocalization of π -electrons of the double bond in three-membered borirenes. Indeed, DFT calculations showed a distinct π -electron delocalization in the borirene rings, in which a significant contribution is made by iron d-electrons.⁸⁹

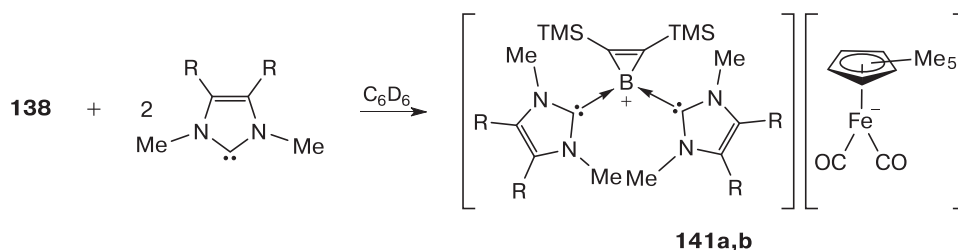
The interaction of B-ferroborene **138** with carbenes proceeds *via* heterolytic B–Fe bond cleavage and leads to a new class of boron-containing heterocycles, *viz.*, boronium cations **141a,b** (Scheme 69).⁹⁰

Compound **141a** immediately precipitates from the solution as an orange-colored salt. Compound **141b** was obtained as a red crystalline precipitate only after removal of the solvent from the reaction mixture followed by washing with pentane and recrystallization from THF. The structure of compounds **141a,b** was reliably proven by the multinuclear NMR spectroscopy and X-ray diffraction. Thus, boronium cations obtained by the reaction of

Scheme 68

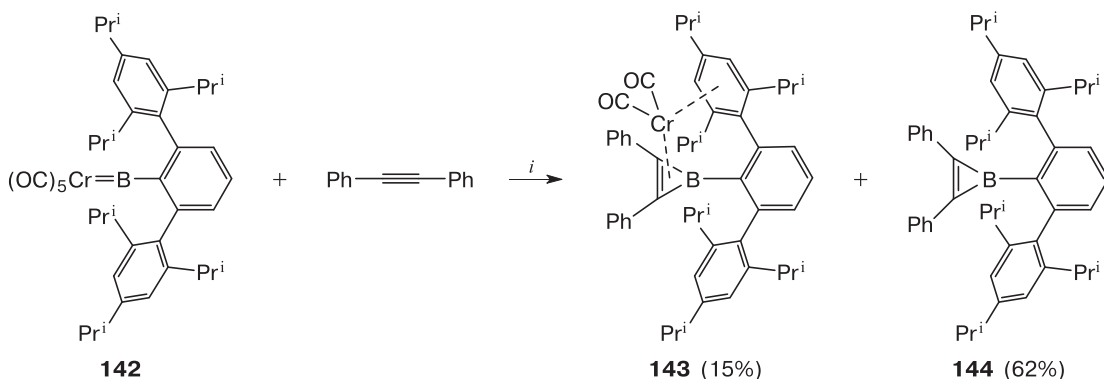


Scheme 69



$\text{R} = \text{H}$ (**a**, 70%), Me (**b**, 50%)

Scheme 70



Reagents and conditions: i . C_6H_6 , $h\nu$, 72 h.

B-ferroborirene with a twofold excess of *N*-heterocyclic carbene are the first compounds in which a boron atom is ligated by two carbenes.⁹⁰

The authors assume that the small size of the boronium rings in compound **141a** is a key factor allowing two bulky carbenes to bind to the boron atom. The reaction is based on the unusual ability of the $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_2]$ anion to act as the leaving group; the use of uncoordinated carbenes for metal—element bond cleavage is a rare phenomenon.

The first example of preparation of a complex with metal η^3 -coordination to a borirene ligand was reported.⁹¹ The synthesis of chromium borirene complex **143** is based on the photolytic transfer of the arylborylene ligand from chromium complex **142** to diphenylacetylene (Scheme 70). The reaction was accompanied by the loss of three CO ligands.

Analysis of the ^1H NMR spectra of the reaction mixture revealed the formation of two compounds **143** and **144** in 1 : 4 ratio. Borirene complex **143** was isolated (15% yield) by recrystallization at -30°C , along with "free" borirene **144** (62%).

X-ray diffraction data showed that complex **143** contains the η^3 -borirene core bound simultaneously to the $\text{Cr}(\text{CO})_2$ moiety and to the $\text{C}_6\text{H}_2\text{Pr}^i_3$ ligand. The authors described this complex as a classical half-sandwich complex in which one CO-group is replaced by the two-electron borirene ligand. It is of interest that the ^{11}B NMR spectrum of compound **143** did not contain a boron signal.

The ^{11}B NMR spectrum of borirene **144**, which was isolated as single crystals, showed the characteristic chemical shift for the boron atom ($\delta_{\text{B}} = 33.0$ ppm). X-ray diffraction data allowed the authors to find the differences between the features of "free" borirene **144** and π -bound mononuclear borirene complex **143**.

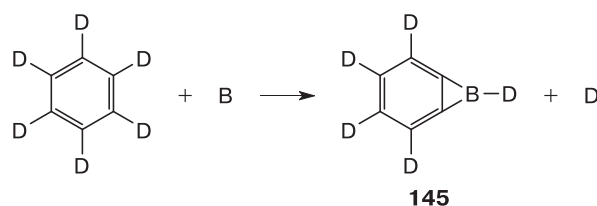
Thus, the aryl-substituted borylene complex of chromium **142**, like more electron-rich amino(iron) organic analogs, can serve as a source of arylborylene to obtain the corresponding borirenes.⁹¹

Synthesis of benzoborirenes

Benzoborirenes are isoelectronic analogs of benzo-cyclopropenyl ions. These compounds are examples of unstable highly strained molecules with an aromatic system conjugated to the boron atom, which is of interest for not only chemists, but also physicists.^{92–98}

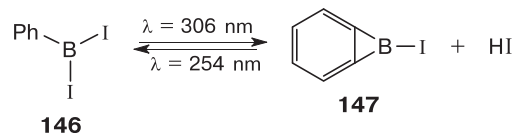
The "elusive" benzoborirene molecule **145**, which is formed in the reaction of atomic boron with deuterobenzene (Scheme 71), was first identified by mass spectrometry in the gas phase at the molecular level using crossed molecular beam experiments.^{92–94} The theoretical computational methods and physicochemical experiments made it possible to describe the radical mechanism of benzoborirene formation.⁹³

Scheme 71

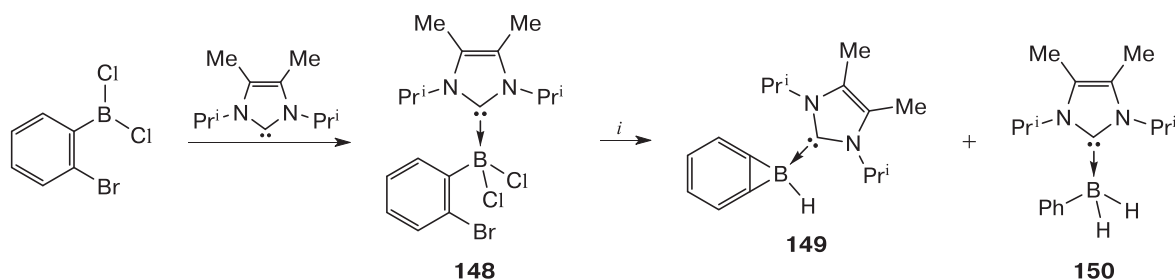


The photoirradiation of diiodophenylborane **146** in solid argon at 10 K gave B-iodobenzoborirene **147** (Scheme 72).⁹⁵ The IR absorption spectrum of a benzoborirene derivative was recorded for the first time.

Scheme 72



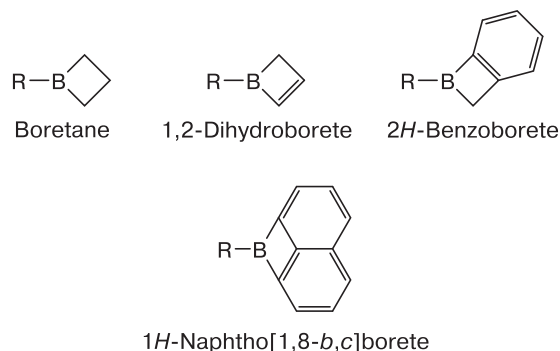
Scheme 73



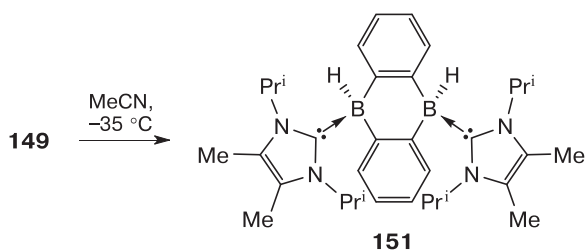
Reagents and conditions: *i.* 2 equiv. Bu^tLi, [D₈]-toluene, 77 K → ~20 °C.

Only in 2018, the benzoborirene molecule was identified using NMR spectroscopy under ambient conditions.⁹⁶ The reduction of borane **148** with *tert*-butyllithium led to benzoannulated borirene as a complex with 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (Scheme 73).⁹⁶ Apart from benzoborirene **149**, this reaction afforded a minor amount of dihydroborane **150**.

Benzoborirene **149** was kept in acetonitrile at -35 °C for a long time to grow single crystals. Its dimerization, however, proceeded under these conditions to give 9,10-dihydro-9,10-diboraanthracene **151** (Scheme 74), which was studied by X-ray diffraction.



Scheme 74



Borirenes are of considerable interest; however, the scope of their applicability as π -conjugated boron-containing structural materials is still little studied.

Saturated and unsaturated four-membered boracyclanes

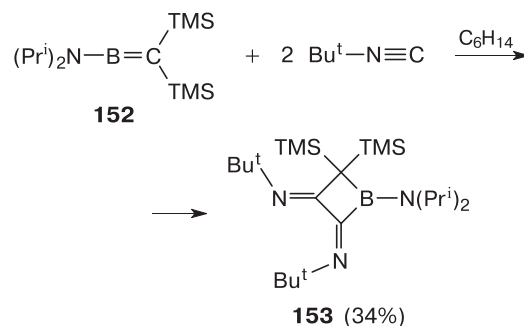
To date, the chemistry of four-membered cyclic organoboron compounds has been little studied. This part addresses the synthesis of boracyclanes such as boretanes and 1,2-dihydro-, 2H-benzo-, and 1H-naphtho[1,8-*b,c*]-boretanes.

In most cases, four-membered boron-containing heterocycles reported in the literature are unsaturated structures and have at least one sp²-hybridized carbon atom in a small ring. Data on the synthesis of their saturated analogs (boretanes) are very scarce, and only a small number of publications are available.

Synthesis of boretanes

Boretane **153** was obtained for the first time in 1989 by the reaction of methyleneborane **152** with *tert*-butyl isonitrile (Scheme 75).⁹⁹

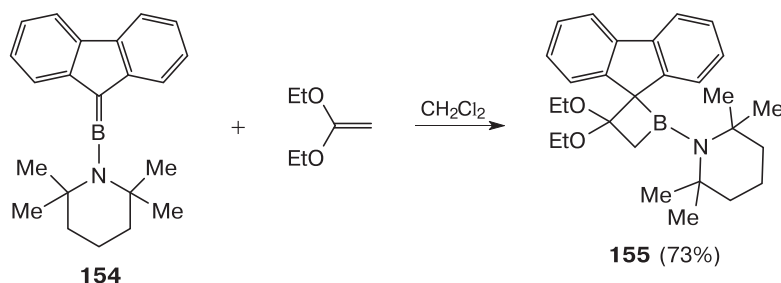
Scheme 75



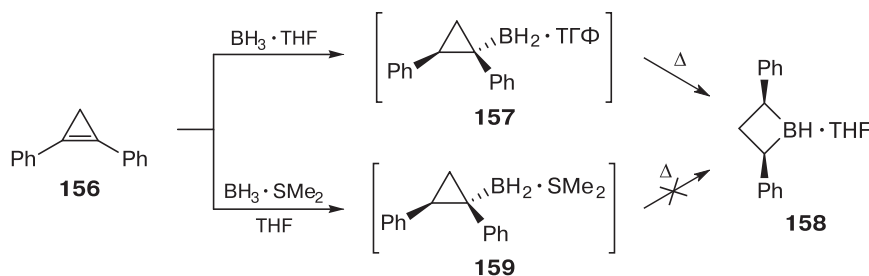
Later, the [2+2]-cycloaddition reaction of 1,1-diethoxyethylene with 9-fluorenylidene tetramethylpiperidineborane **154**, resulting in boretane **155**, was reported (Scheme 76).¹⁰⁰

However, the presented methods for the preparation of boretanes were not further developed. The next publication described the synthesis and spectral identification of the boron-containing four-membered boretane prepared by skeletal isomerization of cyclopropylborane.¹⁰¹ The

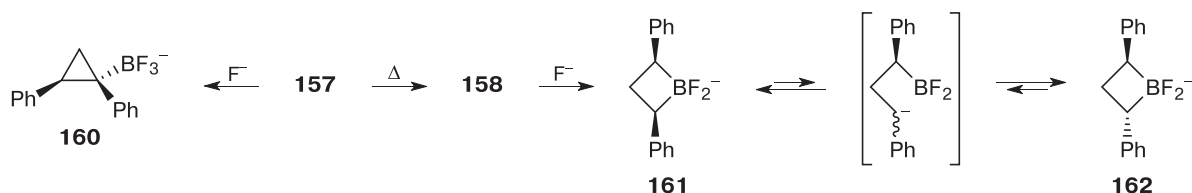
Scheme 76



Scheme 77



Scheme 78



hydroboration of diphenyl-substituted cyclopropene **156** with $\text{BH}_3 \cdot \text{THF}$ led to cyclopropylborane **157**, which was transformed into boracyclobutane **158** by heating to 100°C (Scheme 77).

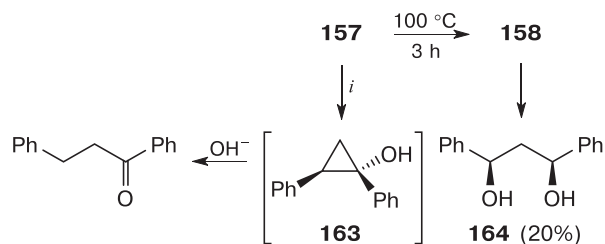
When this reaction is carried out in the presence of $\text{BH}_3 \cdot \text{SMe}_2$ in dry THF, the skeletal rearrangement of cyclopropylborane **159** to boretane **158** did not take place even on long-term heating of the reaction mixture at a temperature of 100°C . The authors assumed that the rearrangement substantially depends on the degree of cationic character of the reaction center and that the reaction can be inhibited by strong Lewis bases.

The dynamics of the above reaction was monitored by the ReactIR spectroscopy, which showed the time variation of the concentrations of the reactants and products. The reaction mixture was treated with KHF_2 to obtain a stabilized four-membered ring as a fluoroborate derivative, in order to collect additional evidence for the formation of boretane **158** (Scheme 78). The ^{19}F NMR spectrum of the reaction mixture demonstrated signals of cyclopropyltrifluoroborate **160** and BF_4^- .

The spectroscopic studies showed that not only difluoroborate **161**, but also thermodynamically more favorable difluoroborate **162** were formed; however, they could not be isolated in a pure state.

Nevertheless, the oxidative treatment of the reaction mixture yielded 1,3-diphenylpropan-1-one, formed *via* the alkali-catalyzed opening of the cyclopropanol ring in **163**, and 1,3-diphenylpropane-1,3-diol **164** (Scheme 79).

Scheme 79



Reagents and conditions: *i.* 30% H_2O_2 /20% NaOH or urea complex of H_2O_2 .

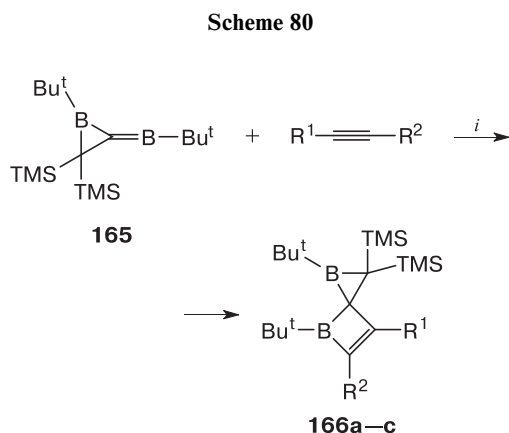
The latter was apparently formed upon oxidation of C—B bonds in boretane **158**, which indirectly confirmed the formation of a four-membered ring.

The oxidation with an H₂O₂/urea complex yielded only the *syn*-diastereomer of diol **164**, whereas the oxidation with H₂O₂/NaOH gave a significant amount of the *anti*-isomer.

The synthesis of boretanes, four-membered saturated boron compounds, is reported only in the papers cited above.^{95–101}

Synthesis of 1,2-dihydroboretetes

Spirodiborabicycloboretetes **166a–c** were synthesized for the first time by the [2+2]-cycloaddition reaction of methyleneborane **165** with acetylenes (Scheme 80).¹⁰²



R¹ = R² = Me (**a**), Ph (**b**); R¹ = H, R² = Bu^t (**c**)

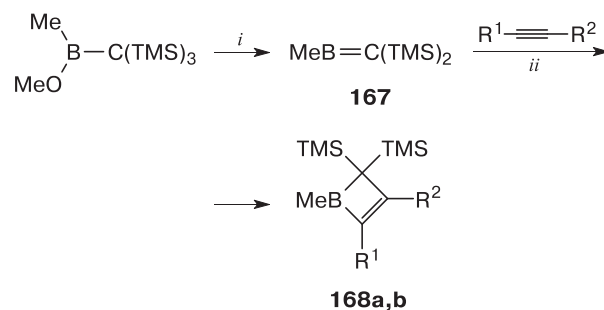
Reagents and conditions: *i*. –60...–20 °C, pentane.

Later, boracyclobutenes **168a,b** (Scheme 81) were obtained in good preparative yields by the reaction of methyl(methylidene)borane **167** with tolane or chloro-(trimethylsilyl)acetylene.¹⁰³ Note that this synthetic route to 1,2-dihydroboretetes was implemented under milder conditions at room temperature. Meanwhile, the synthesis of the initial methyl(methylidene)borane **167** required relatively high temperature (560 °C), which is a considerable disadvantage of this method.

The transmetallation of titanacyclobutenes with boron halides should be attributed to the convenient methods to prepare boracyclobutenes (Scheme 82).¹⁰⁴

The reactions of substituted titanacyclobutenes **169a–d** with phenyldichloroborane afford the corresponding 1-phenyl-2,3-disubstituted boracyclobutenes **170a–d** in high yields under relatively mild conditions (see Scheme 82). The use of other boron halides instead of PhBCl₂ led to unsatisfactory results. A complex mixture of products was formed in the case of BCl₃, and it was impossible to isolate the target 1-chloroboracyclobutene. The attempt

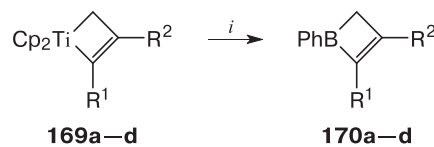
Scheme 81



168	R ¹	R ²	Yield (%)
a	Ph	Ph	86
b	TMS	Cl	70

Reagents and conditions: *i*. 560 °C. *ii*. Pentane, ~20 °C, 30 min.

Scheme 82



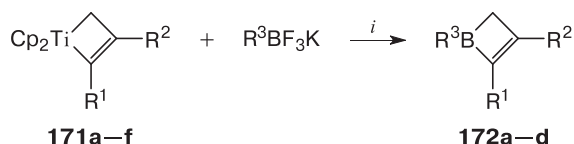
170	R ¹	R ²	Yield (%)
a	Ph	Pr ⁱ	94
b	Ph	cyc/o-C ₆ H ₁₁	98
c	Ph	3-MeAll	77
d	TMS	Bn	85 (NMR data)

Reagents and conditions: *i*. PhBCl₂, toluene, ~20 °C, 12 h.

to identify this product by converting it to 1-phenyl-substituted boracyclobutene by the subsequent addition of PhLi was also unsuccessful.

The transmetallation of titanacyclobutenes **171a–f** with difluoroboranes R³BF₂ (R = Me, Ph, Prⁱ), formed *in situ* under the reaction conditions, resulted in the formation of B-methyl(phenyl, isopropyl)-2,3-disubstituted boracyclobutenes **172a–f** (Scheme 83).¹⁰⁴ The NMR

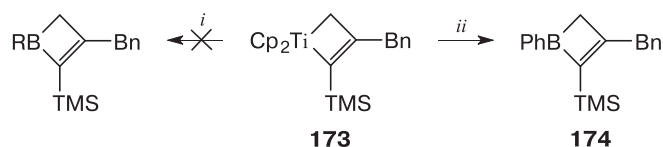
Scheme 83



172	R ¹	R ²	R ³	Yield (%)
a	Ph	Pr ⁱ	Me	99
b	Ph	3-MeAll	Me	—
c	Me	Pr ⁱ	Me	27 (NMR data)
d	Me	Bn	Ph	44 (NMR data)
e	Me	cyc/o-C ₆ H ₁₁	Ph	94
f	Me	Bn	Pr ⁱ	—

Reagents and conditions: *i*. Me₂SiCl₂, toluene, 80 °C, 12 h.

Scheme 84

R = Mes, Prⁱ**Reagents and conditions:** *i.* RBF₃K, Me₂SiCl₂, toluene, 80 °C, 12 h. *ii.* PhBF₃K, Me₂SiCl₂, toluene, 80 °C, 12 h.

spectra of the isolated compounds **172b,f** showed the presence of titanium-containing impurities, which hampered the correct determination of the weight of the obtained boracyclobutenes. Pure samples of the target boracyclobutenes were not isolated.

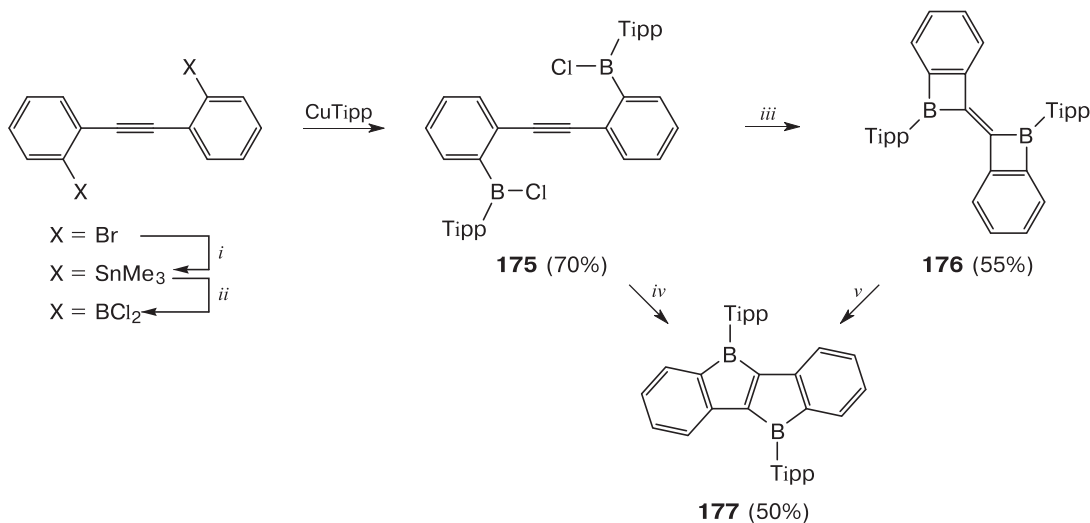
The influence of the substituent structure in potassium organotrifluoroborates RBF₃K on the yield and composition of boracyclobutenes was studied for 2-trimethylsilyl-3-benzyltitanacyclobutene **173**. The target product **174** was formed only when the phenyl-substituted potassium borate was used (Scheme 84). Sterically hindered substituents (R = Mes, Prⁱ) in RBF₃K inhibited the transmetallation of titanacyclobutene.

Synthesis of 2H-benzoboretetes

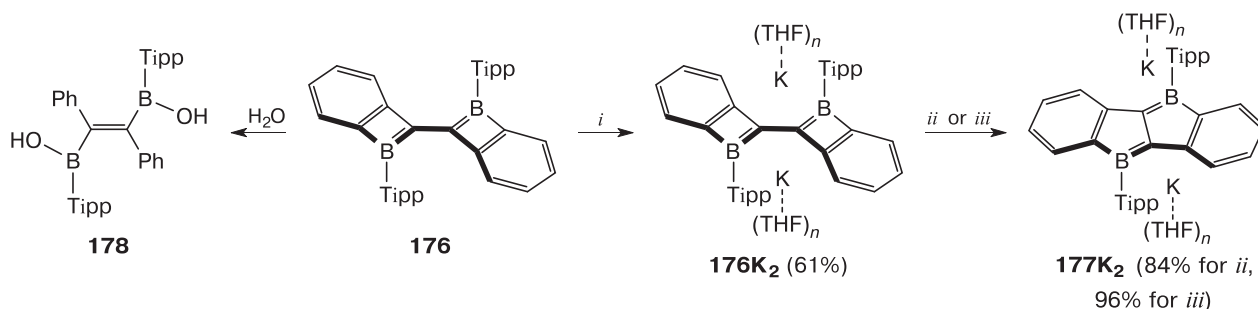
When dihaloborane **175** reacted with potassium naphthalene in THF at −78 °C, dibenzodiboracyclobutylidene **176** was obtained (Scheme 85).¹⁰⁵

Bright yellow compound **176** sensitive to air and moisture, exhibited the green fluorescence both in solution and in the solid state under UV irradiation. X-ray diffraction study of the obtained single crystals showed that the product formed in this reaction was dibenzodiboracyclobutylidene **176**, despite the fact that DFT calculations predicted lower thermodynamic stability for this structural isomer compared to compound **177**. The photoisomerization of compound **176** gave isomer **177** under UV irradiation at 254 nm. The use of light at longer wavelength (>350 nm) did not influence the isomerization. X-ray diffraction data show that the two boracyclobutene rings in compound **176** are connected by the C=C double bond and the boron atoms are in the *trans*-positions relative to this bond. All carbon atoms in dibenzodiboracyclobutylidene **176** are sp²-hybridized, which gives rise to a planar structure of the molecule and provides for conjugation of the whole molecular system. These new boron-containing functional π -conjugated polycyclic aromatic molecular systems, in which the boron atoms are involved into the

Scheme 85

Tipp = 2,4,6-Prⁱ₃C₆H₂, Naph is naphthyl.**Reagents and conditions:** *i.* 1) 4 equiv. BuⁱLi, 2) 2 equiv. SnClMe₃. *ii.* BCl₃ (excess). *iii.* 2 equiv. KNaph, THF, −78 °C. *iv.* 2 equiv. KNaph. *v.* 254 nm.

Scheme 86



Reagents and conditions: *i.* 2 equiv. KNaph, THF. *ii.* Bu^tOH, THF, $\sim 20^\circ\text{C}$. *iii.* 2,6-Me₂C₆H₃OH, THF, 75°C .

electron delocalization owing to the vacant orbital are promising for organic electronics as organic light-emitting diodes, field effect transistors, and photogalvanic devices.

The reaction of dibenzodiboracyclobutylidene **176** with potassium naphthalenide affords the corresponding dipotassium salt **176K₂** (Scheme 86).¹⁰⁶ Compound **176K₂** was isolated by recrystallization from hexane as dark violet crystals sensitive to moisture and air oxygen. The formation of this salt was detected by NMR spectroscopy. It was found that the potassium salt of dibenzodiboracyclobutylidene **176K₂** smoothly undergoes a rearrangement in the presence of weak Brønsted acids (*tert*-butanol or 2,6-dimethylphenol) to give the corresponding dibenzodiborapentalene salt **177K₂** in 89 and 84% yields, respectively. The B—C bonds are cleaved in the reaction between dibenzodiboracyclobutylidene **176** and water to give compound **178**, which was studied by X-ray diffraction.

The reduction of 1,2-bis[2-(dimesitylboranyl)phenyl]ethyne **179** by sodium metal at 10°C was performed to prepare the disodium salt of dibenzodiboracyclobutylidene **180** (Scheme 87).¹⁰⁷ The reaction at 40°C for 96 h contributes to the formation of compound **181**, which is

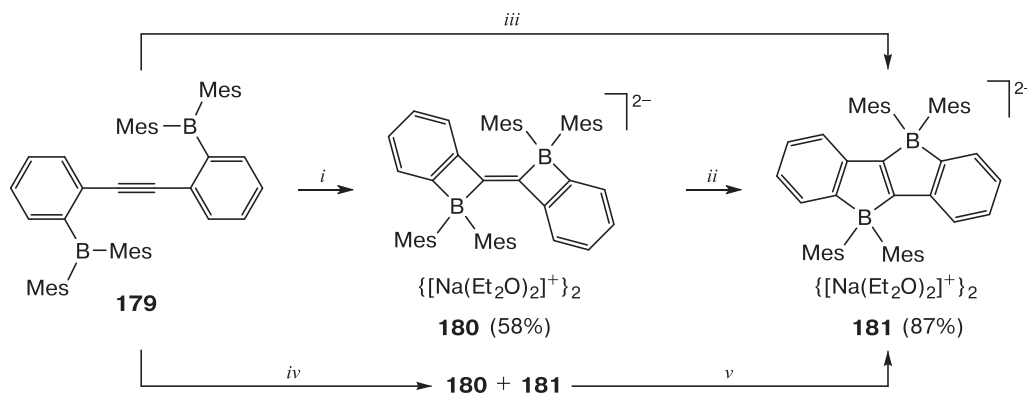
a structural isomer of **180**. A similar result was observed after refluxing dibenzodiboracyclobutylidene **180** in a sealed tube for 48 h.

The reduction of 1,8-bis[2-(dimesitylboranyl)phenyl]ethynyl naphthalene **182** with potassium afforded complex **183**, in which two annulated boracyclobutenes are linked by a butatriene moiety (Scheme 88).¹⁰⁷ The authors noted that the elimination of the naphthalene core during the reaction was unexpected. The structures of *bis*-boracyclobutene complexes **180** and **183** and the structure of dibenzodiborapentalene **177** were confirmed by NMR spectroscopy and X-ray diffraction data.

When diborane **184** was reduced with elemental potassium, the borete dianion salt **185** was formed (Scheme 89).¹⁰⁸ Compound **185** was isolated as colorless crystals and characterized by NMR spectroscopy and X-ray diffraction analysis.

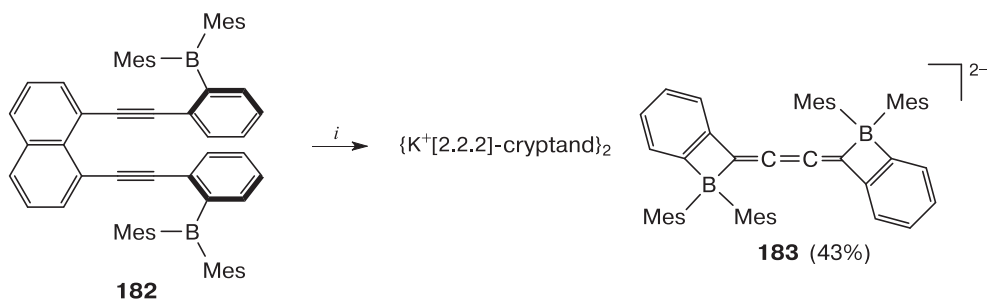
The thermodynamically stable *2H*-benzoborete **185** was formed *via* the intermediate "elusive" boron-centered biradical **186**. This radical has a high reactivity and can initiate homolytic cleavage of the C—H bond in the methyl group attached to the central aromatic ring. It should be noted that boron-based biradicals are very rare.

Scheme 87



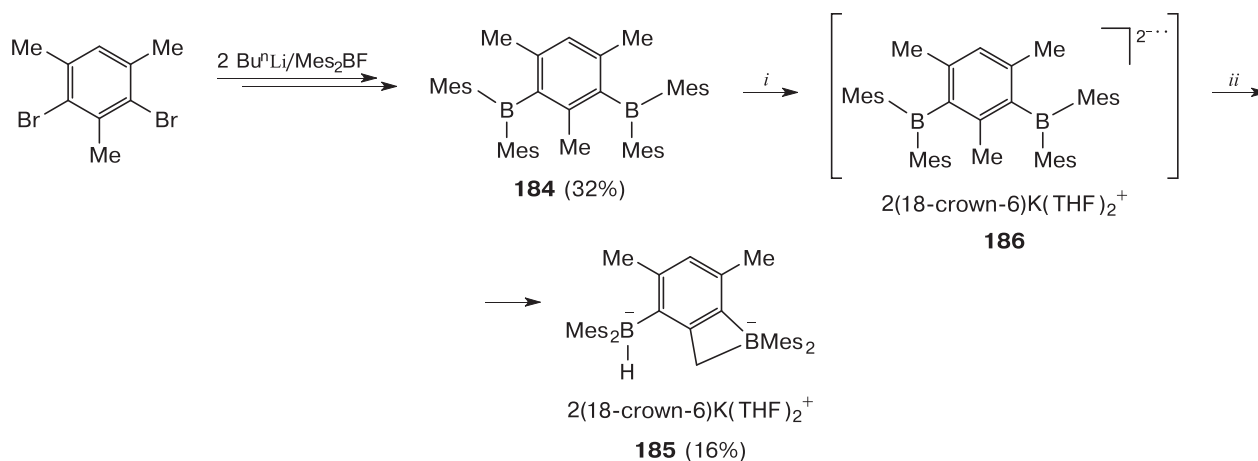
Reagents and conditions: *i.* 2.2 equiv. Na, Et_2O , 10°C . *ii.* Sealed tube, 40°C , Et_2O , 2 days. *iii.* Sealed tube, 2.2 equiv. Na, 40°C , Et_2O , >4 days. *iv.* 2.2 equiv. Na, Et_2O , $\sim 20^\circ\text{C}$. *v.* 40°C , 2 days.

Scheme 88



Reagents and conditions: *i.* 2.2 equiv. ($K^+ \cdot [2.2.2]\text{-cryptand}$), THF, 20 °C, 12 h.

Scheme 89



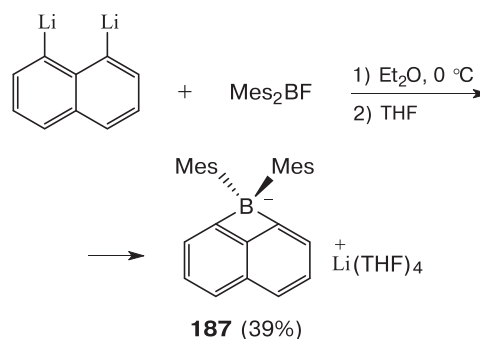
Reagents and conditions: *i.* K, 18-crown-6, THF. *ii.* C–H activation.

Synthesis of 1H-naphthoboretates

Dimesitylfluoroborate Mes_2BF reacts with 1,8-dilithionaphthalene at 0 °C to give a borete fused to a naphthalene molecule: dimesityl(1,8-naphthalenediyl)borate **187**.^{109–111} The reaction is based on the replacement of lithium atoms by a boron atom *via* nucleophilic attack. The product was isolated by recrystallization from THF as the lithium salt of compound **187** in a moderate yield of 39% (Scheme 90).^{109–111}

The crystals of compound **187** are rapidly destroyed at room temperature to lose a THF molecule; therefore, the product should be stored at a temperature no more than –25 °C. When pyridine was used for the recrystallization instead of THF, borete **187** was isolated as a $\text{Li}(\text{Py})_4$ salt, which was more stable at 20 °C. The structure of the obtained compound **187** was confirmed by X-ray diffraction analysis. The borete salt was soluble in polar (THF and pyridine) and aromatic solvents. After being kept in *d*-toluene for a week, according to NMR spectral data, borete **187** was almost completely converted to a rather rare

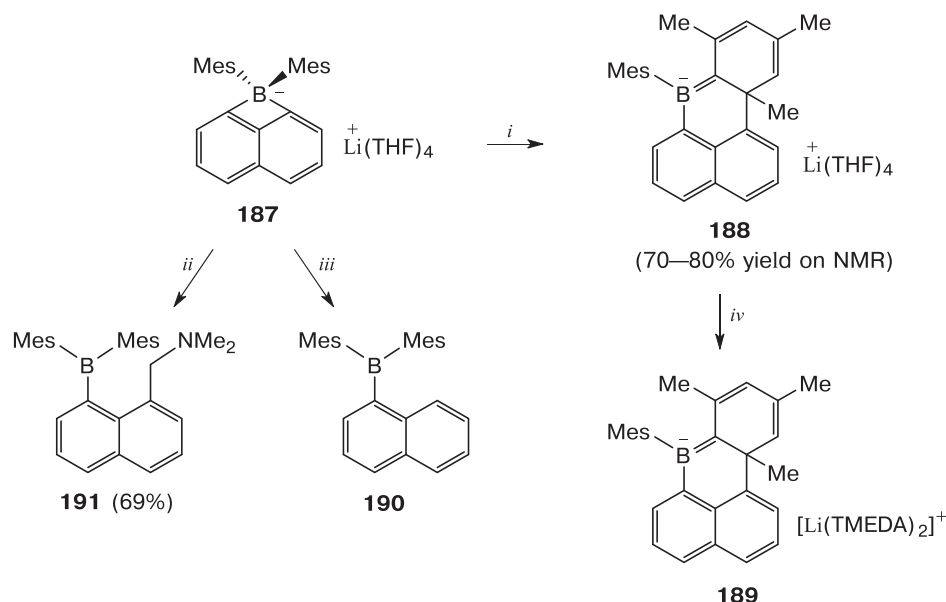
Scheme 90



compound, boranthracene derivative, 8,10,11a-trimethyl-7-mesityl-11a*H*-7-boratabenzo[de]anthracene **188**, which is a structural isomer of **187** (Scheme 91).¹¹²

The addition of tetramethylethylenediamine to a solution of compound **188** and subsequent holding for 12 h at –30 °C in the reaction mixture resulted in the formation of a new crystalline compound **189**. Annulated boracyclo-

Scheme 91

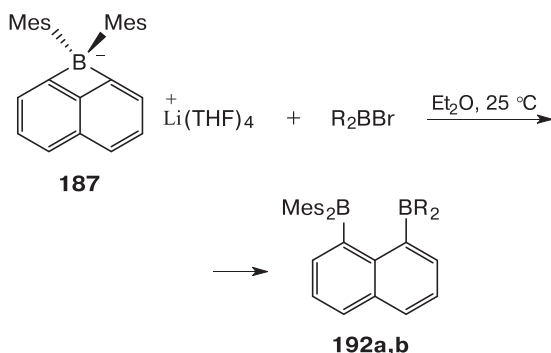


Reagents and conditions: *i.* Toluene, 25 °C, 7 days. *ii.* $[\text{Me}_2\text{NCH}_2]\text{I}$, THF, 25 °C. *iii.* THF–H₂O, 25 °C. *iv.* Tetramethylethylenediamine (TMEDA), –30 °C, 12 h.

butene **187** was hydrolyzed in the presence of moisture to give dimesityl-1-naphthylborane **190**.¹¹² Treatment of borate **187** with $[\text{Me}_2\text{NCH}_2]\text{I}$ in a THF solution at 25 °C resulted in B–C bond cleavage to give compound **191** in a moderate yield of 69%.¹¹³

The reaction of the salt **187** with dialkyl or diaryl bromide in ethyl ether led to acyclic diboryl naphthalene derivatives **192a,b** as a result of the ring opening of the boracyclobutene (Scheme 92).¹¹⁰ This reaction allows easy preparation of organoboron heteronuclear bifunctional Lewis acids.

Scheme 92



R = Me (**a**, 79%), Ph (**b**, 71%)

Borate **187** was reacted with 9-chloro-9-borafluorene (for 12 h) or 5-bromo-10,11-dihydrodibenzo[b,f]borepin

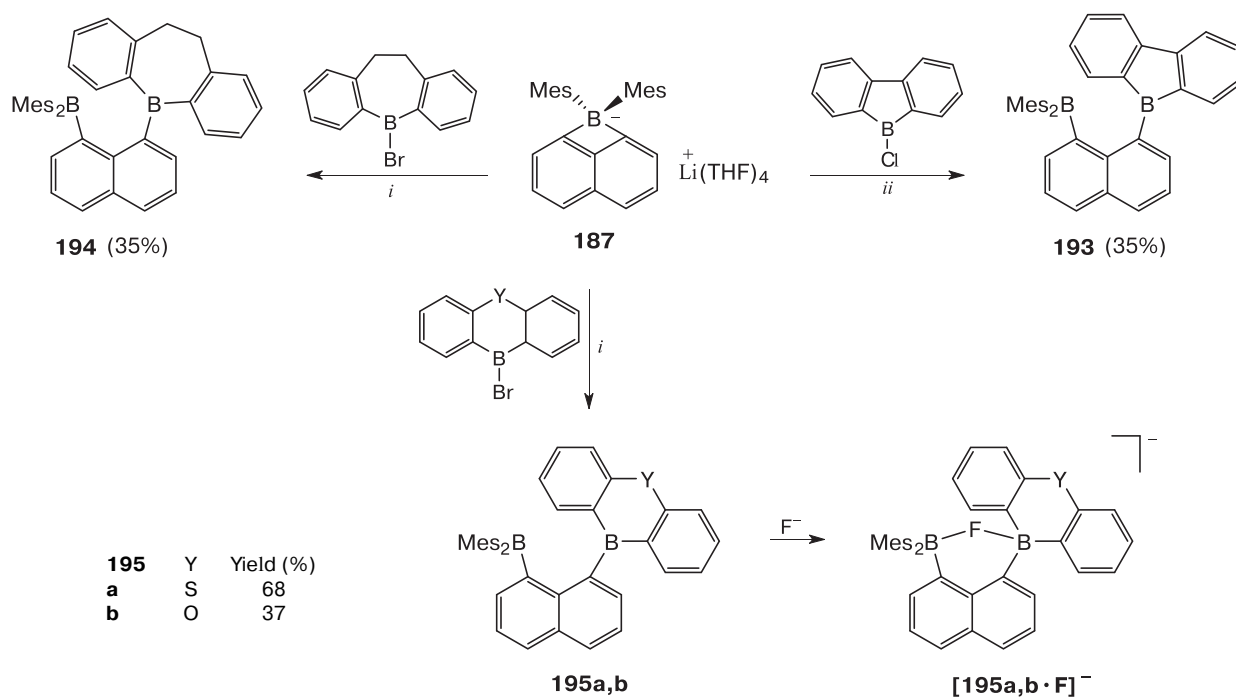
(2 h) in order to introduce planar cyclic boryl moieties into a naphthalene molecule (Scheme 93).¹¹² The obtained diboranes **193** and **194** were characterized by multinuclear NMR spectroscopy and X-ray diffraction analysis.

Treatment of dimesityl-1,8-naphthalenediyl borate **187** with 10-bromo-9-thia(oxa)-10-boraanthracenes led to bidentate (B/B) Lewis acids **195a,b** (see Scheme 93).^{114–116} These Lewis acids easily reacted with fluoride anions in the presence of $[\text{Me}_3\text{SiF}_2]^-[\text{S}(\text{NMe}_2)_3]^+$ in THF to form chelate complexes $[\text{195a,b} \cdot \text{F}]^-$.

Borate **187** was used to prepare heteronuclear bidentate (B/Sn and B/Hg) Lewis acids.^{117,118} For example, the boracyclobutene ring in borate **187** was opened on treatment with trimethyltin chloride in diethyl ether at room temperature to give bifunctional boron- and tin-containing compound **196** (Scheme 94).¹¹⁷ The boryl and stannyl groups in **196** are located in the *peri*-position of the naphthalene core.

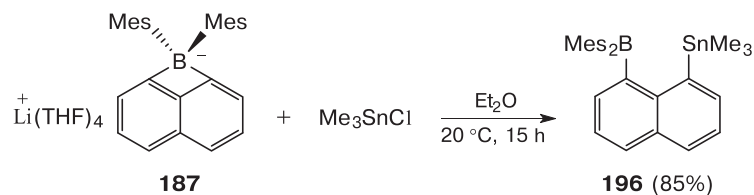
It was shown¹¹⁴ that the bidentate (B/B) Lewis acids **195a,b** can be used as colorimetric fluoride sensors owing to the formation of chelate complexes with fluoride anions $[\text{195a,b} \cdot \text{F}]^-$. Gabbai and co-workers^{118–120} decided to find out whether similar properties are also inherent in heteronuclear derivatives of bidentate Lewis acids containing B and Hg atoms. This choice is due to the fact that multidentate mercury-containing Lewis acids easily bind fluoride ions; furthermore, mercury can induce phosphorescence of hydrocarbon chromophores at room temperature *via* spin–orbit coupling.

Scheme 93

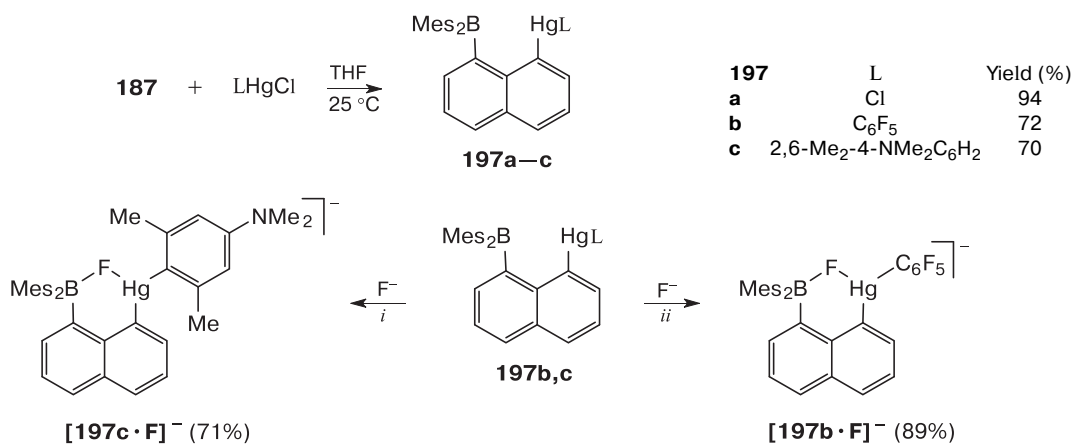


Reagents and conditions: *i.* Et₂O, 25 °C, 2 h. *ii.* Et₂O, 25 °C, 12 h.

Scheme 94



Scheme 95



Reagents and conditions: *i.* [(TMS)F₂]⁻[S(NMe₂)₃]⁺, CH₂Cl₂, 25 °C. *ii.* [(TMS)F₂]⁻[S(NMe₂)₃]⁺, CHCl₃, 25 °C.

The study demonstrated that the reaction of mercury chloride with borate **187** affords bidentate compounds **197a–c** (Scheme 95), which react with fluoride anions to give the corresponding chelate complexes [**197b,c**·F][–]

Note that this is the first example of synthesis of phosphorescent sensors for anions based on heteronuclear derivatives of bidentate Lewis acids containing boron and mercury atoms.

Conclusion

This review is devoted to the synthesis, the study of properties, and the application prospects of a unique class of boron-containing small rings, among which three-membered rings, boriranes and borirenes, are most studied. However, high instability of these compounds in the presence of atmospheric oxygen or during storage at room temperature extremely restricted investigations of their properties and scope of their practical applicability. New preparative approaches to the synthesis of three-membered boracyclanes and their derivatives were developed over the last 15 years. The photochemical isomerization of photochromic chelated organoboranes to the corresponding boriranes is the most promising. The studies in the field of photochromic boron compounds as new photocontrolled molecular switches for electronics and photonics are very promising.

Borirenes are of enormous interest for researchers; however, their practical use as π -conjugated structural materials has not yet been adequately addressed. Considering that these studies are currently at an early stage, previous results attest to good prospects of these compounds for the development of unique boron-containing functional materials for sensor, light-emitting, and electronic devices.

The chemistry of four-membered rings with one boron atom is less studied than that of three-membered boron-containing ones. The review presents methods for the synthesis of these compounds. A practical value is expected for bidentate Lewis acids based on dimesityl-(1,8-naphthalenediyl)borate, which are able to form chelates with fluoride anions. This feature allows the use of these complexes as colorimetric fluorescent fluoride sensors.

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