

Benzoannulated cycloboranes

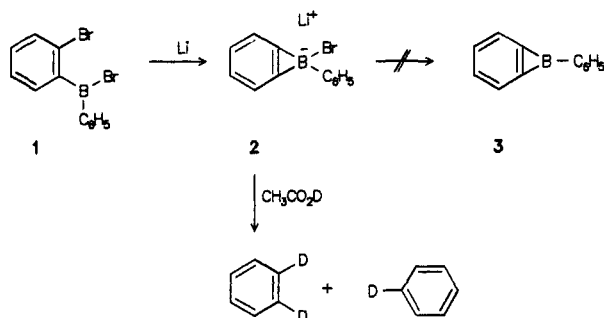
Dieter E. Kaufmann* and Wolfgang Schacht

BAYER AG, Zentrale Forschung and Entwicklung, D-5090 Leverkusen, FRG

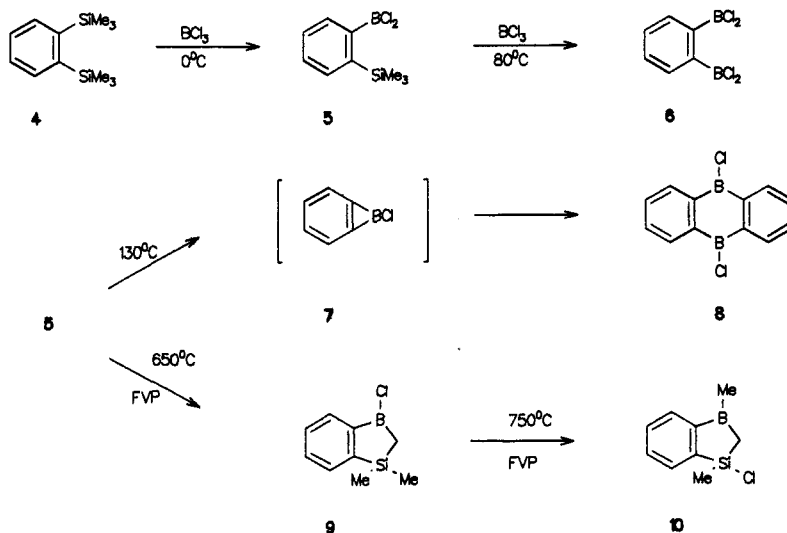
Abstract - Using two synthetic methods, flash vacuum pyrolyses (fvp) and metal supported cyclizations, we were able to open broad access to benzoannulated cycloboranes. Probably the *p*-phenyl substituted benzoborirene could only be synthesized as a borate. *o*-Silylated phenylboranes dimerized in solution giving diboradihydroanthracenes and silanes; the fvp led to borasilaindanes, which isomerized regioselectively at higher temperatures. The fvp of *o*-alkyl-dichlorophenylboranes is a general synthetic way to boraindanes and boratetralines, while the fvp of benzyldichloroborane led to a dimer of the benzodihydroborete, a dibenzotetrahydrodiborocine. When the boron is substituted by a diisopropylamino group, monomeric derivatives of the benzodihydroborete and diborete are accessible via solution chemistry. Fvp of a 1-boraindane led to a highly reactive 8π -antiaromatic benzoborole, which dimerized to a tetracyclus stereoselectively. The benzoborole could be trapped by 2-butyne thus giving a stable 10π -aromatic 1-benzoborepin. A 10π -system also resulted when an aminosubstituted 2-boraindane was lithiated twice.

Since the calculations of the geometries and resonance energies of boron-containing small-ring systems by P. von R. Schleyer et al. in 1981, this field has also proven to be experimentally productive. The benzoannulated small-ring boranes have remained unknown for some more years. Their properties and reactions deserve special interest as these systems represent a unique mixture of the thermodynamic stability of an aromatic system and the kinetic reactivity of a small ring system.

The borirene is the smallest, 2π -heteroaromatic system und isosteric with the cyclopropenyl cation. In 1976 Halton and Burger have already synthesized cationic trisubstituted benzocyclopropenes and investigated their NMR-spectroscopical properties. To synthesize a *p*-phenyl substituted benzoborirene 3 we tried the 1,3-coupling reaction of the dibromide 1 with a lithium suspension. Probably the metallation of the aryllic position will be the first step, followed by an intramolecular attack on the boron atom, generating a borate complex 2 (^{11}B -NMR). But so far all attempts to release the uncomplexed borirene failed. The high stability could be correlated to an increase in ring strain when changing the hybridization of the boron towards sp^2 . Cleaving the reaction product with deuterioacetic acid we got a 1:1-mixture of mono- and dideuterobenzene (MS). This is a further support of the proposed structure. The synthesis of an uncomplexed *tert*-butyl or diisopropylamino substituted benzoborine also failed. So we tried to avoid complexation by extruding a volatile silane.

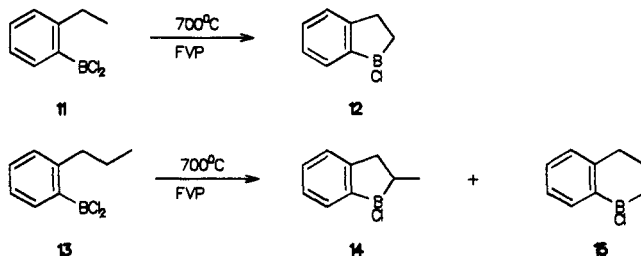


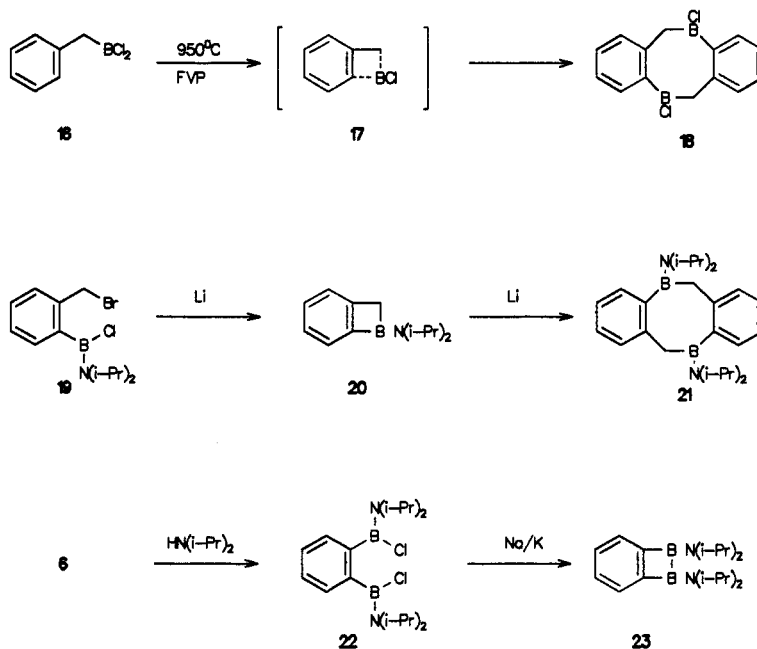
In systematical investigations aryltrimethylsilanes have proved to be versatile starting materials for the synthesis of the corresponding aryldichloroboranes (ref. 1). In case of the 1,2-bis(trimethylsilyl)benzene (4) only one silyl group is borylated to 5 selectively when treated with trichloroborane at low temperatures. At 80°C the *ipso*-borylation of the second silyl group also succeeds, thus generating the bifunctional Lewis acid 6. First a thermolysis in solution was tried. At 130°C there was already a complete formation of dichlorodiboradihydroanthracene (8) and chlorotrimethylsilane (TMSCl) (ref. 2). An *intramolecular* elimination of TMSCl could lead to the benzoborirene 7, which is supposed to dimerize under the reaction conditions. The mutual, synchronous attack of the boryl group of one molecule to the silyl group of another one would form the diboradihydroanthracene in an *intermolecular* reaction. By now it is not possible to distinguish between both possibilities. Almost no higher oligomers were present. Only traces of a benzoborirene trimer could be detected by MS. Certainly under the conditions of a flash vacuum pyrolysis (fvp) an *intramolecular* mechanism should be favoured.



All boranes were flash vacuum pyrolyzed in a standard type glass apparatus with a quartz reactor at about 10^{-3} mbar. All silylated phenyl boranes were pyrolyzed at temperatures around 650°C. Starting with 5 elimination of hydrogen chloride instead of TMSCl took place, yielding the borasilabenzocyclopentane 9, which isomerized at 750°C to 10 regioselectively by mutual migration of a chloride and a methyl group. The intermediate formation of a benzoborirene could be excluded by cocondensation of DCl: no deuterium was incorporated. Such an intramolecular migration is uncommon. Caused by the geometry of the five membered ring and the hybridization of the boron both migrating groups should be too far away from each other to get exchanged directly. 1,2-Diborylated benzenes also dimerized in solution giving diboradihydroanthracenes, while under fvp conditions cyclization to 1,3-diboraindane derivatives occurred already at 550°C. These boranes are interesting new building blocks for multidecker metal complexes.

The pyrolytic HCl elimination is not limited to the presence of an activating silyl group (ref. 3). The *o*-alkylated phenyldichloroboranes 11 and 13 yielded different boraindanes 12 and 14 or boratetraline 15. The formation of five membered products is always favoured. The yields are about 80 %.





As the pyrolytic elimination of hydrogen chloride is a good method to synthesize carbocyclic benzocyclobutenes, we also tried the pyrolysis of 2-methylphenylboranes. Surprisingly they were stable up to 1050°C; at higher temperatures degradation occurred. But the fvp of the isomeric benzyldichloroborane (16) at 950°C led to the crystalline 1,5-dichlorotetrahydrodibenzodiborocine (18), the generation of which can only be explained by the dimerization of a valence isomer of the desired 1-chlorodihydroborete (17). The proton-NMR of the dimer is temperature dependent. The free enthalpie of activation is about 10 kcal/mol.

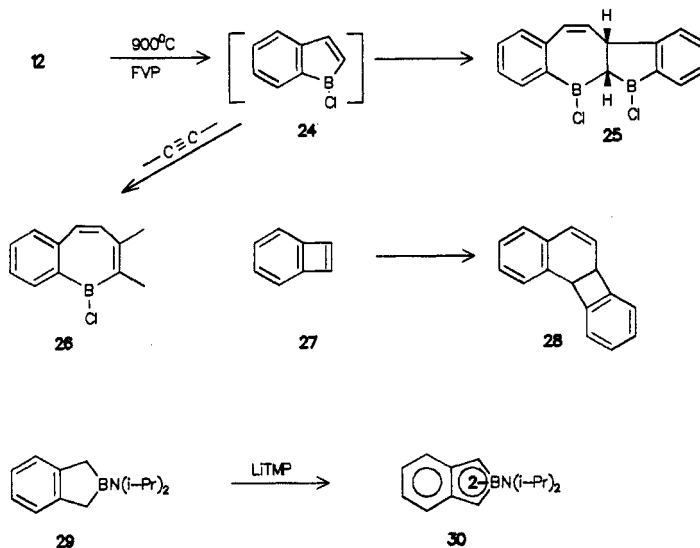
As B-alkylated benzodihydroboretes also proved to be too reactive for an identification, a dialkylamino-stabilized derivative was synthesized (ref. 4). The 1,4-cyclization of 19 was tried with sodium-potassium alloy and with lithium suspension. In the first case the dimer 21 was formed exclusively. The lithium supported cyclization mainly gave the dihydroborete (20), which slowly dimerized in the presence of excess lithium. The monomer is only stable in dilute solution; the pure compound polymerizes within minutes already at room temperature. In contrary to the dichlorotetrahydrodiborocine the proton NMR spectrum of the aminotetrahydrodiborocine 21 is not temperature depending, probably caused by strong (BN)- π bonds and the sterically demanding diisopropylamino groups.

Treating the aminodihydroborete with electrophiles like boron trichloride, we neither got the chlorodihydroborete nor its dimer 18, but a ring cleavage product. Treatment with hydrogen chloride very probably led to the formation of the dichloroborate of the chlorodihydrobenzoborete.

Treating the bisaminoborane 22 with sodium-potassium alloy it was even possible to synthesize the crystalline, thermally stable benzodihydrodiborete 23, which dimerizes only in the presence of certain catalysts. The x-ray data show that the four membered ring is twisted to minimize the strain caused by the sterical demanding diisopropylamino groups.

To get a first access to the 8π -antiaromatic benzoboroles we tried the fvp of boraindanes (ref. 5). At 900°C dehydrogenation of 12 occurred. At 77K the pyrolysate was intense yellow. Warming to room temperature the colour largely disappeared giving crystals of the tetracyclic dimer 25. A direct spectroscopical observation of the monomer 24 was impossible because of the fast dimerization reaction already at -90°C. The five and the seven membered rings were *cis*-connected (x-ray). The exclusive formation of this dimer is also interesting in view of a similar reaction mode between the benzoborole and the related benzocyclobutadiene (27). This antiaromatic hydrocarbon can form two types of dimers, depending on the reaction conditions. One of these dimers 28 structurally corresponds to 25. Its formation can be explained by a regio-specific *cis*-vinylboration of a double bond with the B-C_{vinyl}-bond of a sec-

ond borole molecule when warming up the matrix. Additional reactions proof the intermediate generation of the borole. While it does not react with alkenes, the addition to alkynes like 2-butyne is fast, forming the first 10π -aromatic 1-benzoborepin 26. Only a vinylboration can explain the observed stereochemistry, as the methyl groups are located in the 2- and 3-position. Cocondensation of 24 with monodeuterated methanol led to a *Z*-(β -deuterostyryl)borane, accompanied by some dimethoxydimer. This stereoselective formation can only be explained by cleavage of the B-C(2)-bond of the borole.



In order to get access to the probably even more reactive 2-benzoborole, we investigated the synthesis and fvp of the 2-boraindane. The pyrolytic HCl-elimination of the *o*-(methylbenzyl)dichloroborane succeeded. But the 2-chloroboraindane was completely stable even at high temperatures. We finally tried to get access to a related ionic 10π -system. It was possible to prepare the dianion 30 of the diisopropylamino-2-boraindane by deprotonating the aminoborane (29) with lithium tetramethylpiperidid (TMIP). The orange solution of 30 could be quenched by DCl and TMSCl to yield disubstituted boraindanes.

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