

An outline of the chemistry of bis(9-borabicyclo[3.3.1]nonane)

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Abstract - The distinctive features in the reactivity of $(9H-9-BBN)_2$ compared to other tetraalkyldiboranes(6) arise primarily from the rigid and usually very stable bicyclic structure of the 1,5-cyclooctanediyl residue, which prevents the facile dismutation of the organic groups often observed in the latter, especially at elevated temperatures. - The 1,5-cyclooctanediylboryl group (9-BBN) has gained manifold importance in chemistry for a number of reasons: 1. Highly selective reaction pathways. - 2. Enhanced reactivity of exocyclic BC-bond over the endocyclic BC-bonds in the bicyclic $C_8H_{14}B$ system. - 3. Facile preparations of various pure 9X-9-BBN borane reagents. - 4. New informative, easily isolable 9-BBN crystalline solids.

I. PREPARATION AND CHARACTERISATION OF $(9H-9-BBN)_2$

The first report on the preparation of 9-bis(borabicyclo[3.3.1]nonane) $(9H-9-BBN)_2$ through an alkyl exchange reaction between 9-propyl-9-borabicyclo[3.3.1]nonane and tetrapropyldiborane(6) dates back to 1960 (ref. 1). Subsequently, in an improved procedure, it was obtained according to eq. (a) by the direct reaction of *c,c*-1,5-cyclooctadiene (COD) with excess of tetrapropyldiborane(6) or tetraethyldiborane(6) in 94% yield (ref. 2-4), cf. Fig. 1.

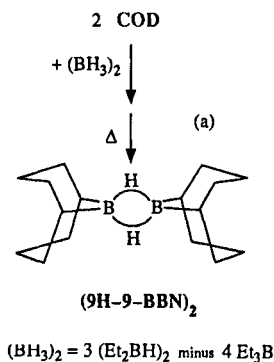


Fig. 1. Preparation procedure for pure $(9H-9-BBN)_2$ with m.p. = 157°C

δEI ($CDCl_3$)	C_8H_{14} moieties (number, conformation)			BH
	α	β	γ	
1H	1.56 (4)	1.62 (8,a) 1.82 (8,e)	1.46 (4,e) 1.93 (4,a) [$^2J_{ae} = -13.7$ Hz]	1.41 (2)
		[$^3J_{ac,ca} = 6.1$ and 5.8 Hz]		
^{13}C	19.1 (br)	[$^3J_{ec} = 2.9$ Hz] 32.9	[$^3J_{aa} = 11.8$ Hz] 23.5	—

Fig. 2. 1H and ^{13}C NMR data of $(9H-9-BBN)_2$

$(9H-9-BBN)_2$ crystallizes from refluxing heptane in long, colourless needles with m.p. $\geq 157^\circ C$ (DSC). The crystals are air stable for several weeks at room temperature. $(9H-9-BBN)_2$ can also be prepared by the reaction of COD with THF-BH₃ (ref. 5). However, the solid $(9H-9-BBN)_2$ obtained by this procedure [apparently the method of choice for its commercial preparation (ref. 6)] is reported to be spontaneously inflammable in air, probably, by unavoidable contamination with THF and THF- $9H-9-BBN$ resp., which easily destabilise the dimeric $(9H-9-BBN)_2$ by dissociation. Other, less widely used procedures have also been reported (ref. 7).

The ir absorption band of $(9H-9-BBN)_2$ at 1567 cm^{-1} shows the presence of $\setminus BH_2B /$ -grouping (ref. 4). - The EI mass spectra (ref. 8) of $(9H-9-BBN)_2$ and $(9D-9-BBN)_2$ resp. show the B_2 mass M^+ and the B_1 mass $(M/2)^+$ with relatively high intensities. Base peaks are the m/z 94 and 95 resp., which presumably are formed from $(M/2)^+$ by elimination of 28 mass units. - The ^{11}B NMR resonance signal at $\delta = 28.0$ is comparable to values obtained for the boron atom of other tetraalkyldiboranes(6) (ref. 9). The 1H and ^{13}C NMR data of $(9H-9-BBN)_2$ are combined in the Fig. 2 (ref. 10). - An X-ray crystal analysis has confirmed the dimeric structure (ref. 11) as an 1,1:2,2-bis(1,5-cyclooctanediyl)diborane(6), in which both 1,2,3-annellated boracyclohexane rings of each $C_8H_{14}B$ residue have chair conformations.

II. THERMAL BEHAVIOUR OF (9H-9-BBN)₂

In early descriptions of its properties, (9H-9-BBN)₂ was considered to be a thermally rather stable molecule (ref. 5). DSC analyses, however, show a relatively rapid thermal degradation of the molecule at 200°C with a half life time $t_{1/2}$ of 0.7 h. Investigation of the degradation products, obtained either from a melt (~170°C) or from a refluxing mesitylene solution, showed them to consist of a mixture of the products (ref. 12). - At somewhat lower temperatures (~140°C) the boron atom of 9H-9-BBN undergoes a topotactical walk over the C₈ ring. Utilizing this internal reactivity, [9D-9(cis-2,3,4,6,7,8-d₆)BBN]₂ could be prepared, which also allow the easy synthesis of cis-d₆-cyclooctane derivatives (ref. 12). - Furthermore, this mobility of the boron atom around the C₈ ring has been used to prepare the long sought isomer (9H-9-borabicyclo[4.2.1]nonane)₂ by way of its 9-quinuclidine adduct (ref. 13).

Interesting transformations of the bis(9-borabicyclo[3.3.1]nonane) (9H-9-BBN)₂ including C-skeleton rearrangements could be observed at higher temperatures (e.g. 350°C) in the gas phase. The products obtained and characterized are monomeric to oligomeric compounds with structures such as the 1-bora- and the 8-borabicyclo[4.3.0]nonanes I and II (ref. 14); cf. Fig. 3.

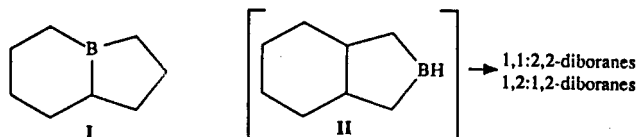


Fig. 3. 1-Bora- and 8-Borabicyclo[4.3.0]nonanes I and II from (9H-9-BBN)₂ by pyrolysis in the gas phase

Flash pyrolysis of (9H-9-BBN)₂ and of 9-alkyl-9-BBN derivatives at 400 - 500°C leads to near exclusive formation of I, which suggests the existence of 9H-9-BBN monomer in the gas phase.

In this connection our results on the thermal regioselective deuteration of the 1,5-cyclooctanediylboryl moiety must be mentioned (ref. 15): The action of deuterium gas on (9H-9-BBN)₂ in heptane at 80°C leads slowly under formation of HD according to eq. (b) to (9D-9-BBN)₂, presumably via pentacoordinate boron atoms such as an intermediate of the type III (ref. 16); cf. Fig. 4. This reaction, at about 120°C, can be utilized to prepare (9D-9(supra-d₆)BBN)₂ with a deuteration content of >90%. The \rightarrow CH/ \rightarrow CD exchange process in the C₈ rings probably proceeds by the topotactical walk mechanism of the \rightarrow BD-borane function (cf. ref. 12). - The relative rapid \rightarrow BD/ \rightarrow CH exchange at elevated temperatures limits the use of (9D-9-BBN)₂ for the elucidation of certain pathways with 9-BBN compounds. By using (9D-9-BBN)₂ a defined transfer of deuterium atoms is achieved only, when the reaction is carried out at temperatures below 100°C. At higher temperatures e.g. at 140°C the boron bonded deuterium atom is lost by the \rightarrow BD/ \rightarrow CH exchange processes (ref. 15).

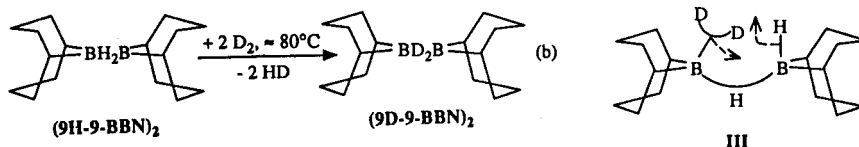
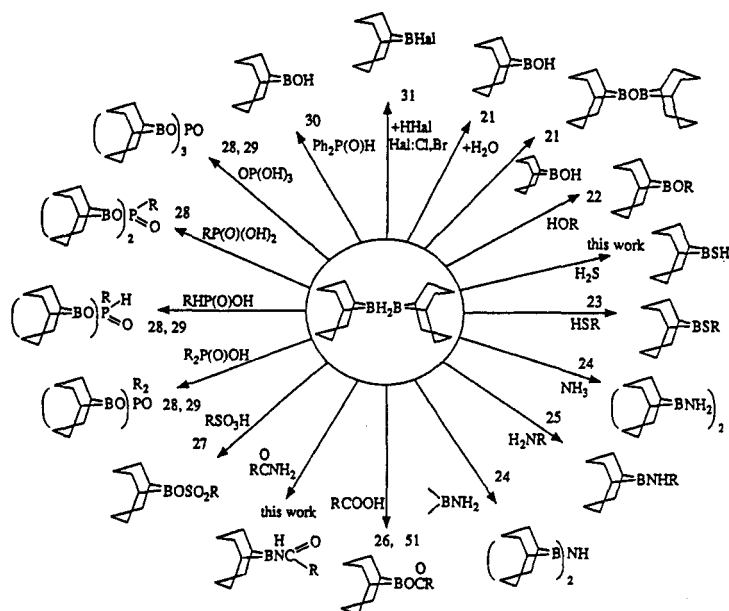


Fig. 4. (9D-9-BBN)₂ from (9H-9-BBN)₂ with D₂ via proposed intermediates of type III

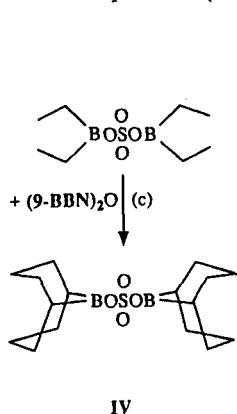
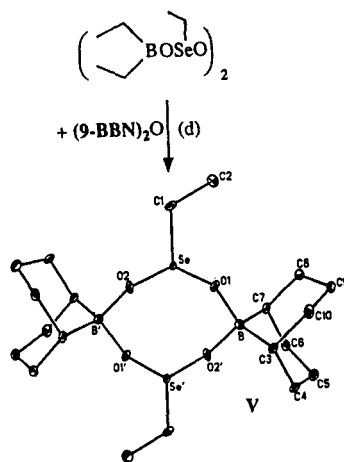
III. REACTIONS WITH RETENTION OF THE 9-BBN-SKELETON (Hydroborations, Borylations)

The 9-BBN skeleton is very often employed as a carrier of organic residues at the 9-position. It can be used to achieve cyclisation (ref. 17) or for ring opening of organic groups (ref. 18) and also for chain lengthening with C₁ groups (ref. 19). The C₈H₁₄B moiety remains unchanged in all of these reactions. - Hydroborations of multiple bonds with (9H-9-BBN)₂ have found the widest general applications of this reagent in synthetic organic chemistry. These reactions have been amply reviewed elsewhere (ref. 7,20). - An uncommon hydroboration reaction is observed when (9H-9-BBN)₂ reduces a variety of metal carbonyls: A mixture 9-alkyl-9-BBN's with a Schulz-Flory distribution is formed. The n- and iso-9-alkyl groups attain chain lengths of up to ten C₁ units. As side-products of this Fischer-Tropsch type C₁ polymerization reaction, quantitative yields of (9-BBN)₂O and the corresponding magnetic-pyrophoric metals are also achieved (ref. 19). The catalysed growth of the carbon chain takes place exclusively without disrupting the bicyclic 1,5-cyclooctanediylboryl skeleton. Therefore the reactions are easy to follow as substituent exchange reactions do not interfere. The 9-BBN species can also be used as a stable boryl reagent.

The reactions of (9H-9-BBN)₂ with Brønsted acids are numerous. Without affecting the C₈H₁₄B bicyclic ring a number of oxy-, thio-, or amino derivatives can be easily prepared (ref. 21-31). The oxy derivatives also include S or P bonded oxygen atoms; cf. Fig. 5. While the double derivatization of H₂O or H₂S is very facile, the indirect route through reaction of (9-BBN)₂NLi with 9-Cl-9-BBN has to be employed for the preparation of (9-BBN)₂N (ref. 24).

Fig. 5. Borylations with $(9H-9-BBN)_2$

O-Transborylations with the oxide $(9-BBN)_2O$ can in certain cases be important for the introduction of the $C_8H_{14}B$ residues to form well-defined crystalline products, which can then be analysed by X-ray diffraction. Two examples are given below, in which the direct O-borylation with $(9H-9-BBN)_2$ is unsuccessful. The O-borylation of H_2SO_4 with $(9H-9-BBN)_2$ leads to reduced products. Therefore the O-transborylations of $[(C_2H_5)_2BO]_2SO_2$ with $(9-BBN)_2O$ according to eq. (c) is adopted as an excellent preparative procedure to compound IV (ref. 32); cf. Fig. 6.

Fig. 6. $(9-BBN)_2$ -sulfate IV (m.p. $74^\circ C$), prepared by transborylation with $(9-BBN)_2O$ Fig. 7. Dimeric 9(ethylseleninyloxy)-9-BBN (V) (dec. $168^\circ C$), prepared by transborylation with $(9-BBN)_2O$

Also the exchange of two $(C_2H_5)_2B$ groups for two 9-BBN residues in the dimeric ethylseleninyloxy-borate product, prepared according to eq. (d), leads to a high melting, crystalline 9-BBN compound V, which has been identified by an X-ray structure analysis (ref. 33); cf. Fig. 7.

IV. REACTIONS WITH 9-BBN TRANSFORMATIONS (Ring expansions, Ring contractions)

There are reactions, which involve a change of the 9-borabicyclo[3.3.1]nonane skeleton. We know ring expansions forming bicyclo[3.3.2] systems, e.g. with C_1 from carbenoides (ref. 34) or nitrenoides (ref. 35). Furthermore, it is known that in reactions of 9-BBN derivatives with a borate intermediate the action of electrophiles result in the removal of an α -hydride with subsequent rearrangement to a 1-boryl-bicyclo[3.3.0]octane (ref. 36). Electrophiles also cause the rearrangement of the bicyclic ring in 1-alkynyl-9-BBN-borates (ref. 37,38). Ring expansion lead to 9-borabicyclo[3.3.2]decanes with 10-alkylidene moieties (ref. 37,39).

The exhaustive oxidation of 9-alkyl-9-BBN compounds with anhydrous trimethylamine-N-oxide leads after a double oxygen insertion in two BC bonds to give the 10-alkoxy-9,10-oxaborabicyclo[3.3.2]decanes (ref. 40). The third BC bond of the bicyclic compound is not attacked by the N-oxide although the oxidation of the first BC bond in the $C_8H_{14}B$ bicyclic system is extremely fast (ref. 40,41).

No reaction of $(9H-9-BBN)_2$ with free carbon monoxide has hitherto been reported. In connection with our investigations on the organoboron Fischer-Tropsch model reaction (ref. 19) we have recently studied the uncatalysed reaction of $(9H-9-BBN)_2$ with carbon monoxide. At about $100^\circ C$ the CO molecule is partially reduced and inserted into one of the BC bonds. A crystalline dimer VI with two [3.3.2]bicyclic rings is formed quantitatively; see Fig. 8. The easily prepared $(COB)_2$ -heterocycle is a good example of the special advantageous application of the 9-BBN residue. Up to now, an intermediate of the hydroborane/CO reactions has not been characterized by a complete crystal structure analysis (ref. 42). - At about $150^\circ C$ $(9H-9-BBN)_2$ reacts with carbon monoxide forming the boroxin VII (ref. 42); cf. Fig. 8.

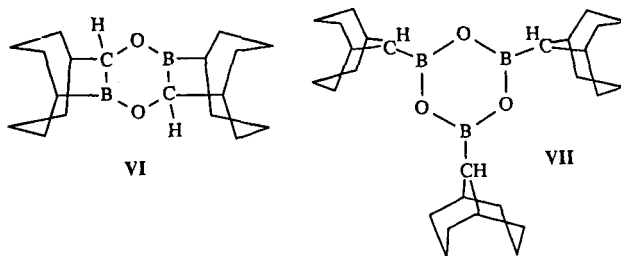


Fig. 8. Products from $(9H-9-BBN)_2$ and CO under pressure: VI at $100^\circ C$ and VII at $150^\circ C$

V. 9-BBN AS A CARRIER OF REACTIVE SUBSTITUENTS (9-BBN reagents)

The halogens Cl_2 , Br_2 , and I_2 react directly with $(9H-9-BBN)_2$ giving 9-halogeno-9-BBN compounds in high yields (ref. 43,44). A convenient and simple procedure for the iodoboration reagent 9-iodo-9-BBN has recently been reported (ref. 45). - Also the hitherto undescribed 9-fluoro-9-BBN VIII can be prepared quantitatively in pure form from $(9H-9-BBN)_2$ by reacting it with the antimony fluorides SbF_3 or SbF_5 (ref. 46) according to eq. (e); cf. Fig. 9.

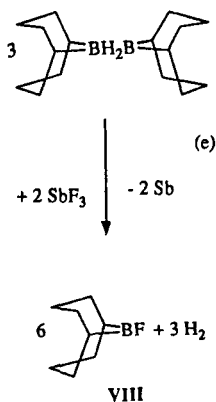


Fig. 9. Preparation of 9F-9-BBN (VIII)

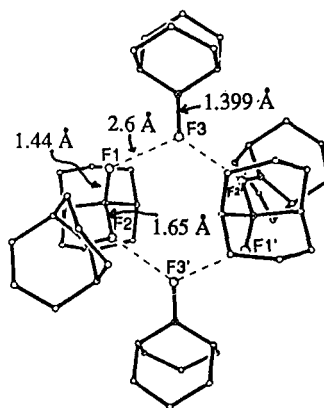


Fig. 10. Packing of 9F-9-BBN (six molecules with three different bonded VIII including one BFB grouping)

9F-9-BBN is monomeric ($\delta^{11}B = 63$) in toluene solution, but exchange of the F-atom between the boron atoms is very rapid (no splitting of the ^{11}B NMR signal is observed). Solid 9F-9-BBN with a melting point of $100^\circ C$ forms crystals with three differently bonded molecules in the asymmetric unit. This arrangement includes a BFB grouping with a FB coordination bond (ref. 46).

The well known reaction of the dimeric dialkyl-hydro-borane $(R_2BH)_2$ with elemental sulfur or selenium leads to the five-membered ring compounds $RBEI_3^VI BR$ (ref. 47) with one $BEI^VI B$ and one $BEI_2^VI B$ grouping. In contrast to these results, the pure compounds $(9-BBN)_2S$ and $(9-BBN)_2Se$ have recently been prepared directly from $(9H-9-BBN)_2$ with sulfur (S_8) or with selenium (Se_x). This method also readily furnishes the pure $(9-BBN)_2S_2$ and $(9-BBN)_2Se_2$ (ref. 48,49). Both 9-HS-9-BBN and 9-HSe-9-BBN (IX; cf. Fig. 11) are also easily obtainable in pure form. The solid $9-HEI^VI-9-BBN$ compounds are dimers, which readily form addition compounds, e. g. X, with $(9H-9-BBN)_2$; cf. Fig. 12.

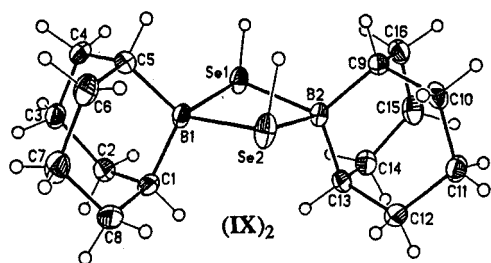


Fig. 11. Molecular structure of solid $\text{cis}-(9\text{HSe-9-BBN})_2$ (IX)₂

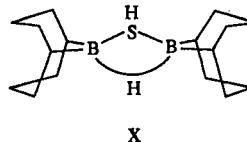


Fig. 12. Structure of the 1:1 adduct X of 9HS-9-BBN and 9H-9-BBN in solution

Compounds IX , XI , and XII (see Fig. 13) are excellent selenidation reagents (ref. 49).

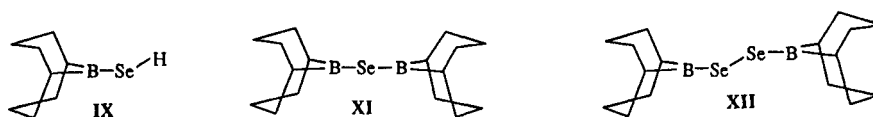


Fig. 13. The three selenium 9-BBN compounds IX , XI , and XII

The compounds $(9\text{-BBN})_2\text{S}$ and $(9\text{-BBN})_2\text{Se}$ have proven to be excellent reagents for the preparation of many sulfidated or selenidated compounds. They readily undergo S/O or Se/O exchanges with e.g. carbonyl compounds (ref. 48,50). The oxygen atoms of carbonyl groups of non-enolisable ketones [e.g. $(\text{C}_6\text{H}_5)_2\text{CO}$, $(\text{C}_6\text{H}_4)_2\text{CO}$], carbonic acid esters [e.g. XIII from $\text{C}_6\text{H}_5\text{COOCH}_3$; $\text{C}_6\text{H}_4\text{-1,4}-(\text{COOCH}_2)_2$], of amides and lactams [e.g. $\text{C}_6\text{H}_5\text{CON}(\text{CH}_3)_2$, $\text{RN}(\text{CH}_2)_3\text{CO}$; $\text{C}_6\text{H}_4\text{-1,2-CONCH}_3\text{CO}$] or of certain N -heterocycles can be substituted by sulfur atoms using the $(9\text{-BBN})_2\text{S}$ reagent. In some cases a stepwise reaction mode is observed (e.g. coffein). A further use of the $(9\text{-BBN})_2\text{S}$ reagent is the sulfoboration of cyclic ethers such as THF or oxepane, which form easily the corresponding thioalcohols. The α,ω -oxy, thio alkanes are formed in a very slow reaction from the cyclic ethers by addition of the $(9\text{-BBN})_2\text{S}$ reagent to one CO bond (ref. 50); cf. Fig. 14.

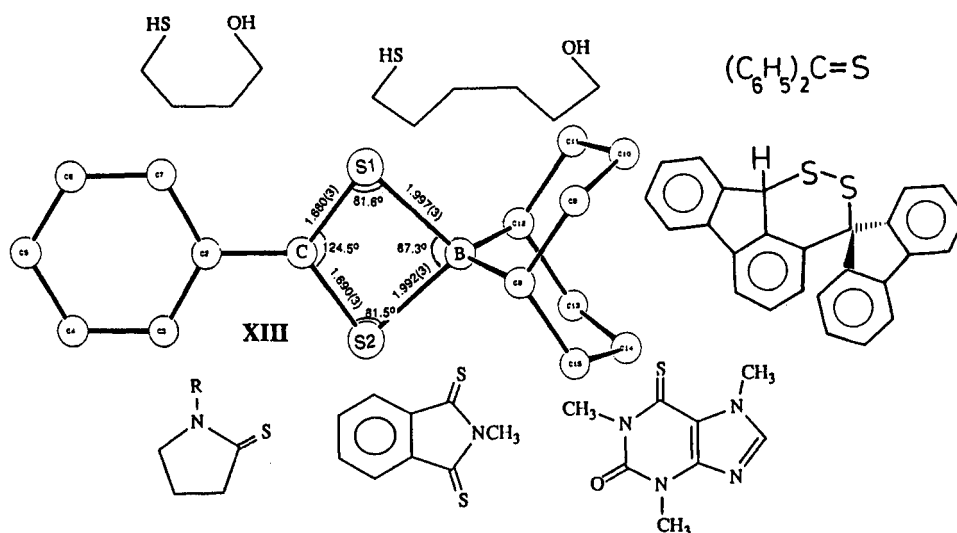


Fig. 14. Compound XIII and some organic sulfur compounds, prepared from the oxygen analogues by sulfidation with $(9\text{-BBN})_2\text{S}$ reagent

VI. STRUCTURES OF NOVEL ADDUCTS WITH 9-BBN RESIDUES

The 9-BBN residue often allows the easy isolation of intermediates (ref. 51,52) and hence information gain on reaction pathways. Some 9-BBN derivatives form the new addition complexes XIV - XVI, which are similar to the previously described (ref. 51) 9-BBN/carboxylic acid dimer XVII.

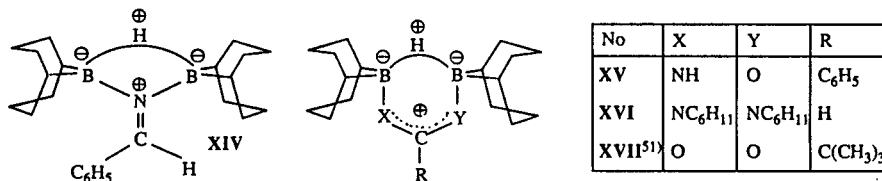


Fig. 15. Cyclic BHB bridged adducts XIV - XVII with two 9-BBN residues

Certain adducts are thermally unstable. When heated in solution they convert to give new products. Compound XIV reacts at about $\geq 80^\circ\text{C}$ by intramolecular hydroboration resulting in (9-BBN)₂benzylamine. The bimolecular condensation of XV according to eq. (f) is complex. The heterocycle XVIII is formed without reduction of the carboxylic acid amide. Compound XVIII has the known borylated N-acyl amidine structure (ref. 42); cf. Fig. 16.

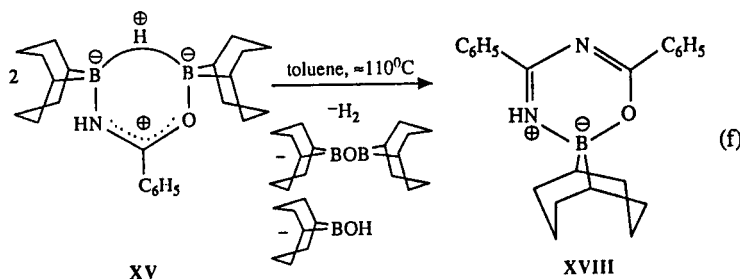


Fig. 16. Formation of the heterocycle XVIII from compound XV by heating in toluene

As expected 9-pyrazolyl-9-BBN derivatives do react with excess of 9H-9-BBN to give the 1 : 1 addition complexes XIX; cf. Fig. 17. However, with pyrazole itself or with monosubstituted pyrazoles only the very stable dimeric products (ref. 53,54), derivatives of the well known so-called pyrazoboles (ref. 55), are obtained.

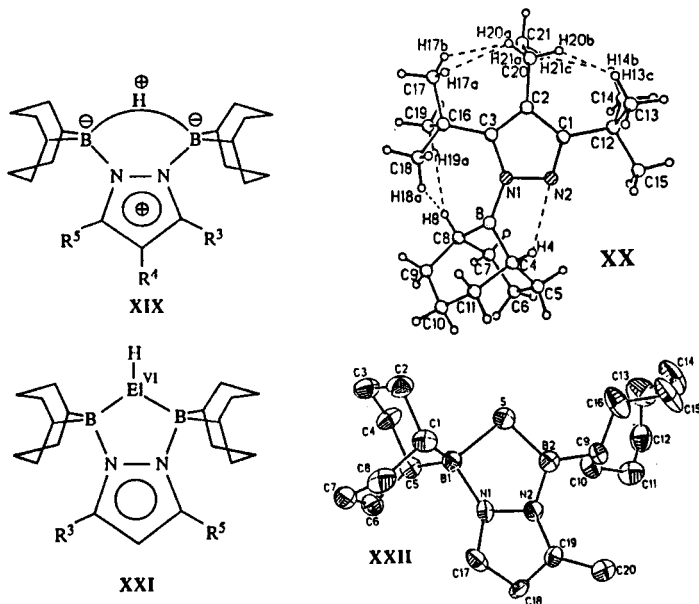


Fig. 17. 9-BBN-Pyrazolyl compounds XIX - XXII from (9H-9-BBN)₂ with substituted pyrazoles

When pyrazoles with very large substituents are employed the monomeric 9-pyrazolyl-9-BBN becomes unreactive towards excess of either 9H-9-BBN or added pyrazole. In solutions of such monomer the 9-BBN moiety fluctuates between the two nitrogen atoms of the pyrazolyl ring (^{13}C NMR). The solid state molecular structure of compound XX (cf. Fig. 17) shows severe intramolecular crowding with a large number of very short intramolecular distances (X-ray; ref. 56). Ab initio calculations have shown, that the energy difference between the acyclic structure and the N_2B heterocycle continuously decreases on increasing the steric factors in the 3,5-position of the pyrazolyl residue. No certain claim for a non-classical boronium ion can be made (ref. 56-58).

Both of the nitrogen atoms of the pyrazolyl moiety form stable bonds to the two boron atoms of all the three $(9\text{-BBN})_2$ -chalcogenides, giving rise to the novel $\text{B}_2\text{El}^{\text{VI}}\text{N}_2$ heterocycles (ref. 53,59). In these, at least formally, an addition complex XXI of 9-pyrazolyl-9-BBN with a 9-hydrochalcogeno-9-BBN is present ($\text{R}^{3,5} = \text{H}$; $\text{El}^{\text{VI}} = \text{O}, \text{S}$; X-ray); cf. Fig. 17. These heterocycles become progressively unstable with substituents on the 3- and/or 5-positions of the pyrazolyl moiety. 3,5-Dimethylpyrazole with $(9\text{-BBN})_2\text{O}$ forms an unstable heterocycle of the type XXI, which in solution is in equilibrium with the usual (NB)-adducts. Larger pyrazole substituents e.g. 3,5-di-*t*-butyl prevent any interaction with $(9\text{-BBN})_2\text{O}$ (ref. 53). - The initially formed heterocycle from $(9\text{-BBN})_2\text{S}$ and 3-methylpyrazole readily reacts by a BC protolysis to give a new heterocycle XXII (X-ray; ref. 59); cf. Fig. 17.

CONCLUSIONS

Although some of the chemistry described above is not unique to $(9\text{H-9-BBN})_2$ because other organodiboranes(6) also show similar reactivities, the special features: Sterically rigid structure, greater Lewis acidity, and restriction of substituent exchanges, generally differentiate this compound from the other hydroboranes. Furthermore, the presence of the bicyclic C_8B skeleton in compounds of this borane generally not only simplifies the analysis of NMR spectra, but the rigid molecule moiety also provide additional stereochemical information on the structures present e.g. in the environment of the boron atom. Finally, since many of these compounds crystallise readily in one conformer, they allow an advantageous and easy resort to X-ray structure analysis. It was demonstrated, that information derived from solid state structure analyses of these, often spatially very crowded 9-BBN derivatives, can lead to the design of new approaches to their chemistry.

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