

Remarkable properties of four-, five-, and six-membered diboraheterocycles

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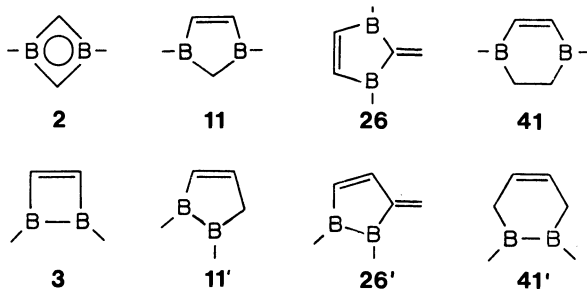
Abstract - Derivatives of the 1,3-dihydro-1,3-diborete 1 and the 1,2-dihydro-1,2-diborete 3 are obtained by dehalogenation of Z-bis(dialkylamino-chloroboryl)alkenes 5 with potassium. X-ray structure analyses prove that 1 is a folded nonclassical Hückel system in agreement with MO calculations (P.v.R. Schleyer). Planar 3 possesses a short C=C bond (1.30 Å) and rearranges around 120°C to puckered 1. Hydrogenation of 1 leads to the corresponding 1,3-diboretanes, which are less folded than 1 (32° vs. 52°). Reduction of 1 (R¹=N*i*Pr₂, R²=SiMe₃) with potassium followed by treatment with ClAu-PPh₃ yields the 2,2-digold compound 9 with a short Au-Au distance (2.98 Å).

2,3-Dihydro-1,3-diborols 11 are obtained via redox reactions between bis(diiodoboryl)methane and alkynes as well as ring contraction of a 1,4-diboracyclohexene derivative 41. 11 possesses remarkable ligand properties: after elimination of hydrogen it functions as a 3e donor in sandwich, oligodecker, and polydecker complexes. Examples of complexes with 11 as a 4e ligand will be given, too.

The formation of the first derivatives of 1,3-dihydro-1,3-diborafulvene 26 as a new isomer of the labile hexaalkyl-1,4-diboracyclohexadiene will be reported. Among the 2,5-dihydro-1-heteroatom-2,5-diborols the thia (10) and phospho heterocycles (29) exhibit interesting ligand properties, as does the 1,4-diboracyclohexene 41. The 1,2-diaza-3,6-diborine 48 and the corresponding nonplanar diphospha heterocycle 49 function as 6e and 4e donor towards Cr(CO)_n, respectively. The dichloro derivative of 49 (R¹=Cl, R²=CMe₃) dimerizes to give 50.

INTRODUCTION

The diboraheterocycles 2,3,11,11',26,26',41, and 41' are the structural analogues of cyclobutadiene, cyclopentadiene, fulvene, and cyclohexadiene, respectively. Formal replacement of two sp²-carbon atoms in the cyclic dienes by two sp²-boron atoms leads to heterocycles with two electrons less. One may expect that transformation of the antiaromatic cyclobutadiene into 1,3-dihydro-1,3-diborete (ref.1) will cause an unusual electronic structure provided a dimerization of the C₂B₂ ring with formation of the C₄B₄ carborane framework (ref.2) is hindered sterically and/or electronically by the substituents at the carbon and boron atoms. MO calculation (ref.3) predict the isomer 3 to be unstable. In agreement, the only known derivative rearranges to the 1,3-isomer 1 around 120°C (ref.4).



The heterocycles 11, 26, and 41 possess a higher reactivity than their carbocyclic analogues. Due to the thermodynamically favored formation of the B-O bond the boron-carbon heterocycles are susceptible to oxygen. Usually compounds with a B-B bond add to alkenes (ref.5). However, dialkylamino substituents at the boron atoms of 3 (ref.4) and 41' (ref.6) reduce the reactivity of the B-B bond and thus prevent intermolecular additions. The compounds 11' and 26' are not known. The diboraheterocycles are capable of accepting electrons to form the corresponding dianions, isoelectronic with the neutral hydrocarbons. With transition metal complex fragments as supplier of electrons and three orbitals the formation of metal complexes occurs (ref.7,8).

1,2- AND 1,3-DIHYDRO-DIBORETES

In the closo carborane series $C_2B_nH_{n+2}$ the smallest members ($n=3$) are the 1,2- and 1,5-isomers of $C_2B_3H_5$ having a trigonal bipyramid structure. For $n=2$ the $C_2B_2H_4$ system does not adopt a closo, tetrahedrane-like structure; ab initio molecular theory predicts a nonclassical folded geometry. Surprisingly, puckered 1 is favored over the planar Hückel system 2, the localized structure 3 and the diborabicyclobutane structure 4.

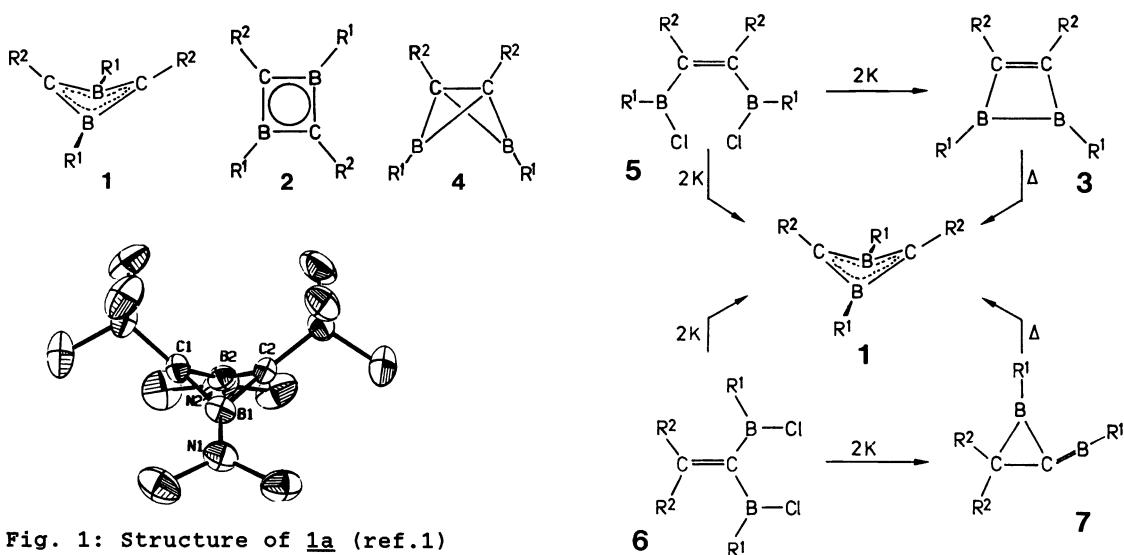


Fig. 1: Structure of 1a (ref.1)

Recently derivatives of 1 have been reported by three groups. Van der Kerk, Schleyer et al., described the formation of $(Me_3C-C)_2(Me-B)_2$ by reacting di-tert.-butylacetylene with $MeBBr_2$ and C_8K together with the corresponding borirene ($n=1$) and/or planar 1,3-dihydro-1,3-diborete 2. However, the products were not separated (ref.9).

In 1979, we have postulated that desulfuration of a 2,5-dihydro-1,2,5-thia-diborol with potassium proceeds via an intermediary labile $(R^2C)_2(R^1B)_2$ molecule 3, which subsequently dimerizes to yield the nido-carborane $(R^2C)_4-(R^1B)_4$ (ref.2). Attempts to stabilize the intermediate by electron-donating substituents at the boron atoms only led to the formation of colored anions without any desulfuration. To synthesize 3 via Z-bis(dichloroboryl) alkenes 5 ($R^1=Cl$) we generated new derivatives of 5 by substituting one chlorine atom of each boryl group for NMe_2 and $NiPr_2$, respectively (ref.1,4).

Dehalogenation of the chloroborane 5a with Na/K alloy does not yield 3a but 1a ($R^2=CMe_3$, $R^1=NMe_2$) in 65% yield (ref.1). The structures of colorless 1a as well as 1b ($R^1=NiPr_2$, $R^2=SiMe_3$; ref.10) and 1c ($R^1=NiPr_2$, $R^2=H$; ref.11) have been elucidated by X-ray crystallography (Fig. 1) which confirm the results of ab initio calculations (ref.3).

At the same time Berndt et al. (ref.12) have studied the dehalogenation of the di-tert.-butyl derivatives of 5 ($R^1=CMe_3$, $R^2=Me$, Et) and obtained the corresponding derivatives of folded 1. Reacting bis(trimethylsilyl)acetylene with $(Me_3C)BCl_2$ they discovered a 1,2-rearrangement with formation of the 1,1-diboryl-2,2-disilylethene 6 ($R^2=SiMe_3$, $R^1=CMe_3$; ref.13), which by dehalogenation gives the unusual three-membered ring boranediylborirane 7 with an exocyclic B=C double bond. On heating 7 rearranges to folded 1 (ref.12). When 6b ($R^1=NiPr_2$, $R^2=SiMe_3$) obtained via $(Me_3Si)_2C_2, B_2Cl_4$ and $HNiPr_2$ is dehalogenated, the formation of 1b is observed (ref.10).

According to MO calculations on the $C_2B_2H_4$ system (ref.3) the 1,2-dihydro-1,2-diborete 3 ($R^1=R^2=H$) should be unstable and rearrange to folded 1. Dehalogenation of 5 ($R^2=Alkyl$) always yields 1. When, however, 5c ($R^2=H$, $R^1=NiPr_2$) is reacted with Na/K alloy, for the first time we isolated the long-sought 1,2-dihydro-1,2-diborete 3c ($R^2=H$, $R^1=NiPr_2$; ref.4). Surprisingly, 3c is stable up to 100°C, and then rearranges to folded 1c. Spectroscopic data (NMR) prove the 1,2-diborete 3c, which is confirmed by the X-ray structure analysis (Fig. 2).

The C1C2 distances (1.80, 181 Å) in 1a and 1b (ref.14) are much longer than C-C in bicyclobutane (1.50 Å). However, in 1c ($R^2=H$, $R^1=NiPr_2$) C1C2 is 1.74 Å (ref.11), the folding along C1C2 46° vs. 52° in 1a. In the derivatives 1a-c short B-N bonds (1.39 - 1.41 Å) are present indicating considerable B=N double bond character. The amino groups in 1a and 1b alter the geometry of the ring only to a small extent, which is in agreement with recent MO calculations for $(CH)_2(B-NH_2)_2$ (ref.15). On the other hand the hydrogen and diisopropylamino substituents in 1c influence the geometry considerably. In planar 3c a remarkable short C=C bond (1.30 Å) is present.

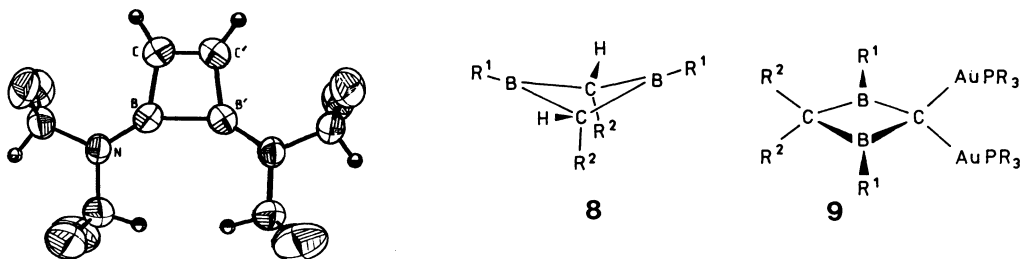


Fig. 2: Structure of 3c (ref.4)

1,3-DIBORETANES

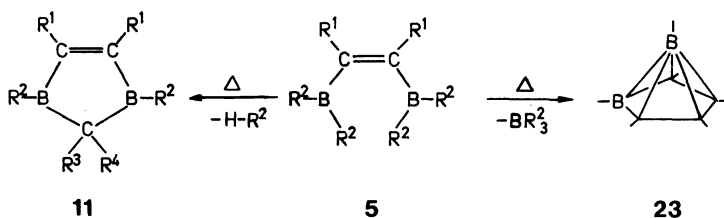
The 1,3-dihydro-1,3-diboretanes 1a and 1b react with Na/K alloy in tetrahydrofuran to give the corresponding radical anions. 1b⁻ undergoes further reduction to diamagnetic 1b²⁻, which on protonation with weakly acidic compounds ($HCCl_3$, $HN(SiMe_3)_2$) results in the formation of colorless 8b (ref.10). It is also formed by hydrogenation of 1b using Pd/active carbon.

Reaction of 1b²⁻ with CH_3I affords the corresponding dimethyl derivative of 8. X-ray structure analysis of 8b shows that the puckering of the four-membered ring along C1C2 (32°) is significantly smaller than for 1a-c. The value is in good agreement with that calculated for the 1,3-diboretane $C_2B_2H_6$ (36°; ref.3). As expected the unsaturated 1b and saturated 8b have different B-C distances (1.520 vs. 1.585 Å) indicating the (B-C) π bond in 1b. The silyl groups of 8b ($R^2=SiMe_3$) are in axial position. When the dianion 1b²⁻ is reacted with $Ph_3P-AuCl$, two products are formed: yellow 2,2-digold-1,3-diboretane 9b and a monogold compound. The formation of 9b is accompanied with silyl group migration. In the planar ring (puckering along C1C2:3°) the Au-Au distance (2.98 Å) is in accord with significant Au-Au interaction (ref.10).

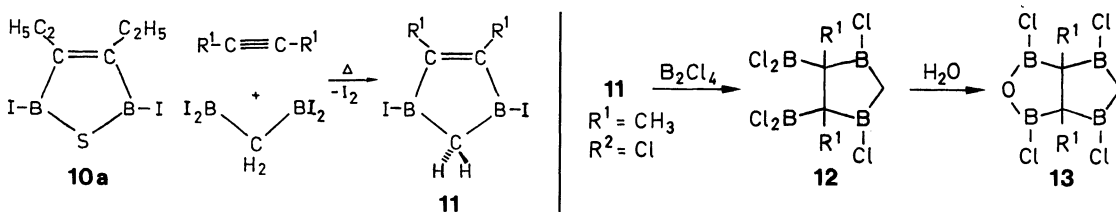
2,3-DIHYDRO-1,3-DIBOROLS 11

The heterocycle 11a ($R^1=R^2=C_2H_5$, $R^3=CH_3$, $R^4=H$) was first obtained by Binger in the thermal ring closure of Z-3,4-bis(dimethylboryl)hexene-3 in 35-40% yield (ref.16).

Heating Z-2,3-bis(dimethylboryl)-2-butene only the nido C_4B_2 carborane 23 is obtained, presumably via rearrangement of the intermediate 1,4-diboracyclohexadiene 22. In our laboratory we developed two routes to derivatives



of **11**. The reaction of 3,4-diethyl-2,5-diiodo-2,5-dihydro-1,2,5-thiadiborol **10a** with the Tebbe reagent $(C_5H_5)_2Ti(Cl)CH_2Al(CH_3)_2$ leads to **11b** ($R^1=C_2H_5$, $R^2=CH_3$, $R_3=R_4=H$) by S/CH₂ and I/CH₃ exchange. However, the yield is small (ref.17), and the reaction is limited since other derivatives of the C₂B₂S-heterocycle are difficult to obtain.

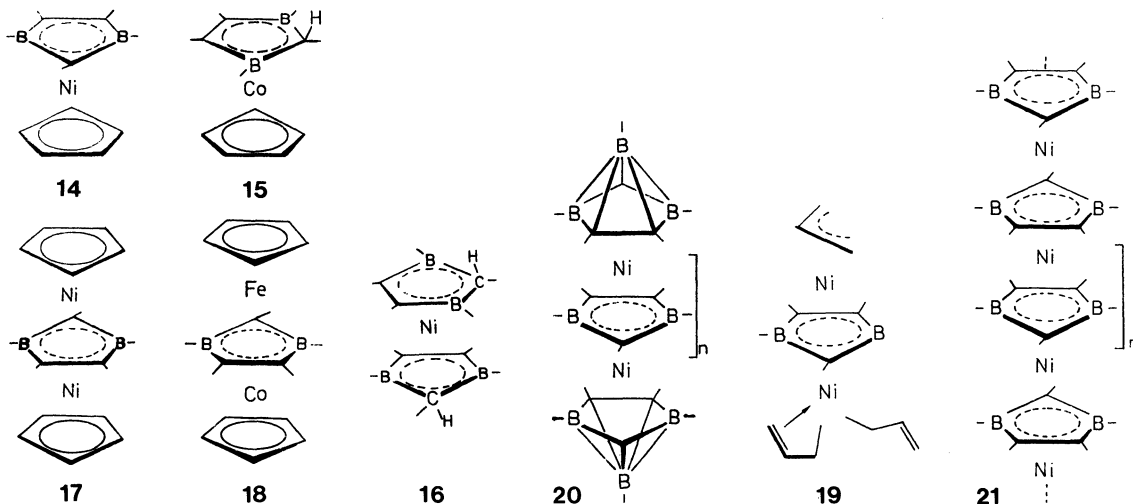


The redox reaction between bis(diiodoboryl)methane and dialkylacetylenes provides a new and versatile approach to **11** (ref.18). Several 1,3-diiido derivatives of **11** have been prepared and subsequently alkylated by using trialkylaluminum. Starting with 1,1-bis(diiodoboryl)alkanes, pentaalkyl derivatives of **11** such as 1,2,3,4,5-pentamethyl-2,3-dihydro-1,3-diborol are accessible. When **11a,b** are treated with excess of potassium in ether, the consumption of 1.4 - 1.8 mol of potassium is observed without evolution of hydrogen. The resulting dark mixtures react with methyl iodide to give methane evolution and methylation of the ring carbon atom C2 occurs (ref.19). B₂Cl₄ adds across the C=C bond of **11** ($R^1=Cl$) to yield **12**. Water transforms **12** to the bicyclic compound **13**.

The heterocycle **11** can act as a three- or four-electron ligand towards transition metal moieties, depending on their electronic requirements (ref.20). Thus with the 15e complex fragment $(C_5H_5)Ni$ it forms the diamagnetic sandwich **14**, while a hydrogen atom of C2 is lost.

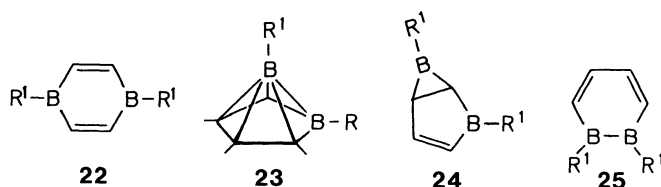
With $(C_5H_5)Co(C_2H_4)_2$ the sandwich **15** is obtained, in which the heterocycle functions as a 4e donor via the C=C double bond and a H-C→Co 3-center/2-electron interaction (ref.21). In the complexes **15** and **16** the C2 carbon atom of the ligand **11** is unique because of its pentacoordination. **14** and **15** may be used as starting materials for bifacial coordination of **11**-H yielding triple-decker sandwich complexes, e.g. **17** and **18** (ref.17).

The green paramagnetic **17** possesses 33 valence electrons (VE), green diamagnetic **18** is the electronic analogue of ferrocene, in which formally the 12 VE diborolylnickel stack has been incorporated. The trisallylnickel complex **19b** is obtained from **11b** and $Ni(\eta^3-C_3H_5)_2$. Both the sandwich **16** and the triple-decker **19** exhibit unusual reactivities. When yellow **16** is heated in benzene, capping and stacking occur leading to a mixture of bis(tricarbahexaboranyl)nickel oligodecker complexes **20**. Complexes with n=1-8 have been identified (ref.22). On heating **19** to more than 120°C in vacuo a polycondensation with elimination of bis(allyl)nickel and hexadiene takes place and a black insoluble product is formed. **21** exhibits a high thermal stability and behaves as a semiconductor. Electrical conductivity measurements yield values of 10^{-2} S/cm (ref.23).

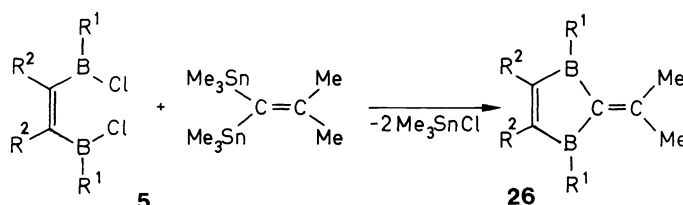


1,3-DIHYDRO-1,3-DIBORAFULVENES

1,4-Diboracyclohexadienes **22** are stabilized by electron-donating substituents at the boron atoms ($R^1 = F, OMe$; ref.8), whereas with hydrogen or alkyl groups ($R^1 = H, CH_3$) the nido carborane structure **23** is favored (ref.16).

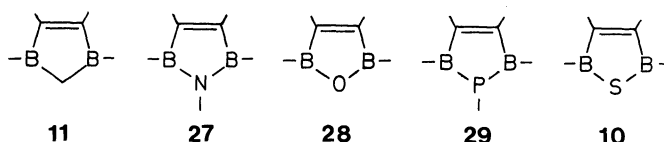


Recently Herberich et al. have prepared the isomers 2,6-diborabicyclo[3.1.0]hex-3-ene **24** ($R^1 = NiPr_2$; ref.24), and 1,2-dibora-3,5-cyclohexadiene **25** ($R^1 = NMe_2$), the latter as ligand in Ru and Rh complexes (ref.6). A further isomer is the 1,3-dihydro-1,3-diborafulvene system **26**, which we obtained by reacting Z-bis(dichloroboryl)alkenes **5** ($R^1 = Cl, R^2 = Et, Me$) with $(Me_3Sn)_2C=CMe_2$ (ref.25). In contrast to **22** ($R^1 = \text{alkyl groups}$) **26** does not rearrange to the carborane at ambient temperature, because cleavage of C-C bonds is energetically unfavored. **26** is a potential synthone for the formation of carboranes, metal complexes and organoboranes.

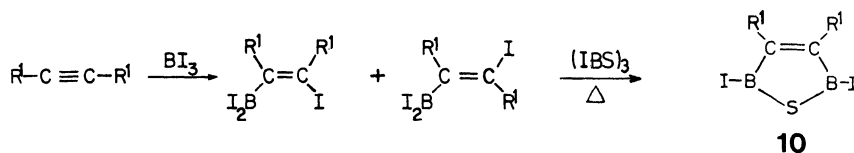


2,5-DIHYDRO-1-HETEROATOM-2,5-DIBOROLS

The heterocycles **11**, **27**, **28**, **29**, and **10** are the structural analogues of cyclopentadiene, pyrrole, furan, phosphole and thiophene, respectively. The π -electron number of the boron heterocycles are two less, therefore reduction of **27-29** and **10** should lead to the corresponding aromatic dianions.

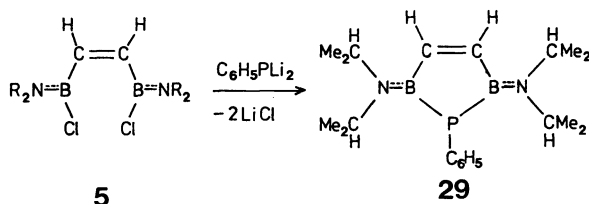


The 2,5-dihydro-1,2,5-thiadiborol **10a** is obtained via redox reaction between hexyne-3, BI_3 and $(IBS)_3$. In the first step BI_3 adds to hexyne-3 yielding cis/trans vinylboranes which react in refluxing hexane with $(IBS)_3$



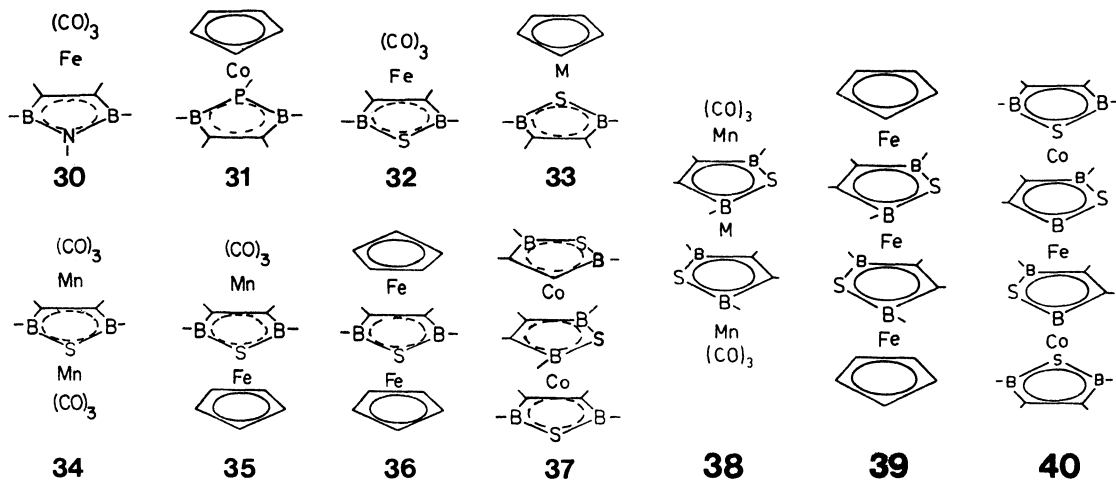
to give **10a** and iodine. Yields of **10a** are up to 80%, while with butyne-2 the dimethyl derivative **10b** is formed only in minute quantities (ref.26). The ring closure proceeds via a diborylsulfane intermediate having δ^+ and δ^- polarized iodine atoms at the carbon and the boron atoms, respectively. Elimination of iodine leads to the formation of the B-C bond. Another approach to **10** starts with Z-diborylethenes **5** and $(Me_3Si)_2S$ (ref.27). Alkylation of **10a** with R_4Sn yields the corresponding alkyl derivatives. Substitution of the iodine in **10a** with diphenylmercury, dialkylamine, bromine, iodochloride, arsenic trichloride, dimethyldisulfane, and diethylether leads to the corresponding derivatives in good yields. The 2,5-dihydro-1,2,5-thiadiborol compounds are sensitive to moisture and oxygen; they are

monomeric in solution with the exception of the iodine derivative 10a, which crystallizes as a dimer formed by two sulfur-boron donor-acceptor bonds. The X-ray structure analysis of 3,4-diethyl-2,5-bis(dimethylamino)-2,5-dihydro-1,2,5-thiadiborol proves the planarity of the C₂B₂S ring having long B-S (1.844 Å) and B-C bonds (1.590 Å). Replacement of the sulfur atom by the CH₂ group with the Tebbe-reagent yields 11 (s. chapter 2,3-DIHYDRO-1,3-DIBOROLS). With heptamethyldistannazane the 2,5-dihydro-1,2,5-azadiborol 27 is formed (ref.28). Attempts to prepare the corresponding oxo- and phospho compounds 28 and 29 from 10 were unsuccessful. However, the reaction of Z-1,2-bis(diisopropylamino-chloroboryl)-ethene with dilithiumphenylphosphide leads to 29a. The ring is nonplanar, and the coordination geometry at the phosphorus atom is pyramidal (ref.29).



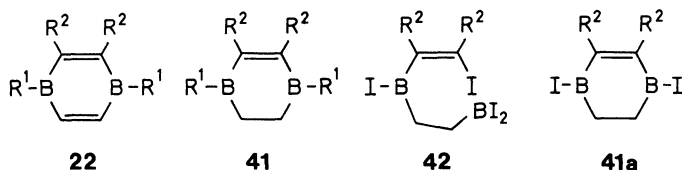
The heterocycles 27, 29, and 10 exhibit Lewis acid/Lewis base properties; they act as four-electron donors and as two-electron acceptors. The azadiborol 27 possesses reduced acceptor qualities, therefore only mononuclear complexes (e.g. 30) are formed. The heterocycle 29 (ref.30) and 10 are coordinated mono- and bifacially leading to 31-33 and to the triple-decker complexes 34-37 (ref.7). These mono- and dinuclear complexes are diamagnetic having closed shells with 18 and 30 valence electrons, respectively.

The 1,2,5-thiadiborol heterocycle 10 gave us the access to the first the tetradeccker complexes 38, 39, and 40 (diamagnetic, 42VE, ref.7). This finding was the proof that metals and boron heterocycles can be stacked.

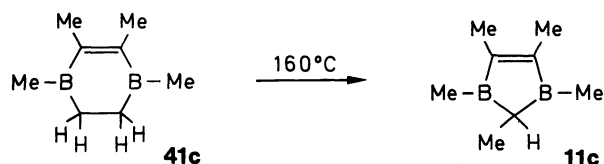


1,4-DIBORACYCLOHEXENES

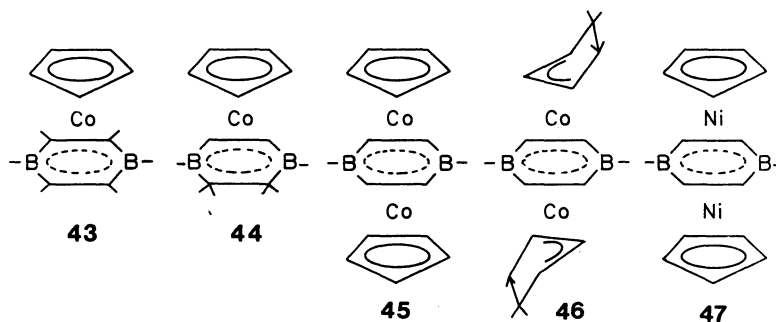
Because of its electron-deficiency 1,4-diboracyclohexadienes 22 (R¹=alkyl, hydrogen) easily rearrange to the nido carboranes 23. Electron-donating substituents (R¹=F, OMe) stabilize the classic structure (ref.8). As these groups hamper the ligand properties of 22, we synthesized 1,4-diboracyclohexenes 41, which are stable even with alkyl substituents at the boron atoms.



The heterocycle **41** is obtained via a redox reaction involving 1,2-bis(diodoboryl)ethane and dialkylacetylenes (ref.31). In the first step addition of one B-I group onto the hexyne-3 with formation of intermediate **42** occurs, which on heating yields elemental iodine and the heterocycle **41a** ($R^2=Et$). With dimethylacetylene **41b** ($R^1=Me$) is obtained. In these compounds the iodo substituents are easily replaced; alkylation with $AlMe_3$ leads to **41c, d** ($R^2=Me, Et$; $R^1=Me$). Reaction with Me_3SiNMe_2 and $HN(iPr)_2$ yields the corresponding bis(dialkylamino) derivatives. Reduction of the alkyl derivatives **41c, d** with potassium leads to colored solutions of the diborabenzene dianions $[22]^{2-}$ which on reaction with MeI yield hexaalkyl-1,4-diboracyclohexens. On heating **41c** for several hours at $160^\circ C$ in benzene, the six-membered ring undergoes a ring contraction to form 1,2,3,4,5-pentamethyl-2,3-dihydro-1,3-diborol **11c** quantitatively (ref.32).

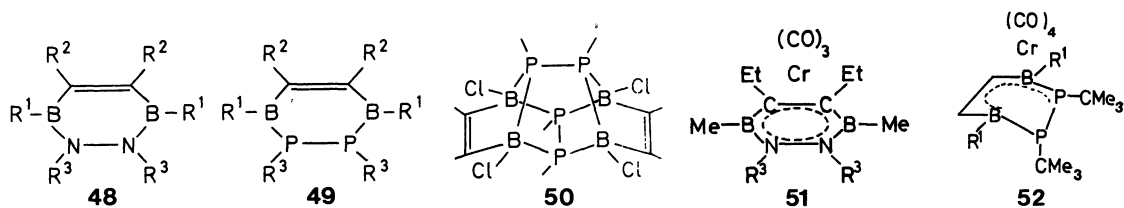


The tetra- and hexaalkyl derivatives of **41** are two-electron donor ligands in which the ethylene bridge is activated by metal centers. This activation results in the elimination of hydrogen and formation of 1,4-diboracyclohexadiene complexes. From $(C_5H_5)Co(C_2H_4)_2$ and **41** the cobalt complexes **43 - 46** are obtained. **46** is a remarkable case, as the hydrogens of **41** are transferred to the cyclopentadienyl to form cyclopentenyl ligands. In $[(C_5H_5)Ni(CO)]_2$ the CO groups are substituted by **41** and the yellow diamagnetic triple-decker **47** is formed. These results demonstrate the applicability of **41** as starting ligand for the construction of mono- and dinuclear 1,4-diboracyclohexadiene complexes (ref.31).



1,2-DIHETEROATOM-3,6-DIBORACYCLOHEXENES

Replacement of the sulfur atom in the 2,5-dihydro-1,2,5-thiadiborol ring **10** with hydrazines yields the planar 1,2-diaza-3,6-diborines (ref.33). **48** exhibits a higher thermal and hydrolytic stability than the 2,5-dihydro-1,2,5-azadiborol **27**, which is due to the increased electron density at the boron atoms of **48**. The corresponding diphospha heterocycle **49** is obtained when Z-bis-(diisopropylamino-chloroboryl)ethene is reacted with $(Me_3CP-SiMe_3)_2$ (ref.30). The yellow heterocycle **49** ($R^1=NiPr_2$, $R^2=CMe_3$) is nonplanar, one phosphorus group being above and the other is below the C_2B_2 plane. In contrast Z-bis(dichloroboryl)ethene and $(Me_3CP-SiMe_3)_2$ yield a dimeric product, which on the basis of ^{11}B - and ^{31}P -NMR was expected to have a cubane-like structure. Surprisingly, in **50** the phosphorus and boron atoms occupy positions like the sulfur and nitrogen atoms do in S_4N_4 (ref.34). Both **48** and **49** form carbonylchromium complexes. **48** is isoelectronic with borazine and benzene and yields the orange-red η^6 -complex **51** with the d^6 -Cr(CO) $_3$ fragment. The nonplanar $C_2B_2P_2$ ring, however, does not allow η^6 -bonding; it complexes in η^4 -fashion to give the d^6 -Cr(CO) $_4$ complex **52**.



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