# Recent advances in boron–nitrogen chemistry—II

Heinrich NÖTH*, Gilbert GEISBERGER, Gerald LINTI, Dirk LODERER,
Wilfried RATTAY, Erik SALZBRENNER

Institute of Inorganic Chemistry, University of Munich,
Meiserstr. 1, 8000 Munich 2 (FRG)

Abstract - The chemistry of dimethylaminopolyboranes $B_n(NMe_2)_nX_2$ (n = 3, 4, 6, X = Cl, Br) has been investigated. Nucleophilic substitution of the halides by NHR, OR, SR and R groups is readily achieved as well as by difunctional nucleophiles which give access to boron rich heterocycles. The characteristic feature of all these new compounds is the almost perpendicular arrangement of the $BNMe_2$ units.

The scope of the chemistry of amino iminoboranes has been expanded by the synthesis of molecules containing two $RN \equiv B$ units. Reactions of amino iminoboranes with boron hydrides lead to hydroboration products in the case of $BH_3 \cdot thf$ or $B_3H_7 \cdot thf$ while a boron-boron bond is formed in the reaction with $B_{10}H_{14}$. While $B_n(NMe_2)_nCl_2$ compounds exclusively chloroborate $tmpB \equiv NCMe_3$ no such reaction is observed employing $Fe_2(CO)_6S_2B_2(NMe_2)Cl$. This is due to the nido-structure of this compound. Its reaction with $LiNMe_2$ converts it into $Fe_2(CO)_6S_2(BNMe_2)_2$ cage containing a diboron unit.

The $R_2N$ group cannot yet electronically stabilize $R_2N \doteq B = PR'$ compounds. However, if the lone pair at the P atom is engaged in bonding with a $M(CO)_5$ group (M = Cr, W) allenic type complexes $R_2N = B = PR'(M(CO)_5)$ containing two coordinated boron and a BP double bond (1.74Å) result.

## INTRODUCTION

Dialkylamino groups exert a stabilizing effect on boron compounds. This is due to electronic and steric shielding of the boron atom to which the $R_2N$ substituent is bonded. Using this effect for more than 25 years a large variety of new kinds of boron compounds have been made accessible by our group (ref. 1). To name a few examples: monomeric phosphino (ref. 2), arsino and stibino boranes (ref. 3), silyl and stannyl boranes (ref. 4, 5), boryl transition metal compounds (ref. 6) or salts of the bis(dialkylamino)boron cations (ref. 7). The present report concentrates on three topics in which this effect plays also an important role:

i)   the chemistry of dimethylamino polyboranes,

ii)  the chemistry of amino imino boranes,

iii) the search for an amino phosphanylidene borane $R_2N \doteq B = PR$.

## SOME NOVEL CHEMISTRY OF DIMETHYLAMINO POLYBORANES

The synthesis of tetrakis(dimethylamino)diborane(4) was independently reported by Brotherton et al. (ref. 8) and by our group (ref. 9) almost 30 years ago. It forms in high yield by dehalogenation of bis(dimethylamino)boron chloride. Using the same procedure higher members of the series $B_n(NMe_2)_{n+2}$ were obtained (ref. 10) including the cyclohexaborane $(BNMe_2)_6$ (ref. 11). Apart from $B_2(NMe_2)_4$ the chemistry of these electron precise polyborane derivatives remained, however, almost unexplored, since they were accessible only in low yield.

We have now optimized the conditions for their preparation, and it proved essential to employ a short path distillation for separating the species $B_2(NMe_2)_4$, $B_3(NMe_2)_5$, $B_4(NMe_2)_6$ and $B_6(NMe_2)_8$ effectively. Representative yields and some characterizing data for the dechlorination on a 1 : 1 mixture of $B_2(NMe_2)_3Cl$ and $(Me_2N)_2BCl$ by Na/K alloy, optimized for the preparation of the triborane(5) derivative are as follows:

|           | $BNMe_2)_3$ | $B_2(NMe_2)_4$ | $B_3(NMe_2)_5$ | $B_4(NMe_2)_6$ | $B_6(NMe_2)_8$ |
|-----------|-------------|----------------|----------------|----------------|----------------|
| Yield (%) | 5           | 8.5            | 23             | 3              | 0.5            |
| bp. °C/Torr | 25/50     | 56/10          | $80/10^{-2}$   | $100/10^{-3}$  | $120/10^{-3}$  |

Thus, the triborane(5) species is now readily accessible, and we have explored its chemistry

to some extent. Using $EtBCl_2$, $MeBBr_2$ and $MeBI_2$ respectively, two $Me_2N$ groups, one each at the terminal boron atoms, can be replaced by a halogen atom. Yields obtained for the 1,3-dihalo-geno-1,2,3-tris(dimethylamino)-triboranes(5) lie in the range of 60 - 80 %. Similarly, compounds $B_4(NMe_2)_4X_2$ (X = Cl, Br, I) were isolated starting from $B_4(NMe_2)_6$. Further substitution of $Me_2N$ groups by $Me_2N$/halogen exchange so far lead neither to defined nor detactable intermediates, mind $B_nX_{n+2}$ electron precise polyboron halides.

The dimethylamino polyboron dihalides nevertheless proved to be suitable for exploring and expanding the substitution chemistry of these and related polyborane species. Using $B_3(NMe_2)_3Br_2$ as an example a series of triboranes $B_3(NMe_2)_3Y_2$ (Y = OR, SR, R) was prepared by nucleophilic substitution of the bromine (or also chlorine) atoms. Most of these compounds are crystalline, and some structures are represented by the following ORTEP plots. It can be noted that the B - B bond lengths increase as the terminal BN bond becomes shorter. Therefore, the B - B bond is influenced by the nature of the substituents Y. More important is the characteristic conformation of the chain: while all boron atoms show a planar arrangement of the substituents, the $BCN_2$ planes are almost perpendicularly oriented to one another. Therefore, there is no $\pi$-interaction between adjacent boron atoms in the chain. This same kind of structural feature is also observed in the X-ray structure of $B_4(NMe_2)_4(SPh)_2$.

ORTEP PLOTS



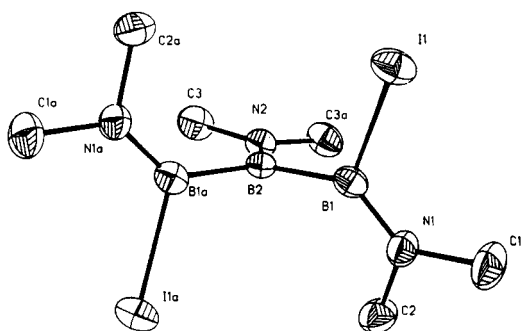Fig. 1: ORTEP-Plot of $B_3(NMe_2)_3I_2$.
B1-B2 1.674(7)Å, B1-B2-B1a
118.7(3)º



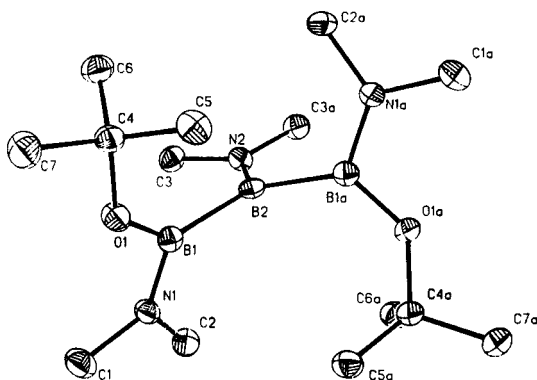Fig. 2: ORTEP-Plot of $B_3(NMe_2)_3(OCMe_3)_2$.
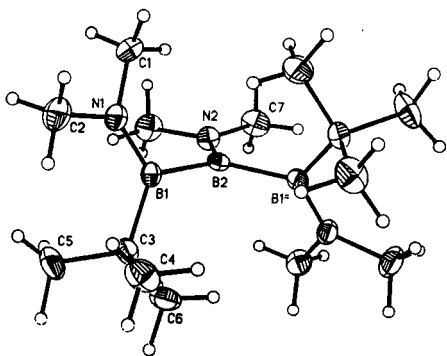B1-B2 1.755(5)Å
B1-B2-B1a 126.7(4)°



Fig. 3: ORTEP-Plot of $B_3(NMe_2)_3(CMe_3)_2$.
B1-B2 1.733(3)Å, B1-B2-B1 121.3(3)°

It is evident from these results that the dihalides $B_n(NMe_2)_nX_2$ can be used as synthons for the construction of new polyboron heterocycles by reacting these dihalides with difunctional molecules. Interestingly, the reaction of $B_3(NM_2)_3Br_2$ with $Me_2Si(NH^tBu)_2$ in the presence of $NEt_3$ produced not the six membered ring 1 but at 120 °C the azatriboretidine 2. Under these conditions Si-N bond cleavage is more rapid than HBr elimination. However, 3 results from $B_3(NMe_2)_3Br_2$, 1,2-diphenylhydrazine and $NEt_3$. Similarly, the six membered ring compounds 4 and 5 are readily obtained from $PhP(O)(OH)_2$ or$(MeHN)_2CO$. Seven and even eight membered
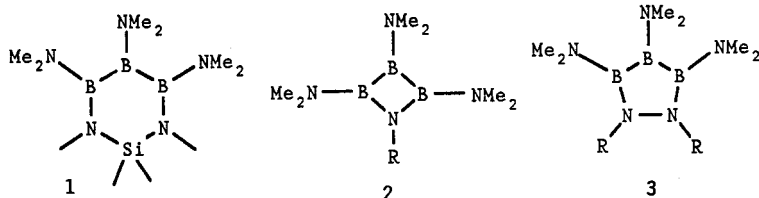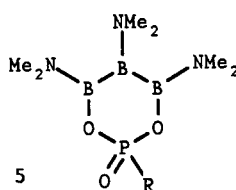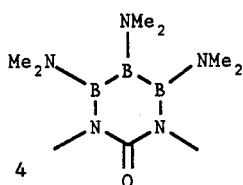
heterocycles, 6 and 7, containing the triboron unit, result from the triboron dibromide $B_3(NMe_2)_3Br_2$ with catechol or 2,2-dimethyl-propylendiamine. The $C_2O_2B_3$ ring in 6 possesses boat conformation as revealed by an X-ray structure determination, and the perpendicular arrangement of the dimethylamino boron units is again observed.

Attempts to synthesize the four membered phosphatriboretane 8 failed. The product obtained from $B_3(NMe_2)_3Br_2$ and $Li_2Pmes$ (mes = mesityl group) is the eight membered ring 9 whose X-ray structure has also been determined.
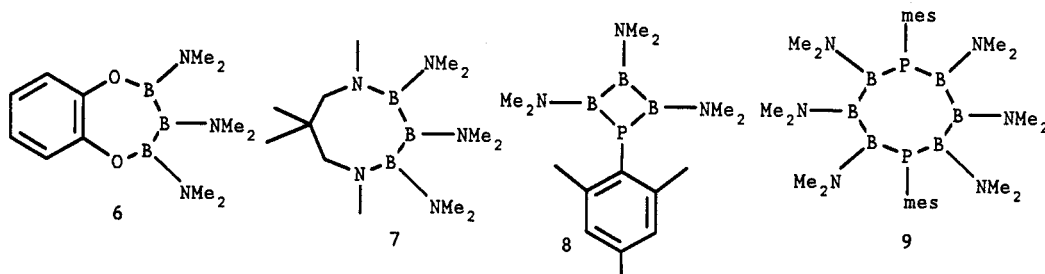
## NEW AMINO IMINO BORANE CHEMISTRY AND A CAGE/CLUSTER REARRANGEMENT

Amino imino boranes $R_2N \rightleftharpoons B \rightleftharpoons NR'$ are extremely versatile reagents (ref. 13). Provided that steric shielding is not too pronounced they dimerize in a (2+2)-cycloaddition reaction to give 1,3,2,4-diazadiboretidines. With this kind of information one can construct and synthesize molecules containing more than one imino borane group. Two representative examples are shown as 10 and 11 (tmp = 2,2,6,6-tetramethylpiperidino group). Stable molecules result if the imino nitrogen atom is bonded to a tert.-carbon atom. If an aromatic group is the substituent then it is essential that the two ortho-positions carry at least methyl groups.
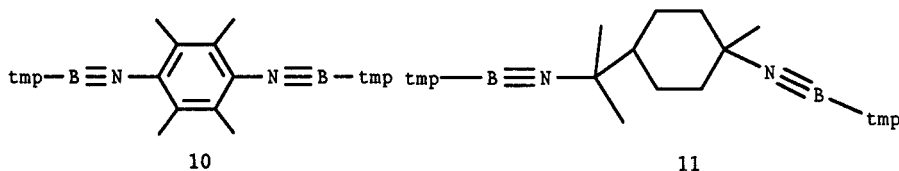
It is well known that "$BH_3$" offered to tmp $\rightleftharpoons$ B $\rightleftharpoons$ N - $CMe_3$ in the form of $BH_3 \cdot THF$, $BH_3 \cdot SMe_2$ or $B_2H_6$ leads to the hydroboration product 12 which is thermally unstable decomposing readily into $tmpBH_2$, $tmpB_2H_5$ and $(Me_3CNBH)_3$ (ref. 13). In contrast, the analogous product derived from 1,8-bis(tetramethyl-piperidino-iminoboryl)-p-menthane gives 13, stable up to 200 °C. The reason for this enhanced stability is not readily understood and may be associated with the solid state of 13.
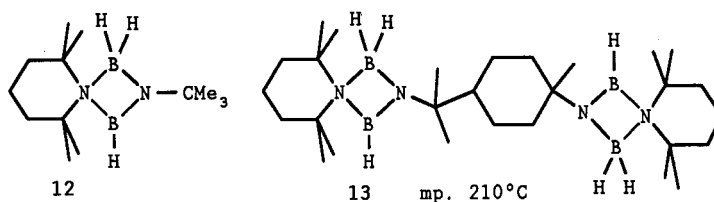
Hydroboration reactions with $B_3H_7 \cdot L$ require usually more drastic conditions as compared to $BH_3 \cdot L$. Indeed, a much slower rate is observed for the reaction of $B_3H_7 \cdot L$ with tmp - B = N - $CMe_3$, allowing the dimerization of the amino imino borane to compete effectively with the hydroboration (about 50 %). The X-ray structure of the hydroboration product is shown as 14. It corresponds with the 1104 rather than the alternative 2013 styx notation. Therefore the structure of 14 is closely related to the structure of $B_3H_7CO$ (ref. 14).

Pentaborane(9) did not react with tmp $\div$ B $\doteq$ N - CMe$_3$ at ambient temperature in contrast to B$_{10}$H$_{14}$. However, the object to achieve the formation of closo-B$_{10}$H$_{10}$(Btmp)NCMe$_3$ with evolution of two mols of H$_2$ could not be accomplished. Not unexpectedly, decaborane acts as a protic acid towards the electron rich amino imino borane: the cation tmp = B = NHCMe$_3$$^+$ and the anion B$_{10}$H$_{13}$$^-$ are most likely intermediates and nucleophilic attack of this anion on the electrophilic boron centre in the cation leads to a novel kind of B - B bond formation. As the structure of the compound 15 shows, an additional proton migrates to give B$_{10}$H$_{12}$(B(Htmp)NHCMe$_3$) as the final product.

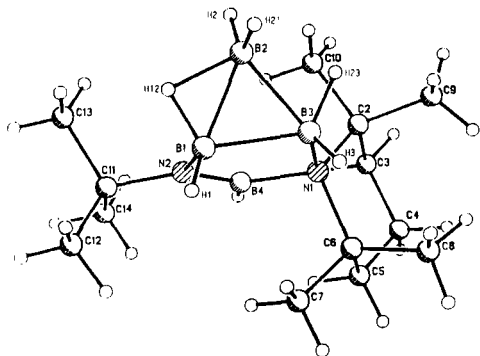

Fig. 4: ORTEP-Plot of 14
   B1-B2 1.756(4), B2-B3 1.844(4),
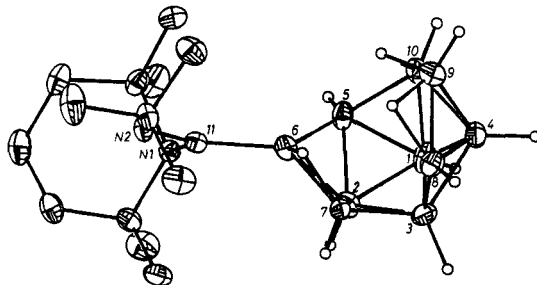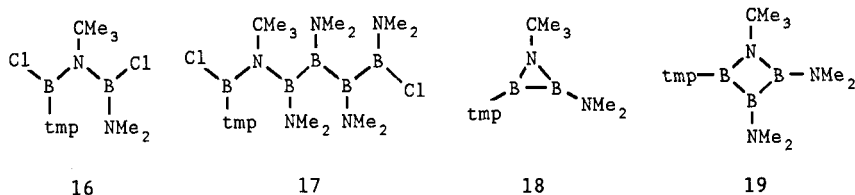   B1-B3 1.842(4), B1-N2 1.530/4),
   B3-N1 1.638(3)Å

Fig. 5: ORTEP-Plot of 15
   B6-B11 1.679(5), B11-N2 1.371(5)
   B11-N1 1.594(4)Å

Haloboration is exclusively observed by reacting tmp $\div$ B $\doteq$ NCMe$_3$ with dimethylamino boron chlorides B$_n$(NMe$_2$)$_n$Cl$_2$ (n = 1 - 4). Products 16 and 17 can be dehalogenated to the small ring heterocycles 18 and 19 respectively.



This kind of a specific reaction was expected to help in the structure elucidation of Fe$_2$(CO)$_6$S$_2$B$_2$(NMe$_2$)Cl, 21, a compound which is obtained from 20 by monohalogenation with e.g. BCl$_3$ or EtBCl$_2$ (ref. 15). Its low field signal at 77 ppm observed in the $^{11}$B NMR spectrum of 21 was not really compatible with the proposed structure. If the structure was correct, then it was to be expected that this compound would chloroborate tmp $\div$ B $\doteq$ N - CMe$_3$. A 1 : 1 reaction does indeed occur, but the mentioned $^{11}$B NMR signal remains almost unaltered. Therefore the structural unit associated with this boron atom remained the same. There are two more $^{11}$B NMR signals for 22 indicative for a BN$_3$ unit as well as for a tetracoordinated boron atom. These data are in accord with the result of an X-ray structure analysis represented as formula 22. Thus, the B - B bond in 20 is broken and its cage structure has changed into a nido-structure in 22. Therefore, one can conclude from the $^{11}$B NMR data that 21 is actually represented by the nido-cluster structure 23, and this has been ascertained for (CO)$_6$Fe$_2$S$_2$B$_2$(NMe$_2$)Br by an X-ray structure analysis. Amidation of 22 by LiNMe$_2$ leads to the dimethylamine derivative whose Fe - B bond to the apex Fe atom has increased by 0.4Å in comparison with 22. This is due to strong $\pi$-bonding in the cluster BNMe$_2$ unit which competes favourably with the multicenter bonding in the cluster. Even more important is the observation that 23 can be reconverted with LiMe$_2$ into 20. Thus, it is the nature of the substituents which controls the stability of these cage/cluster isomers. We conclude from these results that this is true also for other isomers to be described as electron precise/electron deficient.

## AMINO PHOSPHANYLIDENE BORANES

Amino phosphanylidene boranes, R$_2$N $\div$ B = PR, are the P-homologues of amino imino boranes. MO calculations have shown that these two classes of isoelectronic compounds are not isostructural (ref. 16). The phosphorus compounds are not linear like R$_2$N $\div$ B $\doteq$ NR but show a bond angle at the P atom of about 100°. Calculations further indicate, that the amino phosphanylidene boranes are unstable with respect to dimerisation. The activation energy for their
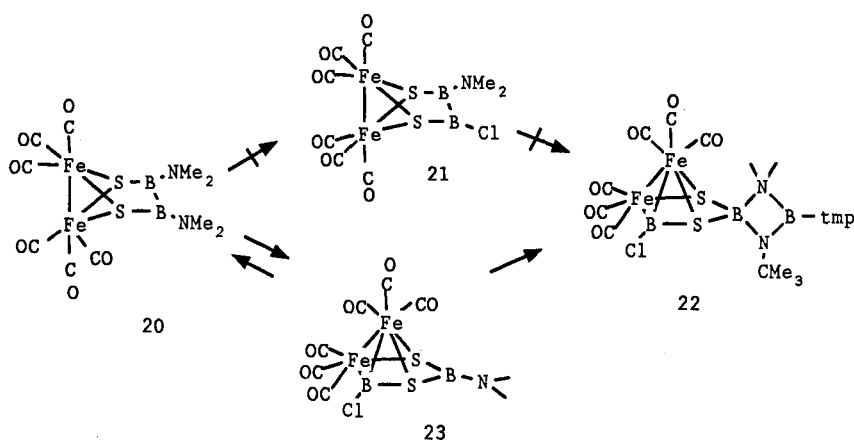
dimerisation to 1,3,2,4-disphosphadiboretanes is only in the order of 5 kcal/mol. This cor-
responds with futile attempts in many research groups to isolate amino phosphanylidene bo-
ranes. However, their stabilisation may be possible, if the lone pair at the P atom of
$R_2N \doteq B = PR$ is occupied by a suitable electron pair acceptor. This approach has been veri-
fied, and results will be discussed elsewhere (ref. 17).

Another strategy is to use diphosphadiboretanes as precursors. For this purpose it is neces-
sary to introduce very bulky substituents into the diphosphadiboretanes. Thus, $(Et_2N - B =$
$Pmes)_2$ reacts readily with $Cr(CO)_5$.thf in a 1 : 1 and 1 : 2 ratio without changing the basic
diphosphadiboretane structure. In contrast, $(tmp - B = PCEt_3)_2$ replaces thf from $M(CO)_5$.thf
(M = Cr, W) to produce 24. The X-ray structure of 24 reveals an allene type arrangement for
the $C_2NBP(Cr)C$ skeleton. Therefore, a two coordinated boron atom is generated during this
process with formation of a very short BP bond (1.74Å) (ref. 18) which is a representative
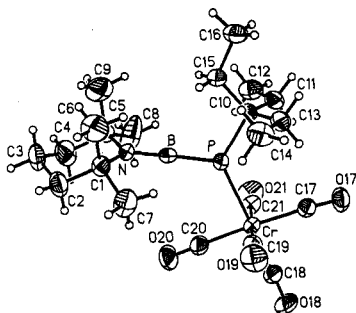example of a BP double bond.



Fig. 6: ORTEP-Plot of 24
       B - P 1.742, B $\overline{-}$ N 1.338(5)Å,
       B - P - N 176.1(3)°

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