

## The borylation of aromatic compounds by dehalogenation products of dialkylamino(dihalogeno)boranes

Anton Meller

Institut für Anorganische Chemie, Universität Göttingen, Tammannstraße 4,  
D-3400 Göttingen, Federal Republic of Germany

**Abstract** - Reactions of subvalent boron species, generated by the dehalogenation of  $X_2BNR_2$  ( $X = Cl, F$ ;  $R = Pr^i$  or  $Bu^i$ ) by Na/K, with aromatic compounds in 1,2-dimethoxyethane lead to polycyclic species in which formal borene units, "BNR<sub>2</sub>", are added across or inserted into the carbon skeleton of the aromate. The highly reactive borene or borenoid intermediates lead to complex product mixtures and lossy high vacuum distillations make it difficult to evaluate the true yields of the respective products. In some cases (compounds **9** and **13**) pure isolated material come up to nearly 50%. Structures have been deduced from MS and NMR (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C and in part <sup>15</sup>N) data as well as by x-ray structure analyses for 14 of the 27 species formulated. Formation of specific compounds depends on the reaction conditions (see the references cited). All species exhibit high thermal stability, some are slowly hydrolysed by atmospheric moisture while others are stable to wet acetone for prolonged periods. With one exception (**20**), the novel species are quite different from carboranes.

### INTRODUCTION

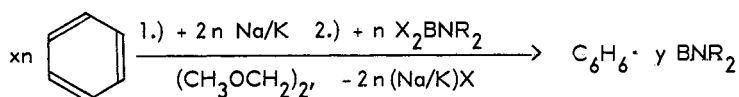
Carbenes, derivatives of divalent carbon are six electron species. They can be described as Lewis acids and (in their singlet state) as Lewis bases at the same time. Without a suitable reaction partner, carbenes will polymerize. With aromatic compounds carbenes will react either by 1,2-addition across a (CC) double bond thus forming norcaradiene derivatives or by insertion into the carbon skeleton thus forming e.g. cycloheptatriene. Cases where the same aromatic ring reacts with two carbene species are extremely rare. A borene is a derivative of monovalent boron and therefore a four electron species. Even its electron deficiency may be diminished by  $\pi$ -donor substituents its reactivity must be higher than that of a carbene.

To be certain that a free borene is acting as the reaction partner to any substrate, the borene has to be generated either in a gas phase reaction or in solution by elimination from cyclic moieties. This has been performed by Timms by the high temperature preparation of boron monohalides and their reaction with alkynes to give 1,4-dihalo-dibora-cyclohexadienes (ref. 1). When borenes are generated in solution, by the dehalogenation of dihaloboranes,  $RBX_2$ , with active metals, reaction products obtained can be formed also by radical reactions of borenoids,  $RB\dot{X}$ , and a subsequent second dehalogenation step. Surprisingly no attempts have been made to react subvalent boron species (borenes or borenoids) with aromatic compounds in the past. - However the borele dianion **A** has been reacted with  $CH_3BBr_2$  to yield the 2,3,4,5-tetracarba-nido-hexaborane(6) derivative **B**, while with  $Pr^i_2NBCl_2$  the 2,6-diborabicyclo[3.1.0]hex-3-en derivative **C** is obtained (ref. 2). Like in the 1,4-dihalogeno-1,4-diboracyclohexadienes classical, cyclic structures are stabilized by the diminution of the electron deficiency at the boron atoms by additional  $\pi$ -bonding from their substituents.

All species marked by letters (denoting the work of others) or by numbers (our work) are depicted in Table 1. All these compounds have been fully characterized by their mass-(MS) and NMR.(<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C and in part <sup>15</sup>N) spectra. Those labeled with an \* have been substantiated by x-ray structure analyses.

### RESULTS AND DISCUSSION

By the reaction of  $X_2BNPr^i_2$  ( $X = Cl$  or  $F$ ) with Na/K and  $C_6H_6$  in  $(CH_3OCH_2)_2$ , species  $C_6H_6 \cdot xBN(i-Pr)_2$  ( $x = 1-6$ ) are formed as shown by field ionization (FI) mass spectrometry.



$$x = 10 - 0.1; \quad y = 1 - 6; \quad X = Cl, F; \quad R = Pr^i, Bu^i$$

By fractionating high vacuum distillation of the viscous mixture of the reaction products, so far three bicyclic species containing two (1) and three (2, 3) formal borene units " $\text{BNPr}_2$ " have been isolated (ref. 3,4). In all these products two double bonds are retained; 3 is a spirocyclic species and hydrogen transfer is observed. The structure of 4 (which is obtained from 1,4-diisopropyl-benzene) presents the same skeleton as 1, while 5 derived from toluene corresponds to 2. Likewise the reaction product of p-xylene with two " $\text{BNPr}_2$ " units, 6 and compounds 7 and 8 which originate from 1,2,4-trimethylbenzene and N-dimethyl(4-trimethylsilyl)aniline belong to a common type of structure (ref. 5). The type of skeleton which is presented by the compounds 6 to 8 seems to be easily formed and is also contained in 9 which is the main product formed in the dehalogenation of  $\text{X}_2\text{BNPr}_2$  by the naphthalene alkali-metal complex in glyme (ref. 3,6,7). These products apparently are formed by the 1,4-addition of a "borene" unit across a six membered aromatic ring and by insertion of the other "borene" under ring enlargement. Again compounds 6 - 9 still contain two double bonds. The inclusion of a part of the remaining aromatic ring into the bonding system of the borolated part of 9 apparently stabilizes the aromatic ring against further attack. The reaction product obtained from m-xylene by the addition of two "borene" units represents a tricyclic structure 10 characterized by a six- and a five membered ring with boron atoms and a cyclopropane unit (ref. 8). The species 11 obtained from toluene contains four "borene" units and consists of a seven- and two five membered rings (ref. 8). Compounds 12 and 13 made from toluene and tert-butylbenzene consist of each a seven-, a six- and a five membered ring (ref. 5). The compounds 11 - 13 still contain one double bond in the seven membered  $\text{B}_2\text{C}_5$  ring. If the starting aromatic species carries substituents (as alkyl, trimethylsilyl, dialkylamino groups or a condensed second ring) double bonds are always retained next to the substituents, thus indicating, that carbon atoms carrying substituents other than H are not attacked by the subvalent boron species formed. Upon reacting 1,2,4,5-tetramethylbenzene with Na/K and  $\text{F}_2\text{BNPr}_2$  in glyme one obtains only the exocyclic disubstituted compound 14, formed by 1,4-addition of the fluoroborenoide moiety. If o-xylene is the starting material however, besides of 15 (which is isostructural to 14) also the bicyclic species 16 is formed by additional insertion of two "borene" units into the carbon skeleton. In 16 the double bond is fixed between the C atoms carrying the two methyl groups (ref. 9).

So far the species  $\text{C}_6\text{H}_6 \cdot \text{BNR}_2$  and  $\text{C}_6\text{H}_6 \cdot 6 \text{BNR}_2$  (or derivatives thereof) have not been isolated. This is due to the fact that the products with just one "borene" oligomerize rapidly and perhaps are less stable than species containing additional boron atoms. From the dianion of cyclooctatetraene (a 10  $\pi$ -species) however 17 has been isolated, which would suggest that a 1,4-addition is the first step of the reaction. However from FI-MS and  $^{13}\text{C}$ -NMR it must be concluded, that also a second species with the same mass is formed, containing the "borene" between two C-atoms with  $\text{sp}^2$ -geometry (ref. 10). On the other hand 18 is apparently the main product with acenaphthylene, a species were no 1,4-addition between two (CH) groups is possible (ref. 6). Also it shows that 1-methylnaphthalene is extremely difficult to be borolated, while 2-methylnaphthalene easily adds up to five borene units (ref. 5).  $\text{C}_6\text{H}_6 \cdot 6 \text{BNPr}_2$  has not been obtained in pure state so far.

According to the structural data obtained, substitution by boron appreciable lengthens the C-C bonds, so in 11 a (CC) bond which is substituted by 3 boron atoms is 159.6 pm, the bond between two C-atoms carrying 4 boron atoms is 164.2 pm long (ref. 8). The two (CC) bonds in D, prepared from  $\text{Pr}_2\text{-NB}(\text{Cl})\text{-CH}=\text{CH-B}(\text{Cl})\text{NPr}_2$  with Na/K and phthalocyanine palladium catalysis, are 165 and 169 pm long (both between C atoms of  $\text{sp}^3$ -geometry which together carry four B atoms) (ref. 11). The (BC) bond lengths are between 158 to 160 pm like those in other 3-dimensional boron carbon structures with classical bonding obtained recently by different methods (ref. 11, 12). Compounds 1 - 18 contain only three coordinated boron and three- or four coordinated carbon ( $\text{sp}^2$  and  $\text{sp}^3$  hybridization) and therefore are different from carboranes. The same is true for 19 which is obtained from norbornene and represents an uncomplexed 1,2,3-triborolane derivative (ref. 5, see also ref. 13). If however norbornadiene is the starting material,  $\text{C}_5\text{H}_6$  is eliminated from the reaction product in a retro Diels-Alder reaction and the corresponding 1,5-dicarba-closo-pentaborane(5) derivative 20 is formed (ref. 5). 20 has not to different structural parameters compared to 1,5-dicarba-closo-pentaborane(5) and its alkyl derivatives (ref. 14, 15), however quite different NMR-data indicating that 20 is rather to be described as a classical bonded system.

Benzene reacts with difluorosilylene to give a compound in which cyclohexadiene is bridged in 1,4-position by a difluorosilylene trimer (2,2,3,3,4,4-hexafluoro-2,3,4-trisilabicyclo[3.2.2]nona-6,8-diene) (ref. 16). This resembles the structure of 19. Also 21, the product of the reaction of the alkali metal complex of 2,2'-dipyridyl and  $\text{Cl}_2\text{BNPr}_2$  (ref. 17), corresponds to a species recently obtained from photolytically generated di-tert-butylsilylene and 2,2'-dipyridyl (ref. 18).

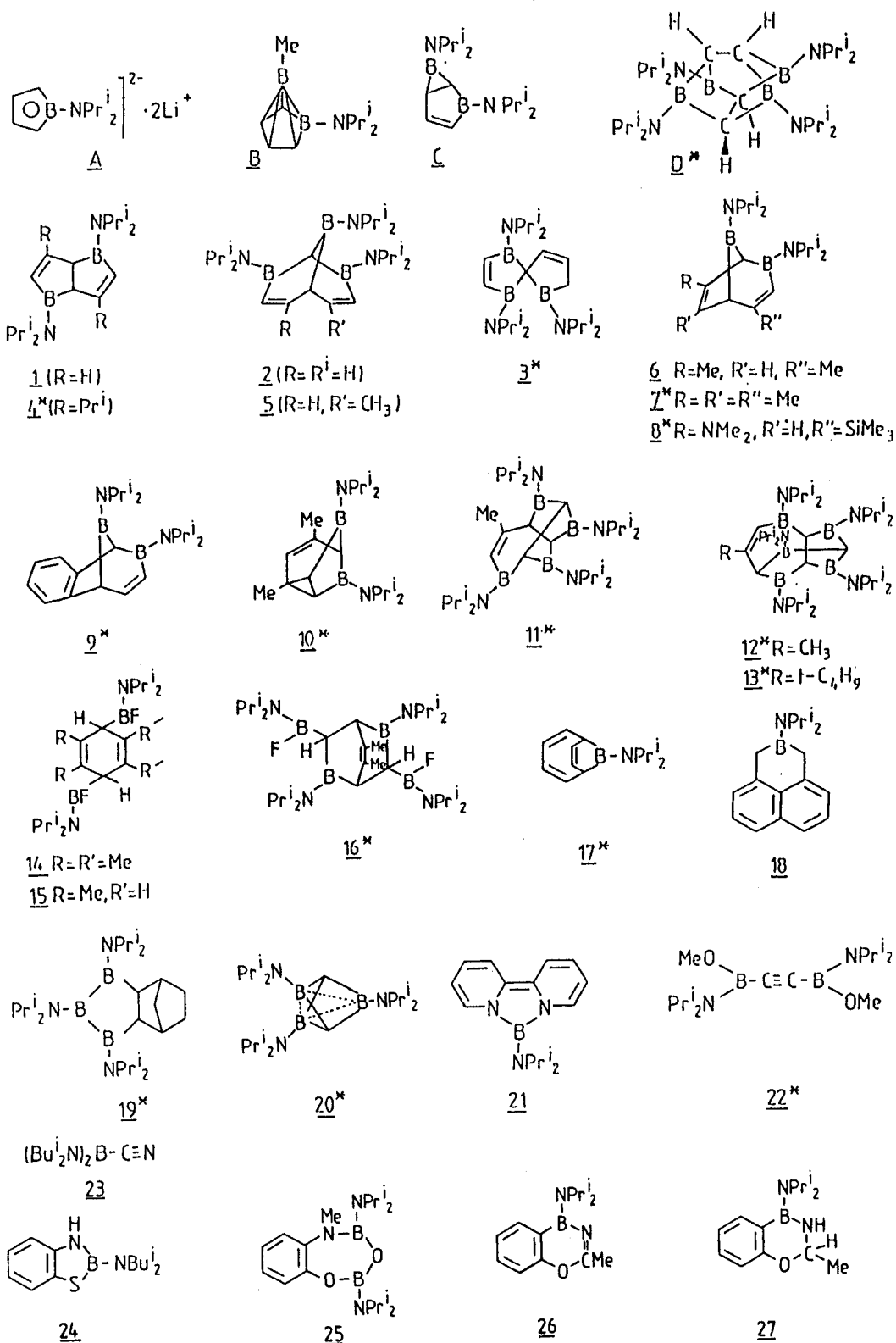
If aromatic compounds are used which show restrained reactivity towards the subvalent boron species generated, the "borene" species will attack the solvent, 1,2-dimethoxyethane, and diborolated ethyne 22 is formed under partial hydrogenation of the aromatic compound (ref. 6, also see ref. 19).

Furtheron the reaction of subvalent boron species has been studied with oxygen-, sulfur- and nitrogen heterocycles (ref. 20, 21). For example with benzothiazole compounds 23 and 24 have been isolated (ref. 20). From 2-methylbenzoxazole besides of  $(\text{PhO})_2\text{BNPr}_2$  and  $(\text{Pr}_2\text{N})_2\text{B-C}\equiv\text{N}$  compound 25 has been isolated and the formation of 26 and 27 substantiated by MS and NMR-spectroscopy (ref. 20).

Subvalent boron compounds generated by active metal dehalogenation of dihalogeno-(diorganyl-amino)-boranes are by far more reactive than carbenes. Even the formation of a free borene species " $\text{BNR}_2$ " in these systems cannot be substantiated unambiguously, products obtained support this assumption.

Certainly it would be of high interest to make use of today's facilities of structural characterization for the only example of a transition metal borenane complex,  $(\text{CO})_4\text{FeBNMe}_2$ , described 20 years ago (ref. 22).

TABLE 1 Letters denote compounds described by other authors. Numbers denote our own results. Compounds labeled with an \* have been characterized by x-ray structure analyses.



## REFERENCES

1. P.L. Timms, Accounts Chem. Research **6**, 118-123 (1973) and literature cited therein.
2. G.E. Herberich, H. Ohst and H. Mayer, Angew. Chem. **96**, 175-176 (1984).
3. A. Meller, D. Bromm, W. Maringgele, D. Böhler and G. Elter, J. Organomet. Chem. **347**, 11-16 (1988).
4. A. Meller, D. Bromm, W. Maringgele, A. Heine, D. Stalke and G.M. Sheldrick, J. Chem. Soc. Chem. Commun. 741-742 (1990).
5. A. Meller et al. unpublished results.
6. A. Meller, W. Maringgele, G. Elter, D. Bromm, M. Noltemeyer and G.M. Sheldrick, Chem. Ber. **120**, 1437-1439 (1987).
7. M. Noltemeyer, F. Pauer, D. Bromm and A. Meller, J. Cryst. C in press.
8. A. Meller, U. Seebold, W. Maringgele, M. Noltemeyer and G.M. Sheldrick, J. Am. Chem. Soc. **111**, 8299-8300 (1989).
9. A. Meller, U. Seebold, W. Maringgele and M. Noltemeyer, Chem. Ber. **123**, 967-970 (1990).
10. W. Maringgele, D. Stalke, A. Heine, A. Meller and G.M. Sheldrick, Chem. Ber. **123**, 489-490 (1990).
11. A. Krämer, H. Pritzkow, W. Siebert, Z. Naturforsch. **44b**, 96-98 (1989).
12. W. Haubold, W. Keller, G. Sawitzki, J. Organomet. Chem. **367**, 19-25 (1989).
13. A. Meller, D. Bromm, W. Maringgele, A. Heine, D. Stalke and G.M. Sheldrick, Chem. Ber. **123**, 293-294 (1990).
14. T. Onak, R.P. Drake and G.B. Dunks, Inorg. Chem. **3**, 1686-1689 (1964).
15. E.A. McNeill, K.L. Gallaher, F.R. Scholer and S.H. Bauer, Inorg. Chem. **12**, 2108/21 (1973).
16. P.L. Timms, D.D. Stump, R.A. Kent and J.L. Margrave, J. Am. Chem. Soc. **88**, 940-942 (1966).
17. W. Maringgele, D. Bromm and A. Meller, Tetrahedron **44**, 1053-1056 (1988).
18. M. Weidenbruch, A. Lesch and H. Marsmann, J. Organomet. Chem. **385**, C47-C49 (1990).
19. W. Maringgele and A. Meller, Z. Naturforsch. **44b**, 67-73 (1989).
20. I. Uzarewicz, W. Maringgele and A. Meller, Z. anorg. allg. Chem. (in press)
21. W. Maringgele and A. Meller, Z. anorg. allg. Chem. **572**, 140-144 (1989).
22. G. Schmid, W. Petz and H. Nöth, Inorg. Chim. Acta **4**, 423-427 (1970).