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Synthesis and characterization of compounds with boron–boron double bonds

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Abstract

The diborane(4) derivatives $Mes_2BB(Mes)Ph$ and $Me_2N(Ph)BB(Ph)NMe_2$ readily react with lithium powder in ether to give the doubly reduced salts $[\{(Et_2O)Li\}_2Mes_2BB(Mes)Ph]$ and $[\{(Et_2O)Li\}_2Me_2N(Ph)BB(Ph)NMe_2]$. Both species, which were isolated as red crystals, have been characterized by X-ray crystallography, ^{11}B NMR and electronic spectroscopy. The structural data reveal planar or almost planar B_2C_4 or $B_2C_2N_2$ cores with B–B distances near 1.63 Å (cf. B–B = 1.71 Å in the neutral non-planar precursors) consistent with the formation of a π-bond between the boron centers. Their ^{11}B NMR spectra display peaks that are shifted upfield relative to the starting compounds. In the case of the amido derivative, two B–N π-bonds were cleaved in the reduction process. The electronic absorption spectrum of this compound in Et_2O displays an intense absorption at 320 nm which may be attributed to the π–π^* transition of the B–B π-bond. This suggests that the strength of this bond is of the order of 40 kcal mol^{-1}. The compounds, which may be considered as boron analogues of the corresponding alkenes, represent the first structurally characterized acyclic species that possess formal B–B double bonds.

Introduction

Since the mid-1970s the isolation and characterization of stable compounds that involve multiple bonding between the heavier main group elements have undergone rapid development [1]. The investigations, however, have been dominated by derivatives of the fourth [2] and fifth [3] main groups that usually have sufficient numbers of electrons to fill their bonding molecular orbitals. In contrast, multiple bonding between the main Group 3 elements is much less well known, even in the case of the lightest element boron. In general, compounds of this group are more notable for their electron deficiency and the consequent absence of sufficient numbers of electrons to form multiple bonds [4]. In certain derivatives, however, the deficiency can be remedied by the use of substituent groups with lone-pairs of electrons. Thus, multiple bonding between boron and nitrogen [5, 6], oxygen [7], sulfur [8], and more recently, carbon [9, 10], phosphorus [11] and arsenic [12] is now well established. In these compounds, the multiple bond is usually formed by donation of lone-pair electron density from the ligand to an empty orbital on the boron. Unfortunately, this strategy is not so easily applied to homonuclear bonds between two boron centers. In this case, an alternative method for providing sufficient electron density for the formation of multiple bonds becomes necessary.

There are a number of reports in the literature where this problem has been partially overcome. For example, B–B moieties have been incorporated in various metal complexes of reduced six-membered quasi-aromatic rings [13–17]. In addition, the structures of a number of uncomplexed three-membered ring compounds containing B–B units in a 2π-electron quasi-aromatic system have been reported [18–20]. In these heterocycles, the stabilized ring π-orbitals provide the impetus for a delocalization that subsumes the B–B moiety. Boron–boron bond lengths as short as 1.58 Å [20] (cf. B–B single bond ~1.71 Å) have been observed in these compounds. Short B–B distances (~1.6 Å) have also been observed in the solid state structures of several binary transition metal borides which contain one-dimensional polyacene-type boron chains embedded in a three-dimensional metallic lattice [21, 22]. In this laboratory the object of some recent work has been the synthesis of reduced acyclic molecular species that have boron–boron multiple bonds. In this paper, the results obtained to date are summarized and, in addition, the prospects for their extension to the heavier elements Al, Ga or In are discussed.

Synthetic approach

Consider the unsaturated skeletal series illustrated by the structures **I–III**.

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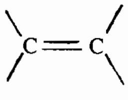
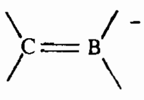
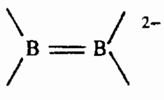


I



II

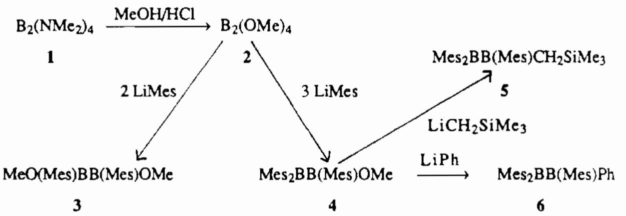


III

In essence, it is possible to sequentially replace C by B$^-$ to give a doubly-reduced diborane(4) species (**III**) that ought to possess a formal B–B double bond in a manner similar to ethylene. Prior work in this laboratory had reported the structural characterization of $[CH_2BMes_2]^-$ (a derivative of **II**) [10(a)] which, in earlier work, had been shown to form in solution [23]. The B–C distance in this compound (*c.* 1.44 Å), in addition to spectroscopic data, demonstrated that a double bond had indeed formed. These results suggested that the isolation of **III** would also be possible provided a suitable synthetic route could be found.

The most obvious pathway to such a compound is the direct double reduction of a B_2R_4 precursor to give a $[B_2R_4]^{2-}$ ion. Unfortunately, the range of B_2R_4 compounds is not large since the obvious synthetic route involving reductive coupling of XBR_2 does not generally give R_2BBR_2 products [24]. Stable examples of B_2R_4 compounds (R = alkyl or aryl group) are, in fact, quite rare and have only been relatively recently authenticated in the case of bulky ligands such as CH_2(t-Bu) and t-Bu [25, 26]. Even with these large groups the compounds decomposed in the relatively low temperature range of 50–100 °C. Interestingly, these compounds had been shown to undergo a one-electron reduction in solution to give the radical species $[B_2R_4]^-$ which presumably has a one-electron π-bond [27, 28]. Apparently, the addition stopped at the one-electron stage and a further reduction was not reported.

The synthetic objective in this laboratory was the isolation of B_2R_4 species with as high a thermal stability as possible and their subsequent double reduction under mild conditions to give the dianions $[B_2R_4]^{2-}$. It was hoped that the latter dianion would form crystals in the presence of suitable counter cations in order to enable these interesting species to be structurally characterized. Noting the utility of mesityl (Mes) substituents in stabilizing unusual boron compounds in other systems [7, 8, 10(a), 11], it was hoped that the use of this group would confer a similar stability on B_2R_4 compounds and related species. Also, encouragement was drawn from calculations on the hypothetical species $Li_2B_2H_4$ which predicted the presence of a strong B–B double bond [29]. Initial results in this area which include the isolation and structural characterization of such compounds are now described.



Scheme 1. Synthetic pathway to tetraorganodiborane(4) compounds.

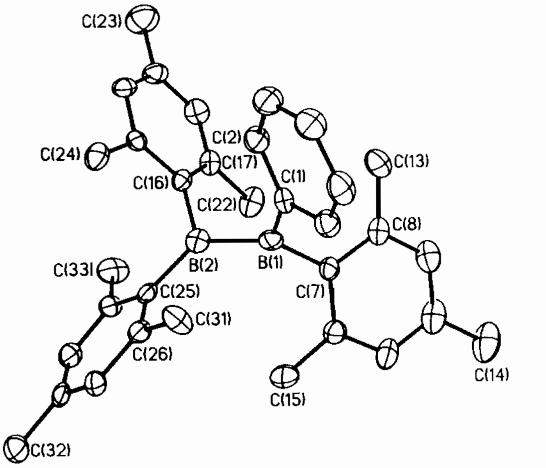
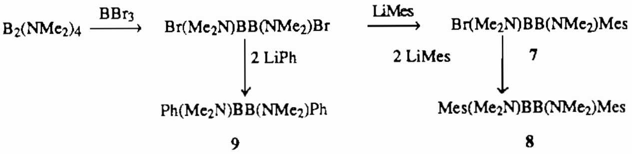


Fig. 1. Thermal ellipsoid plot of **6**. Important bond distances and angles are given in Table 1.



Scheme 2. Synthetic pathway to organoaminodiboron(4) compounds.

Synthesis of organodiboron(4) compounds

Precursor B_2R_4 compounds were made [30] by the sequence illustrated in Scheme 1. This synthetic route is adapted from that previously reported for the alkyl compounds B_2R_4 [25, 26] and is dependent on the readily prepared starting material $B_2(NMe_2)_4$ [31]. Interestingly, it has not proved possible to make B_2Mes_4 by this scheme. Apparently, the steric requirements of four Mes groups are too great and only three such groups can be accommodated. In this respect the reaction of $B_2(OMe)_4$ with LiMes resembles that with Li(t-Bu) which gives the product $(t\text{-}Bu)_2BB(t\text{-}Bu)OMe$ [25, 26]. The fourth–OMe may, however, be replaced by the less crowding CH_2SiMe_3, or Ph, moieties to afford the products **5** or **6** [30]. Compounds **3**–**6** have been characterized spectroscopically and structurally. Their structures [30] may be illustrated by that of **6** (Fig. 1) and they all possess B–B distances of about 1.70 ± 0.02 Å with high > 60° angles between the planes at the boron atoms. Other heteroleptic organodiborane(4) derivatives may be obtained by Scheme 2 [32]. Compounds such as **9** had already been obtained by the simple reduction of the precursor $XB(NR_2)R$ [33, 34]. However, this route has not been shown to give high yields of **8**, perhaps for steric reasons.

Reduction of organodiborane(4) derivatives

Reduction of the species $Mes_2BB(Mes)Ph$ can be readily accomplished in ether solution with lithium powder according to eqn. (1) [35].

$$\underset{\mathbf{6}}{Mes_2BB(Mes)Ph} \xrightarrow[Et_2O]{\text{excess Li}} \underset{\mathbf{10}}{[\{(Et_2OLi\}_2Mes_2BB(Mes)Ph]} \quad (1)$$

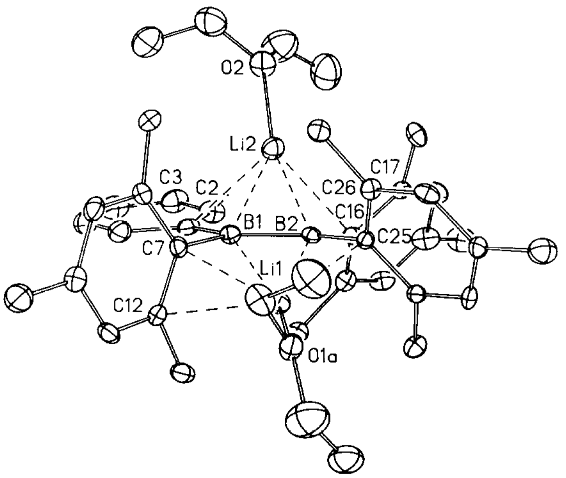
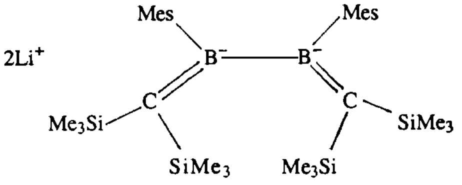


Fig. 2. Thermal ellipsoid plot of **10**. Some important bond distances (Å) and angles (°) not given in the text or in Table 1 are: Li(1)–O(1a) = 1.962(15), Li(1)–O(1b) = 1.927(22), Li(2)–O(2) = 1.918(15). Interplanar angles between the averaged planes at the following atoms are: B(1) and C(1) 6.3, B(1) and C(7) 86.8, B(2) and C(16) 56.8, B(2) and C(25) 56.6.

TABLE 1. Selected bond distances (Å) and angles (°) in **6** and **10**

	6	10
B(1)–B(2)	1.706(12)	1.636(11)
B(1)–C(1)	1.565(12)	1.613(11)
B(1)–C(7)	1.579(11)	1.648(7)
B(2)–C(16)	1.576(9)	1.642(10)
B(2)–C(25)	1.586(12)	1.643(11)
C(1)–B(1)–C(7)	115.1(7)	109.5(5)
C(10)–B(2)–C(25)	119.8(6)	108.9(6)
C(1)–B(1)–B(2)	116.9(6)	124.6(4)
C(16)–B(2)–B(1)	112.0(6)	122.2(6)
C(7)–B(1)–B(2)	127.8(7)	125.8(6)
C(25)–B(2)–B(1)	128.1(6)	128.8(6)
Angle between B(1) and B(2) planes	79.1	7.3

The reduction is accompanied by a change in the ^{11}B NMR chemical shift from about 100 to 25 ppm which is indicative of an increase in electron density at the boron center. The species **10** is obtained from Et_2O solution in good yield as red crystals. It represents the first isolation of a species containing a dianion of the formula $B_2R_4^{2-}$. Its X-ray crystal structure is illustrated in Fig. 2 [35]. The most notable features are the short B–B bond of 1.636(10) Å and near coplanarity of the two $\{BC(\mathit{ipso})\}_2$ moieties. The Li^+ ions, in addition to binding to ether, have close interactions with the borons and various carbon atoms. Further details of the structures of both **6** and **10** are provided in Table 1. The B–B bond is about 0.07 Å shorter than that (1.706(12) Å) in the precursor **6** [30]. This shortening is not as dramatic as the 10–12% expected for a B–B single → double bond transformation (cf. C–C → C=C, 1.54 → 1.34 Å). This can, most probably, be attributed to the Coulombic repulsion between two negative charges located on the two adjacent boron atoms which serves to lengthen the B–B bond in **10**. The significance of this factor in its effect on bond distance may be gauged from the species **11** [36] illustrated by



11

In this compound, which has a B–B single bond involving two negatively charged boron centers, the B–B distance is 1.859(6) Å [36]. Thus, the B–B bond length in **10** represents a shortening of about 0.22 Å relative to this value. The difference is consistent with the presence of a strong B–B π-bond and is in agreement with theoretical data for the hypothetical species $Li_2B_2H_4$ [29].

Although the strength of the B–B π-interaction in **10** is not accurately known at present, indirect experimental evidence that it is quite high comes from the reduction illustrated by eqn. (2) [37].

$$\underset{\mathbf{9}}{Me_2N(Ph)BB(Ph)NMe_2} \xrightarrow[Et_2O]{\text{excess Li}} \underset{\mathbf{12}}{[\{(Et_2O)Li\}_2Me_2N(Ph)BBPh(NMe_2)_2]} \quad (2)$$

The product **12** was isolated as red crystals which have been structurally characterized [37]. The data for **12** and its precursor **9** [32] are summarized in Table 2 and a drawing of **12** is provided in Fig. 3. The reduction is more complex than that in eqn. (1) in that it involves

TABLE 2. Selected bond distances (Å) and angles (°) for **9** and **12**

9		**12**	
B(1)–B(2)	1.714(4)	B(1)–B(1a) B(2)–B(2a)	1.631(9) 1.623(8)
B(1)–N(1)	1.405(3)	B(1)–N(1)	1.560(3)
B(2)–N(2)	1.392(3)	B(2)–N(2)	1.562(5)
B(1)–C(3)	1.584(3)	B(1)–C(8)	1.595(6)
B(2)–C(11)	1.586(3)	B(2)–C(13)	1.591(6)
C(3)–B(1)–N(1)	119.9(2)	C(1)–B(1)–N(1)	114.2(3)
C(11)–B(2)–N(2)	119.7(2)	C(13)–B(2)–N(2)	114.9(3)
C(3)–B(1)–B(2)	118.8(2)	C(1)–B(1)–B(1a)	126.4(4)
C(11)–B(2)–B(1)	117.9(2)	C(13)–B(2)–B(2a)	125.6(4)
N(1)–B(1)–B(2)	121.2(2)	N(1)–B(1)–B(1a)	119.4(3)
N(2)–B(2)–B(1)	122.4(2)	N(2)–B(2)–B(2a)	119.4(3)
Torsion angle between planes at boron	88.7	0	

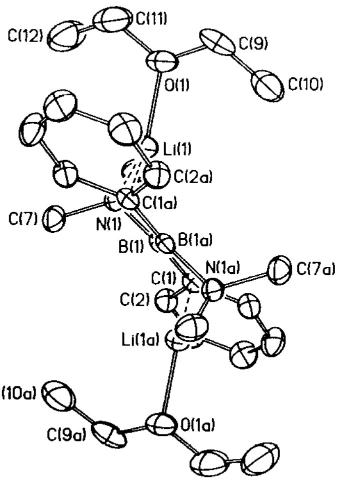
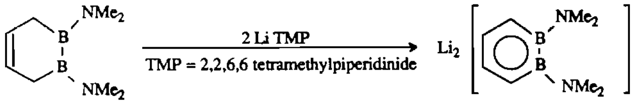


Fig. 3. Thermal ellipsoid plot of **12**. Important bond distances (Å) and angles (°) not given in the test or in Table 2 are: Li–O = 1.920(7) (1.916(7)), Li–N = 1.978(7) (1.977(7)), Li–C(*ipso*) = 2.251(7) (2.249(8)), Li–B = 2.281(8) (2.251(8)), Li–B(a) = 2.337(8) (2.304(8)). Angle between B(1) N(1) C(1) plane and the plane of the C(1) ring = 31.5°.

the cleavage of two B–N π-bonds during the formation of the B–B π-bond. Thus, in **12** the B–N bonds are about 0.16 Å longer than those in the precursor. Moreover, the $-NMe_2$ units are oriented ~90° with respect to the plane of the $B_2\{C(ipso)\}_2N_2$ core. In other words the B–N π-bonds in **9** have been completely broken during the reduction process. The B–B distance in **12**, which averages 1.627 Å long is very close to that seen in **10**. The ^{11}B NMR spectrum of **12** displays a broad singlet at 33 ppm whereas the corresponding peak for **9** appears at 49.3 ppm. The upfield shift upon reduction is indicative of an increase in electron density at the boron centers in spite of the elimination of strong π-donation by the $-NMe_2$ substituents.

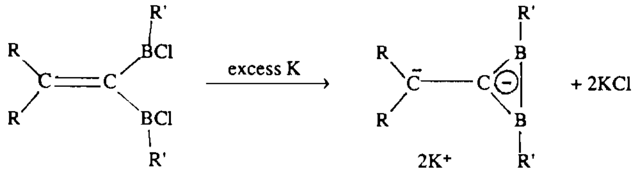
The facile reduction illustrated in eqn. (2), in which two B–N π-bonds are destroyed in the formation of the B–B π-bond, strongly supports the contention that the B–B π-bond is a stable one. The reduction is all the more remarkable in view of the strength of the B–N π-bonds which are probably in the range 20–25 kcal mol^{-1}. Corroborating evidence for considerable B–B π-bond strength comes from the electronic absorption spectrum of **12** which displays an intense peak at 320 nm. If this is taken to be indicative of the π–π* transition of the B–B π-bond, then an energy difference of ~90 kcal between the π and π* levels may be estimated. The energy of the π-bond should be somewhat less than half this value, perhaps near 40 kcal mol^{-1}.

With the exception of the prior report on the generation of the radical species $[B_2R_4]^-$ (R = t-Bu or CH_2(t-Bu) [27, 28] in solution, reductions of the type illustrated in eqns. (1) and (2) have not been previously described. The closest analogy to the species **10** and **12** known in the literature is the ring compound **13** which was synthesized as indicated by the process in eqn. (3).



13 (3)

In this reaction two carbon centers bonded to the borons are deprotonated to generate the dilithium dianion salt **13** [14]. This features an almost planar quasi-aromatic C_4B_2 ring with a B–B distance of 1.706(8) Å and B–C and B–N exocyclic distances of 1.505(6) and 1.495(5) Å. In addition, the diboriranide salt **14** generated according to eqn. (4)



14 (4)

has been reported [38]. The structural data [20] for this interesting species show that a B–B multiple bond of 1.580(12) Å exists in the three-membered ring. The dianions **13** and **14**, as well as the six-membered ring complexes of transition metals and the quasi-aromatic three-membered NB_2 rings mentioned earlier, obviously possess a considerable degree of B–B π-bonding. Nonetheless, compounds **10** and **12** are distinct in that (i) the reduction directly involves the B–B moiety and (ii) the B–B moiety which does not form part of an extended delocalized π-system. In effect, the driving force for the reduction involves only the formation of the B–B π-bond and the solvation of the Li^+ ions by ether and the dianion.

Currently, nothing is known about the reactions of **10** and **12** and it is anticipated that these and related species will possess a rich chemistry. A further point of interest regarding **10** and **12** is that their overall general formula $Li_2B_2R_4$ corresponds to a dimer of a lithiumdiorganoboronide $(LiBR_2)_2$. The differences in structure between these lithium derivatives and the lithium salts of alkyls, aryls or amides also suggest a unique reactivity pattern. It may also be possible to extend the results described above to the heavier members of the group. Several recent reports have disclosed the isolation and structural characterization of compounds of the type M_2R_4 (M = Al, Ga, In; $R = CH(SiMe_3)_2$) [39–41]. Species of this type, or related compounds with aromatic or amide substituents, should also be susceptible to reductions similar to those described in eqns. (1) and (2).

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