Behavior of 1,3-Di(*tert*-butyl)-2,4-bis(tetramethylpiperidino)-1,3,2,4-diphospha-diboretane towards Boron Halides and Adduct Formation of a Bicyclo[1.1.0]diphosphadiboretane with Tris(pentafluorophenyl)borane [1]

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Z. Naturforsch. **61b,** 265 – 274 (2006); received December 8, 2005

Dedicated to Prof. Dr. H.-G. Schnöckel on the occasion of his 65th birthday

While the diphosphadiboretane (*t*BuP=Btmp)$_2$, **1**, reacts with boron trihalides BX_3 (X = Cl, Br, I) with BN cleavage producing a number of unidentifiable products, a new tricyclic BP ring system **2**, containing B_3P_3, PB_2C_2 and C_6 rings, results from the combination of $PhBCl_2$ and **1**. B-Chlorocatecholborane and **1** give access to the diborylphosphane **3**, tmpBCl-P*t*Bu-cat (cat = $C_6H_4O_2B$). This shows that the selectivity of the reactions increases as the Lewis acidity of boron halide decreases. The structure of compounds **2** and **3** were determined by X-ray structure analysis. The bicyclic (tmpBP)$_2$ **4** forms no adducts with MeI, CF_3SO_2Me or $Ph_3C(SnCl_5)$. However, it adds $B(C_6F_5)_3$ to give **10**, the first BX_3 adduct of this bicycle that is fully characterized including its molecular structure.

Key words: Diphosphadiboretanes, Bicyclodiphosphadiboretane, Reactivity, NMR Spectra, X-Ray Structure Analysis

Introduction

The reaction chemistry of 1,3,2,4-diphosphadiboretanes [2 – 7], the bicylic [1.1.0]diphospha-diboretanes $(R_2NBP)_2$ (R_2N=Et_2N, *i*Pr, 2,2,6,6-tetramethylpiperidino (tmp) group) [8, 9], and tricyclic $(R_2NB)_2P_2(EX_n)$ cages [2, 10] has been partially explored with several classical Lewis acids and a multitude of metal carbonyls [2 – 14]. In particular, the trihalides of Al, Ga or In react with 1,3,2,4-diphosphadiboretanes either with formation of adducts $(tmpB{=}PR)_2 \cdot EX_3$ [15, 16] or by BP bond opening to generate a boraphosphinidene molecule $tmpB{=}PR(EX_3)$ [17]. Adduct formation is also observed in the case of the bicyclic $(tmpB)_2P_2$ with metal carbonyls, *e. g.* $CpMn(CO)_3$ [18]. However, the behavior of the two types of BP compounds towards boron halides has not yet been reported except for the formation of the adduct $(tmpBP)_2(BBr_3)_2$ [18], which was characterized only by analytical and NMR methods. Some reactions of boron halides with the diphosphadiboretane (tmpB=P*t*Bu)$_2$, **1**, are reported here, one of them yielding an unexpected new BP heterocyclic system.

Reactions of $(tmpB{=}PCMe_3)_2$ with Some Boron Halides

Reactions of boron trihalides BX_3 with **1** may lead to a variety of interesting and still unknown boron phosphorus compounds. Several possibilities are depicted in Scheme 1. Most likely the first step results in the formation of addition products **A** or **B**. The boron trihalides may of course also attack at the nitrogen atom of the tmp substituent. So far we have never observed BX_3 addition to this group although this might be expected since cleavage of the BN bond of tmp-boranes is quite common. Ring opening of the 1,3,2,4-diphosphadiboretanes generates product **C** which may form a new ring **D**. Provided that BN cleavage occurs to generate the unknown diphosphadiboretanes **E** these may react with more BX_3 to give either compounds of type **G** or **F**. Compounds of type **F** have already been reported [19], but not yet for boron halide groups.

In the present study, we examined reactions of **1** with BCl_3, BBr_3 and BI_3 using reactant ratios from 1 : 1 to 1 : 2. In all cases mixtures of various boron compounds were observed by ^{11}B NMR spectroscopy, but no single reaction product was isolated in a pure

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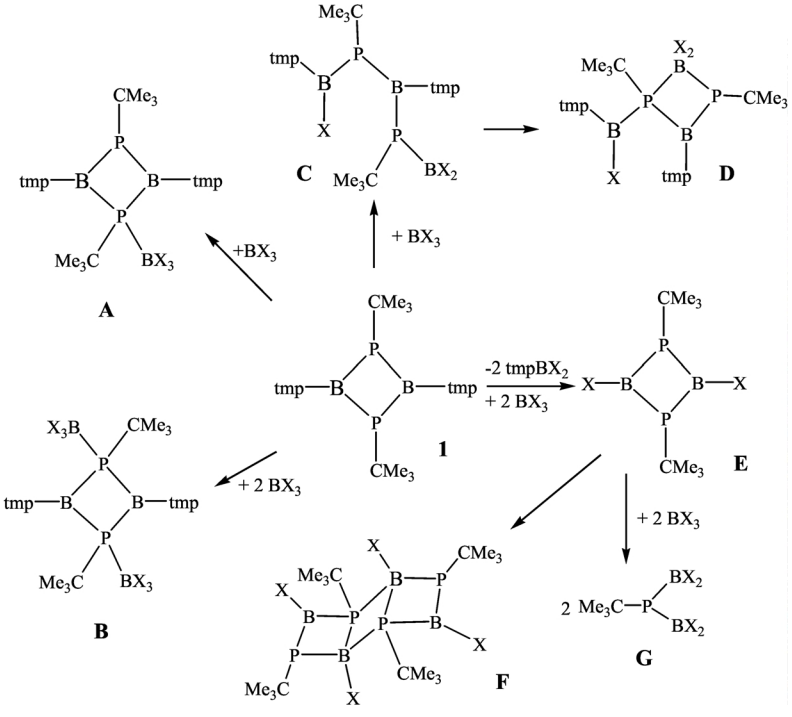
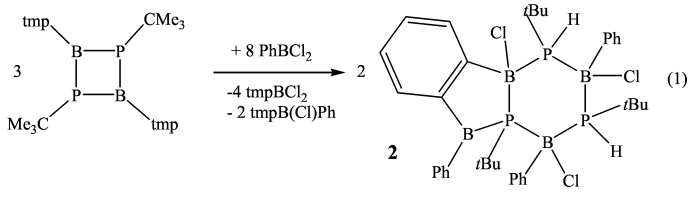


Scheme 1.

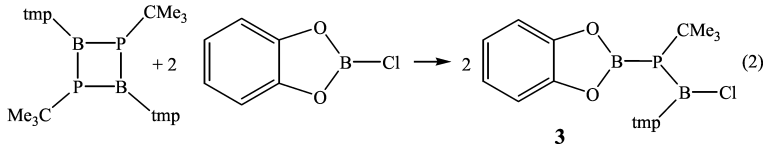


state. In case of BCl_3 the ^{11}B NMR data show clearly that BN bond cleavage takes place with formation of $tmpBCl_2$ ($\delta^{11}B = 33.8$ ppm) [20]). The 1 : 1 reaction of **1** with BBr_3 in toluene at -50° led to two broad ^{11}B NMR signals at -8.8 and 18.4 ppm suggesting the formation of two products, but at room temperature new signals emerged. The reaction of **1** with BI_3 led to the iodoborane tmp_2BI ($\delta^{11}B = 26.5$ ppm) [21]). In addition, during the reaction of BI_3 with **1** a doublet ($\delta^{11}B = -57.4$ ppm, with $^1J(BP) = 40$ Hz) and a triplet ($\delta^{11}B = -43.1$ ppm with $^1J(BP) = 50$ Hz) was observed indicating the formation of BI_3 adducts at the P-atoms.

The boron trihalides are obviously too reactive to allow selective reactions. Therefore, we replaced them by the less Lewis acidic $PhBCl_2$. In this case the reaction products were independent of the stoichiometry used. The tricyclic 9-bora-2,4,6-triboratabicyclo[4.3.0^{1,6}]-nonane, **2**, was the main product accompanied by $tmpBCl_2$ and tmpB(Cl)Ph. For maximal yield of **2** a 3 : 8 (**1** : $PhBCl_2$) stoichiometry was required as shown in eq. (1). Below -40 °C no reaction according to eq. (1) was noted.

It is obvious that a number of consecutive reactions are necessary to arrive at compound **2**.

Most likely $PhBCl_2$ adds to **1** by opening of B-P bonds with formation of the diborylphosphane PhClB-*t*BuP-BCl(tmp). Elimination of $tmpBCl_2$ from this intermediate should generate *t*BuP=BPh which on trimerization could form the six-membered (*t*BuP=BPh)$_3$. Addition of $PhBCl_2$ to this ring across one of its BP bonds would generate a cyclic intermediate ClPhB(*t*BuPBPh)$_3$Cl. Orthoboration of one of the phenyl groups by HCl elimination could then form a benzodiboryl system. Addition of the HCl generated in this process to two BP bonds should finally yield the tricyclic compound **2**. This reaction sequence is, of course, speculative but some of the steps are typi-



3

cal in BP chemistry. According to eq. (1) the yield of **2** should not exceed 51% based on boron. The actual yield was 54%.

The rather unexpected formation of **2** shows, however, that a reduced Lewis acidic character of the boron halide might induce higher selectivity with **1**, and one may surmise that a monohaloborane would be an even better choice than $PhBCl_2$. This is indeed the case as observed for the reaction of **1** with catecholchloroborane which yields the diborylphosphane **3** as shown in eq. (2). In contrast to the formation of **2** no BN bond cleavage was observed in this case.

NMR Spectra and Molecular Structures of 2 and 3

The structure of compound **2** could be deduced from its NMR data. These showed two broad ^{11}B NMR signals at 29.8 and −4.0 ppm in a 1 : 3 ratio, assigned to a tricoordinated boron atom and three tetracoordinated boron atoms, respectively. Although atom B2 is not chemically equivalent to B1 and B3, both are bound to two P atoms, one Cl and one C atom. Therefore, the chemicals shifts for these three boron atoms should not differ much. This explains that only one signal is observed for these two atoms. No BP coupling was noted for all ^{11}B resonances, a well known phenomenon which is due to the large quadrupole moment of the boron atom as well as the asymmetry induced by the substituents. There are three ^{31}P resonances, two of them are doublets in the ^{1}H coupled spectra indicating the presence of PH groups. The assignment to atom P1 is unambiguous as there is no H atom bonded to this P atom. Because δ^{31}P and $^{1}J(^{31}\mathrm{P}^{1}\mathrm{H})$ are rather similar for the PH type P atoms no assignment either to P2 or P3 is possible. This is true also or $^{3}J(^{31}\mathrm{P}^{1}\mathrm{H})$ found for the protons of the *t*Bu groups; although there are three signals for *t*Bu groups, the coupling constants $^{3}J(^{31}\mathrm{P}^{1}\mathrm{H})$ are equal for all on them (14 Hz). In addition there are two signals for the ^{1}HP protons which are doublets of doublets with $^{1}J(^{31}\mathrm{P}^{1}\mathrm{H}) = 370$ and 350 Hz, and $^{3}J(^{31}\mathrm{P}^{1}\mathrm{H}) = 3$ Hz for both. The aromatic CH potons give rise to many signals in the region 5.6 to 7.6 ppm. Unspectacular are the ^{13}C resonances for the *t*Bu group: there are three signals each for the methyl groups and the quarternary C atoms showing $^{1,2}J(^{31}\mathrm{P}^{13}\mathrm{C})$ coupling. In addition, 13 ^{13}C signals were observed for the benzo- and phenyl groups. Obviously the C atoms of two phenyl rings are magnetically equivalent. Actually, 14 signals should be found because NMR signals of ^{13}C atoms bonded to the ^{11}B atoms are generally not recordable. As no specific decoupling experiments had been performed no information regarding the relative positions of the *t*Bu and Ph

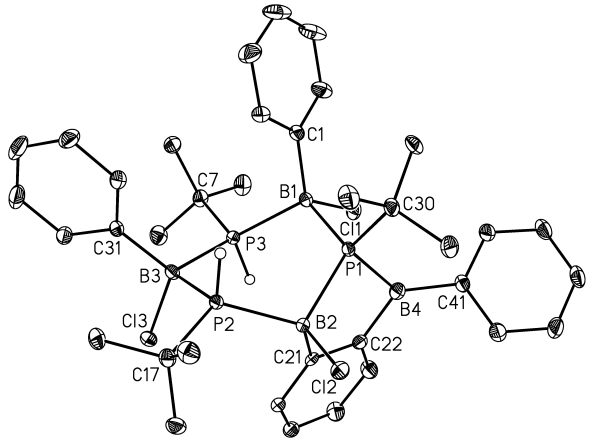


Fig. 1. Plot of the molecular structure of compound **2**. Thermal ellipsoids are presented on a 25% probability scale. Selected bond lengths (in Å): P1–B1 2.029(4), P1–B2 2.013(4), P1-B4 1.956(5), P1–C30 1.887(3), P2–B2 2.003(4), P2–B3 1.995(4), P2–C17 1.880(4), P2–H2 1.24, P3–B1 2.016(4), P3–B3 2.039(4), P3–C7 1.872(4), B1–C1 1.589(5), B1–Cl1 1.909(4), B2–Cl2 1.865(4), B2–C21 1.608(5), B3–C31 1.616(5), B3–Cl3 1.883(4), B4–C22 1.537(5), B4–C41 1.571(6), C7–C10 1.532(5), C7–C8 1.535(5), C22–C23 1.401(6). – Selected bond angles (in degrees): P2–B3–P3 106.0(2), B3–P2–B2 115.0(2), P1–B2–P2 108.1(2), B1–P3–B3 122.3(2), P3–B1–P1 110.3(2), B4–P1–B1 92.2(2), P1-B1-P3 110.4(2), B2–P1–B1 113.3(2), B1–P1–C30 117.1(2), B4–P1–B2 92.2(2), B3–P1–C30 117.0(2), B3–P2–C7 112.0(2), B2–P2–C17 117.3(2), B3–P2–H2 99.7, B2–P2–H2 106.5, B1–P3–C7 112.0(2), B1–P3–H3 102.4, C1–B1–C11 112.6(3), P2–B2–C21 116.4(2), P1–B2–Cl2 111.3(2), C21–B2–Cl2 110.6(3), P2–B2–Cl2 110.1(2), P3–B1–Cl1 104.1(2), P1–B4–C41 130.0(3), Cl3–B3–C31 125.0(3). – Torsion angles: P1–B4–P3–B2 −46.0, B–4–P3–B2–P2 30.2, P3–B2–P2–B3 27.8, B2–P2–B3–P1 −70.4; P2–B3–P1–B4 51.1, B3–P1–B4–P3 1.5, B4–P1–B2–Cl2 89.5, B4-C22-C21-B2 −4.3, C21-B2-P1-B4 −27.3, C21-C22-B4-P1 −17.9, C22–C21–B2–P1 23.2.

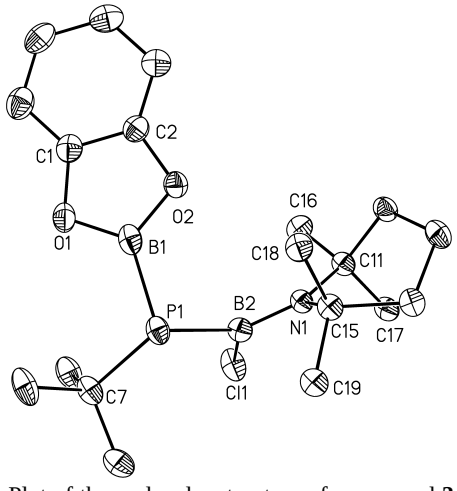


Fig. 2. Plot of the molecular structure of compound **3**. Thermal ellipsoids are presented on a 25% probability level. Selected bond lengths (in Å): P1–B1 884(6), P1–B2 1.933(5), B1–O1 1.389(6), B1–O2 1.390(6), Cl1–B2 1.808(5), B2–N1 1.395(6), N1–C11 1.526(5), N1–C15 1.530(5), O1–C1 1.379(5), O2–C2 1.380(5), C1–C2 1.373(7), C4–C5 1.390(8). – Selected bond angles (in degrees): C7–P1–B1 107.9(2), C7–P1–B2 114.0(2), B1–P1–B2 97.6(2), P1–B1–O1 126.7(3), P1–B1–O2 122.2(3), O1–B1–O2 110.8(4), P1–B2–Cl1 117.5(2), P1–B2–N1 122.8(4), N1–B2–Cl1 119.8(4), C11–N1–C15 117.6(3), B1–O1–C1 105.4(3), B1–O2–C2 105.2(3). Angle between planes (in °): O_2B/P1 B2 C7 = 117.3, C11 N1 C15/ P1 B2 Cl1 127.2.

groups can be given. However, these were determined by X-ray crystallography.

Compound **2** crystallizes in the monoclinic system space group $C/2c$ with $Z = 8$. Fig. 1 depicts its molecular structure. The six-membered B_3P_3 ring adopts a strongly distorted tub shape while the five-membered C_2B_2P ring is present in an envelope conformation with atom P1 flipped up. The phenylene ring is coplanar with the B2C21C22B4 plane. The torsion angles for the six-membered B3P3 ring range from $-70.4°$ to 51.1° with B2–P1–B1–P3 as small as $-1.7°$. The phenyl and *t*Bu groups are arranged in *anti* conformation.

The BP bonds are practically of equal lengths (avg. 2.021(4) Å); only the bond B1–P1 is shorter (1.956(5) Å), a consequence of the tricoordinated B1 atom. This shortening is also observed for the B1–C1 bond (1.550(6) Å) compared with the BC bond lengths of the phenyl groups bonded to tetracoordinated B atoms (range of 1.593(6) to 1.619(6) Å). Two of the three BCl bonds are of equal lengths (1.886 Å) while the bond B3–Cl3 is significantly longer (1.912(5) Å). This may be due to the fact that atom B3 is part of the six- and five-membered rings.

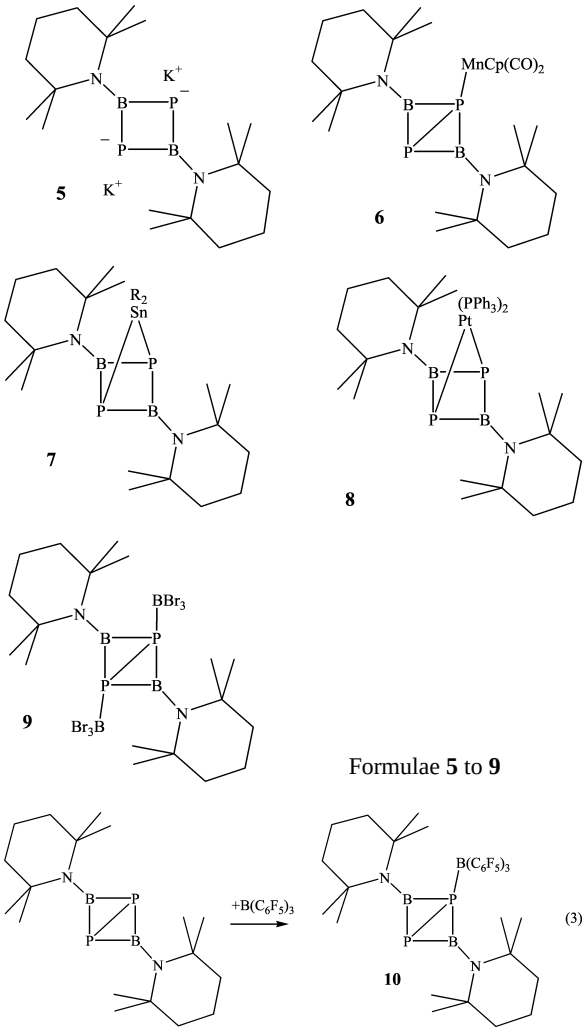
The diborylphosphane **3** is a new type of a diborylphosphane. Its NMR data are in accord with the suggested structure. Fig. 2 shows its molecular structure as determined by X-ray crystallography. The two tricoordinated boron atoms are present in a planar environment, and the structural parameter values of the catecholatoboryl unit compare well with those already reported [22, 23]. Due to an acute OBO bond angle of 110.8(4)°, the two P-B-O bond angles are larger than 120°: 126.7(4) and 122.1(4)°. The BP bonds are 1.884(6) (to B1) and 1.933(5) Å (to B2). The shorter bond to the catecholatoboryl moiety may be due to the stronger Lewis acidic character of this boron atom compared with B2 which carries the tetramethylpiperidino group. Its six-membered ring shows a twist conformation with a planar nitrogen atom, a rather rare conformation for tetramethylpiperidino boranes. The most often observed conformation for the tmp group with its planar N atom is the semichair conformation [24 – 26].

The B2–N1 bond is comparatively long with 1.395(6) Å for an sp^2B-sp^2N bond. The C_2N plane forms an angle with the B2P1Cl1 plane of 37.6°, and this still allows BN-π-bonding. On the other hand, the O_2B plane is twisted against the B1P1B2 plane by 41.8°, while the torsion angle C7P1B2Cl1 is 15.1°, the closest angle to planarity. A pyramidal configuration is found for the P atom.

Reaction of Bis(tetramethylpiperidino)bicyclo(1.1.0)-1,2,3,4-diphosphadiboretane with Lewis Acids

The bicyclic diphosphadiboretane **4** is an interesting molecule. Steric strain in its P_2B_2 three membered rings offers high reactivity. **4** reacts with potassium with opening of the PP bond to form an 1,3,2,4-diphosphadiboretanide anion **5** [8]. It also adds oxidatively stannylenes or platinum(0) complexes with formation of tricyclic systems such as **7** or **8** [22], or adds transition metal fragments such as $CpMn(CO)_2$ to give **6** [18]. Also, BBr_3 adds to **4** in a 1 : 2 ratio to give the adduct **9** [18] while diborane cleaves its B-N bonds with formation of $tmpBH_2$ [18].

Attempts to react **4** with the electrophiles $Ph_3C[SnCl_5]$ or MeI were unsuccessful even under reflux conditions. However, methyltriflate reacted already at -60 °C but no well defined reaction product was found. The Lewis acidic boron compound



$B(C_6F_5)_3$ forms only a 1 : 1 addition product **10** as shown in eq. (3). The addition sets in at about −30 °C.

Two broad ^{11}B NMR signals in a ratio of 1 : 2 were observed for **10** at −7.0 and 40.6 ppm. Also two very broad ^{31}P signals at −294.8 and −244.6 ppm were recorded. We assign the latter to the P atom that is coordinated to $B(C_6F_5)_3$ on the basis of its larger line width because this P atom is bonded to three boron atoms. Compared with the ^{31}P resonances found for compound **4** the tetracoordinated P atom is better shielded by 5 ppm, while the tricoordinated P atom is deshielded by 45 ppm. Due to the large line width no PP coupling could be observed.

Three ^{19}F resonances demonstrate that the pentafluorophenyl groups are magnetically equivalent with free rotation about their BC bonds.

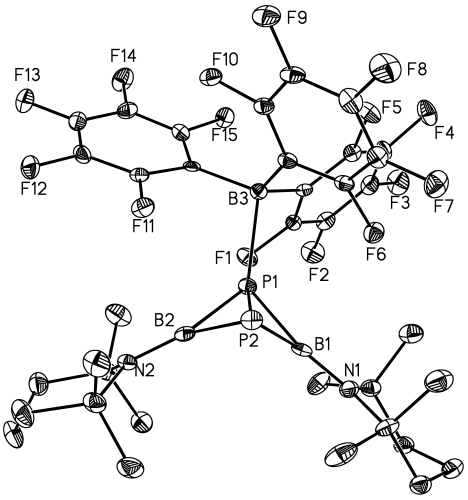


Fig. 3. Plot of the molecular structure of compound **10**. Thermal ellipsoids are presented on a 25% probability scale. Selected bond lengths (in Å): P1–P2 2.280(2), P1–B1 1.919(6), P1–B2 1.909(5), P2–B1 1.905(5), P2–B2 1.896(5), B1–N1 1.368(6), B2–N2 1.380(6), P1–B3 2.120(6), B3 C19 1.636(6), B3–C25 1.622(7), B3–C31 1.632(6); C–F1 to F5: 1.356(5), 1.345(5), 1.341(5), 1.347(5), C 1.351(5). – Selected bond angles (in degrees): B1–P1–B23 81.9(2), B2–P1–B3 132.2(2), B1–P1–B3 132.5(2), B3–P1–P2 52.9(2), B3–P1–P2 115.9(2), B1–P1–P2 53.1(2), B3–P1–P2 115.9(2), B2–P2–B1 82.6(2), B1–P2–P1 53.7(2), B2–P2–B1 82.6(2), B1–N1–C1 118.3(4), B1–N1–C5 120.9(4), C1–N1–C5 120.0(4), B2–N2–10 117.9(4), B2–N2–C14 120.5(4), C10–N2–C14 119.0(4). Angles between planes (in °): P1B2P2/P1B1P2 105.0, C1N1C5/P1B1P2 11.5, C10N2C14/P2B2P1 10.9.

The presence of the tmp group is demonstrated by two proton NMR signals at 1.18 ppm for the methyl groups and a broad multiplet centered around 1.25 ppm for the CH_2 units. The intensity ratio for these two signals is 2 : 1. Compared with other tmp-boranes [24–26] the proton signals are found at unusually high field. There is only a single signal for the methyl groups at 25 °C indicating free rotation of the tmp groups about its BN bond. On the other hand, two ^{13}C NMR signals were observed for the methyl groups besides two singlets for the other *C*H_2 groups of the tmp ring, and a single signal for the *C*Me_2 atom. In case of hindered rotation about the BN bonds four non-equivalent Me groups should be observable.

The molecular structure of **10** is shown in Fig. 3. The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. The bicyclic structure is retained by the addition of $B(C_6F_5)_3$. The roof angle between the two P_2B units is 105.2°, which is close to that found for **4** [8]. However, it is much smaller than in the

cation *t*BuP(Btmp)$_2$P$^+$ [14]. The four B–P bonds are of equal lengths (3σ-criterion). The average length is 1.907 Å, which is practically the same as found in **4** (1.91 Å).

In the solid state, the BN bonds are comparatively short (1.368 and 1.380 Å), close to the value of 1.34 Å for a B=N double bond. Nevertheless, above 30 °C in solution there seems to be free rotation about these bonds, which is obviously frozen in the solid state.

The BP bond to the tetracoordinated B atom is 2.210 Å and lies on the longer side for borane phosphane adducts [27–33], but corresponds to the 2.181 Å found for Ph$_3$P-B(C$_6$F$_5$)$_3$ [34].

Discussion and Conclusions

Reactions of **1** with BX$_3$ (X = Cl, Br, I) were erratic. In case of BCl$_3$ the main product was tmpBCl$_2$. Its ^{11}B NMR signal was accompanied by several other less intense signals indicating to the presence of tetracoordinated boron atoms. None of these signals showed BP coupling. Therefore, it is difficult to assign these resonances to BCl substituted phosphinoboranes. Surprisingly, only two ^{11}B NMR signals were observed by following the reaction of **1** with BBr$_3$ at low temperature. However, the chemical shifts do not fit with a BBr$_3$ adduct to a triorganylphosphane such as Br$_3$B · PMe$_3$ (δ^{11}B = −14.5 ppm [35]) or Br$_3$B · PPh$_3$ (δ^{11}B = −14.2 ppm [36]). Adducts of BBr$_3$ with phosphinoboranes are unknown at present. The reaction of **1** with BI$_3$ furnished only three ^{11}B NMR signals. That at low field seems to be due to tmpBI$_2$ [20], while two more signals in the range for tetracoordinated boron atoms show BP coupling. This indicates the formation of either a BI$_3$ adduct with **1** or a phosphine-borane containing tetracoordinated B and P atoms. So far only phosphinoboranes of the type (X$_2$B-PR$_2$)$_3$ [X = F, R = Me [37]; (X = Cl, R = Me, Et, Ph [37, 38]; X = Br, R = Me, Et, Ph [34–36]; X = I, R = Me. Ph [34, 35]) or of the type [Hal$_2$B-PHR]$_3$, or [HalRB-PR$_2$]$_3$ have been characterized by NMR methods, and the crystal structures of only a few of type [H$_2$P-PR$_2$]$_3$ (R = Me [39]; R = Ph [39]; R = SiMe$_3$ [40]) have been reported.

By contrast, the reaction of **1** with PhBCl$_2$ leads to the well-defined new tricyclic BP compound **2** containing three tetracoordinated P atoms two of which are bonded to a hydrogen atom. One of the four boron atoms of this heterocycle is tricoordinated, the other three are tetracoordinated. The compound is formed by breaking the BN bonds to the tetramethylpiperidino groups of **1** with formation of tmpBCl$_2$ and Ph(tmp)BCl as shown in eq. (2). At which stage the orthoboronation of a phenyl group occurs remains an open question as well as at which stage the PH group formation sets in. In order to formulate a stoichiometric equation for the formation of **2** from PhBCl$_2$ and **1** one has to assume that not only tmpBCl$_2$ is formed, the formation of which is definitely observed amongst the reaction products by ^{11}B NMR (δ = 37.6 ppm) [20], but also Ph(tmp)BCl, to which a signal at δ = 40 ppm can be assigned [34].

The PH groups show up in the ^{31}P NMR spectra as broad doublets, but no BP coupling is observed. The relative orientation of the two P-H bonds and P-CMe$_3$ bonds could not be determined by NMR experiments but turned out to be *trans* as determined by X-ray structure analyses of **2**. The structure determination also showed a planar benzo group, a PB$_2$C$_2$ ring in envelope conformation, and a highly distorted six-membered B$_3$P$_3$ ring as deduced from the ring torsion angles (for data see Fig. 1). In contrast, all known phosphinoboranes of type [R$_2$P-BH$_2$]$_3$ posses a chair conformation. To our knowledge no crystal structure of a six-membered phosphinoborane [R$_2$P-B(Hal)$_2$]$_3$ is known in contrast to known structures for [R$_2$P-BH$_2$]$_3$ [40, 41] and trimeric phosphinoborenes (RP-BR')$_3$ [2]. It is not unexpected that the BP bond at the *tri*coordinated B4 atom is shorter by 0.046 Å than the average B-P bond length to the *tetra*coordinated B atoms. Similarly, the BC bond at the *tri*coordinated B4 atom is 0.043 Å shorter than those at the *tetra*coordinated B atoms. In general, B-P bond lengths of phosphane-boranes are influenced by the boron substituent as well as by the steric demand of the triorganylphosphane components [23–28, 37–43].

Finally it is worthwhile noting that the lengths of the boron-bonded C=C group of the five membered B$_2$C$_2$P ring is elongated by 0.051 Å compared with the other C-C bonds of the benzo ring. Therefore, the endocyclic C-C-C bond angles vary significantly.

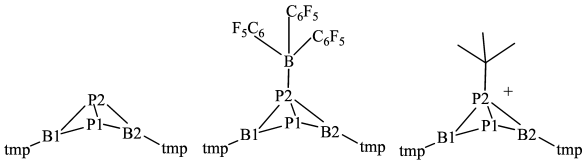
Compound **3** is a typical diborylphosphane, but it is so far unique as no diborylphosphane carrying a O$_2$B and a B(N)Cl boryl group is yet known. Those known either carry aryl groups and/or amino groups [2]. Amongst these, compounds RP(Bmes$_2$)$_2$ and mesP(BmesCl)$_2$ show planar or almost planar configuration at the P atoms (360° and 354.3°, repectively) [44, 45]. In contrast, the P atom of **3** has a pyramidal conformation. The sum of bond angles at the P atom

is 319.5°, while the B-P-B bond angle is 97.6°. Therefore, there is no BP-π-bonding in **3**, and, consequently the BP bonds involving the BO_2 group and the BClN group (1.884(6) Å and 1.933(5) Å) are longer than in $PhP(Bmes_2)_2$ (1.871(2) Å) and $mesP(BClmes)_2$ (1.853(4) Å [44, 45]. The shorter of the two BP bonds in **3** is due to the small O-B-O bond angle (110.8(4)°) and B-O-π-bonding as well as the inductive effect of the oxygen atoms. The longer BP bond results from BN-π-bonding as shown by the short BN bond length of 1.395(6) Å and the presence of a planar N atom. The tmp ring, however, does not show the usual chair or half chair conformation as found for many boranes carrying a tmp group [45–48] but is twisted. However, in solution only a single signal for the Me groups is observed in the ^{13}C NMR spectrum, indicating free rotation about its B-N bond and/or ring inversion.

While the diphosphadiboretanes readily form 1 : 1 and 1 : 2 complexes with transition metal carbonyl fragments [2], there is scarce information about adduct formation of the bicyclic B_2P_2-species **4** particularly with Lewis acids of the main group elements. So far only **4** · BBr_3 has been characterized by NMR spectroscopy, while attempts to prepare $\mathbf{4} \cdot (BH_3)_n$ $(n = 1, 2)$ failed and led to BN bond cleavage (The expected $(HB)_2P_2$ or its oligomer could not be detected amongst the reaction products [19]).

The structure of **4** suggests that this compound should not be a strong Lewis base, neither at the N nor the P atoms, since the lone pair at the P atoms have s-orbital character and the B-N bond is involved in π-bonding. On the other hand, the bicyclic nature of **4** suggests high reactivity. Compound **10** is now the first fully characterized 1 : 1 borane adduct of **4**. In Scheme 2 structural data of three bicyclic P_2P_2 compounds are listed. The PP bond lengths shrink as one moves from the parent compound to the adduct **10** and the cation $(tmpB)_2P(PtBu)^+$. The adduct formation, however, does not result in two very different B-P-B bond angles.

The BP bond to the $B(C_6F_5)_3$ unit (2.120(6) Å) is longer than the BP bonds to the tmpB groups [1.896(5)–1.919(5) Å], a feature that was to be expected, because similar trends have been observed for phosphine boranes [27]. It is also interesting to note that the sum of bond angles for the P_2B_3 unit is 347°, which is larger than found for the $(tmp)_2B_2P_2(tBu)^+$ cation (336°). This is an indication that there is an even higher degree for a *p*,*p*-orbital interaction in **10** than calculated for this cation [17]. Although one might have expected that the formation of **10** would lead to different B1-P1-B2 and B1-P2-B2 bond angles, this is not the case as shown by values of 81.9(2) and 82.6(2)°, respectively. Out of the three examples of the bicyclic BP compounds discussed here there are two which are of a new type. This shows that there are most likely many other still unexpected small and large B_nP_m molecules to be detected, which may also be interesting precursors for new materials.



B1P1P2/B2P1P2	104.1°	B1P1P2/B2P1P2	105.0°	B1P1P2/B2P1P2	123.4°
B1P1B2	84.0(1)°	B1P1B2	53.7(2) °	B1P1B2	90.4(2)°
B1P2B2	84.9(1)°	B1P2B2	82.6(2)°	B1P2B2	87.6(2)°
B1P1P2	52.0(1)°	B1P1P2	53.1(2)°	B1P1P2	53.9(2)°
B2P1P2	51.9(1)(2)°	B2P1P2	53.7(2)°	B2P1P2	51.9(2)°
P1-P2	234.9(2) pm	P1-P2	228.2(2) pm	P1-P2	231.5(2) pm

Scheme 2. Selected bond lengths and angles for three bicyclodiboretanes.

Experimental Section

All experiments have been performed by the Schlenk technique using dry N_2 or Ar as protecting gases. Starting materials were prepared according to literature procedures. Solvents were applied in an anhydrous state stored under N_2. Most NMR spectra were recorded with a JeolEX 400 instrument; chemical shifts are referenced to TMS, $^{11}BF_3OEt_2$, 85% H_3PO_4, and either C_6D_6 or $CDCl_3$ were used as solvents. IR spectra were recorded with a Nicolet-FT-IR spectrometer as Nujol/Hostaflon mulls. Liquids were placed between CsI plates. Data collection for X-Ray structure detgerminations were carried out with a Siemens P4 diffractometer using Mo-K_α radiation, a graphite monochromator, a low temperature device LT2 and an area detector.

7,8-Benzo-1,2,5-tri(tert-butyl)-2,4,6-trichloro-2,4,9-triphenyl-1,3,5-phosphonia-9-bora-2,4,6-triborata-bicyclo-[4,3,0^{1,6}]nonane (**2**)

A solution of $(tmpB\text{-}PCMe_3)_2$ (0.45 g, 1 mmol) in hexane (20 ml) was added within 30 min to a stirred solution of $PhBCl_2$ (0.25 ml, 1.9 mmol) in hexane (10 ml). During this process the orange solution turned yellow. After the addition the solution was reduced to half its volume *in vacuo*. Colorless crystals of **2** separated within one day by storing the solution at −78 °C. Yield 0.21 g (56% based on **1**).

NMR (all in d_8-toluene): ^1H NMR: $\delta = 0.71$ (d, 9H CMe_3), $^2J(PH) = 14$ Hz); 1.16 (d, 9H, CMe_3), $^2J(PH) =$

Table 1. Crystallographic parameters and data relevant for data collection and structure solution of compounds **2**, **3** and **10**.

[a] $w^{-1} = \sigma^2 {F_o}^2 + (xP)^2 + yP$; $P = ({F_o}^2 + 2{F_c}^2)/3$.

Compound	**2**	**3**	**10**
Chem. formula	$C_{39}H_{55}B_4Cl_3P_3$	$C_{19}H_{31}B_2Cl\,N\,O_2P$	$C_{36}H_{36}B_3F_{15}N_2P_2$
Form. wght.	766.33	393.49	876.04
Cryst. size [mm]	$0.07 \times 0.08 \times 0.15$	$0.10 \times 0.10 \times 0.10$	$0.05 \times 0.10 \times 0.10$
Cryst. system	monoclinic	triclinic	triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	38.075(6)	7.9701(8)	11.4667(9)
b [Å]	11.076(3)	10.3649(12)	12.2388(11)
c [Å]	19.859(5)	13.1695(15)	15.0510(13)
α [°]	90.00	81.429(2)	70.609(1)
β [°]	90.45(1)	82.041(2)	75.964(2)
γ [°]	90.00	76.929(2)	89.353(2)
V [Å3]	8375(3)	1041.7(2)	1927.4(3)
Z	8	2	2
ρ(calcd.) [Mg/m^3]	1.216	1.255	1.509
μ [mm^{-1}]	0.360	0.273	0.217
$F(000)$	3240	420	892
Index range	$-42 \le h \le 27$	$-10 \le h \le 8$	$-15 \le h \le 11$
	$-12 \le k \le 12$	$-13 \le k \le 13$	$-15 \le k \le 15$
	$-22 \le l \le 22$	$-16 \le l \le 16$	$-19 \le l \le 19$
2θ [°]	46.50	58.36	57.88
Temp, [K]	193	193(2)	193(2)
Refl. collected	17681	6056	11309
Refl. unique	5000	3212	5939
Refl. observed (4σ)	4470	1870	3117
R (int.)	0.0334	0.0300	0.0722
No. variables	451	243	531
Weighting scheme[a] x/y	0.0326/3.6457	0.1531/0.000	0.0615/0.000
GOF	1.089	1.049	0.950
Final $R(4\sigma)$	0.0454	0.0726	0.0582
Final $wR2$	0.1213	0.2022	0.1134
Larg. res. peak [e/Å^3]	0.921	0.635	0.290

14 Hz); 1.31, (d, 9H C*Me*$_3$), ^2J(PH) = 14 Hz); 4.18 (dd, 1H, P*H*, ^1J(PH) = 370 Hz, ^3J(PH) = 3 Hz); 5.11 (dd, 1H, P*H*, ^1J(PH) = 350 Hz, ^3J(PH) = 3 Hz); 6.92, 6.95, 6.97, 7.00, 7.03, 7.05, 7.11, 7.14, 7.20, 7.23, 7.26, 7.29, 7.31, 7.33, 7.36, 7.38, 7.41, 7.46, 7.52, 7.55, 7.75, 7.77, 7.93(m), 8.27 (m), 8.40, 8.41, 8.44, 8.52, 8.55. – ^{13}C NMR: $\delta = 30.8$ (s, C*Me*$_3$), 31.3 (s, C*Me*$_3$), 31.9 (s, C*Me*$_3$), 37.5 (s, *C*Me$_3$), 38.6 (s, *C*Me$_3$), 40.3 (s, *C*Me$_3$), 127.9, 131,7, 133.5, 134.0, 134.8 135.0, 135.7, 136.5, 136.7, 136.8, 138.6, 138.7. – ^{11}B NMR: $\delta = 29.8$ ($h_{1/2} = 280$ Hz), -4.0 ($h_{1/2} = 420$ Hz). – ^{31}P{^{1}H} NMR: $\delta = -12.5$ ($h_{1/2} = 220$ Hz), -14.23 ($h_{1/2} = 190$ Hz), -21.8 ($h_{1/2} = 220$ Hz). P(H)-NMR: $\delta = -12.3$ (d, ^1JPH) = 370 Hz); -14.7 (d, ^1J(PH) = 350 Hz); -21.8 (s).

Catecholatoboryl(2,2,6,6-tetramethylpiperidinochloroboryl)tert-butylphosphane, ***(3)***

To the clear orange solution of **1** (0.78 g, 1.62 mmol) in toluene (50 ml) was added a toluene solution (10 ml) of B-chlorocatecholborane (0.5 g, 3.24 mmol). The mixture was stirred over night. Then the solution was reduced to half of its volume *in vacuo*. It was kept at -30 °C. Crystals started settling after a few hours. The colorless prisms were isolated after 8 h. Yield: 1.10 g of **3**, 86%, m. p. 154 °C. $C_{19}H_{31}NO_2BClP$ (393.49): calcd. C 57.99, H 7.94, N 3.56; found C 57.11, H 7.86, N 3.56.

NMR (all in d_8-toluene) ^{1}H NMR: $\delta = 1.45$ (s, 3H, tmp*Me*); 1.47 (s, 3H, tmp*Me*); 1.49 (m, 2H, C3H$_2$); 1.50 (s, 3H, tmp*Me*); 1.52 (s, 3H, tmp*Me*); 1.65 (s, 9H, C*Me*$_3$); 1.78 (m, 4H, CH$_2$); 7.06 (m); 7.20 (m, 4H). – ^{13}C NMR: $\delta = 14.4$ (s, C4); 30.0 (C*Me*$_3$); 31.0 (s, *C*H$_2$); 32.1 (s, *C*H$_2$); 32.3 (s, *C*H$_2$); 32.6 (s, *C*H$_2$); 32.7 (s, *C*H$_2$); 35.4 (s, *C*Me$_3$); 57.2 (s, *C*Me$_2$); 112.0 (p-C); 122.3 (m-C); 148.8 (o-C). – ^{11}B NMR: $\delta = 33.4$ ($h_{1/2} = 90$ Hz); 37.4 ($h_{1/2} = 340$ Hz). – ^{31}P NMR: $\delta = -75.6$ ($h_{1/2} = 200$ Hz).

2,4-Bis(tetramethylpiperidino)-1-phosphonia-2-phosphato-3,4-dibora[1,1,0]bicyclobutane-tris(pentafluorpheny)borate ***(10)***

To an orange solution of 3,4-bis(tetramethylpiperidino)-1,2-diphospha-3,4-dibora[1.1.0]-bicyclobutane in toluene (10 ml) was added with stirring a solution of B(C_6F_5)$_3$ (70 mg, 0.13 mmol) in toluene (85 ml). The mixture was stirred for several days until a deep yellow solution had formed. 12 ml of the solvent were removed *in vacuo*. The remaining solution was kept at -30 °C. After standing for three months 0.1 g (85%) of colorless prisms was isolated which had single crystal quality; m. p. 147 – 149 °C.

$C_{36}H_{36}N_2B_3F_{15}P_2$ (875.88): calcd. C 49.36, H 4.14, N 3.20; found C 47.24, H 3.91, N 2.81.

NMR (all in d_8-toluene): ^{1}H NMR: $\delta = 1.18$ (24 H, CH_3); 1.25 (m, 12 H, C4,C3,C5-CH_2). – ^{13}C NMR: $\delta = 16.3$ (t, mp-*C*4), 33.2 (*C*H$_3$); 38.1 (*C*H$_3$); 41.4 (tmp-*C*3,5); 56.5 (*C*Me$_2$). – ^{11}B NMR: $\delta = -7.0$ ($h_{1/2} = 480$ Hz); 40.6 ($h_{1/2} = 400$ Hz). – ^{19}F NMR: $\delta = -163.6$ (m-C*F*); -156.1 (p-C*F*); -127.6 (o-C*F*). – ^{31}P NMR: $\delta = -298.3$ ($h_{1/2} = 2100$ Hz); -244.6 ($h_{1/2} = 2300$ Hz).

MS (70 eV): *m/z* (%) = 512 (45, B(C$_6$F$_5$)$_3^{+\cdot}$), 365 (35, M-B(C$_6$F$_5$)$_3^+$).

X-ray structures

The single crystals were mounted on a glass fibre with perfluoroether oil and fixed on the goniometer head while cooling to -80 °C with a nitrogen cold stream using a LPT2 device. After alignment of the crystal 5 sets of 15 frames each at different setting angles were recorded with an area CCD detector. Reflections on these frames were used to calculate the parameters of the unit cell. Data collection was performed in the hemisphere mode implemented in the SMART program. After data reduction the structure was solved using the SHELXTL program. Non-hydrogen atoms were refined anisotropically, the positions of the PH hydrogen atoms were taken from a difference Fourier map and refined isotropically. All other hydrogen atoms were placed in calculated positions and refined in the riding mode. Crystallographic data are summarized in Table 1 together with data referring to structure solution and refinement. Additional data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 296126 – 296128. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.uk.

Acknowledgements

We are indebted to Fonds der Chemischen Industrie and Chemetall GmbH for continued support, and to Mr P. Mayer for the recording of many NMR spectra. We are also grateful to Dr. J. Knizek for collecting the X-ray data sets and for the cooperation in structure solution.

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