Contribution to the Chemistry of Boron, 232[◇]

Formation, Structure and Reactions of a *P,P'*-Bi(1,3,2,4-diphosphadiboretane)[☆]

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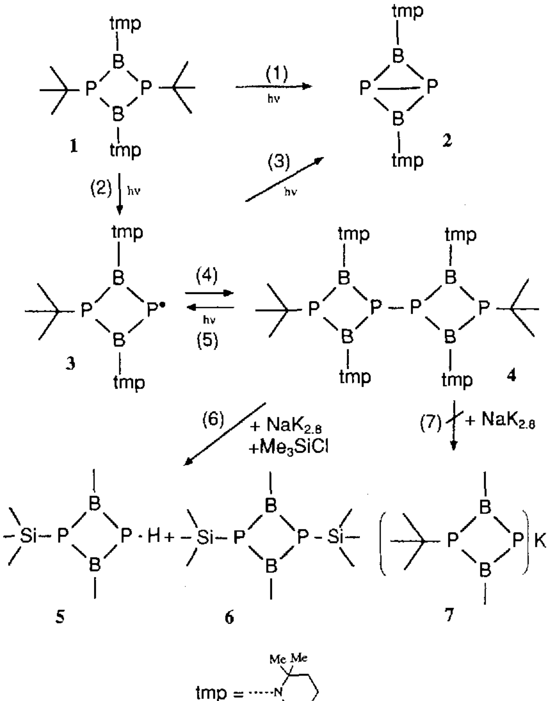
Photolysis of the 1,3,2,4-diphosphadiboretane (tBuPBtmp)$_2$ (**1**) in dilute toluene solution yields the bicyclic diphosphadiboretane **2**. In concentrated toluene solution or in hexane, however, the *P,P'*-connected bi(diphosphadiboretane) **4** is also formed implying that the radical [tBuP(Btmp)$_2$P] **3** is the first photolysis product. On further photolysis, **3** and **4** are converted into bicyclic **2** as the final product. Reduction of **4** with sodium-potassium alloy followed by silylation with Me$_3$SiCl leads to the 1,3,2,4-diphosphadiboretanes (tmpBPSiMe$_3$)$_2$ and [HP(Btmp)$_2$PSiMe$_3$]$_2$. In contrast to many 1,3,2,4-diboretanes, **4** in the absence of photon or thermal promotion does not react with Cr(CO)$_5$ · THF, Fe$_2$(CO)$_9$, or Pd(PPh$_3$)$_4$. However, a mixture of Cr(CO)$_5$ · THF and **4** on photolysis gives the known complex (tmpBP)$_2$ · 2 Cr(CO)$_5$.

Sterically crowded 1,3,2,4-diphosphadiboretanes (RPBtmp)$_2$ (tmp = 2,2,6,6-tetramethylpiperidino group) decompose photolytically with P–C bond cleavage and formation of the bicyclic 1,3-diphospha-2,4-dibora[1.1.0]bicyclobutane (**2**)[2] as described in equation (1). This suggests the formation of a 1,3,2,4-diphosphadiboranyl radical, e.g. **3**, by P–C bond cleavage because **2**[3] can also be generated from **1** in the presence of azabis(butyroisonitrile) as a radical promotor. However, the postulated initial photolysis product **3** has not yet been spectroscopically detected or chemically trapped. We now report on results pertaining to the existence of the anticipated radical **3**.

Scheme 1. Formation and reactions of the bi(diphosphadiborane) **4**



Synthesis of the *P,P'*-Bi(1,3,2,4-diphosphadiboretane) 4

When the diphosphadiboretane **1** in dilute toluene solution is photolyzed with the light from a mercury lamp almost quantitative conversion to the diphosphadibora[1.1.0]bicyclobutane **2** was observed[2]. However, if the photolysis is carried out in concentrated toluene solution, a small amount of a yellow precipitate forms besides the soluble compound **2**. Much larger amounts of this yellow precipitate, which proved to be the *P,P'*-bi(diphosphadiboretane) **4**, are formed by using hexane as a solvent. Yields up to 34% were obtained. Compound **4** is diamagnetic. In its ^{11}B-NMR spectrum there is only a single but rather broad signal at $\delta = 53.5$. This chemical shift is compatible with a diphosphadiboretane structure[4] but would not rule out structure **4a**. Two ^{31}P-NMR signals at $\delta = -30.8$ and -34.5 are observed, and their shape is that of Harris' triplet for AA'BB' spin systems[5] with coupling constants $N = 87$ and 85 Hz, respectively. Finally, four signals for the CH$_3$ groups of the tmp substituent as well as two signals each for the CMe$_2$CH$_2$ carbon atoms appear in the ^{1}H- and ^{13}C-NMR spectra, and coupling of higher order of the CH$_3$ protons to the ^{31}P nuclei is observed. This is typical of tmp

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[◇] Part 231: Ref.[1].

groups with hindered rotation about its BN bond. Hindered rotation about the BN bond is not uncommon in aminoboranes of type tmpBXY[6] and under these circumstances would generate four different methyl groups. Compound **4a** would almost certainly be nonplanar, most likely butterfly-shaped, and this structure should also give rise to four magnetically inequivalent methyl groups (and two chemically nonequivalent NC and CH_2 groups). Evidence that favors structure **4** can be deduced from its mass spectrum although no parent peak is observed, even when the mass spectrum is recorded at 15 eV. The highest mass ion found is at *m*/*z* = 421 which corresponds to the radical cation of 3. Its relative intensity is only 7%. This peak shows the correct isotope pattern from $3^{\bullet+}$ by loss of a Me_3C fragment from 3^+. Further fragmentation occurs by loss of CH_3 groups from tmp, a behavior that is typical of the tmp group containing diphosphadiboretanes[2]. Thus, the fragmentation pattern of **4** under electron impact is more compatible with a *P,P*-bonded dimer of **3** rather than with structure **4a**.

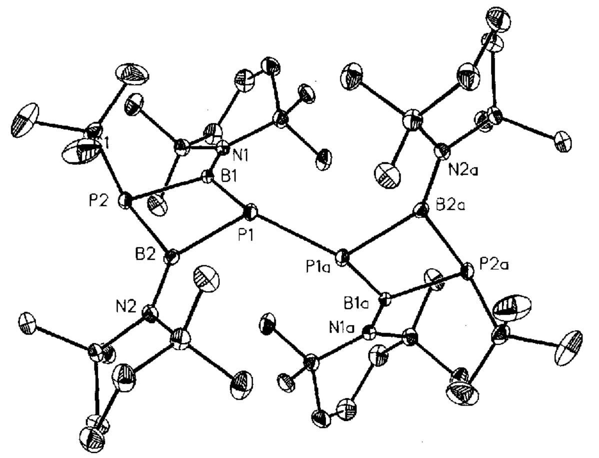
Structure

Final proof of the structure of **4** comes from the determination of its molecular structure by X-ray methods (Figure 1). Compound **4** crystallizes in the orthorhombic space group *Pnna* with *Z* = 4. Its molecular structure consists indeed of two *P,P'*-connected diphosphadiboretane units. A crystallographic twofold axis passes through the center of the P–P bond providing C_2 point group symmetry for the molecule. It should be noted that the P–P bond length, 2.189(1) Å, is slightly but significantly shorter than most of the P–P single bonds of diphosphanes and polyphosphanes[7]. Another point to be considered are the four different B–P bond lengths which fall into two categories, P1–B1, P1–B2 (average 1.933 Å) and P2–B1, P2–B2 (average 1.968 Å). Moreover, the P1a–P1–B angles are also different with 132.7(4) and 121.1 (2)°. The B_2P_2 rings in compound **4** are not planar in contrast to most 1,3,2,4-diphosphadiboretanes[4]. The most important feature is, however, the sum of bond angles at atom P1 which is 340.7° in contrast to 296.9° for atom P2.

Although the BN bonds are of equal length, the interplanar angles C_2N/BP_2 are different as demonstrated by 20.5° for N1 and 32.5° for N2, respectively. This, most likely, represents packing effects in the lattice. However, these rather normal interplanar angles[8] are not prohibitive for BN π bonding. More importantly, the interplanar angle between the $B_2P(1,1a)$ planes of the two B_2P_2 moieties is 98.4°. This, in addition, counts for the fact that the tmp groups are not rotating freely about the BN bond at ambient temperature as is to be expected for comparatively strong BN bonds.

Reactions

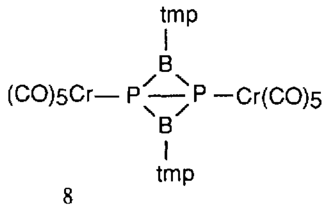
Figure 1. ORTEP representation of the molecular structure of **4** in the crystal; thermal ellipsoids represent a 25% probability; hydrogen atoms have been omitted for clarity[a]



[a] Selccted bond lengths [Å]: P1–P1a 2.189(1), P1–B1 1.896(6), P1–B2 1.955(6), P2–B1 1.968(6), P2–B2 1.970(6), B1–N1 1.400(8), B2–N2 1.399(8), P2–C1 1.931(6); selected bond angles [°]: P1a–P1–B1 132.7(2), P1a–P1–B2 121.1(2), B1–P1–B2 86.9(3), P1–B1–P2 93.1(3), B1–P2–B2 84.6(3), P2–B2–P1 91.2(3); selected interplanar angles [°]: B1–P1–B2/B1–P2–B2 157.2°; B1–P1–B2/B1a–P1a–B2a 98.4.

The structure of **4** suggests two potential reaction pathways: a) Reductive opening of the P–P bond to generate the anion $[Me_3CP(tmpB)_2P]^-$ and b) metal coordination chemistry. Indeed, $NaK_{2.8}$ alloy reacts with **4** in hexane to give an insoluble solid which on treatment with Me_3SiCl produces a solution containing the two known 1,3,2,4-diphosphadiboretanes **5** an **6**[9] in a 2:1 ratio, but not in a 1:1 ratio as suggested by equation (6). Thus, the potassium salt **7** was probably not formed since $Me_3CP(Btmp)_2PSiMe_3$, which should result on silylation of **7** with Me_3SiCl, was not obtained.

Therefore, the reduction of **4** with the $NaK_{2.8}$ alloy not only cleaves the P–P bond but also its P–C bonds. Moreover, **4** surprisingly does not react with $Cr(CO)_5 \cdot THF$, $Fe_2(CO)_9$, and $Pd(PPh_3)_4$ at ambient temperature. But the photolysis of **4** in the presence of $Cr(CO)_5 \cdot THF$ leads finally to the known complex $[tmpBPCr(CO)_5]_2$ (**8**)[10]. This requires not only homolytic cleavage of the P–P but also of the P–C bond.



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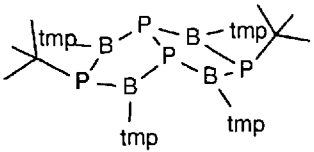

4a

Discussion

Until now, very few reactions involving homolytic P–C bond breaking[11] were known. In the present study clear evidence for the successive homolytic scission of two P–C bonds in **1** is provided by the formation of **3** during UV photolysis of **1**, a radical that dimerizes to **4** when the concentration of **1** is sufficiently high or when **4** rapidly separates from the solution as is the case in hexane solution.

Moreover, isolated examples of **4** decompose on photolysis with formation of **2**; this requires homolysis of the P–P bond as well as of P–C bonds. In contrast to P–C scission, photolytic P–P bond cleavage is quite common. The best known example is the transformation of white phosphorus into red phosphorus[12]. P–P bond cleavage in **4** is also achieved with $NaK_{2.8}$ alloy; the first step in this reaction probably involves the generation of the alkali metal salt $[Me_3CP(tmpB)_2P]K$ (**7**) and the radical **3**. The latter may react further with the alkali metal to also give compound **7**. However, we have at the moment no indication at what stage the P–C bond is broken. This step is not unusual in organophosphorus chemistry. The best example is the formation of Ph_2PK from Ph_3P and K[13]. Taking the structure of **4** into account, it is surprising that $Cr(CO)_5 \cdot THF$ does not react at all with **4** since $(tmpBPCMe_3)_2$ does so with formation of $tmp\text{-}B{=}(PCMe_3)Cr(CO)_5$[10]. Thus, a $tmpB{=}PCMe_3$ fragment is not extruded from **4**, stabilized by $Cr(CO)_5$ addition. This may result from the perpendicular arrangement of the two B_2P_2 rings that would provide steric shielding of the Me_3CP group by the tmp group, thereby hindering $Cr(CO)_5$ attack. In this regard, the shortest nonbonded $CH_3 \cdots P$ distance in **4** is 2.573 Å.

Besides the special orientation of the two diphosphadiboretane rings in **4** we consider the geometry at P1 and P1a which are approaching planarity (sum of bond angles is 340.7°) as particularly noteworthy. There is no comparable example of a cyclic boron-pyramidal phosphorus center. However, a flat environment at the P atoms is observed for some diborylphosphanes[14,15], e.g. $mesP(BClmes)_2$ (360°)[15] as well as for the bis(phosphanyl)boranes $BrB(Pmes_2)_2$ (347.1°)[16] and $Ph_2NB[P(SiMe_3)_2]_2$[17]. This last example comes closest to the structural skeleton of compound **4** because a nitrogen atom is attached to the boron atom, and this is not the case with the other two compounds. Although the geometry at P1 does not suggest pure sp^2 hybridization, the structural data of compound **4** show a shorter BP bond to P1 as compared to P2. The difference in bond length (averaged 0.1 Å) does not necessarily require formal BP π bonding, but may arise from the change in hybridization (increased s character) at the P atoms. On the other hand, the boron nuclei in **4** are better shielded by 10 ppm with respect to **1**, and this reflects some increase of electron density at the boron site which, of course, could be taken as evidence for BP π bonding. At the present time, a complete description of the nature of the B–P bonds in this compound cannot be given.

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Experimental

All experiments were conducted under oxygen-free N_2 or in a vacuo by using Schlenk-type techniques. Anhydrous solvents, stored under N_2, were used throughout. – NMR: Bruker 200 WP, Jeol 270 with $^{11}BF_3 \cdot OEt_2$ (external), 85% H_3PO_4 (external), and TMS as reference. – IR: Nicolet-520-FTIR. – X-Ray: Siemens R3m, SHELXTL-PLUS and SHELXL93 programs for structure solution, refinement and graphic display.

3,3'-Di-tert-butyl-2,2',4,4'-bis(2,2,6,6-tetramethylpiperidino)-1,1'-bi(1,3,2,4-diphosphadiboretane) (**4**): A solution of $(tmpBPCMe_3)_2$[18] (20.6 g, 43.1 mmol) in hexane (140 ml) was photolysed in a Pyrex vessel with unfiltered light from a Hanovia S200W mercury lamp. The body of the lamp was in direct contact with the solution. Shortly after photolysis an intensely yellow-colored precipitate formed depositing mostly on the wall of the reactor. This solid material was twice removed by filtration and the solution used for further photolysis. The product remaining in solution was pure $(tmpBP)_2$ (**2**)[19], yield: 6.85 g (44%), m.p. 138°C. Recrystallisation of the yellow solid from benzene yielded orange-yellow crystals of **4** which were dried in a vacuo; yield: 6.2 g (34%), m.p. 178°C. – MS, *m/z* (%): 421 (7) $[M^{\bullet +}/2]$, 364 (100) $[M^{\bullet +}/2 - CMe_3]$, 349 (37) $[tmpBP)_2 - CH_3^+]$, 126 (31) $[tmpH^+ - CMe_3]$. – IR (Nujol/Hostaflon, cm^{-1}): $\tilde{\nu}$ = 3090 w, 3072 w, 3032 w, 2961 s, 2940 s, 2884 s, 2860 s, 2763 w, 1784 w, 1470 s, 1433 m, 1412 m, 1382 s, 1366 s, 1323 s, 1277 s, 1245 m, 1224 w, 1217 w, 1173 s, 1162 m, 1128 m, 1093 w, 1071 w, 1041 w, 1018 w, 997 m, 975 s, 931 w, 900 w, 842 w, 826 w, 761 w, 752 w, 719 w, 697 w, 674 m, 565 w, 532 w, 500 w, 464 w, 421 w, 397 w, 380 w, 348 w. – $C_{44}H_{90}B_4N_4P_4$ (842.4): calcd. C 62.74, H 10.77, N 6.65; found C 62.27, H 10.93, N 6.55.

Photolysis of **4**: Compound **4** (4.93 g, 5.90 mmol) was dissolved in toluene (140 ml) and photolyzed for 4 h with the light from a Hanovia S200W mercury lamp. After that time ^{11}B- and ^{31}P-NMR data showed the presence of a small amount of $tmpBH_2$ [$\delta^{11}B$ = 36.9, $^1J(BH)1$ = 23 Hz] and **2** ($\delta^{11}B$ = 44.6, $\delta^{31}P$ = −291.4)[17]. Removal of all volatile components afforded **2** (3.93 g, 92%) as a yellow-orange powder.

Reaction of **4** *with NaK Alloy and Me_3SiCl:* To a solution of **4** (0.17 g, 0.18 mmol) in benzene (15 ml) $NaK_{2.8}$ alloy (0.02 ml) was added. The reaction flask was immersed in a water bath and irradiated with ultrasound for 1 h. During this time a light blue solid formed with consumption of the liquid alloy. Then, Me_3SiCl (6 mmol) was added at 6°C, and insoluble material was removed by filtration after stirring of the mixture for 6 h. The benzene was evaporated from the clear solution, and the yellow oil that was involatile at 20°C/10^{-1} Torr was dissolved in pentane/toluene (1:1). The oil proved to be a 1:2 mixture of $(Me_3SiPBtmp)_2$[9] ($\delta^{11}B$ = 61.3, $\delta^{31}P$ = −53.5) and $Me_3SiP(Btmp)_2PH$[9] ($\delta^{11}B$ = 50.7, $\delta^{31}P$ = −108.4 and −129.5).

Formation of $[tmpBPCr(CO)_5]_2$: $Cr(CO)_6$ (1.60 g, 7.26 mmol) was dissolved in THF (70 ml) and transformed into $Cr(CO)_5 \cdot THF$ by photolysis. This solution was then added with stirring to a solution of **4** (1.02 g, 1.21 mmol) in hexane (80 ml). No reaction occurred within 2 weeks when the mixture was stirred in the dark. Then the solution was irradiated with the light from a S200W mercury lamp. A dark brown solution formed readily within 1 h. NMR spectra of the solution showed the formation of $[tmpBPCr(CO)_5]_2$ (δ^1B = 39.3, $\delta^{31}P$ = −180.9)[20]. The residue that remained after evaporation of all volatile materials in vacuo was crystallized from hexane (20 ml) and provided **8**, m.p. 144°C (dec.), yield: 1.01 g (56%).

X-Ray Structure Determination of **4**: Siemens R3m diffractometer, Mo-K_α radiation, graphite monochromator, size of single crystal: 0.25 × 0.2 × 0.68 mm, orange platelet. – *Crystallographic data:* $C_{44}H_{90}B_4N_4P_4 \cdot C_6H_6$, mol. mass 920.43, a =

20.420(9), $b = 25.529(5)$, $c = 10.663(2)$ Å, $V = 5559(3)$ Å^3 at 293 K, orthorhombic, space group *Pnna*, $Z = 4$, $F(000) = 2016$, $d_{calc.} = 1.100$ Mg/m^3, $\mu = 0.171$ mm^{-1}. – *Data collection at 293 K:* scan speed 2.5–29.3°/min, 2Θ range: 3.2–49.6° in h, k, $\pm l$; reflections recorded = 5333, 4785 unique reflections and 3321 considered observed [$F > 4\sigma(F)$]. – *Structure solution and refinement:* Direct methods, nonhydrogen atoms refined anisotropically, H atoms in calcd. positions and refined as riding on the C atom, fixed isotropic U_i; 289 parameters refined, $R1 = 0.099$; $wR2 = 0.223$, GOF = 1.026; largest residual density 3.03 e/Å^3. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404900, the names of the authors, and the journal citation.

☆ Dedicated to Prof. Dr. *O. J. Scherer* on the occasion of his 60th birthday.

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