CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600185

Lewis Base Stabilized Phosphanylborane

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Dedicated to Prof. Dr. Kurt Dehnicke on the occasion of his 75th birthday

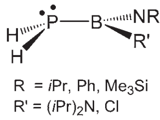
Abstract: The abstraction of the Lewis acid from $[W(CO)_5(PH_2BH_2{\cdot}NMe_3)]$ (**1**) by an excess of $P(OMe_3)_3$ leads to the quantitative formation of the first Lewis base stabilized monomeric parent compound of phosphanylborane $[H_2PBH_2{\cdot}NMe_3]$ **2**. Density functional theory (DFT) calculations have shown a low energetic difference between the crystallographically determined antiperiplanar arrangement of the lone pair and the trimethylamine group relative to the P–B core and the synperiplanar conformation. Subsequent reactions with the main-group Lewis acid BH_3 as well as with an $[Fe(CO)_4]$ unit as a transition-metal Lewis acid led to the formation of $[(BH_3)PH_2BH_2{\cdot}NMe_3]$ (**3**), containing a central $H_3B{-}PH_2{-}BH_2$ unit, and $[Fe(CO)_4(PH_2BH_2{\cdot}NMe_3)]$ (**4**), respectively. In oxidation processes with O_2, Me_3NO, elemental sulfur, and selenium, the boranylphosphine chalcogenides $[H_2P(Q)BH_2{\cdot}NMe_3]$ (Q = S **5b**; Se **5c**) as well as the novel boranyl phosphonic acid $[(HO)_2P(O)BH_2{\cdot}NMe_3]$ (**6a**) are formed. All products have been characterized by spectroscopic as well as by single-crystal X-ray structure analysis.

Keywords: boron · density functional calculations · Lewis bases · phosphorus

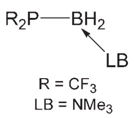
Introduction

The parent compound H_2BPH_2 of the well-known class of substituted phosphanylboranes $(R_2BPR'_2)_n$[1] has not yet been isolated and no experimental approach has been successful. Only ab initio calculations concerning the structure have been performed.[2] Under standard conditions only the poly(phosphanylboranes) of the formulae $[H_2BPH_2]_n$ [3] or $[H_2BPPhH]_n$[4] are known; these were recently obtained by dehydrocoupling catalysis by either $B(C_6F_5)_3$ or Rh^I complexes from corresponding precursor compounds. Looking more closely into the sparse examples of similar monomeric compounds with only a few organic substituents, compounds of type **A**, containing sterically demanding protecting groups such as mesityl, phenyl, or $(i\text{Bu})_2N$ on the boron atom, are found.[1] In these examples some degree of intramolecular π overlap of the P–B bond, caused by the lone pair on the phosphorus atom and the acceptor orbital on the boron atom, adds to their stabilization.

Only one example of a compound stabilized in the reverse manner exists (with a poorly sterically protected phosphorus atom and an unprotected (H-bound) boron atom) and it still requires additional electronic saturation at the boron atom by a Lewis base (type **B**).[5] An alternative route to monomeric parent compounds of phosphanylboranes was developed in our group by using Lewis acid and Lewis base stabilization. By blocking the lone pair and acceptor orbital by a Lewis acid (LA) such as $W(CO)_5$ and a Lewis base (LB)



A



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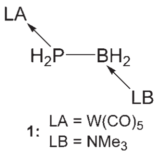
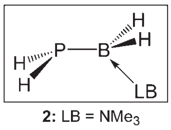


C



D

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such as NMe_3, respectively, compound **1** (type **C**) was synthesized.[6]

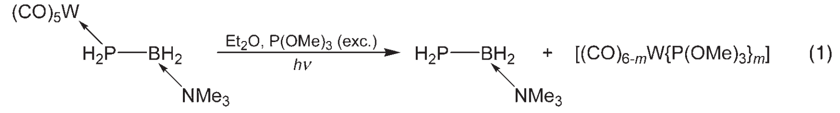
Thermodynamic calculations for the isodesmic reactions between H_2BPH_2 and NMe_3 or $W(CO)_5$ have shown that the monomer should also be stable with only one of the stabilizing moieties (ΔH^0_{298} for $H_2PBH_2NMe_3$ = −98.1 kJ mol^{-1}; for $(CO)_5W(H_2PBH_2)$ = −121.2 kJ mol^{-1}),[6b] although both possibilities have so far not been experimentally realized. To approach the parent compound H_2BPH_2 experimentally a Lewis acid free compound of type **D** is of particular interest, since it is a useful starting material for the synthesis of diverse functionalized phosphinoboranes and furthermore can become an interesting precursor for inorganic materials.

Herein we describe the synthesis and the comprehensive characterization of the first Lewis base stabilized monomeric parent compound of phosphanylborane $[H_2PBH_2{\cdot}NMe_3]$ (**2**), together with the results of theoretical calculations on this system. Furthermore, investigations of the reactivity of **2** in oxidation processes with chalcogens (O, S, Se) and with the Lewis acids BH_3 and $Fe(CO)_4$ were performed. This led to the isolation and characterization of novel boranyl-substituted phosphonic acid as well as phosphine sulfide and selenide derivatives in the former reaction. The latter reactions led to the first structurally characterized compound containing a $H_3B{-}PH_2{-}BH_2$ sequence, for example.[7]

Results and Discussion

Synthesis and characterization of the Lewis base stabilized phosphanylborane $[PH_2BH_2{\cdot}NMe_3]$ (2): The principal methods for removing $W(CO)_5$ fragments from a phosphine are: 1) oxidation with iodine to give $[(CO)_4WI]^+[I]^-$ and complexed phosphine, with subsequent quenching with *N*-methylimidazole to cleave the W−P bond[8] and 2) a ligand-exchange reaction with a bidentate ligand such as 1,2-bis(diphenylphosphino)ethane (dppe).[9] Both of these methods applied to $[W(CO)_5(PH_2BH_2{\cdot}NMe_3)]$ (**1**) did not lead to the Lewis acid free phosphanylborane. Thus, 3) reaction with a strong coordinating ligand, such as trimethylphosphite,[10] was successfully applied for this preparative target as shown in Equation (1). Whereas the classical method for carrying out this reaction under thermal conditions failed,[11] the photochemical activation of a mixture of **1** with an excess of trimethylphosphite led to the quantitative formation of complex **2** [Eq. (1)].

Based on the large excess of phosphite in reaction (1) the characterization of the by-products $[(CO)W\{[P(OMe)_3\}_5]$, *cis*-$[(CO)_2W\{P(OMe)_3\}_4]$, and *fac*-$[(CO)_3W\{P(OMe)_3\}_3]$ by $^{31}P\{^1H\}$ NMR spectroscopy was possible.[10] DFT calculations at the B3LYP/6–31G* level of theory[12,13] (ECP basis set on W[14]) show that reaction (1) in the gas phase with formation of $[(CO)_5WP(OMe)_3]$ at 298 K is slightly exothermic by −3.9 kJ mol^{-1} (Gibbs energy at 298 K is −10.5 kJ mol^{-1}). The same should be valid in solution, but without irradiation no reaction is observed. Thus, the photochemical removal of CO seems to be the initial step necessary for facilitating substitution with phosphite, which weakens the W−P bond of the phosphanylborane unit and leads to the formation of **2**.



$$(CO)_5W{\cdot}H_2P{-}BH_2{\cdot}NMe_3 \xrightarrow[h\nu]{Et_2O,\ P(OMe)_3\ (exc.)} H_2P{-}BH_2{\cdot}NMe_3 + [(CO)_{6-m}W\{P(OMe)_3\}_m] \quad (1)$$

1 2 *m* = 3-5

Compound **2** was isolated at low temperature (<12 °C) as colorless crystals that are readily soluble in solvents such as toluene and CH_2Cl_2. Above 12 °C compound **2** is a colorless liquid with a density of about 0.87 g cm^{-3}. In *n*-hexane it is poorly soluble and above 12 °C forms a two-phase system. The mass spectrum reveals the appropriate molecular ion peak. The IR spectra of **2** show absorptions for the P−H and B−H valence stretching frequencies at 2282 and 2375 cm^{-1}, respectively, which are in accordance with the calculated values.[15a,b] The ^{31}P NMR spectrum of **2** consists of a broad triplet at δ = −215.5 ppm (^1J(P,H) = 189 Hz), which is due to P–H coupling; in the proton-decoupled $^{31}P\{^1H\}$ NMR spectrum the signal is a quartet, owing to coupling with the ^{11}B nucleus. Relative to the starting complex **1** (δ = −184.2 ppm), the signal is shifted to high field, as expected for Lewis acid free compounds,[6] and is in good agreement with chemical shifts found for compounds of the formula R_2BPH_2 (e.g. R = iBu$_2$N, δ = −228 ppm).[16] The structure of **2** was confirmed by an X-ray diffraction study and shows an antiperiplanar orientation of the lone pair at the phosphorus atom and the trimethylamine group at the boron atom (Figure 1).

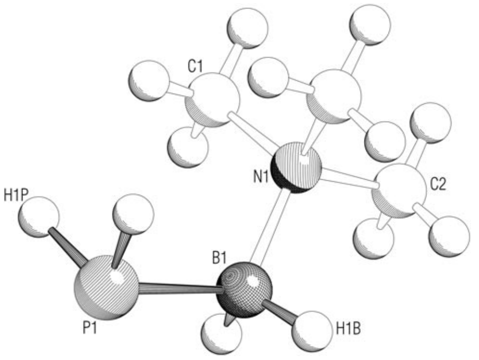


Figure 1. Molecular structure of $[H_2PBH_2{\cdot}NMe_3]$ (**2**) in the crystal. Selected bond lengths [Å] and angles [°]: P1−B1 1.976(2), B1−N1 1.630(2), N1−C1 1.501(1), N1−C2 1.504(2); P1-B1-N1 117.29(11), B1-N1-C1 112.37(9), B1-N1-C2 107.67(12), H1P-P1-B1-H1B 167.15(1).

According to thermodynamic calculations, only a small difference of less than 0.1 kJ mol^{-1} exists between the antiperiplanar (Figure 2, left) and the synperiplanar (Figure 2, right) conformations. In the latter case, possible interaction between the lone pair and an H atom of a methyl group occurs (P···H distance 2.826 Å, com-

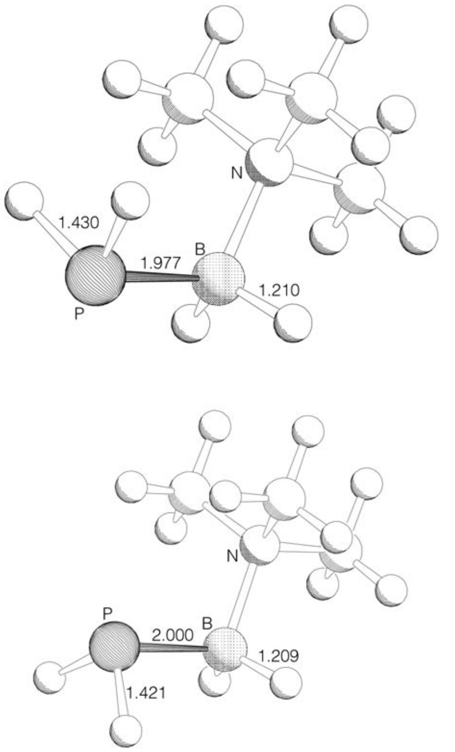


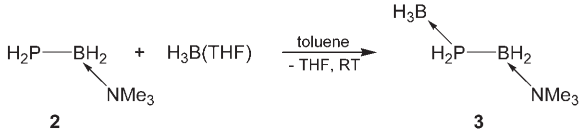
Figure 2. Calculated molecular structures (B3LYP/6–31G* level of theory) of the antiperiplanar (top) und synperiplanar (bottom) conformation of the lone pair and the trimethylamine group relative to the P–B core in **2** (lengths in Å).

pared with 3.087 Å in antiperiplanar conformation), but that seems too insignificant a difference to favor one of the conformers. Thus, the arrangement of the lone pair is not a thermodynamically controlled process but rather a packing effect in the solid state. All experimentally found angles and distances correspond with the calculated values for compound **2** in the gas phase.

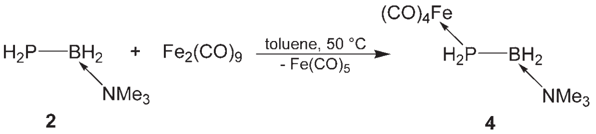
The experimentally observed distance of 1.976(2) Å between the phosphorus and the boron atom is typical for a single bond (1.90–2.00 Å)[1] and close to that of the equivalent bond in reactant **1** (1.955(4) Å).[6] Thus, the coordination of the phosphorus lone pair to the tungsten carbonyl moiety leads to a small decrease of the phosphorus–boron bond length.

Investigations of the reactivity pattern of [$H_2PBH_2{\cdot}NMe_3$] (2):

Synthesis and structural characterization of the Lewis acid/base compounds [(LA)$H_2PBH_2{\cdot}NMe_3$] (LA = BH_3, $Fe(CO)_4$): To gain insight into the Lewis base behavior of compound **2**, reactions of the main-group Lewis acid BH_3 and the transition-metal Lewis acid $Fe(CO)_4$ (generated from $Fe_2(CO)_9$) with **2** were performed to obtain the Lewis acid/base adducts **3** and **4**, respectively [Eq. (2) and (3)].



(2)



(3)

Both reactions were performed in toluene and were complete within a short period with quantitative yield. For the preparation of **3** a solution of BH_3 in THF was added at room temperature to a solution of **2** in toluene. The resulting colourless complex [$(H_3B)H_2PBH_2{\cdot}NMe_3$] (**3**) was purified by sublimation. The corresponding iron tetracarbonyl containing complex [$(CO)_4Fe(H_2PBH_2{\cdot}NMe_3)$] (**4**) was prepared by reacting **2** with [$Fe_2(CO)_9$] at 50 °C in toluene. The colorless compound **3** and the yellow crystalline compound **4** are readily soluble in toluene and CH_2Cl_2. Whereas compound **3** sublimes at 60 °C in a high vacuum, compound **4** decomposes to unidentified products.

In the molecular structure of **3** (Figure 3) all substituents around the B2-P-B1-N core have a distorted tetrahedral conformation. The NMe_3 and H_3B2 moieties adopt a perfectly staggered conformation around the central P–B1 core ($\sphericalangle$(B2-P-B1-N) = 180.0°). In **3** the distances between the phosphorus atom and the boron atoms B1 and B2 are nearly identical (1.962(2) Å, 1.958(2) Å) and are in good agreement with such distances in related phosphanylboranes.[1,7] To our knowledge, compound **3** represents the longest structurally characterized B-P-B chain with only hydrogen substituents.[7]

In the molecular structure of the iron carbonyl compound **4** (Figure 4) the phosphorus lone pair of the central phosphorus-boron core coordinates to the [$Fe(CO)_4$] fragment,

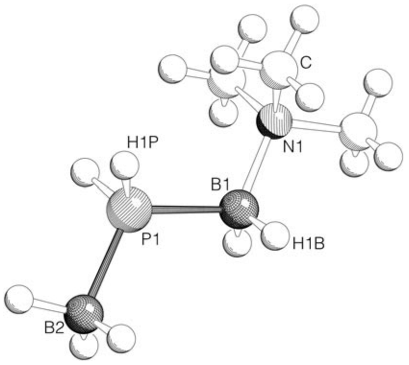


Figure 3. Molecular structure of [$(H_3B)H_2PBH_2{\cdot}NMe_3$] (**3**) in the crystal. Selected bond lengths [Å] and angles [°]: P1–B1 1.962(2), P1–B2 1.958(2), B1–N1 1.620(2); B2-P1-B1 116.38(8), P1-B1-N1 114.70(10), B2-P1-B1-N1 180.00(1). Calculated at the B3LYP/6–31G* level of theory, the structural parameters for **3** in the gas phase (P1–B1 1.967, P1–B2 1.978, B1–N1 1.650; B2-P1-B1 117.1, P1-B1-N1 116.6, B2-P1-B1-N1 180.0) are in good agreement with experimental data from the crystal.

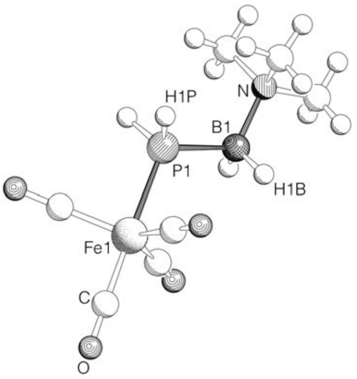
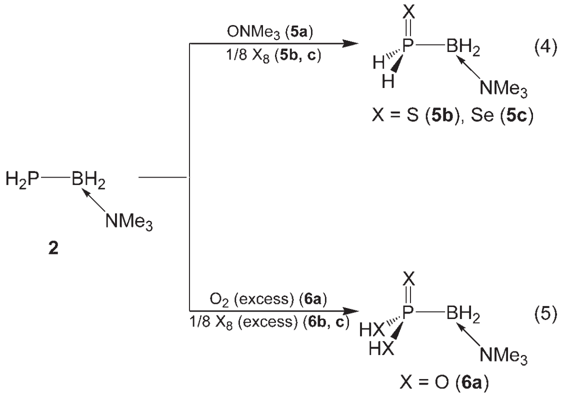


Figure 4. Molecular structure of $[(CO)_4Fe(H_2PBH_2{\cdot}NMe_3)]$ (**4**) in the crystal. Selected bond lengths [Å] and angles [°]: Fe1–P1 2.2790(6), P1–B1 1.964(2), B1–N1 1.610(3); Fe1-P1-B1 114.23(7), P1-B1-N1 116.59(12), Fe1-P1-B1-N1 −175.06(12).

which leads also to a staggered conformation (∢(Fe-P-B-N) = 175.06(12)°). At 2.279(1) Å, the P–Fe bond length is slightly longer than in the comparable compound $[(CO)_4FePPh_3]$ (2.244(1) Å).[17] The P–B bond length in **4** (1.964(2) Å) is also in the range typical of a single bond and is comparable to the distances in compound **3** (1.962(2) Å). Interestingly, coordination of the phosphorus lone pair by the BH_3 and $[Fe(CO)_4]$ units in **3** and **4** leads only to a very small decrease in the P–B1 bond length of the phosphanylborane moiety (≈0.01 Å) relative to that in the starting material **2** (1.972(2) Å).

Oxidation of [$H_2PBH_2{\cdot}NMe_3$] ***2*** *with different chalcogenides*: Another point of interest was the study of the reaction behavior of **2** with Group 16 elements like O, S, and Se to obtain boranylphosphine chalcogenide compounds. To achieve controlled reaction conditions, we first carried out stoichiometric reactions between **2** and elemental sulfur and red selenium, respectively, in CH_2Cl_2 at room temperature, according to Equation (4). This led to the quantitative formation of the new boranylphosphine chalcogenides **5b** and **5c**. Interestingly, to our knowledge, both compounds are the first structurally characterized boranylphosphine sulfides and selenides, respectively, possessing two hydrogen atoms at the phosphorus atom. Additionally, the selenium compound **5c** represents the first structurally characterized primary phosphine selenide.

Attempts to synthesize the oxygen analogue **5a** by using Me_3NO in a stoichiometric reaction at room temperature failed, since no transformation of the starting material **2** was observed. Consequentially, the mixture was refluxed for 12 h in CH_2Cl_2. Workup of the reaction mixture led to a white powder, which was only sufficiently soluble in [D_6]DMSO for spectroscopic characterization. In the $^{31}P\{^1H\}$ NMR spectrum of this solution, we observed unreacted **2** as the main component and two broad signals at $\delta = 49.6$ and 34.1 ppm; at $\delta = 6.4$ ppm a quartet was observed, which is due to coupling with the boron atom ($^1J(P,B) = 110$ Hz). Only the latter signal splits into a triplet in the ^{31}P NMR spectrum,



owing to coupling with the hydrogen atoms ($^1J(P,H) = 355$ Hz). Thus, one could assume that this signal belongs to the boranylphosphine oxide **5a**, which is shifted strongly downfield, as expected for an oxidized primary phosphine; however, it is not shifted as far downfield as the signal for the boranylphosphonic acid **6a** [Eq. (5)], in which the phosphorus atom experiences the deshielding influence of three oxygen atoms. Unfortunately, all attempts to isolate **5a** from this mixture failed.

Reactions of **2** with an excess of the chalcogens proceed in a reversed manner than discussed for the stoichiometric reactions. Whereas a mixture of products were obtained for the reactions with sulfur and selenium, according to ^{31}P NMR investigations of the crude reaction mixture, with spectroscopic evidence of the formation of the trithioboranylphosphonates **6b** and triselenoboranylphosphonates **6c**,[18] the reaction of **2** with an excess of oxygen leads to the isolation of **6a** [Eq. (5)]. The best results for the formation of the novel boranyl phosphonic acid $[(HO)_2P(O)BH_2NMe_3]$ (**6a**) were obtained if **2** was dissolved in THF and exposed to air. After two days, white needles of **6a** were obtained. Compound **6a** is only soluble in solvents of high polarity such as MeOH or DMSO. In water it decomposes slowly under gas evolution.

Spectroscopic properties: In the mass spectra of compounds **3**–**6** the appropriate molecular ion peak is observed. Additionally, a characteristic fragmentation pattern of successive CO group eliminations is observed for **4**. With the exception of the acid **6a**, the IR spectra show typical absorptions for the B–H and P–H valence stretching frequencies at about 2400 and 2300 cm^{-1}, respectively. The boranylphosphine chalcogenides **5b** and **5c** show the P=S (656 cm^{-1}) and P=Se (443 cm^{-1}) stretching vibrations, respectively, which are in good agreement with those of comparable compounds such as $(Me_3Si)_2HCP(S)Cl_2$ (673 cm^{-1}) and $(Me_3Si)_2HCP(Se)Cl_2$ (574 cm^{-1}).[19] In the solid state, **6a** shows a typical P=O stretching frequency at 1217 cm^{-1} and furthermore a broad band at 2954 cm^{-1} for the POH frequency, which indicates hydrogen bonds.

The ^{31}P NMR spectra of **3** and **4** reveal broad triplets at $\delta = -116.0$ ($^1J(P,H) = 323$ Hz) and -110.3 ppm ($^1J(P,H) =$

312 Hz), respectively, which a shifted strongly downfield relative to the initial compound **2**. The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of a quartet ($^1J(P,B) = 78$ Hz) owing to coupling with the ^{11}B nucleus. In the $^{31}P\{^1H\}$ NMR spectrum of **3** the triplet signal changes to a quartet of quartets with two different coupling constants ($^1J(P,B1) = 72$ Hz, $^1J(P,B2) = 36$ Hz) due to coupling with two different boron atoms B1 and B2, respectively. The section of the ^{11}B NMR spectrum of **3** in Figure 5 reveals a triplet of doublets ($^1J(B1,H) = 109$ Hz, ($^1J(B1,P) = 72$ Hz) at $\delta = -10.3$ ppm, which are assigned to the internal H_2B1 group (Figure 5, top) and an additional signal at $\delta = -39.5$ ppm of the terminal H_3B2 moiety as a quartet of doublets ($^1J(B2,H) = 99$ Hz, $^1J(B2,P) = 36$ Hz) (Figure 5, bottom). The chemical shifts correspond to those found in the literature for $R_3N\text{-}BH_2\text{-}PMe_2\text{-}BH_3$ compounds.[20]

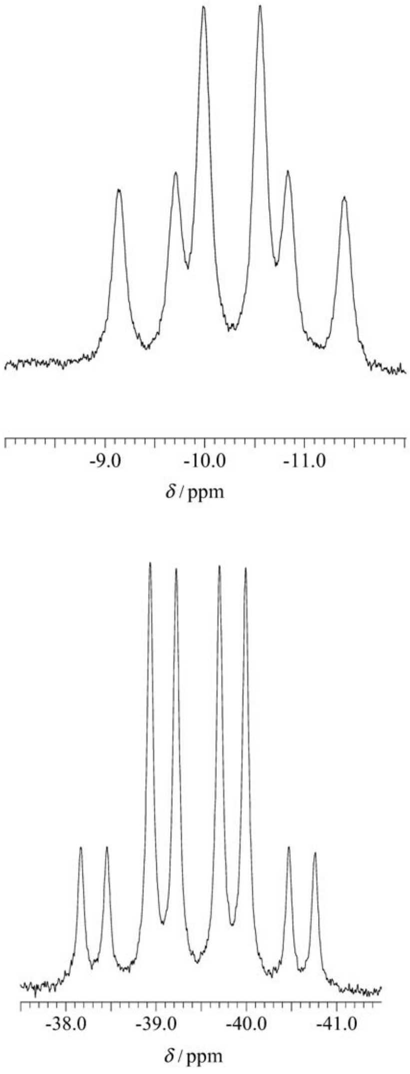


Figure 5. Sections of the ^{11}B NMR spectrum of $[(H_3B)H_2PBH_2{\cdot}NMe_3]$ (**3**) in C_6D_6.

The ^1H NMR spectra of compounds **5b** and **5c** exhibit quartets at $\delta = 2.18$ ($^1J(B,H) = 109$ Hz) and 2.40 ppm ($^1J(B,H) = 111$ Hz), respectively, owing to coupling with the B atom. At $\delta = 5.98$ (**5a**) and 5.04 ppm (**5b**) the hydrogen atoms of the PH_2 group could be detected as a doublet of multiplets, which are shifted strongly downfield because of the deshielding influence of the S and Se atoms, respectively. The chemical shifts correlate with the different electronegativities of the chalcogenides. The ^{31}P NMR spectra of both compounds show a triplet of quartets at $\delta = -45.6$ ppm ($^1J(P,H) = 376$ Hz, $^1J(P,B) = 89$ Hz) for the sulfur compound and $\delta = -84.5$ ppm ($^1J(P,H) = 372$ Hz, $^1J(P,B) = 82$ Hz) for the selenium compound, the latter additionally displaying selenium satellites ($^1J(P,Se) = 575$ Hz). The results for the coupled ^{31}P NMR spectra are in good agreement with those values determined for the NMR characterized compound $PhP(X)H_2$ ($X = S$, $\delta = -15$ ppm, $^1J(P,H) = 464$ Hz; $X = Se$, $\delta = -38$ ppm, $^1J(P,H) = 459$ Hz).[21] The $^{31}P\{^1H\}$ and ^{31}P NMR spectra of **6a** show broad quartets at $\delta = 56.1$ ppm ($^1J(P,B) = 192$ Hz), which are also shifted strongly downfield relative to the starting material **2** as a result of the oxidation of the phosphorus atom. The ^{11}B NMR spectrum of **6a** consists of a broad doublet of triplets at $\delta = -9.6$ ppm ($^1J(B,H) = 103$ Hz, $^1J(B,P) = 192$ Hz) owing to coupling of the boron atom with both hydrogen atoms and additionally with the phosphorus atom. All values are in good agreement with those of the ionic compound $[NH_4]_2[(HO)P(O)_2BH_3]$, which contains a coordinative P−B bond.[22]

Crystal structure analysis of the boranylphosphine chalcogenides and the boranylphosphonic acid: Crystals of **5b** and **5c** suitable for X-ray crystal determination were obtained by slow evaporation of CH_2Cl_2 from the reaction mixture under a stream of inert gas. Compounds **5b** and **5c** crystallize in the acentric orthorhombic space group $P2_12_12_1$ and the molecular structures are depicted in Figures 6 and 7, respectively. In the solid state the free rotation around the P−B bond of the central $H_2(X)PBH_2$ unit is frozen; the *gauche* conformers formed in the structures of compounds **5** (**5b:**

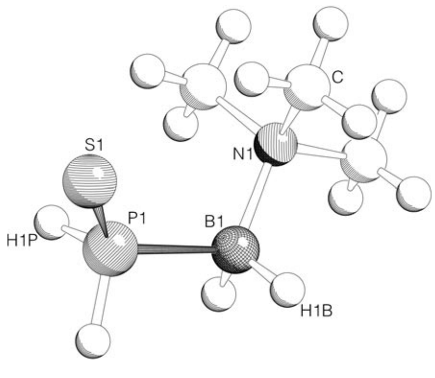


Figure 6. Molecular structure of $[H_2P(S)BH_2{\cdot}NMe_3]$ (**5b**) in the crystal. Selected bond lengths [Å] and angles [°]: S1−P1 1.9995(9), P1−B1 1.964(2), B1−N1 1.604(3); S1-P1-B1 123.51(10), P1-B1-N1 114.75(14), S1-P1-B1-N1 59.7(2).

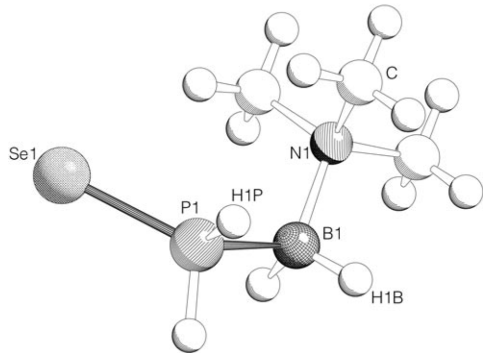


Figure 7. Molecular structure of $[H_2P(Se)BH_2{\cdot}NMe_3]$ (**5c**) in the crystal. Selected bond lengths [Å] and angles [°]: Se1–P1 2.1538(7), P1–B1 1.973(3), B1–N1 1.593(4); Se1-P1-B1 123.67(9), P1-B1-N1 115.1(2), Se1-P1-B1-N1 57.6(2).

−59.7(2)°, **5c:** 57.6(2)°) are thus chiral. Whereas **5b** crystallizes in an enantiometrically pure form, for the selenium compound **5c** both conformers are found to be in a racemic mixture with a ratio of about 1:1. With a value of 2.000(1) Å the P=S distance in **5b** shows no remarkable difference to common phosphine sulfide compounds (c.f. 1.967(1) Å in $[t\mathrm{Bu}_2P(S)H]$[23]). Similar observations were made for the structure of the selenium-containing compound **5c**. The P=Se bond length (2.154(1) Å) is in agreement with those found for $R_3P{=}Se$ compounds (e.g. R = C_6H_{11}: 2.108(1) Å).[24] The P–B bond lengths in both compounds (**5b:** 1.964(2) Å; **5c**: 1.973(3) Å) are similar to the initial compound **2** (1.976(2) Å). Thus, the chalcogenation of the P atom has no significant influence on the B–P bond length of the Lewis base stabilized phosphanylborane. Crystallographic data for compounds **2**–**6** are presented in Table 1.

Only the oxidation and complete transformation of the P–H bonds to POH, as found in the phosphonic acid **6a** (Figure 8 A), leads to significant shortening of the P–B core by 0.045 Å relative to the starting material **2** (1.976(2) Å). The shortest P–O1 bond in **6a** (1.525(2) Å) indicates the double-bond character, whereas the average P–OH bond lengths (1.581(2) Å) are in the typical range of P–O single bonds. Both bond lengths are in agreement with those found in the related ionic compound $[NH_4]_2[(HO)P(O)_2BH_3]$.[22] Owing to the increased steric demand of the double bonded O1 atom in **6a** a deviation from tetrahedral angles around the central phosphorus atom is observed. The torsion angle O3-P1-B1-N1 (172.78(15)°) indicates the staggered conformation of **6a**. An interesting structural feature is the intermolecular association of the molecules of **6a** in the solid state (Figure 8B). The alignment of the molecule of **6a** in the crystal lattice reveals average distances of 2.624(1) and 2.644(1) Å between the O1 atom and the oxygen atoms O2 and O3 of adjacent molecules, respectively. These distances

Table 1. Crystallographic data for compounds **2**–**6**.

	2	**3**	**4**	**5b**	**5c**	**6a**
empirical formula	$C_3H_{13}B_1N_1P_1$	$C_3H_{16}B_2N_1P_1$	$C_7H_{13}B_1Fe_1N_1O_4P_1$	$C_3H_{13}B_1N_1P_1S_1$	$C_3H_{13}B_1N_1P_1Se_1$	$C_3H_{13}B_1N_1O_3P_1$
formula mass [$g\,mol^{-1}$]	104.92	118.76	272.81	136.99	183.88	152.92
collection T [K]	110	123	123	123	123	173
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/m$ (no. 11)	$P2_1/m$ (no. 11)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)
a [Å]	5.5495(7)	5.4339(7)	6.6172(6)	7.7800(11)	7.8969(9)	6.1404(7)
b [Å]	8.8939(16)	8.6621(10)	9.7557(9)	9.0257(10)	9.1264(9)	16.9559(16)
c [Å]	7.3545(10)	8.8879(11)	9.9637(10)	11.3197(12)	11.3441(10)	7.7260(10)
α [°]	90	90	90	90	90	90
β [°]	106.932(15)	101.486(15)	97.741(11)	90	90	96.917(15)
γ [°]	90	90	90	90	90	90
V [Å^3]	347.26(9)	409.97(9)	637.35(11)	794.87(17)	817.57(14)	798.55(16)
Z	2	2	2	4	4	4
ρ_{calcd} [$g\,cm^{-1}$]	1.003	0.962	1.422	1.145	1.494	1.272
μ [mm^{-1}]	0.276	0.238	1.301	0.509	4.691	0.289
$F(000)$	116	132	280	296	368	328
crystal dimensions [mm]	0.16×0.32×0.40	0.04×0.18×0.48	0.12×0.24×0.38	0.02×0.10×0.28	0.08×0.19×0.46	0.06×0.10×0.42
2θ range	2.9–28.2	2.3–27.9	2.9–27.9	2.9–27.0	2.9–26.9	3.5–26.9
index ranges	$-7 \leq h \leq 7$	$-7 \leq h \leq 7$	$-8 \leq h \leq 8$	$-9 \leq h \leq 9$	$-10 \leq h \leq 10$	$-7 \leq h \leq 7$
	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$	$-12 \leq k \leq 12$	$-11 \leq k \leq 11$	$-11 \leq k \leq 11$	$-21 \leq k \leq 21$
	$-9 \leq l \leq 9$	$-11 \leq l \leq 11$	$-13 \leq l \leq 13$	$-14 \leq l \leq 14$	$-14 \leq l \leq 14$	$-9 \leq l \leq 9$
reflections collected	4182	4291	6781	9275	9668	6520
independent reflections	839	1038	3006	1700	1758	1324
goodness-of-fit on F^2	1.110	1.00	1.05	1.00	1.05	1.01
R_{int}	0.082	0.081	0.034	0.035	0.042	0.063
Flack parameter	–	–	−0.005(12)	0.07(14)	0.433(9)	–
parameters	61	56	148	76	77	94
R_1[a] [$I > 2\,s(I)$]	0.0342	0.0392	0.0256	0.0322	0.0218	0.0422
wR_2[b] (all data)	0.0955	0.1022	0.0652	0.0747	0.0505	0.1024
max/min $\Delta\rho$ [e Å^{-3}]	0.47/−0.32	0.38/−0.34	0.60/−0.26	0.31/−0.23/	0.49/−0.24	0.42/−0.19

[a] $R_1 = \Sigma|F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma\omega(F_0^2 - F_c^2)^2]/[\Sigma(F_0^2)^2]^{1/2}$.

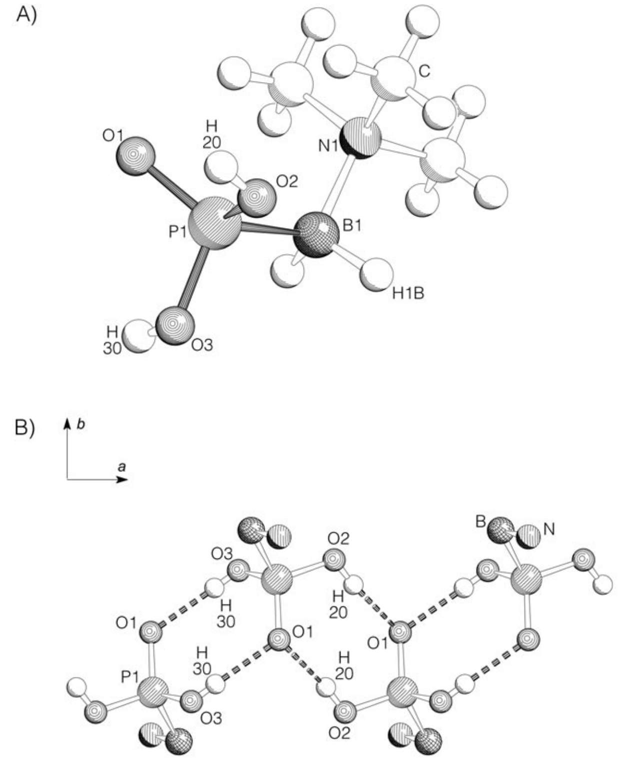


Figure 8. A) Molecular structure of $[(HO)_2P(O)BH_2{\cdot}NMe_3]$ (**6a**) in the crystal. Selected bond lengths [Å] and angles [°]: P1−B1 1.931(2), B1−N1 1.607(3), P1−O1 1.525(2), P1−O2 1.575(2), P1−O3 1.587(2); P1-B1-N1 115.59(15), O1-P1-B1 117.00(10), O2-P1-B1 109.15(10), O3-P1-B1 105.86(10), O1-P1-O2 110.30(9), O3-P1-B1-N1 172.79(0). B) Arrangement of the boranylphosphonic acid chains along the crystallographic *a* axis. The H atoms at the B atom and the methyl groups have been omitted for clarity. Selected interatomic bond lengths [Å]: O3···O1 2.644(1), O2···O1 2.624(1).

indicate hydrogen bonds ($H^{\delta+}\cdots{}^{\delta-}O$) that link the molecules together to form chains along the crystallographic *a* axis as shown in Figure 8B.

Conclusion

Our results have shown that removal of the Lewis acid from the Lewis acid/base stabilized phosphanylboranes $[W(CO)_5(PH_2BH_2NMe_3)]$ leads to the isolation of the first parent compound of a phosphanylborane $[H_2PBH_2{\cdot}NMe_3]$ (**2**) stabilized only by a Lewis base. This compound has a high potential for use in subsequent reactions for the high-yield synthesis of diverse functionalized phosphanylboranes, as was exemplified by the formation of novel Lewis acid substituted phosphanylboranes. Thus, we obtained $[(H_3B)H_2PBH_2{\cdot}NMe_3]$ (**3**), which contains a main-group Lewis acid, as well as $[Fe(CO)_4(H_2PBH_2{\cdot}NMe_3)]$ (**4**), which possesses a transition-metal moiety as a Lewis acid. The BH_3 substituted compound **3** represents the longest structurally characterized B-P-B chain with only hydrogen as a substituent. Furthermore, with the synthesis of the novel boranyl-substituted phosphonic acid **6a** and the boranylphosphine sulfide **5b** and selenide **5c**, insight was obtained into the stepwise oxidation processes of this unusual compound. The phosphonic acid $[(HO)_2P(O)BH_2{\cdot}NMe_3]$ **6a** displays intermolecular association in the solid state through hydrogen bonds. Owing to the high volatility of the Lewis base stabilized compound **2**, it also has the ability to become an interesting precursor in CVD techniques.

Experimental Section

General techniques: All manipulations were performed under an atmosphere of dry nitrogen using standard glovebox and Schlenk techniques. Solvents were purified and degassed by standard procedures. The starting material **1** was prepared according to our literature method.[6a] Photolysis reactions were carried out with a Hanau TQ 150 mercury lamp.

Synthesis of $[H_2PBH_2{\cdot}NMe_3]$ (2): $[(CO)_5W(H_2PBH_2)NMe_3]$ (**1**) (500 mg, 1.166 mmol) in Et_2O (30 mL) and $P(OMe)_3$ (4.1 mL, 30 equiv, 34.76 mmol) were placed in a Schlenk tube sealed with a mercury valve. The bottom of the tube was cooled by an ice-water bath. The solution was irradiated for 12 h by a mercury UV lamp, which was placed 4–5 cm from the Schlenk flask. The volatile by-products were removed under vacuum, to leave a yellow oil. The product was obtained by vacuum transfer from the oily residue at 60–65 °C (1×10^{-3} mbar) and condensation into a nitrogen-cooled Schlenk tube. *n*-Hexane (0.5 mL) was added to the colorless liquid, and **2** precipitated at −25 °C as a white crystalline solid (85 mg, 69 % yield). M.p. ~12 °C; ^1H NMR (400 MHz, $[D_6]C_6D_6$, 300 K, TMS ext.): $\delta = 1.58$ (dm, $^1J(P,H) = 189$ Hz, 2H; PH_2), 1.81 (s, 9H; NMe_3), 2.60 ppm (q, $^1J(B,H) = 106$ Hz, 2H; BH_2); $^1H\{^{31}P\}$ NMR (400 MHz, C_6D_6, 300 K, TMS ext.): $\delta = 1.58$ (m, 2H; PH_2), 1.80 (s, 9H; NMe_3), 2.59 ppm (q, $^1J(B,H) = 106$ Hz, 2H; BH_2); ^{31}P NMR (162 MHz, C_6D_6, 300 K, 85 % H_3PO_4 ext.): $\delta = -215.5$ ppm (br t, $^1J(P,H) = 189$ Hz; PH_2); $^{31}P\{^1H\}$ (162 MHz, C_6D_6, 300 K, 85 % H_3PO_4 ext.): $\delta = -215.5$ ppm (q, $^1J(P,B) = 31$ Hz; PH_2); ^{11}B NMR (128 MHz, $[D_6]C_6D_6$, 300 K, $Et_2O{-}BF_3$ ext.): $\delta = -6.7$ ppm (dt, $^1J(B,P) = 30$, $^1J(B,H) = 107$ Hz; BH_2); $^{11}B\{^1H\}$(128 MHz, C_6D_6, 300 K, $Et_2O{-}BF_3$ ext.): $\delta = -6.7$ ppm (d, $^1J(B,P) = 30$ Hz; BH_2); IR (film): $\tilde{\nu} = 3016$(w), 2998(m), 2943(m), 2917(w), 2375(vs), 2282(vs), 1482(s), 1462(vs), 1403(w), 1252(m), 1153(m), 1123(s), 1091(m), 1056(s), 1019(m), 981(m), 842(s), 576 cm^{-1}(w); EI-MS (70 eV): *m*/*z* (%): 105 (26) $[M^+]$, 72 (100) $[M^+ - PH_2]$; HRMS calcd for $C_3H_{13}N_1B_1P_1$: *m*/*z*: 105.0879, found: 105.0879.

Synthesis of $[(H_3B)H_2PBH_2{\cdot}NMe_3]$ (3): A 1 M H_3B–THF solution (0.48 mL, 0.476 mmol) was added to a solution of **2** (50 mg, 0.476 mmol) in toluene (3 mL) at room temperature. After stirring overnight and purification by sublimation (100 °C, 1×10^{-3} mbar), colorless crystals (46 mg, 82 % yield) were obtained. ^1H NMR (400 MHz, C_6D_6, 300 K, TMS ext.): $\delta = 1.67$ (q, $^1J(B2,H) = 99$ Hz 3H; $B2H_3$), 1.82 (s, 9H; NMe_3), 2.25 (q, $^1J(B1,H) = 109$ Hz, 2H; BIH_2), 3.32 ppm (dm, $^1J(P,H) = 323$ Hz, 2H; PH_2); $^1H\{^{31}P\}$ NMR (400 MHz, C_6D_6, 300 K, TMS ext.): $\delta = 1.67$ (q, ^1J(B2,H) $= 99$ Hz 3H; $B2H_3$), 1.82 (s, 9H; NMe_3), 2.25 (q, $^1J(B1,H) = 109$ Hz, 2H; $B1H_2$), 3.32 ppm (m, 2H; PH_2); ^{31}P NMR (162 MHz, C_6D_6, 300 K, 85 % H_3PO_4 ext.): $\delta = -116.0$ ppm (br t, $^1J(P,H) = 323$ Hz; PH_2); $^{31}P\{^1H\}$ (162 MHz, C_6D_6, 300 K, 85 % H_3PO_4 ext.): $\delta = -116.0$ ppm (qq, $^1J(P,B1) = 72$, $^1J(P,B2) = 36$ Hz; PH_2); ^{11}B NMR (128 MHz, C_6D_6, 300 K, Et_2O–BF_3 ext.): $\delta = -39.5$ (dq, $^1J(B2,H) = 99$, $^1J(B^2,P) = 36$ Hz; $B2H_3$), −10.3 ppm (dt, $^1J(B1,H) = 109$, $^1J(B^1,P) = 72$ Hz); $B1H_2$); $^{11}B\{^1H\}$(128 MHz, C_6D_6, 300 K, Et_2O–BF_3 ext.): $\delta = -39.5$ (d, $^1J(B2,P) = 36$ Hz; B^2H_3), −10.3 ppm (d, $^1J(B1,P) = 72$ Hz); $B1H_2$); IR (KBr): $\tilde{\nu} = 3017$(m), 3002(m), 2956(m), 2928(w), 2900(w), 2420(s), 2374(vs), 2298(m), 2261(m), 1480(s), 1472(s), 1405(m), 1246(m), 1153(m), 1128(s), 1072(vs), 1055(s), 1009(m), 978(m), 877(w), 852 cm^{-1}(s); EI-MS (70 eV): *m*/*z* (%): 118 (7) $[M^+ - H^{\bullet}]$, 105 (56) $[M^+ - BH_3]$, 72 (100) $[H_2BNMe_3]$; HRMS calcd for $C_3H_{15}N_1{}^{10}B_1{}^{11}B_2P_1$ $[(M-H^{\bullet})^+]$: *m*/*z*: 117.1165, found: 117.1165.

Synthesis of $[(CO)_4Fe(H_2PBH_2{\cdot}NMe_3)]$ (4): A suspension containing Fe_2CO_9 (274 mg, 0.752 mmol) in toluene (15–20 mL) was combined with

2 (79 mg, 0.752 mmol) in toluene (5 mL) at room temperature. The reaction was considered complete after all solid disappeared. The resulting red solution was filtered over Celite and the solvent removed under vacuum, to leave a red oil. Toluene (2 mL) was added to the oily residue. At −20 °C **4** was obtained (142 mg, 69 % yield) as yellow crystals. ^{1}H NMR (400 MHz, C_6D_6, 300 K, TMS ext.): δ = 1.56 (s, 9H; NM_3), 3.06 ppm (dm, ^1J(P,H) = 312 Hz, 2H; PH_2); ^{31}P NMR (162 MHz, [D_6]C_6D_6, 300 K, 85 % H_3PO_4 ext.): δ = −110.3 ppm (br t, ^1J(P,H) = 312 Hz; PH_2); ^{31}P{^{1}H} (162 MHz, C_6D_6, 300 K, 85 % H_3PO_4 ext.): δ = −110.3 ppm (q, ^1J(P,B) = 78 Hz; PH_2); ^{11}B NMR (128 MHz, C_6D_6, 300 K, Et_2O–BF_3 ext.): δ = −8.5 ppm (dt, ^1J(B,P) = 78, ^1J(B,H) = 140 Hz; BH_2); ^{11}B{^{1}H}(128 MHz, C_6D_6, 300 K, Et_2O-BF_3 ext.): δ = −8.5 ppm (d, ^1J(B,P) = 78 Hz; BH_2); IR (toluene): $\tilde{\nu}$ = 2436(w), 2403(w), 2265(w), 2042(vs), 1962(vs), 1934(vs), 1261(s), 1098(m), 1403(w), 1015(m), 809 cm^{-1}(m); EI-MS (70 eV): m/z (%): 273 (17) [M^+], 245 (25) [M^+−CO], 217 (9) [M^+−2CO], 189 (47) [M^+−3CO], 161 (61) [M^+−4CO].

Synthesis of [$H_2P(X)BH_2{\cdot}NMe_3$] (X = S (5b), Se (5c)): A solution of **2** (61 mg, 0.581 mmol) in CH_2Cl_2 was combined with either solid sulfur (18.6 mg, 0.581 mmol) or red selenium (45.9 mg, 0.581 mmol). After stirring at room temperature for 2 days, the mixture was filtered and the solvent was removed in vacuo to yield **5b** (66 mg; 83 %) or **5c** (83 mg, 77 %). **5b**: ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS ext.): δ = 2.18 (q, ^1J(B,H) = 109 Hz, 2H; BH_2), 2.91 (s, 9H; NMe_3), 5.98 ppm (br d, ^1J(P,H) = 376 Hz, 2H; (S)PH_2); ^{31}P NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4 ext.): δ = −45.6 ppm (tq, ^1J(P,H) = 376, ^1J(P,B) = 89 Hz; (S)PH_2); ^{31}P{^{1}H} (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4 ext.): δ = −45.6 ppm (q, ^1J(P,B) = 89 Hz, (S)PH_2); ^{11}B NMR (128 MHz, CD_2Cl_2, 300 K, Et_2O–BF_3 ext.): δ = −9.2 ppm (dt, ^1J(B,P) = 89, ^1J(B,H) = 109 Hz; BH_2); ^{11}B{^{1}H}(128 MHz, CD_2Cl_2, 300 K, Et_2O–BF_3 ext.): δ = −9.2 (d, ^1J(B,P) = 89 Hz; BH_2); IR (KBr): $\tilde{\nu}$ = 2996(w), 2945(w), 2435(vs), 2372(vs), 2295(vs), 1483(vs), 1468(vs), 1406(w), 1248(m), 1151(s), 1069(vs), 1007(m), 978(m), 959(m), 914(s), 874(vs), 822(w), 656(vs), 562 cm^{-1}(vs); CI-MS (NH_3): m/z (%): 138 (100) [MH^+], 106 (90) [MH^+−S]. **5c**: ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS ext.): δ = 2.40 (q, ^1J(B,H) = 111 Hz, 2H; BH_2), 2.92 (s, 9H; NMe_3), 5.04 ppm (dm, ^1J(P,H) = 372 Hz, 2H; (Se)PH_2); ^{31}P NMR (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4 ext.): δ = −84.5 ppm (tq, ^1J(P,H) = 372, ^1J(P,B) = 82 Hz; (Se)PH_2); ^{31}P{^{1}H} (162 MHz, CD_2Cl_2, 300 K, 85 % H_3PO_4 ext.): δ = −84.5 ppm (q, ^1J(P,B) = 82 Hz, ^1J(P,Se) = 575 Hz; (Se)PH_2); ^{11}B NMR (128 MHz, CD_2Cl_2, 300 K, Et_2O–BF_3 ext.): δ = −9.2 ppm (dt, ^1J(B,P) = 82, ^1J(B,H) = 111 Hz; BH_2); ^{11}B{^{1}H}(128 MHz, CD_2Cl_2, 300 K, Et_2O–BF_3 ext.): δ = −9.2 (d, ^1J(B,P) = 82 Hz; BH_2); IR (KBr): $\tilde{\nu}$ = 3007(w), 2993(w), 2942(w), 2435(vs), 2369(vs), 2301(s), 1947(m), 1482(m), 1467(s), 1404(m), 1262(w), 1241(m), 1151(s), 1126(s), 1079(m), 1063(vs), 1004(m), 892(s), 872(s), 834(w), 443 cm^{-1}(s); CI-MS (NH_3): m/z (%): 186 (61) [MH^+], 106 (100) [MH^+−Se].

Synthesis of [$(HO)_2P(O)BH_2{\cdot}NMe_3$] (6a): Compound **2** (50 mg, 0.476 mmol) in THF (5 mL) was stirred in a broad Schlenk flask for two days under air until colorless crystals in an oily by-product were obtained. The crystals of **5** were washed with acetone (4 mL) and dried under vacuum to yield 43 mg (59 %). ^{1}H NMR (600 MHz, [D_6]DMSO, 300 K, TMS ext.): δ = 2.06 (br q, ^1J(H,B) = 103 Hz, 2H; BH_2), 2.71 ppm (s, 9H; NMe_3);[25] ^{31}P NMR (243 MHz, [D_6]DMSO, 300 K, 85 % H_3PO_4 ext.): δ = 56.1 ppm (br q, ^1J(P,B) = 192 Hz; PB); ^{31}P{^{1}H} (243 MHz, [D_6]DMSO, 300 K, 85 % H_3PO_4 ext.): δ = 56.1 ppm (br q, ^1J(P,B) = 192 Hz; PB); ^{11}B NMR (193 MHz, [D_6]DMSO, 300 K, Et_2O–BF_3 ext.): δ = −9.6 ppm (td, ^1J(B,H) = 103, ^1J(B,P) = 192 Hz; BH_2); ^{11}B{^{1}H}(193 MHz, [D_6]DMSO, 300 K, Et_2O–BF_3 ext.): δ = −9.6 ppm (br d, ^1J(B,P) = 192 Hz); IR (KBr): $\tilde{\nu}$ = 3015(s), 2954(s), 2813(vs), 2422(s), 2393(s), 2309(m), 1635(w), 1485(s), 1467(s), 1217 (vs), 1137(w), 1102(s), 1082(s), 980(m), 941(s), 902(m), 862 cm^{-1}(s); CI-MS (NH_3): m/z (%): 154 (34) [MH]$^+$, 153 (9) [M]$^+$; HRMS calcd for $C_3H_{12}N_1B_1P_1O_3$: m/z: 152.0648, found: 152.0644.

Computational details: The geometries of the compounds were fully optimized with gradient-corrected density functional theory (DFT) in the form of Becke's three-parameter hybrid method B3LYP[14] with the 6–31G* standard, all electron basis sets as implemented in the Gaussian 98 program package.[15] All structures correspond to the minimum on the potential energy surface (PES).

Crystal structure analysis: The crystal structure analyses of **2**–**6** were performed on a STOE IPDS diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The structures were solved by direct methods with the program SHELXS-97[26a] and full-matrix least-squares refinement on F^2 in SHELXL-97[26b] was performed with anisotropic displacements for non-hydrogen atoms. Hydrogen atoms at the B, P, and O atoms of all compounds could be localized by residual electron density and were freely refined. The other H atoms were located in idealized positions and refined isotropically according to the riding model. All examined crystals of complex **3** consisted of at least two intergrown domains; no twinning law could be found. Therefore the reflections of the crystal with the strongest main domain were used for all calculations, regardless of whether they were influenced by the weak domains or not. This led to a somewhat elevated wR_2 value. The crystal of compound **6a** was found to be a twin (twin axes [100]). Only those reflections that were not influenced by the second domain were used for all calculations. Complexes **4** and **5b**,**c** crystallize in acentric space groups and show Flack parameters that indicate the existence of pure enantiomers for **4** and **5b** and the occurrence of a racemic mixture in the crystal of **5c**.

CCDC-289418 (**2**), CCDC-289419 (**3**), CCDC-296923 (**4**), CCDC-296924 (**5b**), CCDC-296925 (**5c**), and CCDC-289420 (**6a**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was comprehensively supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Received: February 9, 2006