Contributions to the Chemistry of Boron, 227[◇]

The P-centered Chemistry of [(Di-*tert*-butylphosphanyl)imino]-(2,2,6,6-tetramethylpiperidino)borane☆

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The elements oxygen, sulfur, and selenium add to the P atom of the title borane **1**. In contrast to the formation of tmp$-$B$\equiv$N$-$P(X)*t*Bu_2 (X = S, Se), the *P* oxide (X = O) dimerizes to [tmp$-$B$\equiv$N$-$P(O)*t*Bu_2]$_2$ (**5**) with an eight-membered flat boat-shaped $B_2N_2P_2O_2$ ring. Borane **1** reacts readily with MeI to yield a phosphonium salt **8** and with BBr_3 to give an adduct **9** with a B$-$P bond. In contrast, bis(dichloroboryl)methane not only adds to **1** to generate a coordinate B$-$P bond but also chloroborates the B$\equiv$N triple bond, the final product being a new five-membered heterocycle **10**. Similarly, the BH_3 component of $BH_3 \cdot SMe_2$ first adds to the P atom of **1** followed by reaction of a second mol of $BH_3 \cdot SMe_2$ which hydroborates the B$\equiv$N triple bond. Finally, metal carbonyl fragments add only to the P atom of **1**, demonstrating also that the chemistry of the molecule **1** is dominated by the basicity of its P center.

The chemistry of the amino-imino-borane **1**[2,3] which carries a di-*tert*-butylphosphanyl group at the imino nitrogen atom differs considerably from the chemistry of other amino-imino-boranes, for example compound **2**[4]. Thus, hydrogen halides add to the phosphorus atom of **1** with formation of phosphonium salts[2a]. In contrast, hydrogen halides attack the B$\equiv$N triple bond of **2** yielding tmp$-$B(Hal)$-$NHR[5]. In order to get more information about the regiochemistry of **1** we have studied the behavior of this compound towards reagents which are strongly phosphophilic or are known to attack the B$\equiv$N triple bond rapidly.

Reactions with Chalcogens

It is well-known that trialkylphosphanes are readily oxidized by elemental oxygen. We have found that **1** is no exception. It reacts readily with molecular oxygen, and more slowly with air. If air is used to oxidize **1** or if oxygen stays only in short contact with **1** then the seven-membered heterocycle **3** results which can be regarded as the [3 + 4] cycloaddition product of tmp$-$B$\equiv$N$-$P(O)*t*Bu_2 (**4**) with **1**. If oxygen gas is bubbled through a solution of **1** or if air is kept in long contact with **1**, then the eight-membered heterocycle **5** is the product of oxidation. Compound **5** may be looked at as the [4 + 4] cycloaddition product of two molecules of **4**.

Oxidation of the phosphorus center of **1** can also be achieved by elemental sulfur or selenium. The products **6** and **7** show no tendency to dimerize like **4**.

That the reaction of **1** with oxygen produces no **4** is readily seen by the missing ν(B$\equiv$N) band at about 1935 cm^{-1} (as for **1**) in compounds **3** and **5**. Moreover, the mass spectrum of **3** exhibits the peak of the molecular ion at *m*/*z* = 636, however, not with the correct isotope pattern due to formation of the ions $[M - H]^+$ and $[M - 2H]^+$. Further support for the suggested structures of **3** and **5** comes from NMR data. The ^{11}B-NMR spectrum of **5** shows a signal at $\delta = 23$[6] which would also be compatible with the structure tmp$-$B$\equiv$N$-$P(O)*t*Bu_2 (**4**) but also with an environment around a tricoordinate planar boron atom carrying two N atoms and one O atom[7], i.e. the structural element postulated for **5**. Consequently, the structure of **5** cannot be deduced from ^{11}B-NMR data alone. However, there comes support from the ^{11}B-NMR data of compound **3** which shows two signals at $\delta = 29.9$ (atom B4) and 24.1 (B7). These are close to the resonance observed for **5**. The latter signal is just about to be split into a doublet at 233 K as expected for the presence of a boron-phosphorus bond. No splitting due to BP coupling has been observed for the ^{11}B- and the ^{31}P-NMR signal of **5**.

According to the ^{1}H- and ^{13}C-NMR data of **5** all *t*Bu groups are chemically equivalent, and the presence of only four ^{13}C-NMR signals for the tmp group either indicates free rotation about the BN bond or points to a planar eight-membered ring. In contrast, there are two sets of *t*Bu groups in **3**, and the methyl substituents at the piperidino units are represented by three ^{13}C resonances. Considering also the other resonances for the tmp rings this observation would be in accord with two different tmp groups, one group rotating freely, while the other is not dynamic. We

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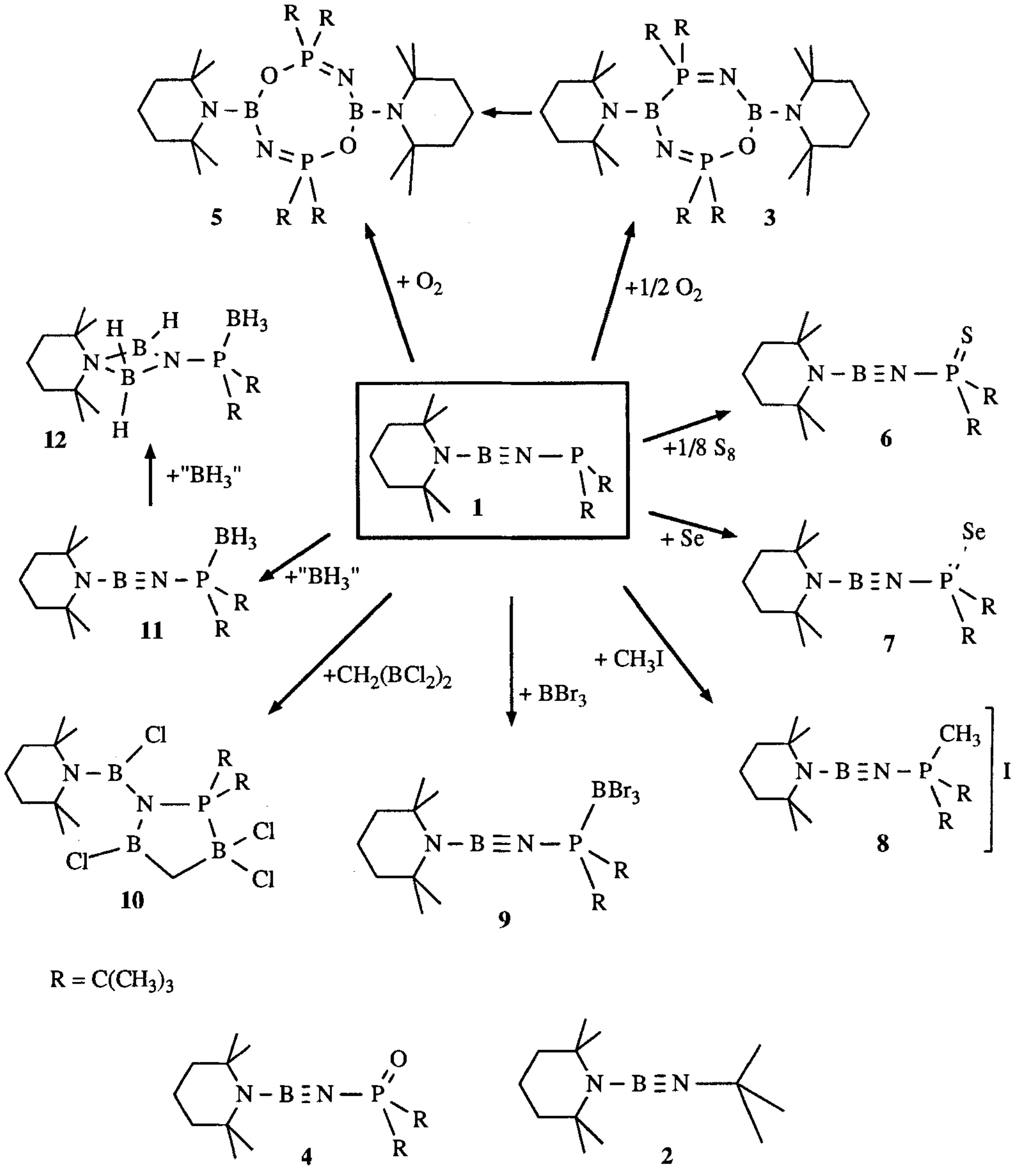
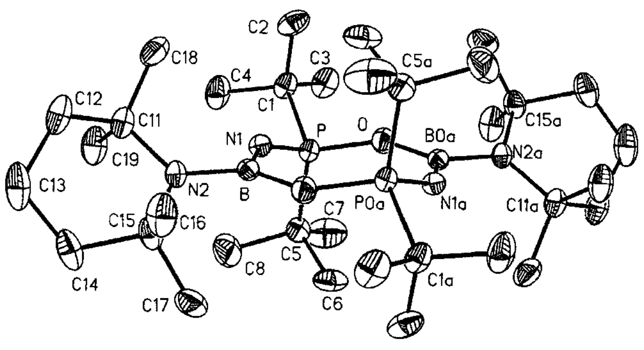
Scheme 1. Some reactions of [(di-*tert*-butylphosphanyl)imino](2,2,6,6-tetramethylpiperidino)borane (**1**)



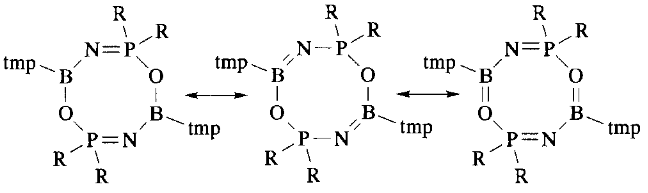
assign the latter group to be linked to the boron atom which is directly bound to a P atom in **3** because steric crowding should be operative at this site. Since the conformation of the rings in **3** and **5** cannot be deduced from NMR data we have determined the molecular structure of **5** by X-ray crystallography.

Compound **5** crystallizes in the triclinic system, space group $P\bar{1}$ with $Z = 1$. Therefore, the molecule must possess a crystallographically imposed center of inversion. This can be readily noticed from Figure 1 which depicts the molecular structure in the crystal. The eight-membered ring is not planar but adopts a flat chair conformation. Intraring angles at the imino nitrogen and oxygen atoms are 141.9 and 141.3°, respectively. These are rather wide for possible sp^2-hybridized atoms and suggest considerable π bonding to their neighboring atoms. Even the O$-$P$-$N bond angle is 121.6°, indicating strong distortions for a tetrahedrally coordinated P atom. However, the C$-$P$-$C bond angle (110.5°) is almost tetrahedral. The only internal ring angle that keeps close to the expected bond angle for an sp^2-hybridized atom subtends at the boron atom with a value of 118.4°. Nevertheless, the difference in P$-$N and P$-$O bond lengths is very small [1.545/1.555(2) Å]. Since the scattering power of N and O atoms are not very different, there may be some ambiguity concerning the positions of the N and O atoms in **5**. However, this can almost certainly be excluded since the thermal parameters for these two atoms differ sufficiently. Calculations with reversed positions not only lead to bond lengths that are practically identical [1.563(2)/1.560(2) Å] but have less likely thermal parameters. Nevertheless, the B$-$O bond is comparatively long [1.410(3) Å] and would not really comply with π-bonding arguments because B$-$O bonds to tricoordinated boron atoms comprise usually the range of 1.35 to 1.38 Å[8]. The same holds for the B–N bond length. However, 1.425(3) Å is compatible with a sufficient π-bond character of the B–N-bond as found in many mono- and diaminoboranes[9]. On the other hand, the B–N bond to the exocyclic tmp group is even longer, 1.459(4) Å, and this fits with the twisting of the C11–N2–C15 plane of the tmp group by 33.6° with respect to the BN_2O plane, reducing its π-bond strength. The tmp group itself adopts a twist conformation.

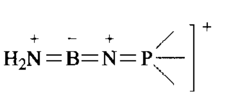
Figure 1. ORTEP-type plot of the molecular structure of **5** in the solid state. Thermal ellipsoids are drawn on a 25% probability scale. Hydrogen atoms are omitted for clarity. Estimated standard deviations are given in parenthesis. Selected bond lengths [Å]: P–N1 1.563(2), P–O 1.560(2), P–C1 1.864(4), P–C5 1.862(3), B–N1 1.424(3), B–O* 1.445(3), B–N2 1.459(4), N2–C11 1.493(5), N2–C15 1.497(4); selected bond angles [°]: C1–P–C5 110.5(1), P–N1–B 141.9(2), B*–O–P 141.3(2), O–P–N1 121.6(1), N1–B–O* 122.7(3), N1–B–N2 118.9(3), N2–B–O* 118.4(2), C1–N2–C15 117.4(3); B* = B0a, O* = equiv. to O



In summary, the bonding in compound **5** is best described by the three structures **A**–**C**, with the first two contributing primarily to the ground state not taking into account the π bonding to the exocyclic tmp group.



A **B** **C**



D

The structures suggested for compounds **6** and **7** correspond fully with their NMR data. $\delta^{31}P$ = 85.6 for **6** represents a typical chemical shift for a $R_2NP(S)R_2$ unit[10], and the ^{31}P-NMR signal for **7** is a doublet at δ = 85.6 with $^1J(^{79}Se^{31}P)$ = 818 Hz. Two bands at 1940 and 1880 cm^{-1} for **6** (one of medium intensity, the other of high intensity as expected for the presence of ^{10}B and ^{11}B isotopes) are typical of an iminoborane. These characteristic bands are found at 1900 and 1840 cm^{-1} for **7**. With these data at hand there is no doubt as to the iminoborane structure of these two compounds.

Reaction with Methyl Iodide

Another reaction that is typical of phosphanes is the formation of phosphonium salts. This holds also for the reaction of **1** with MeI, and the phosphonium salt **8** is readily generated in quantitative yield. All NMR data are in consonance with the suggested structure, and the B≡N stretching bands at 1930/1870 cm^{-1} demonstrate the preservation of the amino-imino-borane structure.

Due to the lack of any detailed structural information on compounds **6** to **8**, we have performed MNDO/CNDO calculations on the model compounds $H_2N–B≡N–PMe_2$, $H_2N–B≡N–P(S)Me_2$, and $H_2N–B≡N–PMe_3^+$. The results are summarized in Table 1.

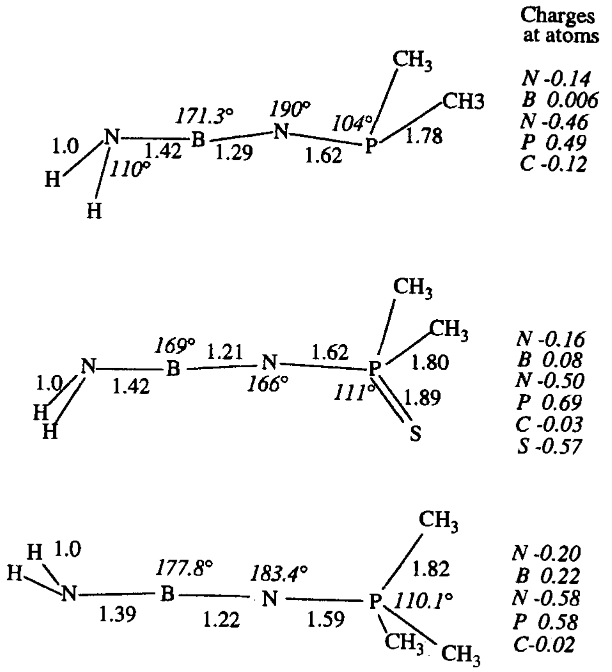
Table 1. MNDO results on model compounds $H_2N–B≡N–P(X)Me_2$

	ΔH_f [kcal/mol]	μ [Debye]	Bond order	HOMO/LUMO [eV]
$H_2N–B≡N–PMe_2$	−57.3	1.68	H_2N–B 1.18 B≡N 2.25 P–N 1.28	10.65
$H_2N–B≡N–P(S)Me_2$	−25.6	4.86	H_2N–B 1.19 B≡N 2.19 P–N 1.27 P=S 2.34	7.72
$H_2N–B≡N–PMe_3^+$	−17.7	17.1	H_2N–B 1.31 B≡N 1.99 P–N 1.49	8.70

The most surprising fact for $H_2N–B≡N–PMe_2$ is that the nitrogen atom of the amino group should be pyramidal and not, as expected and experimentally verified for tmp–B≡N–R[11], planar. The model compound $H_2N–B≡N–PMe_2$ is thermodynamically stable with ΔH_f^0 = −57.3 kcal/mol, and the BN bond order is calculated to be 2.25. This latter value is at the lower end for a series of compounds of imino-substituted amino-iminoboranes[2]. Consequently, the P–N bond order has been calculated as 1.28 and the P–N bond length as 1.62 Å. However, both data are most likely not very correct because it is known that the MNDO method yields too short bond lengths for elements of the third period. The thioxo compound $H_2N–B≡N–P(S)Me_2$ is thermodynamically less favored than $H_2N–B≡N–PMe_2$. Also, the B–N bond order is reduced while the P–N bond order remains unaffected in spite of the slight shortening of the P–N bond. Although one might expect a P–S bond order of 2 for $H_2N–B≡N–P(S)Me_2$, the calculated value is actually 2.34.

The presence of a full positive charge at the cation $H_2N–B≡N–PMe_3^+$ leads to charge localization at the P atom, to a significant decrease of the B≡N bond order to 1.99, and an increase of the B–N bond order for the H_2N–B unit (1.31) and the P–N bond (1.49). Thus, the allene-type mesomeric form **D** contributes significantly to the ground state of the cation. The calculated ground state geometries are depicted in Figure 2.

Figure 2. Structural parameters of $H_2N-B{\equiv}N-P(X)Me_2$ model compounds as calculated by MNDO methods



Reactions with Boron Halides and Borane BH_3

Boron halides are known to react with iminoboranes[12,13] and amino-imino-boranes[14] with haloboration of the $B{\equiv}N$ triple bond. Borane **1** also reacts easily with boron halides. However, BBr_3 only adds to the P atom of **1**. The adduct **9** separates from a hexane solution at −78°C, and BBr_3 in excess will not react further even at ambient temperature. In contrast, bis(dichloroboryl)methane not only adds with one of its boryl groups to the P atom of **1** but also chloroborates the $B{\equiv}N$ triple bond of **1** to produce the ring compound **10**. Therefore, the rather bulky BBr_3 unit may be responsible for preventing the bromoboration of **1**.

This assumption is substantiated by the ready addition of the BH_3 component of $BH_3 \cdot THF$ or $BH_3 \cdot SMe_2$ to **1**. Since the latter reagent has proven to be more effective than $BH_3 \cdot THF$ we have allowed $BH_3 \cdot SMe_2$ to react with **1**, and we studied this interaction in more detail. Using a 1:1 molar ratio, we have obtained the P−borane adduct **11**. Application of additional borane−dimethyl sulfide leads to hydroboration of the $B{\equiv}N$ triple bond of **11**, and the hydroboration product **12** is stabilized by an intramolecular B−N coordinative bond.

The structure of compounds **9** to **12** can be deduced from IR and NMR spectra. IR bands at 1935 and 1876 cm^{-1} observed for **9** proves the presence of an intact $B{\equiv}N$ bond. Similarly, there are two bands at 1964 and 1910 cm^{-1} in the IR spectrum of compound **11**. Bands in this region are missing in compounds **10** and **12**, and this clearly indicates that haloboration and hydroboration, respectively, have occurred in these cases. Further proof that a simple 1:1 addition product is present in the BBr_3 adduct of **1** comes from its ^{31}P-NMR spectrum which shows a 1:1:1:1 quartet at $\delta = 35.2$ with $^1J(^{31}P^{11}B) = 141$ Hz and from its ^{11}B-NMR spectrum which shows a doublet at $\delta = -12.5$. In addition to these sharp signals, there is a fairly broad ^{11}B resonance at $\delta = 21.9$ for the B atom of the iminoborane unit. Four signals for the tetramethylpiperidino group in the ^{13}C-NMR spectrum of **9** indicate free rotation of the $PtBu_2(BBr_3)$ group about the P−N bond, and this fits with the observation of only two ^{13}C resonances for the *t*Bu groups.

The BH_3 adduct of **1** (= **11**) shows also a quartet for its P atom in the ^{31}P-NMR spectrum proving the presence of a B−P bond. However, $^1J(^{31}P^{11}B)$ is only 68.2 Hz, which is much smaller than in compound **9**. There are also two ^{11}B-NMR signals: a broad one at $\delta = 20.7$ results from the iminoborane group, the second one at $\delta = -33.7$ is indicative of a tetracoordinated B atom. This signal shows a fine structure, and on proton decoupling a doublet with $^1J(PB) = 97.2$ Hz and a doublet of a quartet [$^1J(BH) = 95.5$ Hz] prove the presence of a BH_3 group. Finally, there is free rotation about the B−P and/or the B−N bond of the tmp group since there are only four ^{13}C resonances for the tmp group.

The most relevant structural information about compound **10** is provided by its ^{11}B- and ^{31}P-NMR spectra. There are three ^{11}B-NMR signals, two for tricoordinated boron moieties ($\delta = 53.2, 33.5$) and one for a tetracoordinated B atom. The latter is a doublet [$^1J(PB) = 83$ Hz]. The ^{31}P-NMR resonance appears as a quartet (partially relaxed). This indicates the presence of a BP bond to a tetracoordinated boron atom. The shielding of the other two B resonances is indicative of the presence of an BC(N)Cl and a $BClN_2$ moiety[7]. Again, only four ^{13}C resonances for the tmp group appear in the ^{13}C-NMR spectrum, and this group therefore rotates freely at ambient temperature.

The structures deduced from NMR data for compounds **10** and **12** have been confirmed by X-ray structural analysis. Figure 3 shows a molecule of compound **10**. The five-membered B_2PCN ring is present in an envelope conformation, the P atoms lying 0.66 Å outside of the B_2CN plane. This corresponds with a folding angle of 148.6° between the planes B1PN1 and B1CB2N1. There is also a twist angle of 135.6° of the BCl3N2 plane and the best plane through atoms B1CB2N1 but of only 21.6° with the B1PN1 plane, while the C11N2C15 plane of the tmp group is oriented against the Cl3BN2 plane by 51.6°. This twisting should prohibit strong BN-π bonding to N2, but the B−N2 bond length is actually fairly short with 1.403(3) Å and the shortest B−N bond in this molecule. The longest B−N bond [1.472(4) Å] is the B3−N1 bond. This can be understood more readily because N1 is not only part of a "diborylamine" system, but also connected to the P atom. Its P−N bond [1.738(2) Å] is rather long for a trigonal-planar nitrogen atom bound to a phosphorus atom and has to be considered a P−N single bond[15], and this holds also for the P−B bond [2.041(4) Å]. Finally, the BCl bonds to the tetracoordinated boron atom B1 are significantly longer than those to the tricoordinated boron atoms.

Figure 3. ORTEP-type representation of the molecular structure of **10** in the crystal. Thermal ellipsoids are represented on a 25% probability limit. Selected bond length [Å]: B1–Cl1a 1.863(3), B1–Cl1b 1.866(4), B2–Cl2 1.777(3), B3–Cl3 1.810(3), B1–P 2.041(4), B1–C 1.595(4), P–N1 1.738(2), N1–B2 1.451(4), N1–B3 1.472(4), N2–B3 1.403(3). – Selected bond angles [°]: C–B1–P 99.2(2), B1–P–N1 94.8(1), P–N1–B2 106.9(2), N1–B2–C 119.1(2), B2–C–B1 109.2(2), N1–B3–N2 125.9(2), N1–B3–Cl3 115.3(2), N2–B3–Cl3 118.8(2), C–B1–Cl1a 116.5(2), C–B1–Cl1b 110.4(2), C1–P–C5 115.2(1), C–B2–Cl2 119.5(2)

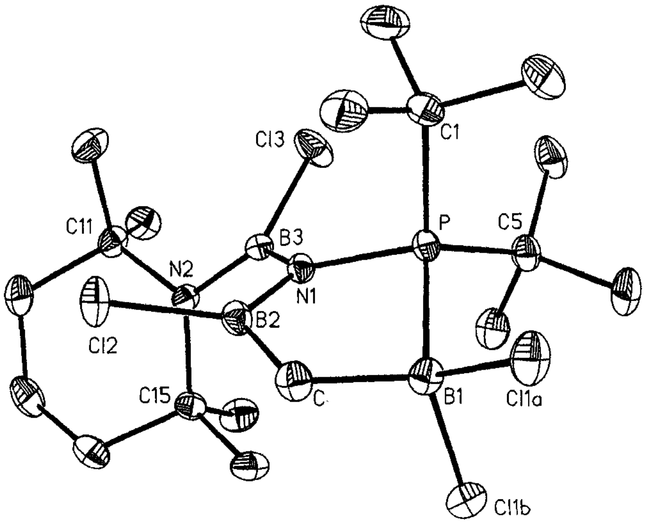
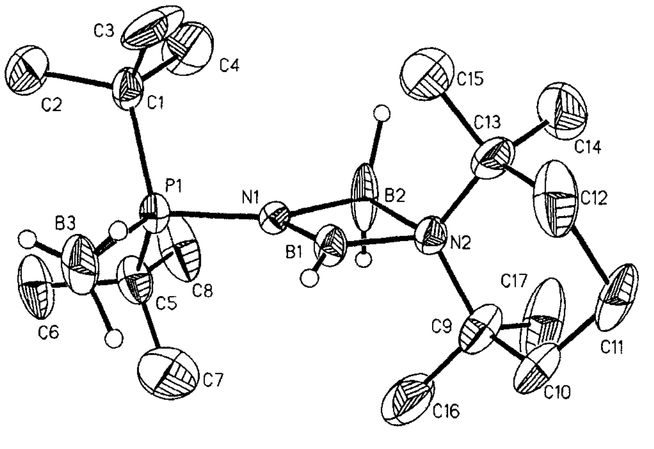


Figure 4. ORTEP-type representation of one of the two independent molecules of **12**. Thermal ellipsoids are drawn on a 25% probability level. Hydrogen atoms, except those at the B atoms, are omitted for clarity. E.s.d.s are given in parenthesis. – Selected bond lengths [Å]: P1–N1 1.703(7), N1–B2 1.57(1), B2–N2 1.69(1), B1–N2 1.50(1), B1–N1 1.35(1), N2–C9 1.52(1), N2–C13 1.49(2), P1–B3 1.92(29), P1–C1 1.835(9), P1–C5 1.83(1). – Selected bond angles [°]: B3–P1–N1 111.9(5), N1–B2–N2 86.6(9), B2–N2–B1 80.4(7), N2–B1–N1 103.4(9), B1–N1–B2 89.6(8), B1–N1–P1 129.4(7), B2–N2–C9 115.3(9), B2–N2–C13 116.1(8)



The molecular structure of the hydroboration product of **1** is depicted in Figure 4. There are two crystallographically independent molecules in the unit cell which differ primarily by torsion angles. The four-membered B_2N_2 ring is planar. The most noticeable feature of this ring system is the presence of four different B–N bond lengths which cover the range from 1.35 to 1.69 Å. The two shorter bonds are associated with the tricoordinated boron atom B1, and the short B1–N1 bond exhibits high double bond character. The B–N bonds to the tetracoordinated atom B2 are significantly longer, and the bond B2–N2 (atom distance 1.69 Å) has to be considered a very weak B–N bond. In contrast, we observe a rather normal coordinative B3–P1 bond length of 1.92 Å[16].

Reactions with Metal Carbonyls

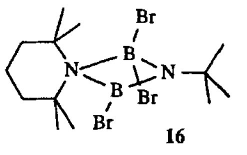
Hexacarbonylchromium and -tungsten react with **1** under photochemical conditions with evolution of 1 mol of CO and formation of the P-metal pentacarbonyl complexes of the ligand **1** as shown in eq. (1). Methylcymantrene behaves similarly and yields complex **15** as orange-colored crystals.

$$\mathrm{tmp\text{-}B{\equiv}N\text{-}P(CMe_3)_2 + M(CO)_6 \xrightarrow[(1)]{h\nu} tmp\text{-}B{\equiv}N\text{-}P(CMe_3)_2{\cdot}M(CO)_5 + CO}$$

$$\begin{array}{c|cc} \mathrm{M} & \mathrm{Cr} & \mathrm{W} \\ \hline & \mathbf{13} & \mathbf{14} \end{array}$$

$$\mathrm{tmp\text{-}B{\equiv}N\text{-}P(CMe_3)_2 + MeCpMn(CO)_3 \xrightarrow{h\nu}} \tag{2}$$

$$\underset{\mathbf{15}}{\mathrm{tmp\text{-}B{\equiv}N\text{-}P(CMe_3)_2{\cdot}MeCpMn(CO)_2}} \mathrm{+CO}$$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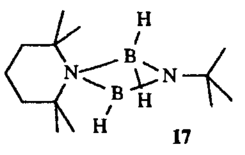
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The structure of compound **14** is ascertained by the ^{183}W satellite in its ^{31}P-NMR spectrum, and, in addition, by the $^{31}P^{13}C$ coupling to the ^{13}C nuclei of the carbonyl moiety, both in **13** and **14**. Moreover, these compounds exhibit B≡N stretching bands showing the intact iminoborane unit. $^{31}P^{13}C$ coupling is also observed both for the cyclopentadienyl carbon atoms and the carbonyl ^{13}C atoms of **15**. The coupling constant $^2J(^{31}P^{13}C)$ is 16 Hz, i.e. the same value as found for compounds **13** and **14**. The presence of a Mn–P bond is also indicated by the ^{31}P-NMR signal of **15** which is rather broad (56 Hz), due to coupling of the ^{31}P nucleus with ^{55}Mn ($I = 5/2$). This coupling should actually give rise to a sextet which can neither be observed at low or higher temperature. Therefore, quadrupolar relaxation must be fast. The ^{31}P nucleus in **15** is much more deshielded than in compounds **13** and **14**, and this holds also for the ^{11}B nucleus. These effects are most likely due to a stronger paramagnetic effect of the methylcymantrene unit than of the more symmetric $M(CO)_5$ groups.

Discussion

The present study clearly reveals a P-centered chemistry of the amino-imino-borane **1** as many of the observed reactions are typical of triorganylphosphanes. However, due to the presence of the iminoborane unit with its dicoordinated boron atom, reactions at these site modify the chemistry of **1** and make its chemistry more interesting. This is readily demonstrated by the reactions of **1** with oxygen which generate new boron-containing heterocycles, and this formation is best explained by cycloaddition reactions of the assumed intermediate $\mathrm{tmp{-}B{\equiv}N{-}P(O)}t\mathrm{Bu}_2$ (**4**). That **4** is not monomeric, as is the case with **6** and **7**, is due to the high thermodynamic driving force which is provided by the formation of boron-oxygen links.

A comparison of the B≡N stretching modes of **6**, **7**, **8**, **9**, and **11** reveals that the strength of this bond, in a first approximation, decreases as the group X in $\mathrm{tmp{-}B{\equiv}N{-}P(X)}t\mathrm{Bu}_2$ changes from BH_3 via S, BBr_3, CH_3^+ to Se. This weakening may be explained by a strengthening of the P−N bond. Thus, BBr_3 is a stronger Lewis acid than BH_3, and this will impose more positive charge on the P atom. This effect is even stronger in the case of CH_3^+. The fact that the selenide **7** has a weaker B≡N bond as compared to **6** is most likely due to the fact that the P=Se bond has less double bond character, and this would favor an increase of the P=N double bond character. Although the results of the MNDO calculations can be considered only as a first and preliminary approximation they tend to confirm the qualitative interpretation of the influence of X on the strength of the B≡N triple bond.

The addition of metal carbonyl fragments to the P atom of **1** changes the strength of the B≡N bond to a smaller extent than the BX_3 units and the chalcogen atoms. Compared with $Ph_3P \cdot M(CO)_5$ (M = Cr, W)[17] the ligand **1** is a slightly more effective donor than Ph_3P, and this also holds for the cymantrene compound **15** in comparison with $MeCpMn(CO)_2PPh_3$[18].

Although haloborations of iminoboranes[12,19] and amino-imino-boranes[4,14] occur readily this type of reaction has not been observed with **1** and BBr_3 in contrast to the reaction of **1** with $Cl_2BCH_2BCl_2$. This proves that the boron halides attack at the imino nitrogen atom to induce haloboration, and this step is sterically prevented in the case of the addition of BBr_3 to **1**. Additional support for this stepwise reaction comes from the formation of **12** which proceeds via the BH_3 addition product **11**. Compound **12** is a molecule which not only contains a BH, BH_2 and a BH_3 unit at the same time but also four different types of B−N bonds [$B(sp^2){-}N(sp^2)$, $B(sp^2){-}N(sp^3)$, $B(sp^3){-}N(sp^2)$, and $B(sp^3){-}N(sp^3)$] within one molecule. These kinds of molecules have been reported previously for three cases; the haloboration product of $\mathrm{tmp{-}B{\equiv}N{-}CMe_3}$ with BCl_3 and BBr_3, **16**[14], and the hydroboration product **17**[20]. However, the latter compound was characterized by NMR methods only.

A comparison of the structure of **12** with those of compound **16** reveals an even longer $B(sp^3){-}N(sp^3)$ bond (1.72 Å) and a shorter $B(sp^2){-}N(sp^2)$ bond (1.34 Å) in **16**. The latter can be explained by the −I-effect of the halogen atoms and by the larger steric effect of the BBr_2 unit as compared to the BH_2 moiety, which obviously dominates over the stronger Lewis-acidic character of the BBr_2 unit.

It appears from the study of the chemistry of **1** and related N-functionalized iminoboranes that these can be used as model systems to better understand regiospecific reactions in boron-nitrogen chemistry.

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Experimental

All experiments were conducted under dry nitrogen or in vacuo. Solvents were dried by standard methods. Starting materials were either commercially available or prepared by literature procedures[3,21]. – IR: Perkin-Elmer 325. – NMR: Bruker WP 200 (^{11}B), Jeol 270 (^{31}P), Jeol 400 (^{1}H, ^{13}C), standards are iTMS (^{1}H), C_6D_6 (^{13}C), $eBF_3 \cdot OEt_2$ (^{11}B), and 85% H_3PO_4 (^{31}P). Numbering scheme for the tmp group: N−C2(C7,8)−C3−C4−C5−C6(C7,8). – X-ray analyses: Siemens P4, Enraf Nonius CAD4, Mo-K_α radiation, graphite monochromator; SHELXL plus PC programs for structure solutions and refinements. – MS: Varian CH7 (70 eV).

2,2,5,5-Tetra-tert-butyl-4,7-dihydro-4,7-bis(2,2,6,6-tetramethylpiperidino)-1,3,6,2λ^5,5λ^5,4,7-oxadiazadiphosphadiborepine (**3**): Oxygen (1−2 bubbles per s) was passed for a period of 10 min through a stirred solution of $\mathrm{tmp{-}B{\equiv}N{-}P}t\mathrm{Bu}_2$ (**1**) (0.99 g, 3.2 mmol) in 15 ml of CH_2Cl_2. Stirring was continued for 3 h. Then the solution was cooled to −78°C and kept at this temp. for 16 h. At the end of that time crystals were floating on top of the solution. After the solution had attained a temp. of about −30°C the solution was separated from the crystals by removing the liquid with a syringe. The crystals turned into a powder during drying in vacuo. Yield: 0.14 g of **3** (7%), m.p. 249−252°C. Additional **3** (0.67 g, 34%) was obtained from the mother liquor. – NMR (C_6D_6): $\delta^{1}H$ = 1.23 [d, $^{3}J(^{31}P^{1}H)$ = 14.7 Hz, 18H, CMe_3], 1.33 (s, 6H, CMe_2), 1.44 (s, 6H, CMe_2), 1.46 [d, $^{3}J(^{31}P^{1}H)$ = 13.2 Hz, 18H, CMe_3], 1.68 (s, 12H, CMe_2), 1.74 [m, 12H, $(CH_2)_3$], and additional signals in this area resulting from the remaining H atoms of methylene groups of the tetramethylpiperidine rings]. – $\delta^{11}B$ = 24.1 (B7), 29.9 (B4). – $\delta^{13}C$ = 15.9 (s, C4), 20.9 (s, $\mathrm{C}\mathit{Me}_2$), 32.6 (s, C7,8), 34.7 (s, C7,8), 37.9 (s, C3,5), 40.8 (s, C3,5), 52.4 (s, C2,6), 59.4 (s, C2,6), 28.0 (s, $\mathrm{C}\mathit{Me}_2$), 28.5 (s, $\mathrm{C}\mathit{Me}_3$), 36.0 [d, $^{1}J(^{31}P^{13}C)$ = 48.2 Hz, $\mathit{C}\mathrm{Me}_3$], 36.3 [d, $^{1}J(^{31}P^{13}C)$ = 95.4 Hz, $\mathit{C}\mathrm{Me}_3$]. – $\delta^{31}P$ = 37.5 [$^{1}J(^{31}P^{11}B)$ = 171 Hz (at 333 K), P5], 50.5 (s, P2). – $C_{34}H_{72}B_2N_4OP_2$ (636.5): calcd. C 64.16, H 11.40, N 8.80; found C 63.12, H 11.50, N 8.50.

2,2,6,6-Tetra-tert-butyl-4,8-bis(2,2,6,6-tetramethypiperidino)-4H,8H-1,5,3,7,2λ^5,6λ^5,4,8-dioxadiazadiphosphadiborocine (**5**): A solution of **1** (0.61 g, 2.0 mmol) in 20 ml of dichloromethane was placed in a 150-ml round-bottom Schlenk flask filled with nitrogen. Stirring was started and the nitrogen replaced by oxygen. After 18 h the clear solution was cooled to −78°C, and the crystals that had formed within 3 d were separated. On drying in vacuo the crystals turned into a powder. Yield: 150 mg of **5** (12%), m.p. >220°C. Additional **5** (600 mg, 48%) was obtained after removal of 2/3 of the solvent from the mother liquor. Single crystals were grown at −78°C from a CH_2Cl_2 solution. – NMR (C_6D_6): $\delta^{1}H$ = 1.38 [d, $^{3}J(^{31}P^{1}H)$ = 14.6 Hz, 36H, CMe_3], 1.61 (s, 24H, CMe_2), 1.68 [m, 12H, $(CH_2)_3$]. – $\delta^{11}B$ = 23.0. – $\delta^{13}C$ = 15.9 (s, C4), 32.9 (s, C7,8, $\mathrm{C}\mathit{Me}_2$), 37.1 (s, C3,5), 52.3 (s, C2,6), 28.2 (s, $\mathrm{C}\mathit{Me}_3$), 37.3 [d, $^{1}J(^{31}P^{13}C)$ = 100.7 Hz, $\mathit{C}\mathrm{Me}_3$]. – $\delta^{31}P$ = 29.4. – $C_{34}H_{72}B_2N_4O_2P_2$ (652.5): calcd. C 62.58, H 11.12, N 8.59; found C 61.86, H 10.35, N 8.60.

X-Ray Structural Analysis: Enraf Nonius CAD4 diffractometer, crystal size = 0.32 × 0.28 × 0.45 mm, colorless prism. – Crystallographic data: a = 9.637(1), b = 11.182(1), c = 11.450(1) Å; α = 119.02(2), β = 92.69(1), γ = 109.87(2)°, V = 980.6(3) Å^3, triclinic, space group = $P\bar{1}$ (no. 2 Int. Tab.), $d_{calc.}$ = 1.105 Mg/m^3, μ = 0.144 mm, F(000) = 360. – Data collection: ω scans, 2-Θ range = 2–50° in h, $+/-k$, $+/-l$, scan speed = 2.9°/min, scan width = 0.9°, 4036 collected reflections, 3200 unique reflections ($R_{int.}$ = 0.0195) of which 2679 were considered observed [$F > 4\sigma(F)$]. – Structure solution and refinement: Direct methods, full-matrix least-squares refinement on nonhydrogen atoms with anisotropic temperature parameters and H atoms in calculated positions, refined with a riding model, 298 variables, reflection/parameters = 9.0:1, R = 0.051, R_w = 0.071, largest difference peak = 0.43 e/Å^3, GOOF = 1.67[22].

[(Di-tert-butylthioxophosphoranyl)imino](2,2,6,6-tetramethylpiperidino)borane (**6**): A solution of **1** (1.1 g, 3.5 mmol) in 20 ml benzene/pentane (1:1) was treated with elemental sulfur (141 mg, 4.4 mmol S) dissolved in 10 ml of benzene. After stirring of the mixture for 2 h the solvents were evaporated in vacuo, and the remaining solid was dissolved in a minimum amount of pentane. Some insoluble material had to be removed by filtration. The filtrate was cooled to –78°C. A yellowish crystalline powder of pure **6** settled from the solution within a few hours. Yield: 0.87 g of **6** (73%), m.p. 62–66°C. – NMR (C_6D_6): δ^1H = 1.19 (Me-7,8), 1.43 [CMe$_3$, ^1J(PH) = 1.50 Hz], 1.7 (m, CH$_2$). – δ^{11}B: 22.5. – δ^{13}C = 17.2 (C4), 27.9 [C*Me*$_3$, ^2J(PC) = 2.0 Hz], 31.9 (C7,8), 37.7 (C3,5), 39.1 [*C*Me$_3$, ^1J(PC) = 61.6 Hz], 52.8 (C2,6). – δ^{31}P = 85.6. – $C_{17}H_{36}BN_2PS$ (342.4): calcd. C 59.65, H 10.60, N 8.18; found C 58.99, H 10.58, N 7.65.

[(Di-tert-butylselenoxophosphoranyl)imino](2,2,6,6-tetramethylpiperidino)borane (**7**): 220 mg of grey selenium powder (2.8 mmol) was added in five portions to a solution of **1** (0.58 g, 1.8 mmol) in 10 ml of benzene. Most of the selenium went into solution by stirring the suspension for 16 h. Excess selenium was removed by filtration (G4 frit) and benzene distilled off from the yellow solution. An orange-colored viscous material remained which was crystallized from a minimum amount of pentane at –78°C. Yield: 470 mg of **7** (76%), m.p. 68–72°C. – NMR (C_6D_6): δ^1H = 1.21 (CMe$_2$), 1.45 [CMe$_3$, ^3J(PH) = 15.7 Hz], 1.6 (m, CH$_2$). – δ^{11}B = 23.6. – δ^{13}C = 17.2 (C4), 28.7 [C*Me*$_3$, ^2J(PC) = 2.0 Hz], 32.0 (C7,8), 37.7 (C3,5), 35.1 [*C*Me$_3$, ^1J(PC) = 52.5 Hz], 37.7 (C3,5), 53.0 (C-2,6). – δ^{31}P = 84.0 [^1J(^{179}Se^{31}P) = 818 Hz]. – $C_{17}H_{36}BN_2PSe$ (389.2): calcd. C 52.46, H 9.32, N 7.20; found C 50.09, H 9.33, N 6.84.

Di-tert-butylmethyl[(2,2,6,6-tetramethylpiperidinoborylene)-imino]phosphonium Iodide (**8**): A solution of methyl iodide (0.1 ml, 1.9 mmol) in 10 ml of pentane was added at –30°C to a stirred solution of **1** (0.46 g, 1.5 mmol) in 20 ml of pentane. On warming the mixture a solid started to separate at about –20°C. After 3 h approximately 1/3 of the pentane was evaporated in vacuo after the solution had attained ambient temp. Then the colorless solid was recovered by filtration, washed with cold pentane and dried in vacuo. Yield 0.66 g of **8** (97%), m.p. 158–161°C. – NMR (D_6D_6): δ^1H = 1.28 [CMe$_3$, ^3J(PH) = 15.7 Hz], 1.29 (CMe$_2$), 1.85 (PMe), signals of the CH$_2$ groups not clearly separable. – δ^{11}B = 23.2. – δ^{13}C: 8.6 [PMe, ^1J(PC) = 59.4 Hz], 16.5 (C4), 26.1 (C*Me*$_3$), 31.6 (C7,8), 35.1 [*C*Me$_3$, ^1J(PC) = 56.6 Hz], 36.9 (C3,5), 53.4 (C2,6). – δ^{31}P = 56.9. – $C_8H_{39}BIN_2P$ (452.2): calcd. C 47.82, H 8.69, N 6.19; found C 47.30, H 8.84, N 5.69.

[(Di-tert-butylphosphanyl)imino](2,2,6,6-tetramethylpiperidino)borane(P–B)–Tribromoborane (**9**): BBr$_3$ (0.60 g, 2.4 mmol) was diluted with 10 ml of hexane and the solution dropped into a stirred solution of **1** (0.75 g, 2.4 mmol) in 15 ml of hexane at –78°C. A solid separated during the addition of the BBr$_3$ solution. Stirring was continued for 1 h. After this period the mixture was allowed to attain ambient temp., and the solid was then removed by centrifugation, washed with 5 ml of cold hexane and dried. Yield: 1.06 g of **9** (79%) colorless powder, m.p. 108–115°C (dec.), which fumed slightly in contact with air. – $C_{17}H_{36}B_2Br_3N_2P$ (560.8): calcd. C 36.41, H 6.47, N 5.00; found C 36.03, H 7.03, N 4.90.

2,2-Di-tert-butyl-3,3,5-trichloro-1-[chloro(2,2,6,6-tetramethylpiperidino)boryl]-1-aza-2-phosphonia-3-borata-5-boracyclopentane (**10**): A solution of $Cl_2BCH_2BCl_2$[21] (0.6 ml, 4.5 mmol) in 10 ml of hexane was added to a stirred solution of **1** (1.41 g, 4.5 mmol) in 10 ml of hexane at –78°C. A colorless suspension formed immediately which on warming to ambient temp. turned into a clear solution. A solid remained after evaporation of all volatile components in vacuo. Crystallization from trichloromethane furnished pure **10**; m.p. 158–162°C. Yield: 0.41 g (19%). Additional material could be obtained by addition of pentane to the filtrate leading to an increase of the yield to 80%. Single crystals were obtained by allowing pentane to diffuse via the gas phase into a saturated solution of **10** in CHCl$_3$. – NMR (C_6D_6): δ^1H = 1.18 [d, ^3J(PH) = 12.5 Hz, 4-H$_2$], 1.38 (s, 6H, 2 CH$_3$), 1.45 (s, 6H; 2 CH$_3$), 1.50 (m, 6H, 3 CH$_2$), 1.64 [d, ^3J(PH) = 14.9 Hz, 18H, CMe$_3$]. – δ^{11}B = 53.2, 33.5, 4.8 [d, ^1J(PB) = 83 Hz]. – δ^{13}C: 17.3 (s, C4), 29.4 (s, C*Me*$_3$), 36.3 (s, C7,8), 36.5 (s, C7,8), 39.3 (s, C3,5), 40.7 [d, ^1J(PC) = 12.1 Hz, *C*Me$_3$], 55.7 (s, C2,6). – δ^{14}N = –245 [h(1/2) = 775 Hz]. – δ^{31}P = 83.8 [^1J(PB) = 83 Hz]. – $C_{18}H_{38}B_3Cl_4N_2P$ (487.7): calcd. C 44.33, H 7.85, N 5.74; found C 44.02, H 7.67, N 5.78.

X-Ray Structural Analysis: Siemens P4 diffractometer, single crystal of dimensions 0.2 × 0.5 × 0.7 mm. – Crystallographic data: a = 8.397(2), b = 11.486(2), c = 14.164(3) Å, α = 112.36(1), β = 91.79(2), γ = 97.61(2)°, V = 1247.3(4) Å^3, triclinic, space group $P\bar{1}$ (no. 2 Int. Tab.), Z = 2, $d_{calc.}$ = 1.299 Mg/m^3, μ = 0.548 mm^{-1}, F(000) = 516. – Data collection: ω scans, 2Θ range = 3–47° in h, $+/-k$, $+/-l$ scan width = 1.2°, scan speed = 2.5–29.3°/min, 4005 data collected, 3710 unique reflections ($R_{int.}$ = 0.038), and 3082 considered observed [$F > 3\sigma(F)$]. – Structure solution and refinement: Direct methods, nonhydrogen atoms were refined anisotropically, most of the H atoms were located from a difference Fourier map. Nevertheless, H atom positions were calculated and included in the final cycles of refinement with a riding model and fixed isotropic U_i. R = 0.038, R_w = 0.051 with 367 variables, data/parameter = 8.4:1, largest residual electron density = 0.44 e/Å^3, GOOF = 1.10[22].

[(Di-tert-butylphosphanyl)imino](2,2,6,6-tetramethylpiperidino)borane(P–B)–Borane (**11**): H$_3$B · SMe$_2$ (0.31 ml, 3.3 mmol) was added through a syringe to a stirred solution of **1** (0.96 g, 3.1 mmol) in 15 ml of hexane kept at –78°C. This caused formation of a suspension. After 1 h the suspension was allowed to attain ambient temp. The mixture was filtered and the filtrate cooled to –78°C. The crystalline **11** was isolated by filtration and dried in vacuo. Yield: 0.57 g (57%), m.p. 50–52°C. – NMR (C_6D_6): δ^1H = 1.01 [m, 6H, (CH$_2$)$_3$], 1.16 (s, 12H, CMe$_2$), 1.33 [d, ^3J(^{31}P^{1}H) = 12.7 Hz, 18H, CMe$_3$], 1.39 [d, ^2J(^{31}P^{1}H) = 13.4 Hz, ^{11}B-decoupled, BH$_3$]. – δ^{11}B = –37.7 [dq, ^1J(^{11}B^{1}H) = 95.5 Hz]. – δ^{13}C = 17.2 (s, C4), 27.5 [d, ^2J(^{31}P^{13}C) = 3.2 Hz, C*Me*$_3$), 34.2 [d, ^1J(^{31}P^{13}C) = 33.6 Hz, *C*Me$_3$), 31.8 (s, C7,8), 37.7 (s, C3,5), 52.4 (C2,6). – δ^{31}P = 80.4 [q, ^1J(^{31}P^{11}B) = 68.2 Hz]. – $C_{17}H_{39}B_2N_2P$ (324.1): calcd. C 63.00, H 12.13, N 8.64; found C 60.99, H 11.64, N 8.30.

2-(Di-tert-butylphosphanyl)-5,5,9,9-tetramethyl-2-aza-4-azonia-1-borata-3-boraspiro[3.5]nonane(P–B)–Borane (**12**): Prepared as **11** from **1** (1.17 g, 3.8 mmol) and H$_3$B · SMe$_2$ (0.69 ml, 7.3 mmol) in 20 ml of hexane. Product **12** crystallized from the solution at

−28°C which was subsequently cooled to −78°C to increase the yield (0.92 g, 72%), m.p. 132−135°C. − NMR (C_6D_6): $\delta^{1}H = 0.93$ (m, H, CH_2), 1.06 (s, 6H, CMe_2), 1.25 (m, 4H, CH_2), 1.30 (s, 6H, CMe_2), 1.36 [d, $^{3}J(^{31}P^{1}H) = 12.7$ Hz, 18H, CMe_3], 1.36 [d, $^{2}J(^{31}P^{1}H) = 13.1$ Hz, 3H, BH_3), 3.62 (s, 2H, BH_2), 5.06 (s, 1H, BH); the last three resonances refer to ^{11}B-decoupled spectra. − $\delta^{31}B = -40.2$ [dq, $^{1}J(^{31}P^{11}B) = 61.7$, $^{1}J(^{11}B^{1}H) = 95.5$ Hz], −1.3 [t, $^{1}J(^{11}B^{1}H) = 126.5$ Hz, BH_2], 39.5 [d, $^{1}J(^{11}B^{1}H) = 158.7$ Hz, BH]. − $\delta^{13}C = 16.7$ (s, C4), 25.4, 30.6 (s, C7,8), 28.3 [d, $^{2}J(^{31}H^{13}C) = 2.1$ Hz, C*Me*$_3$], 35.1 [d, $^{1}J(^{31}P^{1}H) = 30.4$ Hz, *C*Me$_3$], 36.8 (s, C3,5), 57.6 (s, C2,6). − $\delta^{31}P = 87.4$ [q, $^{1}J(^{31}P^{11}B) = 64.4$ Hz]. − $C_{17}H_{42}B_3N_2P$ (337.9). calcd. C 60.42, H 12.53, N 8.29; found C 59.91, H 11.63, N 7.99.

X-Ray Structural Analysis: Siemens P4 diffractometer, single crystals obtained from a hexane solution, crystal size = 0.35 × 0.4 × 0.5 mm, data collected at 20°C, crystal mounted in a glass capillary. − Crystallographic data: $a = 27.485(7)$, $b = 10.959(3)$, $c = 15.407(4)$ Å, $\beta = 105.36(1)°$, $V = 4475(3)$ Å^3, monoclinic, space group = $P2_1/c$ (no. 14 Int. Tab.), $d_{calc.} = 1.003$ Mg/m^3, $Z = 8$, $\mu = 0.123$ mm^{-1}, $F(000) = 1504$. − Data collection: ω scans, 2Θ range = 2−47° in $+/-h$, $-k$ to 1, $+/-l$; scan width = 1.20°, scan speed = 3−60°/min, 7115 data collected, 5589 unique data, 3048 considered observed [$F > 4\sigma(F)$]. − Structure solution and refinement: Direct methods, nonhydrogen atoms refined anisotropically, B-bound H atoms kept fixed in found positions, all other H atoms in calculated positions and refined with a riding model and fixed isotropic U_i. Refined parameters = 421, data/parameter = 13.5:1, full-matrix least-squares refinement on F^2 (SHELX 93), $R = 0.0909$, $R_w = 0.175$ (all data), $wR2 = 0.2122$, GOOF = 1.068, largest residual peak = 0.244 e/Å^3[22].

Pentacarbonyl{[(di-tert-butylphosphanyl)imino](2,2,6,6-tetramethylpiperidino)borane-P}chromium (**13**): A solution of **1** (0.45 g, 1.4 mmol) and $Cr(CO)_6$ (0.34 g, 1.54 mmol) in 50 ml of hexane was irradiated with a UV source (Hanovia S 200 W). After 180 min the evolution of CO gas had ceased and the solution had adopted a green-yellow color. Then the solvent was evaporated in vacuo and the residue heated to 70°C in vacuo to remove excess $Cr(CO)_6$. Crystallization of the non-volatile material from 2 ml of pentane (cooling to −78°C) gave 0.40 g of **13** (56%), m.p. 94°C, as a light yellow microcrystalline solid. − NMR (C_6D_6): $\delta^{11}B = 17.8$ [$h(1/2) = 480$ Hz]. − $\delta^{13}C = 17.2$ (C4), 28.9 [C*Me*$_3$, $^{3}J(PC) = 6$ Hz], 31.9 (C7,8), 37.8 (C3,5), C40.7 [*C*Me$_3$, $^{1}J(PC) = 13$ Hz], 52.5 (C2,6), 219.4 [CO, $^{2}J(PC) = 15$ Hz]. − $\delta^{31}P = 88.8$. − IR (cm^{-1}): $\tilde{\nu} = 1977$ ($^{10}B{\equiv}N$), 1910 ($^{11}B{\equiv}N$), 2060, 1990, 1930 (νCO). − $C_{22}H_{36}BCrN_2O_5P$ (502.3): calcd. C 52.60, H 7.22, N 5.38; found C 52.83, H 7.56, N 5.37.

Pentacarbonyl{[(di-tert-butylphosphanyl)imino](2,2,6,6-tetramethylpiperidino)borane-P}tungsten (**14**) was prepared in analogy to **13** from **1** (0.48 g, 1.5 mmol) and $W(CO)_6$ (0.56 g, 1.6 mmol). Yield: 0.58 g of **14** (60%), m.p. 100−100°C, yellow powder. − NMR (C_6D_6): $\delta^{11}B = 17.8$ [$h(1/2) = 600$ Hz]; − $\delta^{13}C = 17.2$ (C4), 28.9 [C*Me*$_3$, $^{2}J(PC) = 7.5$ Hz], 32.0 (C7,8), 37.8 (C3,5), 40.7 [*C*Me$_3$, $^{1}J(PC) = 16$ Hz], 52.2 (C2,6), 199.9 [C_{eq}, $^{2}J(PC) = 7.5$, $^{1}J(^{183}W^{13}C) = 119$ Hz], 200.0 [C_{ax}, $^{2}J(PC) = 22$, $^{1}J(^{183}W^{13}C) = 134$ Hz]. − $\delta^{31}P = 92.4$ [$^{1}J(^{183}W^{31}P) = 255$ Hz]. − IR (cm^{-1}): $\tilde{\nu} = 1970$ (m $^{10}B{\equiv}N$), 1900 (sst, $^{11}B{\equiv}N$), 2060, 1990, 1930 (νCO). − $C_{22}H_{36}BN_2O_5PW$ (631.2): calcd. C 41.67, H 5.72, N 4.42; found C 41.66, H 5.84, N 4.23.

Dicarbonyl{[(di-tert-butylphosphanyl)imino](2,2,6,6-tetramethylpiperidino)borane-P}(methylcyclopentadienyl)manganese (**15**): Prepared in analogy to **13** from **1** (0.5 g, 1.6 mmol) and $MeCpMn(CO)_3$ (0.34 g, 1.6 mmol). Yield: 0.33 g of **15** (42%), m.p. 28−31°C, yellow powder. − NMR (C_6D_6): $\delta^{11}B = 18.8$ [$h(1/2) = 550$ Hz). − $\delta^{13}C = 14.0$ (*Me*Cp), 17.3 (C4), 29.8 [C*Me*$_3$, $^{2}J(PC) = 5$ Hz], 32.0 (C7,8), 38.2 (C3,5), 42.4 [*C*Me$_3$, $^{1}J(PC) = 16$ Hz], 52.5 (C2,6), 80.4, 81.3, 82.0 (Cp), 235.0 [CO, $^{2}J(PC) = 24$ Hz]. − IR (cm^{-1}): $\tilde{\nu} = 1970$ (m, $^{10}B{\equiv}N$), 1925 (sst, $^{11}B{\equiv}N$), 1910 (st, CO), 1855 (st, CO). − $C_{25}H_{43}BMnN_2O_2P$ (500.4): calcd. C 60.01, H 8.66, N 5.26; found C 59.90, H 8.70, N 4.60.

☆ Dedicated to Professor *Helmut Werner* on the occasion of his 60th birthday.

[1] H. Feulner, N. Metzler, H. Nöth, *J. Organomet. Chem.*, in press.

[2] P. Kölle, Ph. D. Thesis, University of Munich, **1987**. Further results will be published shortly.

[3] [3a] H. Nöth, H. Stolpmann, *Chem. Ber.* **1944**, *127*, 82−86. − [3b] H. Nöth, K. Polborn, H. Stolpmann, M. Thomann, *Chem. Ber.* **1993**, *126*, 1995−2002.

[4] H. Nöth, *Angew. Chem.* **1988**, *100*, 1664−1684; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1603−1623.

[5] H. Nöth, M. Schwartz, S. Weber, *Chem. Ber.* **1985**, *118*, 4716−4723.

[6] Chemical shifts $\delta^{11}B$ for amino-imino-boranes range from δ = 10 to 25. See ref.[2].

[7] H. Nöth, B. Wrackmeyer, *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, NMR, Basic Principles and Progress* (Eds.: P. Diehl, E. Fluck, R. Kosfeld), Springer Publ., Heidelberg, Berlin, New York, **1987**, vol. 14.

[8] N. N. Greenwood, A. Earnshaw, *Chemie der Elemente*, VCH Publ., Weinheim, New York, **1988**; B−O bond lengths for BO_3 groups: 1.28−1.43 Å, for BO_4 groups: 1.43−1.55 Å.

[9] B−N bond lengths of monoaminoboranes range from 1.35 to 1.44 Å while the span covered by diaminoboranes is 1.42 to 1.48 Å, and for triaminoboranes B−N distances are known from 1.42 to 1.48 Å.

[10] C. I. Tebby (Ed.), *CRC Handbook of Phosphorus − 31 NMR Magnetic Resonance Data*, CRC Press, Boca Laton, Ann Arbor, **1981**.

[11] S. Weber, Ph. D. Thesis, University of Munich, **1984**, X-ray structure of tmp−B≡N−smes (smes = 2,4,6-tri-*tert*-butylphenyl).

[12] P. Paetzold, *Adv. Inorg. Chem. Radiochem.* **1987**, *31*, 123−170.

[13] P. Paetzold, B. Redenz-Stormanns, R. Boese, *Chem. Ber.* **1992**, *124*, 2435−2442.

[14] H. Nöth, S. Weber, *Z. Naturforsch., Teil B*, **1983**, *38*, 1460−1466; *Angew. Chem.* **1984**, *96*, 998; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 994−995.

[15] D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Elsevier Publ. Comp., Amsterdam, New York, **1974**.

[16] P. S. Bryan, R. L. Kuczowski, *Inorg. Chem.* **1972**, *11*, 553; W. C. Hamilton, *Acta Crystallogr.* **1955**, *8*, 199.

[17] F. A. Cotton, C. S. Kraihanzel, *J. Chem. Soc.* **1962**, *84*, 4432−4444.

[18] T. A. Magee, C. N. Matters, T. S. Wang, J. H. Wotig, *J. Am. Chem. Soc.* **1961**, *83*, 3200.

[19] G. Schröder, H. Butenschön, R. Boese, T. Lendval, A. de Meijere, *Chem. Ber.* **1991**, *124*, 2423−2428.

[20] D. Männig, H. Nöth, M. Schwartz, S. Weber, U. Wietelmann, *Angew. Chem.* **1985**, *97*, 979−980; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 998−999.

[21] B. Ederer, N. Metzler, H. Nöth, *Chem. Ber.* **1993**, *126*, 2003−2010.

[22] Further details of the crystal structure investigations are available on request from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the depository number CSD-58496, the names of the authors, and the journal citation.

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