# Adducts of Diaminophosphines with Organoboranes

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Dedicated to our dear colleague Prof. Dr. Thomas Schleid on the occasion of his 65th birthday.

Reactions of chlorodiaminophosphines $(R_2N)_2PCl$ (R=Et, *i*Pr) with organoborohydrides $M[BR'_nH_{4-n}]$ (M=Na, Li; n=1–3; R'= alkyl, Ph, CN) proceed via H/Cl metathesis to furnish secondary phosphines and boranes which may either combine to afford isolable donor-acceptor adducts $(R_2N)_2P(H)–BR'_nH_{3-n}$, coexist without any sign of mutual interaction, or give rise to mixtures comprising both a labile phosphine borane and its constituents in a temperature dependent equilibrium. Stable phosphine complexes of BH_2CN and BH_2Ph react with $KN(SiMe_3)_2$ under PH-bond metalation to afford spectroscopically detectable diaminophosphide boranes whose usability as nucleophilic building blocks is illustrated by trapping one specimen in a PC-bond formation reaction with an alkyl halide. The selectivity of the individual H/Cl-metathesis and electrophilic substitution steps as well as the thermal stability of the various reaction products depend subtly on the Lewis acidity of the borane fragment and on steric factors. Several complexes of (iPr_2N)-substituted phosphines with cyano- and phenylborane were characterized by single-crystal XRD.

Introduction

Borane coordination is not only a well-recognized measure to protect non-tertiary phosphines against unwanted oxidation or quaternization with electrophiles,[1] but may also enhance their PH-acidity and thus facilitate phosphide formation.[2] We have recently shown that borane coordination can be used to overcome the notorious reluctance of secondary diaminophosphines **Ia** and phosphonites **IIa** (Scheme 1) to undergo metalation at their PH-bond and enables the forthright generation of thermally stable – and in some cases even isolable – phosphide boranes **Ib** and **IIb**, respectively.[3][4] Such species, which previously only been described as elusive intermediates,[5] make attractive synthetic tools that can serve, like the traditional PH- or P(SiR₃)-substituted phosphides (**IIIb**, **IVb**), as nucleophilic building blocks for the synthesis of functional phosphines.[6] However, whereas the products formed by quenching **IIIb/IVb** with electrophiles retain nucleophilic character at phosphorus (implying that further derivatization requires as well electrophilic reagents), the substituents in **Ib/IIb** impose electrophilic
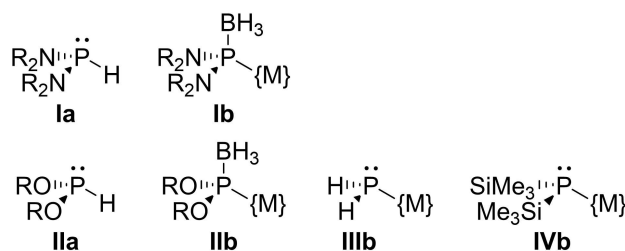
Scheme 1. Generic molecular structures of secondary diaminophosphines **Ia**, phosphonites **IIa**, and known phosphide reagents **Ib**–**IVb** (R=alkyl, aryl; M=(alkali)metal).

character on the P-atom in a resulting phosphine and make **Ib/IIb** reagents that can decorate an *electrophilic* substrate with an *electrophilic* R₂P-fragment allowing for post-functionalization with nucleophiles.[3,4] In this respect, the reactivity of both classes of phosphide reagents can be considered as complementary.

Like the majority of known studies on the chemistry of phosphine boranes in general, our previous exploration of the metalation of O/N-substituted derivatives[3,4] focused on adducts with parent borane (BH₃). Nonetheless, there is also a considerable body of reports on phosphine complexes of various organoboranes.[7] As the substituents on boron affect both the Lewis acidity and steric properties of a borane, their variation can be expected to offer a possibility for fine-tuning the acidifying effect on a bound phosphine. With this prospect in mind, we considered that adducts of hetero-substituted phosphines with organoboranes might make a further appealing synthetic target. Herein, we report on our studies on the formation of the appropriate adducts of secondary diaminophosphines and their metalation properties.

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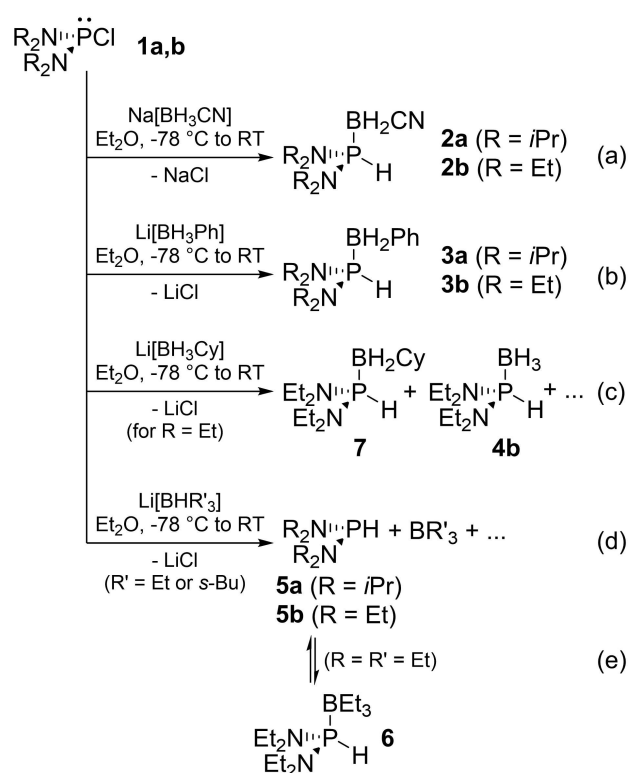*E-mail: gudat@iac.uni-stuttgart.de*
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Results and Discussion

Generation of diaminophosphine boranes. Elaborating on our earlier approach to access secondary diaminophosphine boranes by borohydride reduction of chlorophosphine precursors,[3] we investigated the reactions of **1 a,b** with selected substituted borohydrides. The reactions of both starting materials with Na[BH$_3$CN] and Li[BH$_3$Ph] (Scheme 2(a), (b)) proceeded with

Scheme 2. Reaction of chlorophosphines **1 a,b** with borohydrides M[BH$_n$R'$_{4-n}$] (Cy = cyclohexyl).

high selectivity to afford the expected diaminophosphine boranes **2 a,b** and **3 a,b** that were readily identified by multi-nuclear NMR spectroscopy. The presence of Lewis pairs with the targeted >PH–BH$_2$-unit follows unmistakably from the multiplet structures of the ^{31}P and ^{11}B NMR signals arising from spin coupling of each nucleus with the adjacent proton(s) as well as mutual coupling with each other. Moreover, the ^{1}H NMR spectra reveal coupling between B- and P-bound hydrogens via $^3J_{HH}$ (see Experimental Section). The magnitudes of the one-bond coupling constants ($^1J_{PB}$, $^1J_{PH}$, $^1J_{BH}$, see Table 1) in **3 a,b** roughly match those in the parent borane complexes (R$_2$N)$_2$P(H)BH$_3$ **4 a,b** (R=iPr, Et)[3] and increase further in **2 a,b** upon formal replacement of the phenyl group on boron by a more electron withdrawing cyano group.

Work-up furnished **2 a** as a crystalline solid and **3 a** as a colorless oil that crystallized upon standing, and characterization of both materials by single-crystal XRD studies confirmed the molecular structures inferred from the NMR data (see further below). Whereas **2 a** proved thermally stable as a solid and in solution (a toluene solution showed no significant degeneration upon heating to 100 °C for 1 h), solid **3 a** was found to turn yellow and undergo slow decomposition (which also impeded obtaining a satisfactory elemental analysis) even at ambient temperature, but could be stored for a limited time at −28 °C. Applying the same work-up scheme to N-ethylated phosphine borane **2 b** furnished only a crude product in the form of a yellowish oil that could not be freed from impurities. Even more extensive and faster decomposition occurred as well during the attempted purification of phenyl borane complex **3 b** which, although being rather stable in solution, remained up to now inaccessible in pure form.

Action of alkyl borohydrides on **1 a,b** (Scheme 2(b), (c)) resulted likewise in hydride transfer from boron to phosphorus, but the reactions were mostly less selective (with Li[CyBH$_3$], Li[Et$_3$BH], Li[B(s-Bu)$_3$H]) or even unselective (with Lithium-9-boratabicyclo[3.1.1]nonane) and gave generally labile adducts that were in dynamic equilibrium with their components (Scheme 2, (e)), or Lewis pairing was completely absent. While this behavior thwarted the isolation of well-defined products, ^{31}P and ^{11}B NMR studies still provided a clear picture of the ongoing processes.

Regarding phosphine formation, we found that hydride transfer from Li[s-Bu$_3$BH] to both **1 a,b** and from Li[CyBH$_3$] to **1 a** proceeds with a comparable degree of selectivity as with cyano and phenyl borohydride. Action of Li[Et$_3$BH] on **1 a** yielded a 93:7 mixture of secondary phosphine (iPr$_2$N)$_2$PH (**5 a**)[8] and a by-product identified as P-ethylated (iPr$_2$N)$_2$PEt. We attribute the formation of the latter to a competing ethyl transfer reaction between both reactants.

Delineation of the Lewis pairing behavior of the phosphines formed was feasible from a closer analysis of ^{31}P NMR chemical shifts and $^1J_{PH}$ coupling constants. The data for all borohydride reduction products derived from **1 a** match the values reported for **5 a**,[8] indicating that the phosphine and any boranes formed coexist in solution without significant mutual interaction. This hypothesis is in the case of the reactions of **1 a** with Li[R$_3$BH] (R=Et, s-Bu) corroborated by the detection of the signals of the

Table 1. ^{31}P and ^{11}B NMR data of phosphine boranes (R$_2$N)$_2$P(X)-borane.

	R	X	borane	δ^{31}P	$^1J_{PB}$ [Hz]	$^1J_{PH}$ [Hz]	δ^{11}B	$^1J_{BH}$ [Hz]
2 a	iPr	H	BH$_2$CN	32.2	99	435	−36.1	104
2 b	Et	H	BH$_2$CN	66.5	100	453	−38.4	100
3 a	iPr	H	BH$_2$Ph	42.0	67	407	−25.2	99
3 b	Et	H	BH$_2$Ph	77.7	70	423	−25.9	95
4 a[a]	iPr	H	BH$_3$	46.3	73	407	−35.6	107
4 b[b]	Et	H	BH$_3$	80.3	73	433	−39.1	93
6[c]	Et	H	BEt$_3$	81.4	—[d]		−8.9	—[d]
8 a	iPr	K	BH$_2$CN	55.6	66	–	−35.1	92
8 b	Et	K	BH$_2$CN	118.4	62	–	−36.0	95
9 a	iPr	K	BH$_2$Ph	60.5	62	–	−17.8	81
9 b	Et	K	BH$_2$Ph	135.5	51	–	−21.2	87
10 a[a]	iPr	K	BH$_3$	53.4	64	–	−29.5	84
10 b[b]	Et	K	BH$_3$	130.7	52	–	−32.3	85

[a] data from ref. [3b]. [b] data from ref. [3a]. [c] at −90 °C. [d] obscured by line broadening effects.

respective boranes (δ^{11}B 87.4 (Et$_3$B), 85.6 (s-Bu$_3$B)), and is also in accord with the identification of an oily residue obtained after reduction of **1a** with Li[Et$_3$BH] and removal of all insoluble and volatile components as crude **5a**.

Reduction of **1b** with Li[s-Bu$_3$BH] gave, according to the ^{31}P and ^{11}B NMR spectra, also a non-interacting mixture of the known secondary phosphine ((Et_2N)$_2$PH, **5b**[8]) and the respective tertiary borane. Formation of a secondary diaminophosphine was likewise confirmed for the reaction of **1b** with Li[Et$_3$BH], but an observed $^1J_{PH}$ coupling constant of 274 Hz exceeds in this case perceptibly the value of 259 Hz reported[8] for **5b**. Considering that $^1J_{PH}$ coupling constants in diaminophosphine boranes are usually about twice as large as in the free phosphines (see the data for **2a,b**–**4a,b** in the experimental and in ref [3]), we interpret our findings as a hint to the presence of a dynamic equilibrium between the separate components and a respective Lewis pair (**5a**/BEt$_3$ and **6**, Scheme 2). Confirmation of this hypothesis was obtained from VT NMR studies, which revealed a further numerical increase in $^1J_{PH}$ and a concomitant decline in δ^{11}B with falling temperature (Figures 1, S22, S23) indicating that the molar fraction of **6** in the equilibrium increases upon cooling and approaches unity at temperatures between -70 and $-90\,^\circ$C. Similar thermally induced dissociation of Lewis pairs has also been observed in other cases.[9] Titration experiments indicated that adduct formation can also be promoted at ambient temperature by adding excess borane (see Figure S24).

Finally, formation of a mixture of two room-temperature stable Lewis pairs as main products along with further byproducts was observed for the reduction of **1b** with Li[CyBH$_3$]. Based on the multiplicities of the ^{11}B NMR signals, we assign one major product as the expected adduct **7** (δ^{31}P 78.8, δ^{11}B -26.7, doublet ($^1J_{PB}=61$ Hz) of triplets ($^1J_{BH}=97$ Hz)), while the second one is identified as known **4b**[3] (δ^{31}P 83.7, δ^{11}B -40.2, doublet ($^1J_{PB}=66$ Hz) of quartets ($^1J_{PB}=100$ Hz)). The origin of **4b** is not yet understood in detail, but it may arise from similar transalkylation processes as had been observed during hydroboration reactions with CyBH$_2$.[10] The unselective formation and long-term instability of **4b** (as evidenced by an eventual decay
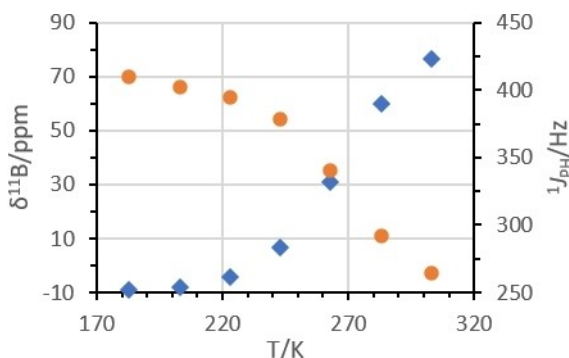
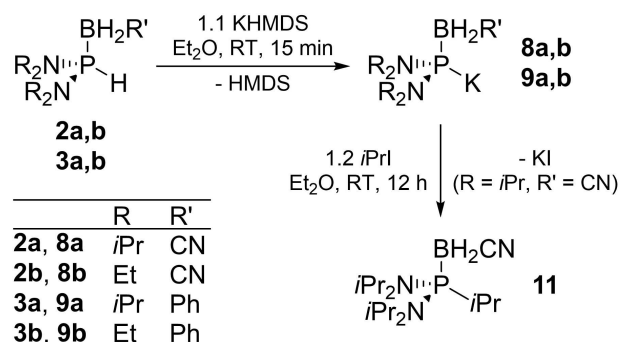of the NMR signals at prolonged reaction times) prevented until now its isolation in pure form.

Comparing the outcome of all our attempts on the synthesis of diaminophosphine boranes (R_2N)$_2$PH–**B** (R = Et, iPr) with both parent (**B** = BH$_3$) and substituted borane acceptors (**B** = BH$_2$CN, BH$_2$Ph, B(alkyl)$_3$), we note that the relative thermal stabilities of the adducts reveal a similar trend as the hydride affinities of the respective boranes,[11] which decrease in the order BH$_2$CN $\gg$ BH$_3$ > BH$_2$Ph $\gg$ B(alkyl)$_3$ and can be considered as a measure of declining Lewis-acidity. Varying Lewis-pairing behavior of a given acceptor towards different donors (**5a**, **5b**, (Me_2N)$_2$PH[3]) indicates, however, that the stability of the adducts depends not only on the borane Lewis-acidity, but as well on the nucleophilicity of the phosphine and steric influences. Regarding this last aspect, it seems that a certain steric protection of the phosphorus atom seems to be needed for selective reactions while accruing steric bulk around boron obviously has a detrimental effect.

Metalation studies. Metalation of phosphine boranes **2a,b** and **3a,b** was achieved by treatment with potassium hexamethyl disilazide (KHMDS) in diethyl ether, which had previously been identified[3] as suitable approach to diaminophosphide boranes (Scheme 3). With the exception of **9b**, which precipitated as a colorless solid from the reaction mixture and was separated in crude form after filtration, the high sensitivity of the metalation products impeded work-up and isolation, and **8a,b** and **9a** were only characterized *in situ* by NMR spectroscopy. Evaluation of the ^{31}P NMR spectra indicated that all products had formed with 86–99% selectivity.[12] The molecular structure as phosphides followed undeniably from the absence of the signal of a P-bound hydrogen atom in the ^{1}H NMR spectra and the disappearance of the diagnostic $^1J_{PH}$ splitting in ^{31}P NMR spectra. The appearance of the ^{11}B NMR signal as doublets of triplets further confirm that the P–BH$_2$R (R = CN, Ph) moieties remained intact. The increase in ^{31}P NMR chemical shifts and numerical decrease in $^1J_{PB}$ coupling constants upon metalation is similar as for previously reported diaminophosphide boranes (R_2N)$_2$P(BH$_3$)K (**10a,b**, Table 1).[3]

Diaminophosphine borane **6**, although being unstable towards dissociation into its constituents **5b** and BEt$_3$ under ambient conditions, still forms the main phosphorus-containing constituent at low temperature or in the presence of an excess

Figure 1. Temperature dependence of the observed values of δ^{11}B (diamonds) and $^1J_{PH}$ (circles) for the equilibrium mixture **5b** + BEt$_3$/**6** formed *in situ* upon reaction of equimolar amounts of **1b** and Li[BEt$_3$H] in Et$_2$O.


Scheme 3. Metalation of **2a,b**/**3a,b** and ensuing alkylation of **8a**.

borane, and might under these conditions in principle be also amenable to deprotonation. Performing the reaction of the equilibrium mixture of **5b**/BEt$_3$ and **6** with KHMDS at $-78\,°C$ gave, however, no spectroscopic evidence for any phosphide formation. Identical behavior was also observed when the reaction was conducted in the presence of a 10-fold excess of BEt$_3$ or at higher temperatures. We presume that the inert behavior of the secondary phosphine in these reactions is either due to the fact that the boost of PH-acidity induced by coordination of a noticeably weaker Lewis-acid than BH$_2$CN, BH$_3$ or BH$_2$Ph is either insufficient for successful metalation, or that this reaction is inhibited by the steric demand of the substituents on boron.

Having succeeded in deprotonation of **2a,b** and **3a,b**, we further investigated the coupling of the resulting phosphide boranes with selected electrophiles. Treatment of **8a** with 2-iodopropane afforded the expected metathesis product **11** (Scheme 3), which was isolated in 65% yield after crystallization and characterized by NMR spectroscopy and a single crystal XRD study. NMR studies provided preliminary evidence that Me$_3$SiCl and Ph$_2$PCl might react similarly, but less selectively, and we could neither isolate nor unambiguously identify any products until now. The reactions of **8b** and **9a,b** with the same set of electrophiles were unselective and usually furnished mixtures of several phosphorus-containing species from which likewise no pure compounds could be isolated.[13]

In total, it appears that organic substituents on the boron atom of a phosphide borane disfavor clean reactions with electrophiles, causing either less selective transformations as have been observed for adducts with parent borane (BH$_3$),[3] or introducing additional complications during work-up. Moreover, our findings seem to confirm that not only the formation of stable donor-acceptor bonds but also a successful boost of PH-acidity upon borane coordination require boranes with sufficiently high Lewis-acidity. Finally, while a certain steric protection of the phosphorus atom seems to be needed for selective reactions, accruing steric bulk around boron obviously has a detrimental effect.

Crystal structure studies. The crystals of phosphine boranes **2a**, **3a** and **11** (Figure 2) contain isolated molecules with the expected tetrahedral coordination at the phosphorus and boron atoms, with crystalline **11** being special due to the presence of two conformers with slightly different disposition of the N*i*Pr$_2$-moieties (Figure S1). The P–B distances in **2a** (1.929(4) Å), **3a** (1.934(5) Å), and **11** (1.955(5) and 1.964(5) Å) fall into the typical region of P–B dative bonds in diaminophosphine boranes (1.915 ± 0.059 Å[14]). The substituents at all P–B bonds adopt a staggered conformation in which the non-hydrogen substituent on boron and one of the amino groups on phosphorus adopt a trans-periplanar orientation granting minimal steric interactions. The P–B bond lengthening in **11** is at first glance counter-intuitive if one considers that formal replacement of a P-bound hydrogen in **2a** by an alkyl should render the phosphine a stronger donor. However, as this trend coincides with a parallel elongation of the P–N distances, we presume that both trends are sterically induced. That the variation of P–B distances in
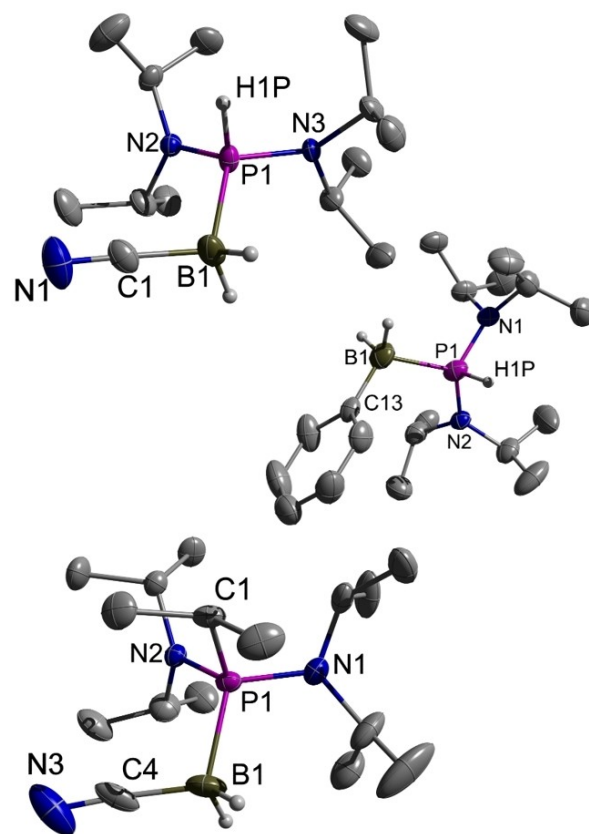
Figure 2. Representations of the molecular structures of **2a**, **3a** and one of the crystallographically independent molecules of **11** (from top to bottom) in the crystal. Hydrogen atoms, except those on boron and phosphorus atoms, were omitted for clarity and thermal ellipsoids were drawn at the 50% probability level. Selected distances and angles are listed in Table S2.

phosphine boranes is controlled by steric rather than electronic factors had been noted before.[15]

Conclusions

Reactions of bis(dialkylamino)chlorophosphines with organo-borohydrides compare to those with parent borohydride in involving an initial Cl/H-metathesis step, but differ in that the resulting secondary phosphines and boranes may either coexist without mutually interacting or combine to form more or less stable donor-acceptor complexes. Highly stable adducts of this type derived from boranes whose electron accepting power matches (BH$_2$Ph) or even exceeds (BH$_2$CN) that of parent BH$_3$ undergo metalation and post-functionalization of the newly formed PH-bond upon treatment with KHMDS and an electrophile. While a certain steric protection of the phosphorus atom is obviously needed to render these reactions selective, accruing steric bulk around boron seems to reduce both adduct stabilities and the selectivity in post-functionalization steps. Since these obstacles render work-up procedures more tedious and less effective than for complexes with parent borane, using

organoboranes instead of BH_3 for PH-bond activation does not seem to offer any particular advantage, except in cases where the higher Lewis acidity of BH_2CN compared to BH_3 may assist in enforcing the derivatization of low reactive PH bonds.

Experimental Section

All manipulations were carried out under an atmosphere of inert argon inside glove boxes or by using standard vacuum line techniques. Solvents were dried by refluxing over Na (toluene) or NaK (Et_2O, pentane) and distilled before use. NMR spectra were recorded on Bruker Avance 250 (^1H 250.0 MHz, ^{11}B 80.2 MHz, ^{13}C 62.9 MHz, ^{31}P 101.2 MHz) or Avance 400 (^1H 400.1 MHz, ^{11}B 128.4 MHz, ^{13}C 100.5 MHz, ^{31}P 161.9 MHz) instruments at 293 K if not stated otherwise. ^1H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent ($\delta ^1H = 7.15$ (C_6D_6), 1.73 (THF-D_8)) as secondary reference. Spectra of heteronuclei were referenced using the Ξ-scale[16] employing TMS ($\Xi = 25.145020$ MHz, ^{13}C), $BF_3 \cdot OEt_2$ ($\Xi = 32.083974$ MHz, ^{11}B) and 85% H_3PO_4 ($\Xi = 40.480747$ MHz, ^{31}P) as secondary references. Coupling constants involving boron nuclei refer to the isotope ^{11}B if not stated otherwise. The $^{13}C\{^1H\}$ NMR signals of carbon atoms next to boron were mostly unidentifiable due to insufficient signal-to-noise ratio and signal broadening effects. Conversions and selectivities derived from NMR data are based on the evaluation of the relative integrals in $^{31}P\{^1H\}$ NMR spectra recorded with 30° excitation pulses and neglecting influences of different relaxation times. Elemental analyses were determined on a Thermo Micro Cube CHN analyzer. Phenyl and cyclohexyl borohydrides were prepared as reported elsewhere.[17]

Diaminophosphine cyanoboranes 2a,b. A solution of the appropriate chlorophosphine (**1a**: 1.50 g, 5.62 mmol, **1b**: 137 mg, 0.65 mmol) in Et_2O (5 ml) was added to a cooled ($-78\,°C$) suspension of Na[BH_3CN] (0.42 g, 6.7 mmol/49 mg, 0.78 mmol) in Et_2O (20 ml). The mixture was allowed to warm to ambient temperature and stirred for 12 h. Volatiles were then evaporated under reduced pressure and the solid residue extracted with three portions of pentane (20 ml). The extracts were combined and volatiles removed in vacuum to leave a colorless powder (**2a**) or yellow oil (**2b**), respectively. Recrystallization of **2a** from pentane (5 ml) at $-28\,°C$ furnished colorless crystals, whereas **2b** could not be freed from impurities resulting from partial decomposition during work-up and was only characterized spectroscopically.

2a: Yield 1.14 g (4.21 mmol, 75%). – ^1H NMR (C_6D_6): $\delta = 6.53$ (dt, 1 H, $^1J_{PH} = 435$ Hz, $^3J_{HH} = 5.1$ Hz, PH), 3.25 (d sept, 4 H, $^3J_{PH} = 14.6$ Hz, $^3J_{HH} = 6.8$ Hz, CH), 1.94 (br q, 2 H, $^1J_{BH} = 104$ Hz, BH_2), 0.99 (d, 12 H, $^3J_{HH} = 6.8$ Hz, CH_3), 0.84 (d, 12 H, $^3J_{HH} = 6.8$ Hz, CH_3). – ^{11}B NMR (C_6D_6): $\delta = -36.1$ (dt, $^1J_{PB} = 99$ Hz, $^1J_{BH} = 104$ Hz). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 47.1$ (d, CH, $^2J_{PC} = 4.8$ Hz), 22.5 (d, CH_3, $^3J_{PC} = 3.4$ Hz), 22.4 (d, CH_3, $^3J_{PC} = 3.2$ Hz). – $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 32.2$ (q, $^1J_{PB} = 99$ Hz). – $C_{13}H_{31}BN_3P$ (271.20 g/mol), calcd. C 57.58 H 11.52 N 15.49, found C 56.92 H 11.67 N 15.15. The deviation in carbon content may arise from the presence of minor impurities visible in the ^1H NMR spectrum.

2b: Yield 51 mg of crude product. – ^1H NMR (C_6D_6): $\delta = 5.89$ (dt, 1 H, $^1J_{PH} = 453$ Hz, $^3J_{HH} = 5$ Hz, PH), 2.61 (ddq, 4 H, $^2J_{HH} = 15.3$ Hz, $^3J_{HH} = 7.4$ Hz, $^3J_{PH} = 3.0$ Hz, CH_2), 2.52 (ddq, 4 H, $^2J_{HH} = 15.3$ Hz, $^3J_{HH} = 7.3$ Hz, $^3J_{PH} = 4.6$ Hz CH_2), 0.71 (t, 12 H, CH_3, $^3J_{HH} = 7.4$ Hz), signal from BH_2CN not identified. – ^{11}B NMR (C_6D_6): $\delta = -38.4$ (q, $^1J_{PB} \approx {}^1J_{BH} \approx 100$ Hz). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 41.3$ (d, $^2J_{PC} = 3.1$ Hz, CH_2), 13.6 (d, $^3J_{PC} = 2.5$ Hz, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 66.5$ (q, $^1J_{PB} = 100$ Hz).

Diaminophosphine phenylboranes 3a,b. A solution of the appropriate chlorophosphine (**1a**: 150 mg, 0.56 mmol, **1b**: 164 mg, 0.78 mmol) in Et_2O (5 ml) was added to a cooled ($-78\,°C$) suspension of Li[BH_3Ph] (61 mg, 0.62 mmol/85 mg, 0.86 mmol) in Et_2O (20 ml). The mixture was allowed to warm to ambient temperature and stirred for 12 h. Volatiles were then evaporated under reduced pressure and the solid residue extracted with pentane (30 ml). The extracts were combined and volatiles removed in vacuum to leave the crude product as colorless oil, which in the case of **3a** eventually solidified to produce a crystalline material. Both products decayed slowly (**3a**) or rapidly (**3b**) to produce yellowish, gummy materials when stored in substance whereas solutions in inert solvents proved to be reasonably stable as long as air and moisture were excluded.

3a: Yield 152 mg (0.47 mmol, 84%) of crude product. – ^1H NMR (C_6D_6): $\delta = 7.53$ (br m, 2 H, o-H), 7.30 (m, 2 H, m-H), 7.16 (m, 1 H, p-H), 6.73 (dt, 1 H, $^1J_{PH} = 407$ Hz, $^3J_{HH} = 6.5$ Hz, PH), 3.37 (d sept, 4 H, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 14.0$ Hz, CH), 2.7 (br, 2 H, BH_2), 0.94 (d, 12 H, $^3J_{HH} = 6.8$ Hz, CH_3) 0.89 (d, 12 H, $^3J_{HH} = 6.8$ Hz, CH_3). – ^{11}B NMR (C_6D_6): $\delta = -23.2$ (dt, $^1J_{PB} = 67$ Hz, $^1J_{BH} = 99$ Hz). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 147.4$ (br, i-C), 136.1 (d, $^3J_{PC} = 10.1$ Hz, o-C), 127.2 (d, $^4J_{PC} = 3.0$ Hz, m-C), 124.5 (d, $^5J_{PC} = 4.5$ Hz, p-C), 47.0 (d, $^2J_{PC} = 4.5$ Hz, CH), 22.9 (d, $^3J_{PC} = 2.3$ Hz, CH_3), 22.5 (d, $^3J_{PC} = 2.3$ Hz, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 42.0$ (m).

3b: Yield not determined. – ^1H NMR (C_6D_6): $\delta = 7.74$ (br m, 2 H, o-H), 7.34 (m, 2 H, m-H), 7.20 (m, 1 H, p-H), 6.09 (dt, 1 H, $^1J_{PH} = 423$ Hz, $^3J_{HH} = 5.7$ Hz), 2.76 (ddq, 8 H, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 9.3$ Hz, CH_2), 2.78 (br, 2 H, BH_2), 2.65 (ddq, 8 H, $^2J_{HH} = 14.4$ Hz, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 11.0$ Hz, CH_2), 0.69 (t, 12 H, $^3J_{HH} = 7.1$ Hz, CH_3). – ^{11}B NMR (C_6D_6): $\delta = -25.9$ (dt, $^1J_{PB} = 70$ Hz, $^1J_{BH} = 95$ Hz). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 146.6$ (br, i-C), 136.3 (d, $^3J_{PC} = 9.0$ Hz, o-C), 127.2 (d, $^4J_{PC} = 3.0$ Hz, m-C), 124.7 (d, $^5J_{PC} = 4.5$ Hz, p-C), 41.5 (d, $^2J_{PC} = 2.3$ Hz, CH_2), 13.7 (d, $^3J_{PC} = 2.4$ Hz, CH_3) – $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 77.7$ (m).

Reactions of diaminochlorophosphines with trialkylborohydrides. In a typical procedure, Li[$BHEt_3$] (3.78 ml of a 1 M soln in Et_2O, 3.78 mmol) was added to a cooled (-78 °C) solution of **1b** (404 mg, 1.92 mmol) in Et_2O (8.1 ml). The mixture was allowed to warm to room temperature and solid precipitates were removed by filtration. The filtrate analyzed using ^{31}P and ^{11}B NMR spectroscopy. For the study of donor/acceptor equilibria, aliquots (4×2 ml, 1×0.1 ml) of the aforementioned filtrate were transferred to five separate flasks. Defined portions of Et_3B (0.38/1.52/3.43/8.50 ml of a 1 M solution adding up to 1/4/9/500 equivalents) were added to flask #2 to #5, respectively. The content of the first flask was analyzed by ^{31}P and ^{11}B VT-NMR spectroscopy and the remaining solutions by ^{31}P NMR spectroscopy at ambient temperature (see Figures S22–S24).

Potassium diaminophosphide boranes 8a,b and 9a. The appropriate crude diaminophosphine borane (**2a**: 25 mg, 90 μmol, **2b**: 25 mg, 11 μmol, **3a**: 25 mg, 80 μmol) and KHMDS (20 mg, 10 μmol/26 mg, 13 μmol/25 mg, 85 μmol) were dissolved in Et_2O (5 ml). The resulting solution was stirred for 15 min. Volatiles were evaporated under reduced pressure. The residue was dissolved in THF-d_8 (**8a,b**) or C_6D_6 (**9a**) and the resulting mixture of metalated diaminophosphine borane and residual $HN(SiMe_3)_2$ characterized NMR spectroscopically.

8a: conversion $> 99\%$ (by ^{31}P NMR); ^1H NMR (THF-D_8): $\delta = 3.48$ (d sept, 4 H, $^3J_{PH} = 9.4$ Hz, $^3J_{HH} = 6.7$ Hz, CH), 1.12 (d, 12 H, $^3J_{HH} = 6.7$ Hz, CH_3), 1.04 (m, 12 H, $^3J_{HH} = 6.7$ Hz, CH_3), 0.85–1-3 (br, 2H, BH_2). – ^{11}B NMR (THF-D_8): $\delta = -35.1$ (dt, $^1J_{PB} = 66$ Hz, $^1J_{BH} = 92$ Hz). – $^{13}C\{^1H\}$ NMR (THF-D_8): $\delta = 47.3$ (d, $^2J_{PC} = 5$ Hz), 24.1 (s, CH_3), 24.0 (s, CH_3). – $^{31}P\{^1H\}$ NMR (THF-D_8): $\delta = 55.6$ (m).

8 b: conversion $>86\%$ (by ^{31}P NMR); ^1H NMR (THF-D_8): $\delta = 3.11$ (ddq, 4 H, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 9.7$ Hz, CH_2), 2.98 (ddq, 4 H, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 7.1$ Hz, $^3J_{PH} = 9.9$ Hz, CH_2), 0.95 (dt, 12 H, $^3J_{HH} = 7.1$ Hz, $^4J_{PH} = 1.2$ Hz, CH_3), 0.5-1.0 (br, 2 H, BH_2). – ^{11}B NMR (THF-D_8): $\delta = -36.0$ (dq, $^1J_{PB} = 62$ Hz, $^1J_{BH} = 95$ Hz). – $^{13}C\{^1H\}$ NMR (THF-D_8): $\delta = 45.0$ (d, $^2J_{PC} = 8.0$ Hz, CH_2), 14.4 (d, $^3J_{PC} = 4.0$ Hz, CH_3). – $^{31}P\{^1H\}$ NMR (THF-D_8): $\delta = 118.4$ (m).

9 a: conversion 90% (by ^1H NMR); ^1H NMR (C_6D_6): $\delta = 7.48$ (br m, 2 H, o-H), 7.18 (m, 2 H, m-H), 7.01 (t, 1 H, p-H, $^3J_{HH} = 7.2$ Hz), 3.69 (d sept, 4 H, $^3J_{HH} = 6.7$ Hz, $^3J_{PH}$ 8.6 Hz, CH), 1.7 (br q, $^1J_{BH} = 81$ Hz, BH_2), 1.42 (d, 12 H, $^3J_{HH} = 6.7$ Hz, CH_3), 1.15 (d, 12 H, $^3J_{HH} = 6.7$ Hz, CH_3). – ^{11}B NMR (C_6D_6): $\delta = -17.8$ (dq, $^1J_{PB} = 62$ Hz, $^1J_{BH} = 81$ Hz). – ^{13}C NMR ($^1H,^{13}C$ gs-HSQC, C_6D_6) $\delta = 135.1$ (o-C), 127.8 (m-C), 124.1 (p-C), 48.6 (d, $^2J_{PC} = 4$ Hz, CH), 24.9 (d, $^3J_{PC} = 6.2$ Hz, CH_3), 24.5 (d, $^3J_{PC} = 5.4$ Hz, CH_3). – $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 60.5$ (q, $^1J_{PB} = 62$ Hz).

Potassium bis(diethylamino)phosphide borane 9 b. A solution of **1 b** (149 mg, 0.71 mmol) in Et_2O (5 ml) was added to a cooled (-78 °C) suspension of Li[BH_3Ph] (76 mg, 0.78 mmol) in Et_2O (10 ml). The mixture was allowed to warm to ambient temperature and stirred for 1 h. Volatiles were removed under reduced pressure and the residue right away extracted with pentane. Volatiles were evaporated once more and the residual yellowish oil immediately dissolved in Et_2O (5 ml). Addition of a solution of K[$N(SiMe_3)_2$] in Et_2O (5 ml) produced a colorless precipitate which was allowed to settle. The supernatant solution was decanted off and the residue washed with Et_2O (10 ml) and pentane (10 ml) to afford crude **9 b** (75 mg, 0.25 mmol, 35%) as a highly air and moisture sensitive, colorless solid.

^1H NMR (THF-D_8): $\delta = 7.42$ (br s, 2 H, o-H), 6.90 (m, 2 H, m-H), 6.74 (m, 1 H, p-H) 3.20 (ddq, 4 H, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 6.2$ Hz, CH_2), 3.08 (ddq, 4 H, $^2J_{HH} = 13.2$ Hz, $^3J_{HH} = 7.0$ Hz, $^3J_{PH} = 7.5$ Hz, CH_2), 1.87 (br q, $^1J_{BH} = 87$ Hz, BH_2), 0.92 (t, 12 H, $^3J_{HH} = 7.0$ Hz, CH_3). – ^{11}B NMR (THF-D_8): $\delta = -21.2$ (dq, $^1J_{PB} = 51$ Hz, $^1J_{BH} = 87$ Hz). – $^{13}C\{^1H\}$ NMR (THF-D_8): $\delta = 135.5$ (d, $^3J_{PC} = 9.9$ Hz, o-C), 125.7 (br m, m-C), 121.3 (d, $^5J_{PC} = 2.7$ Hz, p-C), 45.5 (br m, CH_2), 14.5 (d, $^3J_{PC} = 3.8$ Hz, CH_3). – $^{31}P\{^1H\}$ NMR (THF-D_8): $\delta = 135.5$ (q, $^1J_{PB} = 51$ Hz). – $C_{14}H_{27}BKN_2P$ (304.27 g/mol), calcd. C 55.27 H 8.94 N 9.21, found C 54.56 H 9.01 N 8.73.

Bis(di*iso*propylamino)*iso*propylphosphine borane 11. **2 a** (29 mg, 0.11 mmol) and KHMDS (23 mg, 0.12 mmol) were dissolved in Et_2O (10 ml). The solution was stirred for 15 min, 2-iodopropane (11 μl, 19 mg, 0.12 mmol was added, and stirring was continued for 12 h. Volatiles were then removed under reduced pressure and the residue extracted with pentane (10 ml). Volatiles were evaporated once more and the residual colorless solid dissolved in a minimum volume of a mixture of pentane and toluene (approx. 1 : 1). Storage at −28 °C furnished colorless crystals of **11** (yield 22 mg, 70 μmol, 65%). The purity of the product was established by NMR spectroscopy.

^1H NMR (C_6D_6): $\delta = 3.49$ (d sept, 4 H, $^3J_{HH} = 6.9$ Hz, $^3J_{PH} = 11.4$ Hz, NCH), 1.9 (br q, 2 H, $^1J_{BH} = 100$ Hz, BH_2), 1.79 (d sept, 1 H, $^3J_{PH} = 17.9$ Hz, $^3J_{HH} = 7.1$ Hz, PCH), 1.15 (dd, 6 H, $^3J_{PH} = 16.6$ Hz, $^3J_{HH} = 6.8$ Hz, $PCCH_3$), 1.12 (d, 12 H, $^3J_{HH} = 6.9$ Hz, $NCCH_3$), 1.08 (d, 12 H, $^3J_{HH} = 6.9$ Hz, $NCCH_3$). – ^{11}B NMR (C_6D_6): $\delta = -37.6$ (dq, $^1J_{PB} = 109$ Hz, $^1J_{BH} = 100$ Hz). – $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 48.5$ (d, $^2J_{PC} = 3.6$ Hz, NCH), 25.2 (d, $^1J_{PC} = 58.3$ Hz, PCH), 24.8 (d, $^3J_{PC} = 2.5$ Hz, $NCCH_3$), 24.4 (d, $^3J_{PC} = 2.9$ Hz, $NCCH_3$), 18.0 (d, $^2J_{PC} = 2.9$ Hz, $PCCH_3$). – $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 89.0$ (m).

Crystallographic studies. X-ray diffraction data were collected on a Bruker Kappa Apex II Duo diffractometer equipped with an APEX II CCD-detector and a KRYO-FLEX cooling device with Mo-K_α radiation ($\lambda = 0.71073$ Å) at 130(2) K. The structures were solved with direct methods (SHELXS-2014[18]) and refined with a full-matrix least squares scheme on F^2 (SHELXL-2014[18]). Semi-empirical absorption corrections were applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms except those bound to phosphorus and boron using a riding model. Further details on the refinement are given in the supporting information (Table S1), the cif-files, and the incorporated res-files. CCDC-2171774 to CCDC-2171776 contain the crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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