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ARTICLE

Phosphines with N-heterocyclic boranyl substituents†

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A lithio-diazaborole reacted with diamino-chlorophosphines via metathesis to yield previously unavailable phosphinoboranes bearing amino substituents at both the phosphorus and boron atoms, and with Ph_2PCl and Mes^*PCl_2 via chloride transfer and reductive PP coupling to give a chloro-diazaborole and the corresponding diphosphine or diphosphene, respectively. Diazaboroles with phenylphosphino- and PH_2-substituents were nonetheless accessible via inverse metathesis upon treatment of a bromoborane precursor with phosphides $Ph_nPH_{2-n}M$ (n = 0 – 2, M = Li, K). The products were characterised by spectroscopic data and in most cases by single-crystal X-ray diffraction studies which show the molecules to exhibit strongly pyramidal coordination at the phosphorus atom and long BP bonds of 1.93 – 1.95 Å. The insensitivity of the BP distance towards substituent effects and the tolerance of large sterically induced torsional twists along the BP bond axis suggest the presence of pure single bonds without any contribution from P→B dative π-interactions. This view was confirmed by DFT studies which indicate further that the molecules lack a significant electrophilic character at boron but may act as potential σ-donor/π-acceptor ligands through the phosphorus atom.

Introduction

Phosphinoboranes (boranyl phosphines) $R_2BPR'_2$ [1] have drawn a good deal of attention as heavier congeners of the more familiar aminoboranes, $R_2BNR'_2$. Both types of molecules can draw sizable stability from E→B Lewis-acid/base interactions which may in principle occur intermolecularly via creation of dative σ-bonds between boron and pnictogen atoms of different molecules, or intramolecularly via dative π-bonding (Chart 1). Intermolecular interactions generate usually cyclic oligomers (frequently dimers) of rather low reactivity that are often perceived as analogues of cycloalkanes and have dominated the early stages of the development of phosphinoborane chemistry.[1]

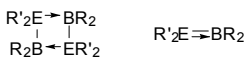

Chart 1 Schematic representation of the stabilisation of amino- and phosphino-boranes by intermolecular and intramolecular E→B electron donation (E = N, P)

Dedicated strategies for the stabilisation of monomeric phosphinoboranes have systematically been developed since the 1980ies. Monomer formation is generally fostered by increasing steric demand of substituents, in particular at boron. In addition, tuning of the Lewis-acidity and -basicity at the B and P atoms by specific substituent effects has been employed to overcome the preference of trivalent phosphorus atoms for a pyramidal coordination geometry with a high energetic barrier towards planarization, which reduces the π-overlap of the phosphorus lone-pair with the empty p-orbital at boron and thus the BP double bond character.[1] In particular, the groups of Power [2] and Stephan [3] have reported on phosphinoboranes with nearly or exactly planar coordination at both the boron and phosphorus atoms and concomitantly short BP bonds (cf. [3] PB = 1.786(4) Å for monomeric $tBu_2PB(C_6F_5)_2$ (**1**) vs. PB_{avg} = 2.057(3) Å for dimeric $[R_2PB(C_6F_5)_2]_2$ with R = Et, Ph). Even if the presence of a strong π-bonding contribution in **1** and related systems is beyond doubt,[1,2] it is remarkable that these species still seem to display some Lewis-ambiphilic character; e. g. the capability of **1** to effect heterolytic cleavage of H_2 [3] resembles closely the analogous reactivity of frustrated Lewis pairs.

As alternative approach to the strengthening of PB π-bonding contributions, monomeric phosphinoboranes have also been successfully stabilised by the introduction of amino groups at boron.[4] The low inversion barrier at nitrogen facilitates N→B-π-donation to saturate the Lewis-acidity at boron, which renders

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P→B-π-bonding energetically unattractive and removes hence the main driving force for planarization at phosphorus. Phosphinoboranes with *B*-amino-substituents like **2** [4a] and **3** [4f] (Chart 2) exhibit therefore pyramidal coordination at phosphorus and elongated B–P distances (BP 1.948(3) Å for **2** and 1.982(5) Å for **3**) which slightly exceed the sum of covalent radii (1.93 Å [1a]) and are addressed as single bonds.[1] Aside from the structural aspects, the weakening of the electrophilic character at boron brings also the phosphine character to the fore, and B-NR_2 substituted phosphinoboranes act therefore as well behaved as 2e-donor ligands towards transition metals via their phosphorus lone pair.[1b]

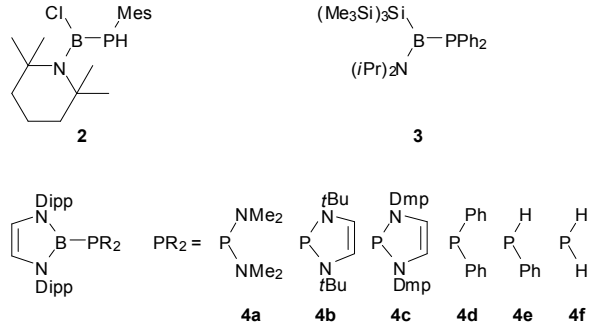


Chart 2 Molecular structures of selected *B*-amino substituted phosphinoboranes (Mes = mesityl, Dmp = 2,6-dimethylphenyl, Dipp = 2,6-di-isopropylphenyl)

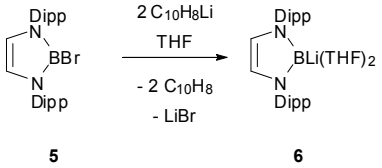
Before this background, we became interested in preparing derivatives like **4a-c** which combine an *N*-heterocyclic borolyl (NHB) fragment [5] with a *diamino*phosphinyl unit. Incorporation of the boron atom into a rigid and electron rich heterocycle maximises N→B-π-conjugation and should eliminate any residual electrophilic character at this site, so that the NHB unit may be simply regarded as strong σ-donor substituent at the diaminophosphinyl unit (a similar concept has been pursued in case of NHB-stabilised silylenes and their homologues [6]). Phosphino-diazaboroles are thus expected to behave no more as Lewis ambiphiles but as monofunctional phosphines which should perform as strong donor ligands in metal complexes. Apart from the fact that phosphinoboranes carrying exclusively amino substituents are so far unknown, these species seem appealing as they can be formally viewed as dimerization products of two carbene analogues (a nucleophilic *N*-heterocyclic diazaborolyl and an electrophilic diamino-phosphenium ion) via dative B→P interaction.

We report here the synthesis and full characterisation of tetra-amino-substituted phosphinoboranes which combine NHB moieties with acyclic (**4a**) or *N*-heterocyclic phosphinyl units (**4b**,**c**). In addition, the preparation and characterisation of some diamino-substituted phosphinoboranes grouping NHB and nucleophilic phosphinyl fragments (**4d-f**) will be described.

Results and discussion

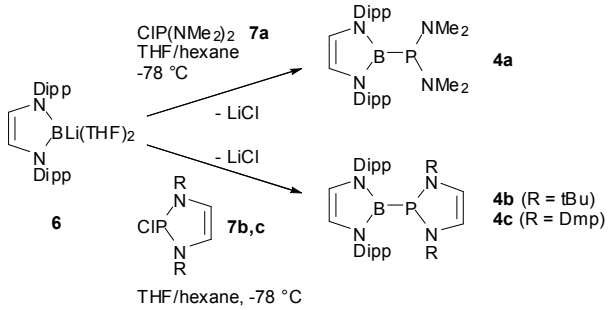
Syntheses and spectroscopic studies

Phosphinoboranes $R_2BPR'_2$ are generally prepared by salt metathesis starting from haloboranes R_2BX (X = halogen) and metal phosphides R'_2PM (M = alkaline metal).[1b] As the anion stabilising effect of amino substituents is very limited [7] and *P*-amino substituted phosphides are not known, this route is obviously unsuitable for the synthesis of target compounds **4a-c**. Considering that the phosphorus atoms in $P(NR_2)_2$ units exhibit, however, distinct electrophilic character, metathesis with a boron-centred nucleophile should be a viable alternative. A suitable reagent is *N*-heterocyclic lithio-borane **6** which was first prepared by Nozaki et al. (scheme 1) in 2006,[8] and has since developed into a versatile tool for the creation of boron-element bonds in metathesis reactions with various organic and organometallic electrophiles.[6,9] The bulky *N*-Dipp (Dipp = 2,6-di-isopropyl-phenyl) substituents in this species must be considered an additional benefit as they provide efficient steric protection at the boron centre which should help to stabilise phosphinoborane monomers.



Scheme 1 Preparation of lithiated *N*-heterocyclic borane **6** according to Nozaki et al. [8]

Following the protocol of Nozaki et al.,[8,9b] lithio-borane **6** was generated by reaction of bromo-diazaborole **5** with excess lithium powder in the presence of naphthalene. We noted that quantitative conversion of the starting materials (as established by ^{11}B NMR spectroscopy) required more forcing conditions than originally reported (24 h reaction time at -18 °C rather than 12 h at -40 °C [8]), presumably due to lower reactivity of the Li powder used. After the reaction was complete, unreacted metal and precipitated salts were removed by filtration through celite. The synthesis of **4a** was carried out by cooling the deep purple solution of crude **6** to -78 °C and subsequent addition of a hexane solution containing an excess of chloro-bis(dimethylamino)phosphine **7a** (Scheme 2).



Scheme 2 Synthesis of phosphinoboranes **4a-c**

For the synthesis of bis-heterocyclic derivatives **4b,c**, lithio-borane **6** was first purified by extraction into hexane and separation of all hexane-insoluble components. Metathesis reactions were then carried out by addition of THF solutions

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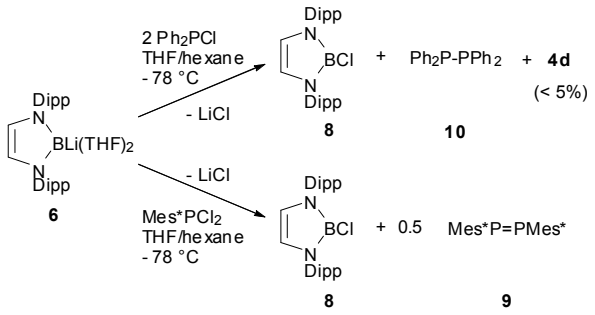
containing equimolar amounts of *N*-heterocyclic chloro phosphines **7b,c** at -78 °C (Scheme 2). Reaction monitoring by ^{31}P and ^{11}B NMR disclosed that **4a-c** constituted the only detectable reaction products in addition to unreacted starting material (**7a**) and minor amounts of hydrolysis products.

Target phosphinoboranes **4a-c** were isolated in decent yields as colourless, air and moisture sensitive solids and were identified and characterised by spectroscopic and single-crystal X-ray diffraction studies. The presence of direct phosphorus- boron bonding was immediately evident from the broadening of ^{31}P NMR signals due to partially relaxed spin coupling to the quadrupolar ^{10}B (19.9% nat. abundance, I = 3) and ^{11}B (80.1% nat. abundance, I = 3/2) nuclei. Determination of $^{1}J_{BP}$ coupling constants was feasible from neither ^{11}B nor ^{31}P NMR spectra. The ^{31}P chemical shifts of **4a-c** (70 – 100 ppm) compare to those of related symmetrical diphosphines (80 – 90 ppm for $(i\text{Pr}_2\text{N})_2\text{PP}(\text{NiPr}_2)_2$ and bis-diazaphospholenyls [10]), and the ^{11}B chemical shifts (23.5 – 25.9 ppm) are slightly larger than those of **5** [9b] (20.9 ppm) and the diazaborole **5-H** [9b] (22.9 ppm) featuring a hydrogen instead of the bromo-substituent at boron.

An unexpected result was obtained when **6** was reacted with chloro-diazaphospholene **7d** (R = Dipp) in hexane. Reaction monitoring by ^{31}P and ^{11}B NMR revealed that a mixture of **5-H** and two phosphorus containing products (with ^{31}P chemical shifts of 95.8 and 117.4 ppm) had formed. Even if none of these species was as yet positively identified, a phosphinoborane structure is definitely excluded as both signals appear as narrow lines that show no sign of ^{31}P,$^{10/11}$B spin coupling. We presume that metathesis is impeded due to steric overcrowding, and that the observed products arise rather from a process involving cleavage of a coordinated THF molecule in **6**. Investigations aiming at further elucidation of the reaction pathway (including reaction studies in deuterated solvents) are currently under way but have not yet provided any decisive results, and we want to refrain at this point from a further discussion of this aspect.

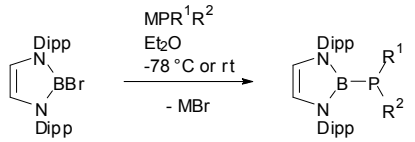
Trying to extend the metatheses of **6** to further halophosphines in order to access phosphino-diazaboroles with a wider range of substitution patterns, we further investigated reactions with Mes*PCl_2 (Mes* = 2,4,6-tri-tert-butylphenyl) and Ph_2PCl. The ^{31}P and ^{11}B NMR spectra of reaction mixtures revealed that treatment of **6** with Mes*PCl_2 at -78 °C produced a mixture of chloroborane **8** [9a] (δ^{11}B 22 ppm) and diphosphene **9** [11] (Scheme 3) which was identified by means of its characteristic ^{31}P chemical shift of 573.5 ppm and a single-crystal X-ray diffraction study of a crystalline sample isolated in low yield from the reaction mixture. The NMR spectroscopic survey of the reaction of **6** with $ClPPh_2$ (complete conversion of the starting material required addition of two equivalents) disclosed that a product addressed as phosphinoborane **4d** (broad ^{31}P NMR signal at -61.1 ppm,) had formed in low yield (< 5% according to integration of ^{31}P NMR signals) whereas the main products were identified as chloroborane **8** and tetraphenyl diphosphine **10** (δ^{31}P -15.6, Scheme 3).



Scheme 3 Reactions of **6** with Ph_2PCl and Mes*PCl_2

The outcome of these reactions is easily rationalised if one acknowledges that main-group organometallics like **6** are not only potent nucleophiles, but may also act as reducing agents. The generation of **10** is then readily explained via a formal two-step pathway involving first Li/Cl exchange between **6** and $ClPPh_2$ to give **8** and $LiPPh_2$, followed by salt metathesis of the formed phosphide with a second equivalent of the chloro-phosphine. A similar mechanism may be invoked to explain the formation of **9**. A heuristic explanation for the preference of **6** to react with Mes*PCl_2 and Ph_2PCl via reductive coupling and with diamino chlorophosphines (in the reactions leading to **4a-c**) via salt metathesis becomes feasible if one relates the observed reactivity of a substrate R_2PCl to the electronic properties of R: amino groups permit better delocalisation of the positive partial charge in the R_2P fragment by π-(hyper)-conjugation than halogen or phenyl substituents and render the phosphorus atom a weaker electrophile,[12] which obviously disfavours the formal reduction of the phosphorus centre in a coupling process and brings metathesis reactions to the fore.

In order to verify the phosphinoborane nature of the side product in the reaction of **6** with $ClPPh_2$, we tried to access this species via conventional metathesis [1b] of a boron electrophile with a phosphorus nucleophile. The expected product **4d** was indeed formed selectively in the reaction of **5** with $LiPPh_2$ and isolated in good yield after standard work-up. Analogous transformations permitted to convert secondary or primary phosphides PhPHLi and KPH_2 into PH-functionalised phosphinoboranes **4e,f** (Scheme 4).



4d (R^1 = R^2 = Ph)
4e (R^1 = Ph, R^2 = H)
4f (R^1 = R^2 = H)

Scheme 4 Synthesis of phosphinoboranes **4d-f** (M = Li (**4d,e**), K (**4f**))

All three compounds **4d-f** are colourless, thermally stable solids which are much less sensitive to air and moisture than **4a-c**; in particular, **4e** was found to be perfectly stable in contact with air or water in the solid state and in solution. Characterisation was accomplished by spectroscopic data and in case of **4e,f** by

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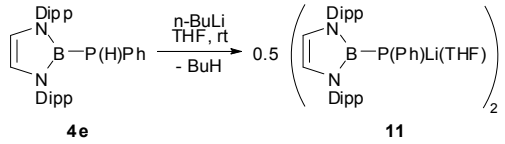
single-crystal X-ray diffraction studies. The ^{11}B NMR data of **4d-f** are very similar to those of **4a-c** whereas the ^{31}P chemical shifts follow the same trend as those of phenyl phosphines $Ph_{3-n}PH_n$ (n = 0 – 3), moving to progressively higher field with increasing number n of hydrogen substituents.

A primary exploration of the chemical properties revealed that **4e** reacts with n-butyl lithium to afford phosphidoborane **11** (Scheme 5) which gives rise to a singlet at slightly larger chemical shift (δ^{31}P -116.1 vs. -130.4 for **4e**) in the ^{31}P NMR spectrum. A similar reactivity had previously been noted by Power et al. for secondary phosphinoboranes $Mes_2BP(H)R$ (R = alkyl, aryl, $SiMe_3$).[13] The identification of **11** was confirmed by a preliminary single-crystal X-ray diffraction study. Even if severe disorder and limited data quality impeded satisfactory refinement of the molecular structure, the data prove the existence of dimeric molecules featuring a central Li_2P_2 ring formed by association of two monomeric units via pairwise Li···P interactions, trigonal planar coordination at boron as well as tetrahedral coordination at phosphorus, and a strongly twisted arrangement of the C_{Ph}–P–BN_2 unit (a representation of the molecular structure is included in the ESI). We attribute the deviation of these structural features from those of Power's monomeric boryl phosphides $[Mes_2BPMes][Li(12\text{-crown-}4)_2]$ and $Mes_2BP(R)Li(THF)_2$, which exhibit planar arrangement of the C–P–BC_2 skeleton and substantial boron-phosphorus double bond character,[13] to a combination of insufficient steric protection at phosphorus and the repression of BP double bond character due to the reduced Lewis-acidity of the boron atom.



4e **11**

Scheme 5 Generation of a phosphidoborane by lithiation of **4e**

Single-crystal X-ray diffraction studies

The molecular structures of **4a-c**, **4e**, and **4f** are displayed in Figs. 1 and 2, and selected structural parameters are listed in Table 1.

All molecules exhibit the expected monomeric structures. The BN_2C_2 rings are planar (which implies implicitly trigonal planar coordination geometries for both the boron and the endocyclic nitrogen atoms), and endocyclic distances (B–N 1.418(4) to 1.445(2) Å, C–N 1.397(3) to 1.405(3) Å, C–C 1.332(2) to 1.344(2) Å) differ not significantly from the structural data of previously reported diazaboroles.[6,8,9] Likewise, the PN_2C_2 rings in **4b,c** exhibit bond distances (P–N 1.737(1) to 1.753(1) Å, N–C 1.420(2) to 1.428(2) Å, C–C 1.329(2) to 1.334(3) Å) and envelope conformations which repeat well-known features of *P*-substituted diazaphospholenes.[14] The slightly pyramidal coordination at the *P*-bound nitrogen atoms in **4a-c** reflects the influences of steric congestion and mutual repulsion between lone-pairs at the adjacent N and P atoms.[14]

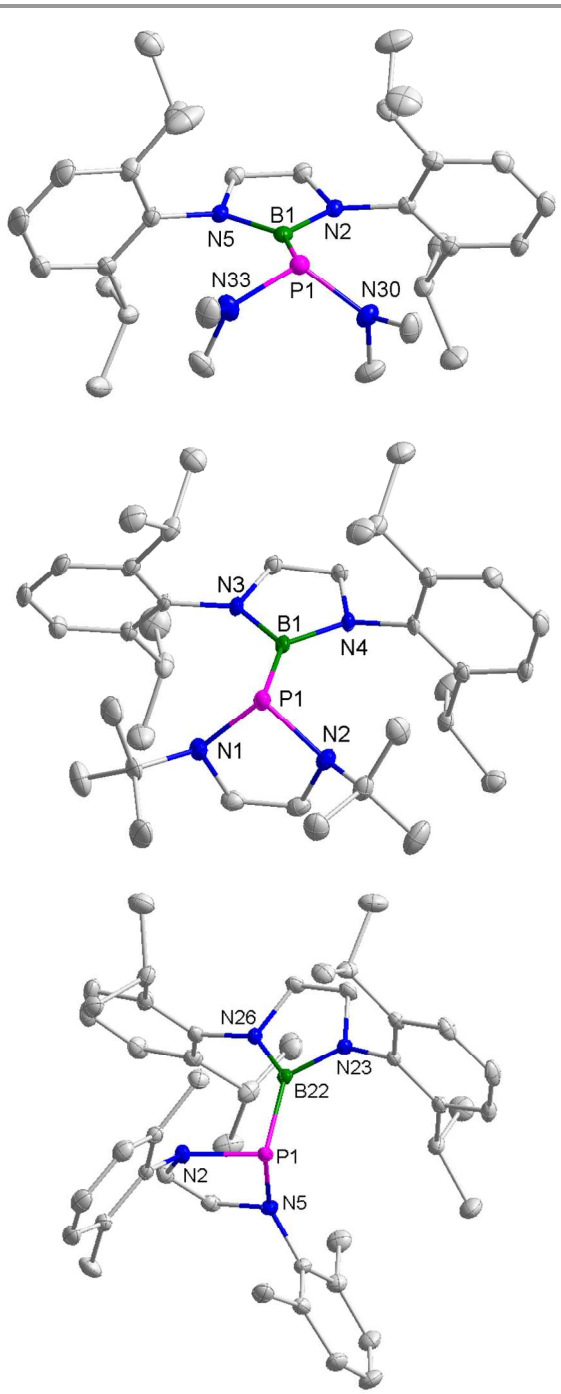


Figure 1 ORTEP-style representation of the molecular structures of (from top to bottom) **4a-c** in the crystal. Thermal ellipsoids are drawn at 50% probability level; hydrogen atoms are omitted for clarity.

The phosphorus atoms exhibit distinctly trigonal pyramidal coordination geometry, with the sums of bond angles ranging at the lower end of the span reported for phosphinoboranes (296° – 360°).[15] The B–P distances are rather insensitive to changes of the substituents at phosphorus (a slight bond elongation by 2 pm in **4b,c** is attested to reflect the effect of increasing steric congestion) and lie at the upper end of the range of known bond distances in acyclic monomeric phosphinoboranes (1.786 to

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1.986 Å, mean value 1.897(6) Å).[15] The coincidence of strong pyramidalisation at phosphorus and elongated B–P bond distances goes with the previously observed inverse correlation between both parameters which has been attributed to two sources, viz. variation of PB-π-bonding and rehybridisation at phosphorus.[2] Comparison with the available reference data [15] gives a first indication that π-bonding in **4** is negligible and the BP bonds should therefore be addressed as pure single bonds.

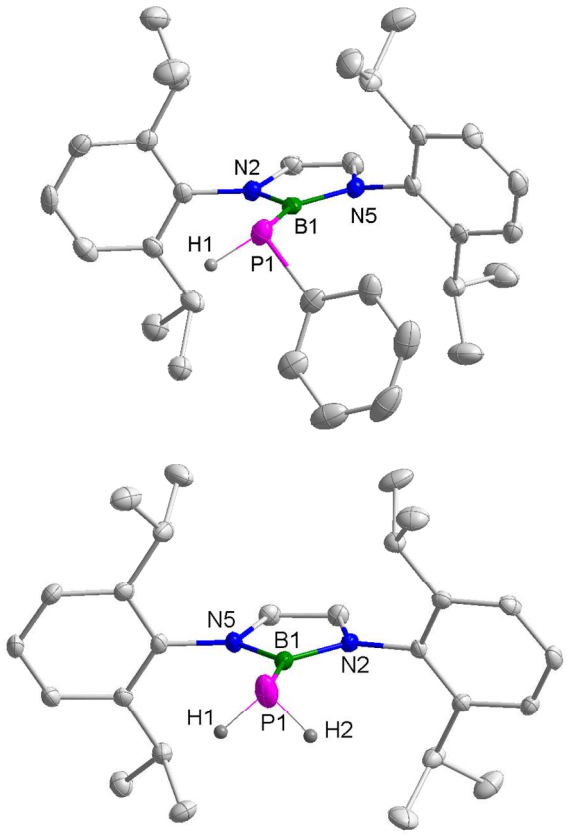

Figure 2 ORTEP-style representation of the molecular structures of **4e** (top) and **4f** (bottom) in the crystal. Thermal ellipsoids are drawn at 50% probability level; hydrogen atoms of CH bonds are omitted for clarity. One orientation of the disordered iso-propyl group in **4e** is displayed.

Table 1 Selected structural parameters for **4a-c**, **4e** and **4f**

	B–P [Å]	Sum of bond angles [°] at B	at P	at $N^{P\ a)}$	twist angle ϕ [b)] [°]
4a	1.9303(15)	357.9(3)	317.3(2)	354.1(3) 354.5(3)	7(1)
4b	1.951(2)	359.1(4)	292.1(2)	348.1(4) 343.1(4)	3(1)
4c	1.953(2)	360.0(4)	293.8(2)	348.5(3) 351.3(4)	67(1)
4e	1.931(3)	359.3(6)	299(2)	-	1(3)
4f	1.923(2)	359.6(4)	284(4)	-	3(5)

[a)] nitrogen atoms in P –N bonds; [b)] angle between the perpendiculars to the local P and B planes when viewed down the P–B bond axis (cf. ref. 2)

Further support for this interpretation is gained from an analysis of the torsional alignment of R'_2P and BR_2 fragments with respect to the BP bond axis. The twist angles ϕ (as defined in Table 1) in **4a,b,d,e** of 1° to 7° come close to the ideal value of 0° – which grants optimum π-overlap between the lone-pair at phosphorus and the empty p-orbital at boron – and confirm that these compounds exhibit the same conformational preference as most previously known phosphinoboranes (including beside species with strong π-bonding contributions also derivatives with a low degree of double bond character like **2** [4a] with ϕ = 6°). In contrast, **4c** exhibits a strongly twisted structure (ϕ = 67°) which approaches a situation where π-bonding is totally blocked by orthogonal arrangement (ϕ = 90°) of the R'_2P and BR_2 units. A similar distortion has previously been established for **3** [4f] (ϕ = 62°) and is consistently explained as being enforced by steric repulsion between the extremely bulky substituents. Quite remarkably, the strong torsional distortion of **4c** as compared to **4b** leaves the BP distance invariant, which is hardly compatible with the presence of a perceptible π-bonding contribution [1a] and gives thus further support to the perception of the BP bonds as pure single bonds.

Computational studies

In order to verify our interpretation of the structural features of the phosphino-diazaboroles under study, we performed DFT calculations, using **4b** and a simplified derivative **4'** featuring the same heterocyclic framework with methyl instead of the bulkier *t*Bu and Dipp substituents at all nitrogen atoms as archetypal model compounds. The computations were carried out with the ωB97X-D functional,[16] which includes long-range and dispersion corrections, in combination with a cc-pVDZ basis set; the same computational model has recently been shown to allow a realistic structural modelling of sterically encumbered bis-diazaphospholenyls.[10c] Energy optimisation of the molecular structures of **4b** and **4'** produced results that are not only quite similar to each other, but show also qualitatively and quantitatively good agreement with the experimentally determined structural parameters of **4b** (see Table 2 and ESI).

Table 2 Comparison of selected calculated structural parameters (at the ωB97X-D/cc-pVDZ level) for **4'** and **4b** with experimental data for **4b**

		B–P [Å]	Sum of bond angles [°] at B	at P	at $N^{P\ a)}$	twist angle ϕ [°]
4'	Calcd.	1.948	359.5	290.6	337.9	0
4b	Calcd.	1.950	358.8	294.5	344.4 344.4	0
4b	Exp.	1.951(2)	359.1(4)	292.1(2)	348.1(4) 343.1(4)	3(1)

[a)] Nitrogen atoms in P –N bonds

Experimentally determined and computed molecular structures of **4b** differ mainly in the alignment of the tert-butyl- and Dipp-substituents, which we attribute to the unfeasibility of modelling computationally the influences imposed by crystal packing effects. The structural features of the bis-heterocyclic core of **4'** deviate from those of **4b** chiefly in showing an even stronger pyramidalisation at the N- and P-atoms in the PN_2C_2 ring, which indicates that steric repulsion between the *N*-tert-butyl groups and the diazaphospholene ring in **4b** is presumably more important than between substituents at the boron and phosphorus heterocycles. Without going into detail, this finding

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corroborates also that the pyramidal coordination of the diazaphospholene-nitrogen atoms is mainly of electronic origin (i.e. attributable to mutual repulsion of the nitrogen and phosphorus lone-pairs).

Inspection of the Kohn-Sham (KS) orbitals of **4'** reveals that the HOMO (we will use HOMO and LUMO instead of the clumsy – even though more exact – notations "highest occupied/lowest unoccupied KS-orbital") is strongly delocalised, containing contributions from the π-electron systems of both heterocycles and the phosphorus lone-pair with a weakly BP-σ-bonding contribution (Fig. 3). The LUMO is merely an antibonding σ*(PN) orbital and has no prominent coefficient at boron, whereas the LUMO+1 exhibits contributions from all atoms of the central N_4BP unit and can be characterised as σ*(PN) and π*(BN) antibonding, and π(BP) bonding; the largest coefficients are likewise found on the phosphorus atom.

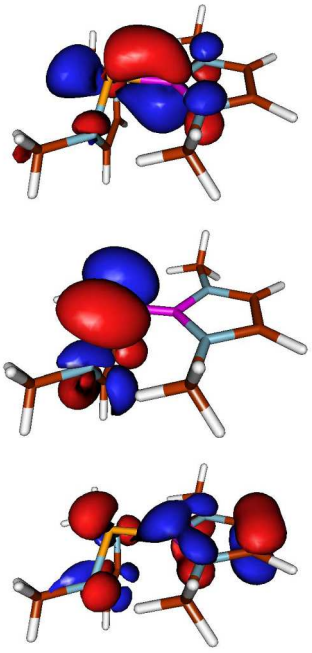

Figure 3 Visual representations of selected Kohn-Sham orbitals of **4'** calculated at the ωB97X-D/cc-pVDZ level of theory (top, LUMO+1; middle, LUMO; bottom, HOMO). Isodensity surfaces were drawn for a value of 0.05 a.u.

Analysis of the remaining occupied KS-orbitals in the frontier orbital region discloses that π-bonding interactions are confined to the heterocyclic PN_2C_2 and BN_2C_2 moieties, and that in no case any significant π(BP) interaction is present. These findings are in accord with an NBO analysis [17] which shows that the BP bonding interaction arises from a single LMO that is rather evenly distributed between both atoms (45% B, 55% P), indicative of a covalent σ-bond. Second-order perturbation theory analysis of the Fock matrix in the NBO basis indicates that the empty p-orbital at boron participates in strong π-conjugation in the BN_2C_2 ring, which is dominated by N→B π-interactions with second order perturbation energies $E(2)$ of 92.9 kcal mol^{-1}; P→B donation remains marginal ($E(2)$ = 7.8 kcal mol^{-1}). Delocalisation in the PN_2C_2 ring is small and confined to the N_2C_2 framework as in other *P*-substituted diazaphospholenes.[14]

Similar results as for **4'** were also obtained from analysis of the KS-orbitals of **4b**, with the exception that the first four unoccupied orbitals constitute π*-orbitals of the aromatic rings of the Dipp substituents, and the σ*(PN)-type orbitals are assigned only to the two next higher levels.

The perception of a true covalent boron-phosphorus bond (rather than a dative Lewis-donor/acceptor interaction) is also supported by calculated energies for BP bond breaking reactions of **4'**: comparison of the values of $\Delta E_{zpe,corr}$ (which include corrections for vibrational zero-point energies and basis set superposition error) computed at ωB97X-D/cc-pVDZ level reveals that heterolytic bond cleavage to give a phosphenium cation/diazaborolide anion pair requires, not surprising, by far more energy ($\Delta E_{zpe,corr}$ = 174.9 kcal mol^{-1}) than homolytic cleavage to produce a radical pair ($\Delta E_{zpe,corr}$ = 64.6 kcal mol^{-1}).

Taken together, the computational results consistently confirm our initial hypotheses that the effect of amino-substituents suppresses both the electrophilic character at boron and the development of BP-π-bonding. The phosphorus-boron bond is best described as a pure σ-bond, leaving the idea to describe species like **4b** as Lewis-donor/acceptor adducts of carbene-analogue phosphenium and diazaborolyl fragments a purely formal analogy. The structure of the KS-orbitals indicates that phosphino-diazaboroles may serve as P-donor ligands.

Conclusions

It has been established that nucleophilic lithio-diazaboroles show two-sided reactivity towards chlorophosphine substrates. Reactions with diamino-chlorophosphines proceed like those with silyl and transition metal halides [9] via metathesis to produce phosphino-diazaboroles, and gave for the first time access to phosphinoboranes bearing *P*-amino-substituents. Synthesis of a diazaphospholenyl-diazaborole bearing *N*-Dipp substituents on both rings was impeded by steric overcrowding, but the detection of products pointing to a possible THF activation stimulates further investigation of this reaction with the prospect to prove involvement of a phosphenium-borolide ion pair as transient intermediate. In contrast, reactions with aryl (di)chlorophosphines occur via formation of a chloro-diazaborole and reductive coupling of the phosphine substrate to create a diphosphine or diphosphene, respectively. The expected *P*-arylphosphino-diazaboroles were nonetheless accessible via metatheses of a bromo-diazaborole with phosphides $Ph_nPH_{2-n}M$ (n = 0 – 2, M = Li, K).

Crystallographic studies showed the products formed to possess phosphorus atoms with strongly pyramidal coordination sphere, and elongated boron-phosphorus bonds which do not show large variation in length upon change of substituents and tolerate large sterically induced torsional distortions around the bond axis. These findings fully back the anticipation that the boron-phosphorus interaction is best described as a pure σ-bond which is unaffected by any dative P→B-π-overlap. The results of DFT studies corroborate this view and indicate that

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phosphino-diazaboroles are potential ligands which are inclined to engage in σ-donor/π-acceptor interactions with a transition metal through the phosphorus atom, but display apparently no electrophilic character at boron. It remains to be seen if the marked delocalisation of the HOMO permits also to develop alternative coordination modes (at least for derivatives with less steric protection around the boron heterocycle). We are currently exploring possible uses of phosphino-diazaboroles as strongly electron donating ligands, as well as further ways to use the functionality of derivatives with primary and secondary phosphino groups for further transformations.

Experimental

Materials and Methods

All manipulations were carried out under dry argon using standard Schlenk technique. Solvents were purified by standard procedures. NMR spectra: Bruker Avance 250 (^{1}H: 250 MHz, ^{11}B: 80.2 MHz, ^{13}C: 62.9 MHz, ^{31}P: 101.2 MHz) in C_6D_6 or $CDCl_3$ at 30 °C. Chemical shifts were referenced to ext. TMS (^{1}H, ^{13}C), $BF_3(OEt_2)$ (^{11}B; Ξ = 32.083974 MHz), or 85 % H_3PO_4 (^{31}P; Ξ = 40.480742 MHz). Coupling constants are given as absolute values. Elemental analysis: Perkin-Elmer 2400CHSN/O Analyser and Elementar Micro Cube. The large deviations between calculated and found analytic compositions for **4a-c** are attributable to the high air-sensitivity of these compounds. Melting Points were determined with a Büchi B-545 melting point apparatus in sealed capillaries.
Diazaborole **5**,[9b] diazaphospholenes **7b,c**,[19] $PhPH_2$,[20] and KPH_2 [21] were synthesised as described. Lithium powder was prepared by washing commercially available lithium dispersion (Sigma Aldrich, 25 wt % in mineral oil, > 0.05% Na) with hexane and drying under vacuum.

Synthetic Procedures

1-(1,3-BIS(2,6-DI-ISOPROPYLPHENYL)-1,3,2-DIAZABOROLYL-N,N,N',N'-TETRAMETYL-PHOSPHINEDIAMINE (4A)
A solution of **5** (500 mg, 1.07 mmol), lithium powder (74 mg, 10.7 mmol), and naphthalene (69 mg, 0.56 mmol) in THF (10 mL) was cooled to -18 °C and stirred for 24 h. The dark purple suspension was filtrated through celite. The deep purple filtrate was cooled to -78 °C, and excess chloro-bis(dimethylamino) phosphine (0.1 mL) was slowly added with stirring. The solution turned yellow, and stirring was continued for 30 min at -78 °C und further 30 min at rt. All volatiles were removed under reduced pressure. The residue was dissolved in 40 mL hexane and filtered through celite to remove insoluble salts. The filtrate was concentrated to a volume of 20 mL and stored at -20 °C to yield 620 mg (yield 57%) of **4a** of m.p. 130 °C. – ^{1}H NMR (C_6D_6): δ = 7.16 (m, 6 H, C_6H_3), 6.31 (d, 2 H, $^{4}J_{PH}$ = 1.1 Hz, =CH), 3.30 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, CH), 2.46 (d, 12 H, $^{3}J_{PH}$ = 9.2 Hz, $PNCH_3$), 1.32 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH_3), 1.18 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH_3). – ^{11}B{^{1}H} NMR: δ = 25.9 (broad). – ^{13}C{^{1}H} NMR (C_6D_6): δ = 145.8 (s, *o*-C_6H_3), 139.9 (s, *i*-C_6H_3), 127.3 (s, *p*-C_6H_3), 123.1 (s, *m*-C_6H_3), 121.4 (d, $^{3}J_{CP}$ = 3.3 Hz, =CH), 46.5 (d, $^{2}J_{CP}$ = 3.3 Hz, NCH_3), 28.7 (d, $^{5}J_{CP}$ = 3.3 Hz, *C*H(CH_3)$_2$), 26.3 (s, CH(*C*H$_3$)$_2$), 22.6 (d, $^{6}J_{CP}$ = 2.5 Hz, CH(*C*H$_3$)$_2$). – ^{31}P{^{1}H} NMR: δ = 100.0 (broad). – Anal. for $C_{30}H_{50}BN_4P$ (508.54 g mol^{-1}): calcd. C 70.86, H 9.91, N 11.02%; found C 69.27, H 9.12, N 10.59%.

2-(1,3-BIS(2,6-DI-ISOPROPYLPHENYL)-1,3,2-DIAZABOROLYL)-1,3-DI(TERT-BUTYL)-1,3,2-DIAZAPHOSPHOLENE (4B)
A solution of **5** (1.00 g, 2.14 mmol), lithium powder (148 mg, 21.4 mmol) and naphthalene (137 mg, 1.07 mmol in THF (20 mL) was cooled to -18 °C and stirred for 24 h. The dark purple suspension was filtered through celite and evaporated to dryness. The residue was taken up in 30 mL of hexane, and again filtered through a layer of celite to remove insoluble components. The dark red filtrate was cooled to -78 °C. A solution of **7b** (502 mg, 2.14 mmol) in THF (10 mL) was added drop wise with stirring. The suspension turned yellow, and stirring was continued for 30 min at -78 °C and then 1 h at rt. Insoluble salts were removed by filtration through celite. Volatiles were evaporated under reduced pressure to yield 680 mg of **4b** (yield 54 %). A crystalline sample (m. p 175 °C) was obtained by recrystallisation from hexane. – ^{1}H NMR (C_6D_6): δ = 7.11-7.25 (m, 6 H, C_6H_3), 6.09 (d, 2 H, $^{4}J_{PH}$ = 0.9 Hz =CH), 5.94 (d, 2 H, $^{3}J_{PH}$ = 5.7 Hz, =CH), 3.36 (sept, 4 H, $^{3}J_{HH}$ = 6.8.Hz, CH), 1.41 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH_3), 1.19 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH_3), 0.79 (s, 18 H, *t*Bu). – ^{11}B{^{1}H} NMR: δ = 25.8 (broad). – ^{13}C{^{1}H} NMR: δ = 146.0 (s, *o*-C_6H_3), 141.2 (s, *i*-C_6H_3), 127.1 (s, *p*-C_6H_3), 124.0 (d, $^{2}J_{PC}$ = 4.8 Hz, =CH), 123.4 (s, *m*-C_6H_3), 121.7 (d, $^{2}J_{PC}$ = 2.6 Hz, =CH), 54.8 (d, $^{2}J_{PC}$ = 11.6 Hz, N*C*(CH$_3$)$_3$), 29.4 (d, $^{3}J_{PC}$ = 8.7 Hz, NC(*C*H$_3$)$_3$), 28.6 (d, $^{5}J_{PC}$ = 1.6 Hz, *C*H(CH$_3$)$_2$), 26.0 (s, CH(*C*H$_3$)$_2$), 22.8 (d, $^{6}J_{PC}$ = 1.5 Hz, CH(*C*H$_3$)$_2$). – ^{31}P{^{1}H} NMR: δ = 70.1 (s). – Anal. for $C_{36}H_{56}BN_4P$ (586.65 g mol^{-1}): calcd. C 73.71, H 9.62, N 9.55%; found C 72.10, H 9.47, N 9.20%.

2-(1,3-BIS(2,6-DI-ISOPROPYLPHENYL)-1,3,2-DIAZABOROLYL)-1,3-BIS(2,6-DIMETHYLPHENYL)-1,3,2-DIAZAPHOSPHOLENE (4C)
The synthesis was carried out analogously to that of **4b** starting from 1.00 g of **5** and 708 mg of **7c**. Crude **4c** was isolated in 56 % yield. A crystalline sample (m. p. 181 °C) was obtained by recrystallisation from hexane. – ^{1}H NMR (C_6D_6): δ = 7.20-7.08 (m, 6 H, C_6H_3), 6.90-6.70 (m, 6 H, C_6H_3), 6.21 (d, 2 H, d, J_{PH} = 2.0 Hz, =CH), 5.49 (d, 2 H, J_{PH} = 2.9 Hz, =CH), 3.26 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, C*H*(CH$_3$)$_2$), 2.30 (d, 12 H, $^{5}J_{PH}$ = 0.9 Hz, CH_3), 1.15 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.06 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$). – ^{11}B{^{1}H} NMR: δ = 23.5 (broad). – ^{13}C{^{1}H} NMR: δ = 145.6 (s, *o*-C_6H_3), 140.8 (s, *i*-C_6H_3), 144.0 (d, $^{2}J_{PC}$ = 11.2 Hz, *i*-C_6H_3), 133.2 (d, $^{3}J_{PC}$ = 2.5 Hz, *o*-C_6H_3), 129.8 (s, *m*-C_6H_3), 127.3 (s, *p*-C_6H_3), 124.9 (d, $^{2}J_{PC}$ = 4.8 Hz, =CH), 123.9 (s, *m*-C_6H_3), 123.5 (s, *m*-C_6H_3), 121.5 (d, $^{2}J_{PC}$ = 2.5 Hz, =CH), 28.8 (d, $^{5}J_{PC}$ = 1.1 Hz, *C*H(CH$_3$)$_2$), 26.4 (s, CH(*C*H$_3$)$_2$), 22.9 (s, CH(*C*H$_3$)$_2$), 20.9 (s, CH_3), 20.7 (s, CH_3). – ^{31}P{^{1}H} NMR: δ = 80.1 (broad). – Anal. for $C_{44}H_{56}BN_4P$ (682.74 g mol^{-1}): calcd. C 77.41, H 8.27, N 8.21%; found C 75.78, H 8.03, N 7.94%.

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1,3-bis(2,6-di-isopropylphenyl)-2-diphenylphosphino-1,3,2-diazaborole (4d)

N-butyl lithium (0.675 mL of a 1.6 M solution in hexane, 1.08 mmol) was added at rt to a solution of diphenylphosphine (187 µL, 1.08 mmol) in Et_2O (10 mL). The mixture was stirred for 30 min. The resulting dark yellow solution was added to a cooled (-78 °C) solution of **5** (500 mg, 1.08 mmol) in Et_2O (15 mL). The reaction mixture was stirred for 30 min at this temperature and then allowed to warm slowly to rt. Solvents and volatiles were removed under reduced pressure. The residue was taken up in hexane (20 mL) and filtered through celite. The filtrate was concentrated to a volume of 5 mL and stored at -20°C to yield 386 mg (yield 63 %) of **4d** as crystalline precipitate, m. p. 174 °C. – ^{1}H NMR (C_6D_6): δ = 7.29 (m, 4 H, *o*-Ph), 7.13 (m, 2 H, *p*-C_6H_3), 7.00 (m, 4 H, *m*-C_6H_3), 6.90-6.78 (m, 6 H, *m/p*-Ph), 6.34 (d, 2 H, d, $^4J_{PH}$ = 1.5 Hz, =CH), 3.25 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH_3)$_2$), 1.14 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.09 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$). – ^{11}B{^{1}H} NMR: δ = 26.0 (broad). – ^{13}C{^{1}H} NMR: δ = 145.8 (s, *o*-C_6H_3), 139.2 (s, *i*-C_6H_3), 136.3 (d, $^2J_{PC}$ = 6.7 Hz, *i*-Ph), 135.3 (d, $^3J_{PC}$ = 19.5 Hz, *o*-Ph), 127.9 (s, *p*-C_6H_3), 127.8 (*m/p*-Ph), 123.5 (s, *m*-C_6H_3), 122.1 (d, $^2J_{PC}$ = 2.5 Hz, =CH), 28.8 (d, $^5J_{PC}$ = 1.5 Hz, *C*H(CH_3)$_2$), 26.2 (s, CH(*C*H$_3$)$_2$), 22.7 (d, $^6J_{PC}$ = 1.4 Hz, CH(*C*H$_3$)$_2$). – ^{31}P{^{1}H} NMR: δ = -60.7 (broad d). – Anal. for $C_{38}H_{46}BN_2P$ (572.57 g mol^{-1}): calcd. C 79.71, H 8.10, N 4.89%; found C 79.31, H 7.99, N 4.87%.

1,3-bis(2,6-diisopropylphenyl)-2-(phenylphosphino)-1,3,2-diazaborole (4e)

N-butyl lithium (1.06 mL of a 1.6 M solution in hexane, 1.71 mmol) was added at -78 °C to a solution of phenylphosphine (185 µL, 1.71 mmol) in Et_2O (15 mL). The mixture was stirred for 1 h at -78 °C and then allowed to warm to rt. The resulting solution was added to a suspension of **5** (850 mg, 1.71 mmol) in Et_2O (20 mL). The reaction mixture was stirred for 30 min and then evaporated to dryness under reduced pressure. Soxhlet extraction of the residue with hexane and subsequent removal of solvent under reduced pressure gave 650 mg of **4d** (yield 81 %). Crystals of m. p. 118 °C were obtained by recrystallisation from hexane. – ^{1}H NMR ($CDCl_3$): δ = 7.31 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.23 (dd, 2 H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, *m*-C_6H_3), 7.10 (dd, 2 H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, *m*-C_6H_3), 6.94 (m, 1 H, *p*-Ph), 6.83 (m, 4 H, *m*-Ph), 6.63 (m, 4 H, *o*-Ph), 6.31 (d, 2 H, d, $^4J_{PH}$ = 1.1 Hz, =CH), 3.30 (d, 1 H, $^1J_{PH}$ = 225 Hz, PH), 3.12 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH_3)$_2$), 2.79 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, C*H*(CH_3)$_2$), 1.28 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.15 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.10 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.84 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$). – ^{11}B{^{1}H} NMR: δ = 26.3 (broad d). – ^{13}C{^{1}H} NMR: δ = 146.3 (s, *o*-C_6H_3), 145.7 (s, *o*-C_6H_3), 138.4 (s, *i*-C_6H_3), 134.0 (d, $^2J_{PC}$ = 15.8 Hz, *o*-Ph), 131.1 (d, $^1J_{PC}$ = 7.5 Hz, *i*-Ph), 127.8 (d, $^3J_{PC}$ = 7.5 Hz, *m*-Ph), 127.4 (s, *p*-C_6H_3), 126.3 (s, *p*-Ph), 123.35 (s, *m*-C_6H_3), 123.33 (s, *m*-C_6H_3), 120.8 (d, $^2J_{PC}$ = 2.1 Hz, =CH), 28.4 (d, $^5J_{PC}$ = 1.7 Hz, *C*H(CH_3)$_2$), 28.2 (s, *C*H(CH_3)$_2$), 25.2 (s, CH(*C*H$_3$)$_2$), 23.5 (d, $^6J_{PC}$ = 2.5 Hz, CH(*C*H$_3$)$_2$), 22.8 (d, $^6J_{PC}$ = 2.2 Hz, CH(*C*H$_3$)$_2$). – ^{31}P NMR: δ = -130.4 (broad d, $^1J_{PH}$ = 225 Hz). – Anal. for $C_{32}H_{42}BN_2P$ (496.47 g mol^{-1}): calcd. C 77.41, H 8.53, N 5.64 %; found C 76.35 H 8.570 N 5.53 %.

1,3-bis(2,6-diisopropylphenyl)-2-phosphino-1,3,2-diazaborole (4f)

Et_2O (15 mL) was added to a mixture of **5** (500 mg, 1.08 mmol) and KPH_2 (86 mg, 1.2 mmol). The suspension was stirred for 24 h at rt. Solvents and volatiles were removed under reduced pressure. The residue was taken up in hexane (20 mL) and the resulting suspension filtered through celite. The filtrate was stored at -20 °C to yield 370 mg of **4f** (yield 82 %) as crystalline precipitate of m. p. 149 °C. – ^{1}H NMR (C_6D_6): δ = 7.21 (m, 2 H, *p*-C_6H_3), 7.14 (m, 4 H, *m*-C_6H_3), 6.24 (d, 2 H, $^4J_{PH}$ = 0.6 Hz, =CH), 3.16 (sept, $^3J_{HH}$ = 6.9 Hz, C*H*(CH_3)$_2$), 1.58 (d, $^1J_{PH}$ = 198 Hz, PH_2), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$). – ^{11}B{^{1}H} NMR: δ = 27.5 (broad). – ^{13}C{^{1}H} NMR: δ = 146.2 (s, *o*-C_6H_3), 138.7 (s, *i*-C_6H_3), 128.0 (s, *p*-C_6H_3), 123.7 (s, *m*-C_6H_3), 120.8 (d, $^2J_{PC}$ = 1.4 Hz, =CH), 28.5 (s, *C*H(CH_3)$_2$), 24.6 (s, CH(*C*H$_3$)$_2$), 23.9 (d, $^6J_{PC}$ = 2.0 Hz, CH(*C*H$_3$)$_2$). – ^{31}P NMR: δ = -250.3 (broad t, $^1J_{PH}$ = 200 Hz). – Anal. for $C_{26}H_{38}BN_2P$ (420.38 g mol^{-1}): calcd. C 74.29, H 9.11, N 6.66%; found C 73.86, H 9.31, N 6.63%

Reactions of 6 with Mes*PCl_2 and PH_2Cl and 4d:

The preparation of **6** and reaction with the appropriate chlorophosphines was carried out by analogy to the syntheses of **4b,c**. The resulting mixtures were analysed by ^{31}P and ^{11}B NMR spectroscopy. Applying the same work-up procedure produced crystalline borane **5-H** (in the reaction with **4d**) and diphosphene **9** (in the reaction with Mes*PCl_2) as only isolable products.

Metalation of 4e:

n-Butyl lithium (250 µL of a 1.6 M solution in hexane, 0.40 mmol) was slowly added to a solution of **4e** (200 mg, 0.40 mmol) in THF (10 mL). The resulting yellow solution was stirred for 30 min. Solvents and volatiles were removed under reduced pressure, and the residue taken up in hexane (20 mL). The resulting suspension was filtered through celite. The crude product was isolated by removal of the solvent under reduced pressure and characterised by ^{31}P and ^{11}B NMR spectroscopy. Recrystallisation from hexane produced a small crop of crystalline material which was further identified by a single-crystal X-ray diffraction study. – ^{11}B NMR: δ = 32.4 (broad s). – ^{31}P NMR: δ = -116.1 (broad s).

X-ray diffraction studies

Crystals of **4a-c**, **4e**, and **4f** suitable for X-ray diffraction analysis were obtained by recrystallization of purified products from hexane. Diffraction data were collected at 100 K (**4a-c**, **4e**), or 110 K (**4f**) using a Bruker Kappa APEXII Duo diffractometer with Mo-K_α radiation (λ = 0.71073 Å). A combination of ω and Φ scans was carried out to obtain at least

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a unique data set. The crystal structures were solved by direct methods (SHELXS-97 [22]), and refined with a full-matrix least-squares scheme on F^2 (SHELXL-97 [22]). Non-hydrogen atoms were refined anisotropically and H atoms (except those on phosphorus in **4e,f**) with a riding model. The positions of the hydrogen atoms at phosphorus in **4e,f** were localised by electron density determination and refined freely using isotropic thermal displacement parameters. One isopropyl group in **4e** is disordered. Details of the crystal structure are listed in Table 3 and in the ESI.

Table 3 Summary of crystallographic data for **4a-c**, **4e**, **4f**

	4a	**4b**	**4c**	**4e**	**4f**
Formula	$C_{30}H_{48}BN_4P$	$C_{36}H_{56}BN_4P$	$C_{44}H_{56}BN_4P$	$C_{32}H_{42}BN_2P$	$C_{26}H_{38}BN_2P$
CCDC	957947	957948	957949	957950	957951
Mol. Wt.	506.50	586.63	682.71	496.46	420.36
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a/Å	17.9692(13)	11.7029(8)	12.4257(4)	12.0947(13)	7.5063(5)
b/Å	10.7572(9)	12.3599(8)	12.4802(5)	13.6131(12)	9.4119(6)
c/Å	17.2353(14)	24.3641(18)	13.2635(5)	17.9876/14)	18.3880(14)
α/°	90	90	97.682(2)	90	77.441(3)
β/°	114.004(2)	96.785(3)	98.396(2)	90	86.774(4)
γ/°	90	90	103.761(2)	90	78.004(3)
V/Å^3	3043.4(4)	3499.5(4)	1945.80(12)	2961.6(5)	1240.23(15)
Z	4	4	2	4	2
Calcd. density (g cm^{-3})	1.105	1.113	1.165	1.113	1.126
Abs. coeff. (mm^{-1})	0.114	0.108	0.106	0.115	0.126
F(000)	1104	1280	736	1072	456
Crystal size (mm)	0.65 x 0.52 x 0.44	0.26 x 0.18 x 0.18	0.60 x 0.41 x 0.21	0.27 x 0.13 x 0.10	0.47 x 0.27 x 0.22
θ range (°)	2.97 to 30.51	1.67 to 26.47	1.58 to 25.35	1.88 to 25.35	2.26 to 27.47
R(int)	0.046	0.053	0.037	0.060	0.039
Reflections measured	34117	48124	31455	20575	23221
Reflections unique [$I > 2\sigma(I)$]	9269	7217	7097	5423	5671
Completeness to θ	0.997	0.996	0.998	1.00	0.999
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.7128	0.6370 to 0.7454	0.7457 and 0.7223	0.7451 and 0.7129	0.7461 and 0.7086
Data/restraints/parameters	9269 / 0 / 325	7217 / 0 / 393	7097 / 0 / 455	5423 / 13 / 327	5671 / 0 / 277
Goodness of fit on F^2	1.004	1.055	1.033	1.012	1.036
R_1 ($I > 2\sigma(I)$)	0.046	0.0528	0.0389	0.0462	0.0503
$wR(F^2)$ (all data)	0.120	0.1498	0.0979	0.0910	0.1245
Largest diff. (e Å^{-3})	0.402 and -0.291	0.695 and -0.485	0.316 and -0.369	0.237 and -0.222	1.025 and -0.901
Flack parameter	-	-	-	0.06(11)	-

Computational studies

DFT calculations were carried out with the Gaussian 09 [23] package using the ωB97X-D functional by Head-Gordon [16] in combination with a cc-pVDZ basis set as obtained from the basis set exchange homepage.[24] Numerical integrations were performed on an ultrafine grid. Energy optimisation of molecular geometries was carried out in C_1 symmetry. Harmonic frequencies and zero-point energies (ZPE) at optimized structures were calculated at the same level and showed all molecular geometries to present local minima (only positive eigenvalues of the Hessian matrix) on the potential energy surface. MOLDEN [25] was used for visualization. Listings of computed energies and molecular coordinates are given in the Supporting Information.

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Notes and references

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† Dedicated to Professor Dr. Werner Uhl on the occasion of his 60th birthday.

Electronic Supplementary Information (ESI) available: crystallographic data of **4a-c,e,f** (cif-files, CCDC-957947 to 957951), plots of ^{31}P and ^{11}B NMR spectra of **4a-f**, graphical representation of the molecular structure of crystalline **11**, graphical representations, atomic coordinates, and energies of computed molecular structures of **4b** and **4'**. See DOI: 10.1039/b000000x/

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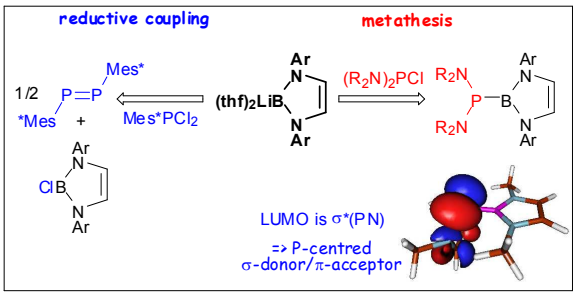

Metathesis of *N*-heterocyclic lithioboranes and diaminochlorophosphines yields previously unavailable tetraamino-phosphinoboranes predicted to feature phosphorus rather than boron centred electrophilicity.