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The Reaction between Diazadienes and Element Tribromides EBr_3 (E = P, B) Revisited: Metal-Free Synthesis of Halogenated N-Heterocyclic Phosphanes and Boranes

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Reactions of selected diazadienes with PBr_3 and BBr_3 in the presence of a tertiary amine yielding N-heterocyclic phosphanes (NHPs) and N-heterocyclic boranes (NHBs) were studied. It is demonstrated that heterocycle formation occurs even without an amine or another auxiliary reagent, and the amine acts mainly as scavenger of Br_2 formed as by-product, but also that the additive speeds up reactions and has an influence on the product selectivity. In extension of the results of earlier studies it is shown that the reactions can follow two different pathways to give either 2-bromo- or 2,4-dibromo-substituted heterocycles. Computational studies enabled to propose a reaction mechanism, which relates the observed behaviour to the availability of two competing reaction channels and provides also a rational explanation for the different behaviour of ECl_3, EBr_3, and EI_3 (E = B, P) in cycloaddition reactions with diazadienes, which is empirically well established. In the borane series, a tribromo-NHB is formed in a follow-up reaction between the initial products and Br_2, which seems to be the first example of an electrophilic backbone functionalization in an NHB. The 2-bromo derivative is formed exclusively when PPh_3 is used as auxiliary reagent. Selected products are isolated and fully characterised, proving the synthetic utility of the reactions studied.

Introduction

The ground-breaking discovery of stable N-heterocyclic carbenes **Ia**[1] (Scheme 1) kicked off a still ongoing boom of carbene chemistry with applications in synthesis, coordination chemistry, or catalysis.[2] In its wake, this upsurge raised (or, in some cases, revived) interest in inorganic carbene analogues, which are derived from the prototype by formal isoelectronic replacement of the divalent carbon atom by neutral or charged elements of groups 13–16 (**Ib**–**l**).[3] Many of these species are accessed by reductive or Lewis-acid-induced cleavage of halides from halogen-substituted derivatives **IIb**–**j**.[4] Apart from serving as precursors of carbene analogues, such compounds have been employed to access heterocycles with functional substituents at the main-group element by halide displacement. Some of these species exhibit unique chemical properties; for instance, boron heterocycles (**IIe**) with *B*-stannyl or -stannylenyl substituents[5] and phosphorus heterocycles (**IIh**) with *P*-phosphanyl groups[6] add selectively and easily to organic multiple-bond systems, and *P*-hydrogen-substituted phosphorus heterocycles behave as hydride transfer agents under stoichiometric[7] and catalytic[8] conditions. That even halogen-substituted heterocycles display peculiar reactivity is exemplified by a *P*-chloro derivative of type **IIh**, which acts as electrophilic organocatalyst in a PC cross coupling reaction.[9]

Ia (E= C) **Ie** (E = B^-) **Ii** (E = As^+) **IIe** (E = B) **IIi** (E = As)
Ib (E = Si) **If** (E = Ga^-) **Ij** (E = Sb^+) **IIb** (E = SiX) **IIj** (E = Sb)
Ic (E = Ge) **Ig** (E = N^+) **Ik** (E = S^{2+})
Id (E = Sn) **Ih** (E = P^+) **Il** (E = Se^{2+}) **IIh** (E = P)

Scheme 1. Structures of N-heterocyclic carbenes and their analogues (**Ia**–**k**) and halogenated precursors **IIb**–**j**. (R = alkyl, aryl; X = halogen).

Synthetically, **IIb**–**j** are usually accessed by starting from 1,4-diazadienes (diimines). The most widely used protocol is a two-step reaction involving first treatment of the diazadiene with a metal-based reducing reagent to produce the corresponding dianion, and subsequent metathetic ring closure (either directly or after quenching with an acid) with a suitable electrophile to give the target hetero-

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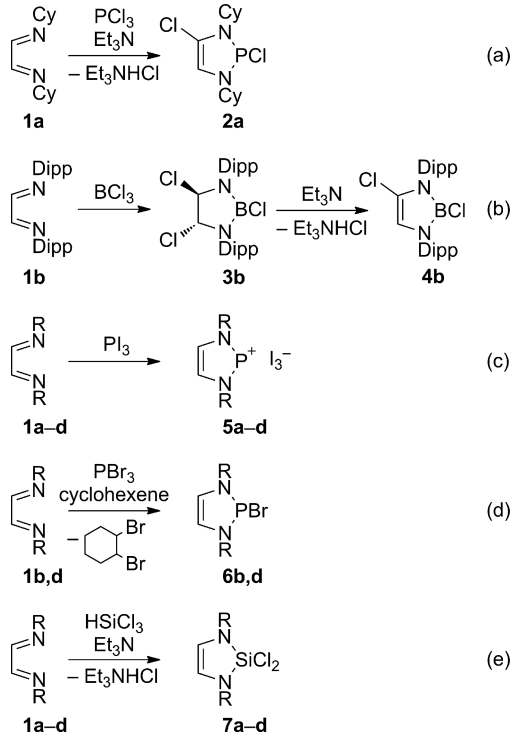
cycle.[4a,4b,4d,4e,7b,10] In special cases, the order of both steps may be reversed.[4b,10]

Alternatively, the conversion can also be achieved in a single step without a metal-based reductant. An early example is the reaction of *N*,*N*′-dialkyldiazadiene **1a** with PCl_3 in the presence of a tertiary amine to afford the 2,4-dichloro-substituted N-heterocyclic phosphane **2a** [Scheme 2 (a)].[11] Even if no intermediates were observed, the reaction was explained through double addition of P–Cl bonds across the diimine double bonds followed by dehydrohalogenation. This pathway was positively established for the reaction of diazadiene **1b** with BCl_3. The initial addition product **3b** was in this case isolated and structurally characterized, and decayed in polar solvents under spontaneous cleavage of HCl to give **4b** [Scheme 2 (b)].[12]



Scheme 2. One-step syntheses of N-heterocyclic halogeno-element compounds from diazadienes and element halides. R = Cy (**1a**, **5a**–**7a**), 2,6-*i*$Pr_2C_6H_5$ (**1b**, **5b**–**7b**), *t*Bu (**1c**, **5c**, **7c**), Mes (**1d**, **5d**–**7d**).

In contrast, a different outcome was observed for the reaction of the heavier phosphorus halides with diazadienes. Phosphorus triiodide reacted to give phosphenium triiodides **5** [Scheme 2 (c)].[13] Reaction of *N*-aryldiazadienes with PBr_3 alone was reported to be unselective, but clean conversion to N-heterocyclic phosphanes **6b**,**c** was noted in the presence of cyclohexene.[14] The heterocycles **5**, **6** lack a halogen substituent in 4-position, and product formation was explained by a formal cycloaddition of a monovalent "P–X" synthon with the diazadiene. Formation of ionic **5** involved further an I^- abstraction from the initial cycloadduct by I_2. In principle, these reactions resemble the synthesis of N-heterocyclic silanes **7** by action of a tertiary amine on a mixture of $HSiCl_3$/diazadiene,[15] which was assumed to proceed by a cycloaddition of a transient silylene to the diimine. Further parallels may be drawn to the assembly of an N-heterocyclic iodoborane from a diazadiene and BI_3.[10]

Altogether, these findings suggest that the "metal-free" syntheses of N-heterocyclic phosphanes and boranes can follow different pathways and may yield either mono- or dihalogenated products, respectively. A report on the simultaneous formation of both types of species[16] gives a hint that the reaction channels may not be mutually exclusive but competitive. Considering that metal-free, one-step protocols can offer a synthetically valuable approach to N-heterocyclic element halides, further elucidation of this matter is needed in order to exploit the full potential of this methodology. We have therefore re-examined the reactivity of phosphorus and boron trihalides towards selected diazadienes, aiming at a mechanistic analysis of this transformation, which allows us to understand the origin and implications of the two-sided reactivity. Apart from clarifying the academically interesting question whether the cycloadditions may possibly involve any subvalent E–X species, we reckoned that the results may provide valuable guidelines for the development of selective access routes to particular target compounds. The experimental studies focused on the element tribromides since we anticipated that these offer the best chance to observe two-sided reactivity.

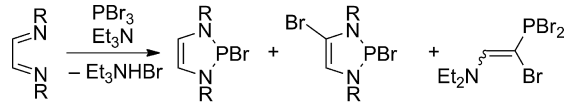
Results and Discussion

Reactions of Phosphorus Tribromide with Diazadienes

Previous reports on reactions of PBr_3 with diazadienes mention only 2-bromo-substituted N-heterocyclic phosphanes (NHPs) as products.[14,17] Considering that a possible generation of 2,4-dibromo-substituted species from these starting materials is accompanied by the formation of HBr, we studied reactions of the diazadienes **1a**–**c** and PBr_3 in the presence of triethylamine as acid scavenger in order to bring any two-sided reactivity to the fore. The individual reactions were carried out by adding PBr_3 to a solution containing the diazadiene and the amine, and the phosphorus-containing products were analysed by ^{31}P NMR spectroscopy. The NHPs formed were identified by comparison of the observed spectroscopic data with those of authentic samples.

Analysis of the NMR spectra revealed that in the reactions with **1a**,**b** complete consumption of PBr_3 was achieved at ambient temperature within 1 h, whereas the reaction with **1c** was slower and required approx. 18 h. All three reactions gave a mixture of two phosphorus-containing species (see Scheme 3). The major components were identified in all cases as the 2-bromo-NHPs **6a**–**c** (**6a**,**b** 75%; **6c** 67% by evaluation of ^{31}P NMR signal intensities). The by-product in the reactions of **1b**,**c** – although it could not be isolated and fully characterized – was on the basis of an analysis of NMR spectra of the reaction mixture tentatively assigned as phosphanyl-enamine **9**.[18] Optimizing the conditions for the reaction of **1b** allowed to reduce the amount

of this species and to isolate **6b** in 90% yield. The by-product of the reaction of **1a** with PBr_3 was identified as 2,4-dibromo-substituted NHP **8a**. Structural assignment obtained from NMR spectroscopic data was in this case confirmed by a single-crystal X-ray diffraction study of a mixed crystal containing both **6a** and **8a**, which was serendipitously isolated from the reaction mixture. The crystal contains molecular pairs (Figure 1) that are held together by a halogen bond connecting the Br1 atom of **6a** with the C-bound Br23 atom in **8a** [Br1–Br23 3.248(7) Å]. The structures of both molecular subunits are, as expected, closely similar to each other and those of **6b** (see Supporting Information), **6c**[19] and **6d**[14] (R = Mes). The most prominent differences lie in the pronounced deviation in P–Br distances – the bond length in **6a** [P1–Br1 2.907(1) Å] comes close to the extreme value observed for **6c** [2.947(1) Å[19]], whereas the bond in **8a** [2.764(1) Å] is significantly shorter but still exceeds the length in **6b** [2.591(1) Å] and **6d** [2.618(1) Å[14]], respectively. A similar trend had been previously observed in chloro-substituted NHPs[20] and is mainly attributable to fine-tuning of the n(N)–σ*(P–X) hyperconjugation by the inductive effects associated with the electron-releasing *N*-alkyl and the electron-withdrawing 4-halogeno substituents.



1a–c	R	6a–c	8a–c	9
	Cy	75%	25%	–
	Dipp	75%	–	25%
	*t*Bu	67%	–	33%

Scheme 3. Reactions of diazadienes **1a**–**c** with PBr_3 in the presence of excess Et_3N at ambient temperature.

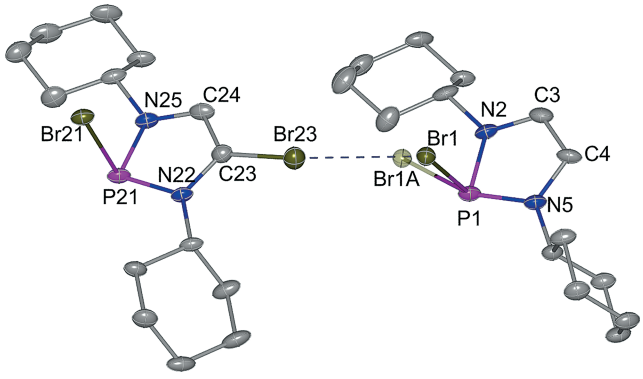


Figure 1. Representation of the molecular structures of **6a** and **8a** in the crystal. Thermal ellipsoids are drawn at 50% probability level, H atoms and solvent molecule are omitted for clarity. The Br1 atom is disordered over two positions with occupancies of 0.9 (Br1)/0.1 (Br1A). Selected bond lengths [Å]: **6a**: Br1–P1 2.9069(12), Br1A–P1 2.940(5), P1–N5 1.659(4), P1–N2 1.666(4), N2–C3 1.392(6), C3–C4 1.360(6), C4–N5 1.383(5); **8a**: Br21–P21 2.7640(12), P21–N25 1.664(4), P21–N22 1.671(4), N22–C23 1.382(6), Br23–C23 1.854(5), C23–C24 1.348(6), C24–N25 1.375(6); intermolecular: Br1–Br23 3.248(7).

Further experiments on the reaction of **1a** with PBr_3 revealed that the product ratio **6a/8a** depends crucially on the presence or absence of triethylamine and the reaction temperature, whereas the choice of solvent had no prominent influence. Thus, the amount of disubstitution product **8a** decreased substantially (to a ratio **6a/8a** > 95:5) when the reaction was performed as described by Macdonald et al.[14] at room temperature in the presence of cyclohexene, but without triethylamine. This finding indicates that the formation of **8a** is indeed promoted by the base. Interestingly, the presence of cyclohexene as Br_2 scavenger is in this case not mandatory, and even the two-component reaction between **1a** and PBr_3 in THF at 0 °C resulted in selective formation of **6a**, which was isolated in moderate yield after crystallization.[21] No spectroscopically detectable amounts of **8a** were observed when the reaction was conducted in the presence of triethylamine at 0 °C, but **8a** became the major product when the reaction was carried out at 70 °C. Under these conditions, also a small amount of **9** (ca. 5% of phosphorus-containing products) was produced.

The formation of the elusive enamine **9**, which was under certain conditions observable in the reactions of all diazadienes studied, can be explained as arising from a reaction of PBr_3, Et_3N, and Br_2. The latter react, as was shown by Belucci et al.,[22] to yield iminium salts $[Et_2N^{(+)}{=}CHCH_nBr_{3-n}]Br$ (n = 0–3). Attempts to detect these species in the reaction mixtures were unsuccessful, and we assume that they are quenched by the reaction with PBr_3 to give **9**. The amount of this by-product increased when PBr_3 was rapidly injected into a mixture of **1a**. Even if a final proof for the constitution of **9** and a mechanistic explanation of its formation are still pending, its occurrence indicates that triethylamine acts in this reaction, like cyclohexene, in the first place as Br_2 scavenger.

The main conclusions to be drawn from these experiments are: (a) auxiliary reagents (triethylamine, cyclohexene) are not mandatory for the formation of NHPs from diazadienes and PBr_3 but can suppress unwanted follow-up reactions of starting materials or products with Br_2 formed as by-product; (b) whereas diazadienes react with PCl_3 and PI_3 to give only 2,4-dihalo- *or* 2-halo-NHPs, respectively, the reaction with PBr_3 may yield both mono- *and* dihalogenated products; (c) the product ratio varies with the molecular structures of the reactants and the reaction conditions, but the use of base as auxiliary reagent favours the formation of mixtures of mono- and dihalogenated products;[23] (d) using triethylamine can still be advantageous for diazadienes with low preference for the formation of dihalogenated products (like **1b**) as it allows to speed up the reactions.

In order to cast further light on the mechanistic aspects of the dual-sided reactivity to mono- and dihalogenated NHPs, we set out to perform a computational study of the reaction of PX_3 (X = Cl, Br) with the *N*-methylated model diazadiene **1e**. Density functional calculations were carried out at the b3lyp/def2-tzvp level with inclusion of solvent effects by using a polarizable continuum model. For the sake of simplicity, the diazadiene was assumed to adopt the

cisoid conformation needed for the heterocycle formation. The minimum free energy reaction pathway connecting **1e** with **6e** is represented in Figure 2a; further data (including calculated energies and molecular geometries) are given in the Supporting Information.

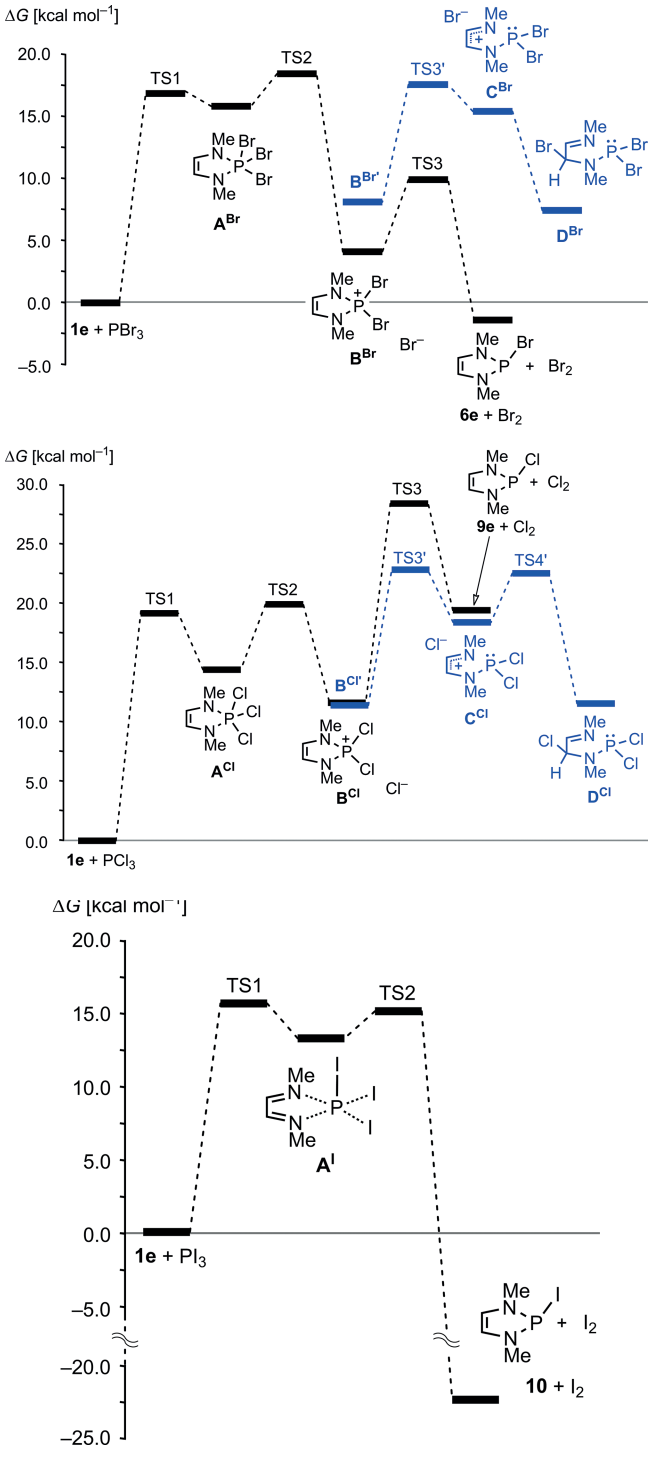


Figure 2. Calculated minimum free energy pathways for the reactions of diazadiene **1e** with (a) PBr_3 (top), (b) PCl_3 (middle), and (c) PI_3 (bottom) at the b3lyp/def2-tzvp level. Solvent effects were modelled by using a PCM approach. $\mathbf{B^X}$ and $\mathbf{B^{X'}}$ (X = Br, Cl) denote contact ion pairs with different ion arrangement.

The reaction is initiated by formation of a van der Waals complex (not shown in Figure 2a) which is a local minimum on the energy hypersurface and preorganized for a [4+1]-cycloaddition step to give phosphorane $\mathbf{A^{Br}}$. The geometry of transition state TS1 suggests describing this step as concerted. The computations predict for $\mathbf{A^{Br}}$ an unusual square-pyramidal coordination geometry at the phosphorus atom with short apical and long basal P–Br bonds (2.230 vs. 2.595 Å). However, a trigonal-bipyramidal conformer representing the transition state to Berry pseudorotation is only by 1.5 kcal mol^{-1} higher in energy, and the molecule is thus best addressed as fluxional. Phosphorane $\mathbf{A^{Br}}$ can readily ionize under P–Br bond heterolysis. We found that the resulting contact ion pair may exist in (at least) two energetically different (ΔG = 5.0 kcal mol^{-1}) configurations $\mathbf{B^{Br}}$ and $\mathbf{B^{Br'}}$, which differ in the spatial orientation of cation and anion relative to each other. Both configurations are local minima on the energy hypersurface and can presumably easily interconvert by ion diffusion.

Formation of **6e** is completed by nucleophilic attack of Br^- on a *P*-bound bromine atom in one of the ion pair configurations ($\mathbf{B^{Br}}$). The search for a transition state for this step yielded only a higher-order stationary point with three imaginary vibrational modes. However, both ionic constituents are at this point confined in separate solvent cages, and a relaxed potential energy scan indicated the absence of a transition state at a later reaction stage. We assume therefore that the activation barrier for this step is intimately connected with solvent reorganization around the reactants, which cannot be satisfactorily modelled in the PCM approach, and that the energy and location on the reaction coordinate of the real transition state (TS3) are close to the stationary point found. In total, formation of **6e** and Br_2 from **1e** and PBr_3 is calculated to be slightly exergonic (ΔG = –1.3 kcal mol^{-1}), and the initial conversion of **1e** to $\mathbf{A^{Br}}$ is the rate-determining step with $\Delta G^{\neq}$ = 16.8 kcal mol^{-1}.

Assuming initially that the 2,4-dibromo-NHP **8e** is formed by addition of a P–Br bond to a C–N double bond, we also tried to locate a transition state for this process. However, all such attempts converged to the already known transition state TS1, and we conclude that a reaction involving direct addition of PBr_3 to an imine double bond of **1e** is unlikely. Looking for an alternative pathway to a *C*-halogenated product, we found that the contact ion pair $\mathbf{B^{Br'}}$ can isomerize to a ring-opened product $\mathbf{C^{Br}}$. This species can then react under ion recombination and C–Br bond formation to the formal imine addition product $\mathbf{D^{Br}}$. Further conversion to a dibromo-NHP **8e** may proceed by tautomerization to an ene-diamine MeN(H)–CH=C(Br)–N(Me)PBr_2 ($\mathbf{E^{Br}}$) and ring closure by base-induced dehydrohalogenation, and was not analysed further.[24] Formation of $\mathbf{D^{Br}}$ (ΔG = 7.6 kcal mol^{-1}) and $\mathbf{E^{Br}}$ (ΔG = 10.7 kcal mol^{-1}) is endergonic and thermodynamically and kinetically less favourable than that of **6e**. This result is qualitatively in accord with the experimental finding that formation of **6a** is generally preferred over that of **8a**. However, it must be considered that $\mathbf{D^{Br}}$ and $\mathbf{E^{Br}}$ are not the

final products, and base trapping of the HBr formed in the final ring closure step to yield **8e** may shift the reaction further to this side. Consequently, the relative free energies calculated for the formation of **6e** and $\mathbf{D^{Br}/E^{Br}}$ do not necessarily provide a quantitative measure of the expected product ratio.

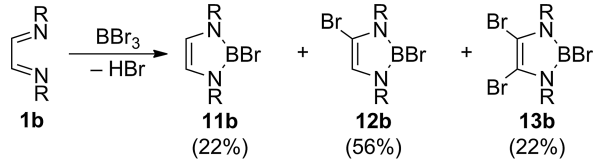
Qualitatively similar reaction pathways to produce either a chloro-substituted heterocycle **9e** or a formal addition product $\mathbf{D^{Cl}}$ were also identified in the computational analysis of the reaction of **1e** with PCl_3 (Figure 2b). Contrary to the reaction with PBr_3, the phosphorane intermediate $\mathbf{B^{Cl}}$ displays the expected trigonal-bipyramidal geometry (with a calculated activation barrier to pseudorotation of $\Delta G^{\neq}$ = 1.7 kcal mol^{-1}). More importantly, formation of monochloro-NHP **9e** is even more endergonic (ΔG = + 19.4 kcal mol^{-1} vs. **1e** + PCl_3) than that of the formal addition product $\mathbf{D^{Cl}}$ (ΔG = +11.4 kcal mol^{-1}), which is also reached by a lower activation barrier. The endergonic nature of the transformation **1e** + PCl_3 → $\mathbf{D^{Cl}}$ + HCl implies that trapping of hydrogen chloride by a base is again indispensable as driving force for the product formation.

For comparison, we also studied the reaction of **1e** with PI_3. Again, the first step produces a pentacoordinate intermediate $\mathbf{A^{I}}$ with square-planar geometry at the phosphorus atom. However, this species is different as it represents, according to an NBO analysis, no phosphorane but rather a charge-transfer complex of the diazadiene with PI_3. Furthermore, its decay does not lead to a dihalophosphonium salt but results essentially in the loss of I_2 to furnish directly the N-heterocyclic phosphane **10** (Figure 2c). A formal imine addition product ($\mathbf{D^{I}}$) was also identified as a local minimum on the energy hypersurface, but was in view of its prohibitively high energy (the calculated ΔG is 24.3 kcal mol^{-1} above that of $\mathbf{G^{I}}$) not further considered as alternative reaction product. The calculations indicate that I^- abstraction from **10** by I_2 to the experimentally observed phosphenium triiodide [Scheme 2 (c)][13] is also slightly exergonic.

In total, the computational studies suggest that the reactions of PBr_3 and PCl_3 with diazadienes can follow two competing reaction channels, which may both be classified as oxidative addition/reductive elimination sequences. The oxidative addition proceeds as concerted [4+1]-cycloaddition of the diazadiene to PX_3 to give a phosphorane. The reductive elimination occurs in two steps, the first of which – ionization of the phosphorane by heterolytic P–X bond fission – is common to both reaction channels. Monosubstituted NHPs are then formed by nucleophilic substitution (S_N) at a covalently bound X atom. Alternatively, the ion pair can rearrange to a formal imine addition product, which may undergo further transformations to yield a dihalogenated NHP. The different product selectivity in reactions of PBr_3 and PCl_3 is due to the fact that in each case a different reaction channel (leading to **6e** or $\mathbf{D^{Cl}}$/**8e**, respectively) is thermodynamically and kinetically favoured. In simple terms, the failure to observe monosubstituted NHPs in reactions of PCl_3 with diazadienes is attributable to the fact that formation of Cl_2 as oxidative by-product is thermodynamically unfavourable unless an external reducing agent is applied. The predicted preference of the PBr_3 reaction for the monobromo-NHP and its exergonic nature are qualitatively in accord with the experimental findings. The calculations gave no evidence for the participation of subvalent P–X species.

Reactions of Boron Tribromide with Diazadienes

Studies of syntheses of N-heterocyclic boranes (NHBs) focused on derivatives bearing sterically demanding *N*-(2,6-diisopropylphenyl) (Dipp) substituents. Reaction of BBr_3 with **1b** proceeded smoothly at room temperature to furnish a mixture of three products, which were later identified as mono- to tribromo-NHBs **11b**–**13b** (Scheme 4).



NR_3	11b	12b
NEt_3	16%	84%
$N(Et)iPr_2$	94%	6%

Scheme 4. Reactions of diazadiene **1b** (R = Dipp) with BBr_3 or BBr_3–NR_3 adducts [NR_3 = NEt_3, $N(Et)iPr_2$] at ambient temperature.

As with PBr_3, selectivity increased upon addition of a tertiary amine. Reaction of **1b** with BBr_3 in the presence of 1 equiv. of triethylamine (as an alternative to adding the amine to the reaction, also the preformed BBr_3–amine adduct could be used) gave a mixture containing only **11b** and **12b** (16:84 ratio according to ^{1}H NMR analysis of the crude reaction product) and amine hydrobromide. Interestingly, **11b** became the main product (ratio **11b**/**12b** = 94:6) when the reaction was carried out with Hünig's base. We explain the different product ratio by the fact that this bulky amine cannot form a stable Lewis pair with BBr_3 and is thus more active in quenching Br_2 and suppressing the formation of **12b**. The major products of both reactions were isolated in moderate yields (limited by losses during crystallisation) and fully characterized.

Monitoring the progress of a reaction of **1b** with BBr_3 and triethylamine in [D_8]THF by ^{1}H NMR spectroscopy revealed that the product ratio remained constant throughout the reaction. This finding makes it unlikely that **11b** is formed as initial product and undergoes a follow-up reaction to **12b**. Rather, both species are presumably formed through competing reaction channels, and the mechanistic scenario is thus similar as in reactions of PBr_3 with **1a**–**c**.

In contrast, the tribromo-NHB **13b** (which is only formed in the absence of amines) arises possibly from subsequent bromination of **11b** or **12b**. In order to verify this hypothesis, we treated **11b** with 1 and 2 equiv. of Br_2 in the presence of Hünig's base. NMR spectroscopic analysis of the products disclosed that in the first case a mixture of **11b**–**13b** (with **12b** as main product) had formed, and in the second case near quantitative (> 95%) conversion to **13b** had taken place. In both cases, the tertiary ammonium bromide formed as by-product. Tribromide **13b** was isolated in satisfactory yield after workup and was fully characterized. The molecular structures of **12b** and **13b** (Figure 3) exhibit planar five-membered rings as expected. The endocyclic bond lengths differ not significantly from each other or from those in **11b**,[25] indicating that the Br substitution has no visible structural impact on the heterocycle. The B–Br bond lengths [**12b**: 1.911(3) Å; **13b**: 1.915(3) Å] are similar as in **11b** [1.898(7) Å[25]], and the C–Br bonds are normal.

Computational studies of the reaction of diazadiene **1e** with BBr_3 support the idea that mono- and dibromo-NHBs are, in a similar manner as with PBr_3, formed through competing reaction channels (Figure 4).

The reaction starts with the formation of a contact ion pair $\mathbf{F^{Br}}$ consisting of a doubly donor-stabilized heterocyclic dibromoborenium cation and a bromide anion. This intermediate can further rearrange via a transition state TS2′ under migration of a bromine atom from the boron atom to the carbon atom and formation of two Br–C bonds to give the addition product $\mathbf{G^{Br}}$, which can then loose HBr to yield the final product **12e** in a slightly exergonic step.[27] Alternatively, attack of Br^- on a *B*-bound Br atom can produce Br_2 and monobromo-NHB **11e** via transition state TS2. The latter transformation starts from an alternative configuration $\mathbf{F^{Br'}}$ of the ion pair, which exhibits a larger ion separation and is therefore higher in energy ($\Delta\Delta G$ = 14.2 kcal mol^{-1}). Although an energy difference this size seems at first glance prohibitive, the transition states TS2 and TS2′ themselves are energetically much closer ($\Delta\Delta G$ = 5.3 kcal mol^{-1}), making competition between both pathways a viable option. This is even more so if one considers that in a real reaction an intermolecular process involving the anion of an adjacent ion pair may be feasible.

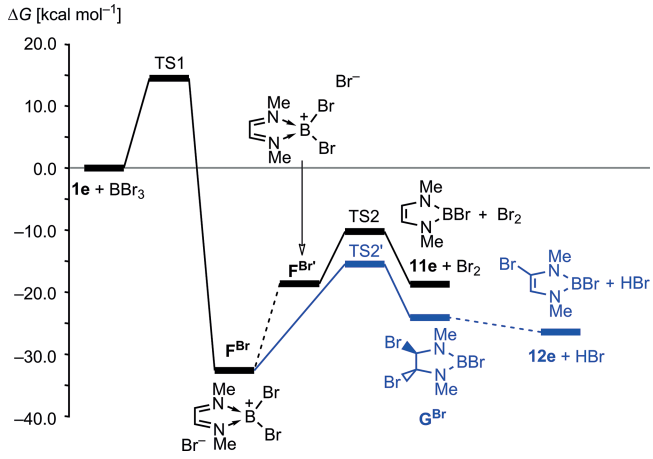


Figure 4. Calculated minimum free energy pathways for the reactions of diazadiene **1e** with BBr_3 at the b3lyp/def2-tzvp level. Solvent effects were included by using a PCM approach. $\mathbf{F^{Br}}$ and $\mathbf{F^{Br'}}$ denote contact ion pairs with different arrangement of ions.

Evaluation of the relative free energies of transition states (TS2′ and TS2) and products (**11e** + Br_2 and **12e** + HBr; $\Delta\Delta G$ = 7.7 kcal mol^{-1}) indicates that formation of **12e** is kinetically and thermodynamically preferred, in line with the observed product distribution in the reaction of BBr_3 with **1b**. Quite interestingly, the final products are less stable than the donor-supported borenium salt $\mathbf{F^{Br}}$. This is in accord with the fact that creation of such cations from boron trihalides and diazadienes is well known,[4b,10,16,26] and several specimens have been isolated and structurally characterized.[16,28] While the transformation of such stable adducts into NHBs requires an external reductant,[4b,10] reaction of **1b** with BBr_3 proceeds directly to the three-coordinate boranes, and a donor-supported borenium salt can neither be spectroscopically observed nor isolated. This difference implies that the borenium salt is in this case destabilized, possibly by the influence of the bulky *N*-aryl groups.

Calculations on analogous chloroboranes were carried out for comparison and revealed a similar picture. A difference lies mainly in the fact that the free energy of **3e** + Cl_2 exceeds that of **4e** (the chloro analogue of $\mathbf{F^{Br}}$) by 28.4 kcal mol^{-1}. As in the case of the phosphane reactions,

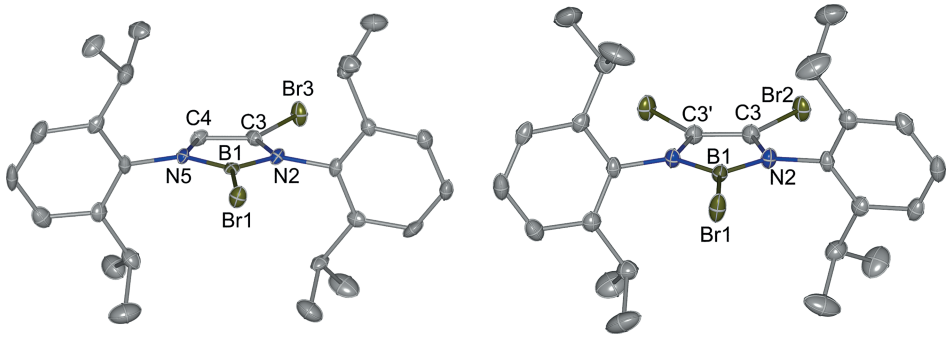
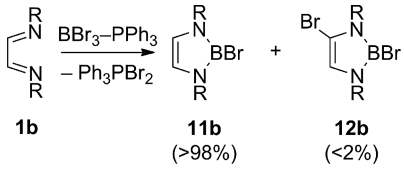


Figure 3. Representation of the molecular structures of **12b** (left) and **13b** (right; the molecule has crystallographic C_2 symmetry) in the crystal. Thermal ellipsoids are drawn at 50% probability level, H atoms and solvent molecule are omitted for clarity. Selected bond lengths [Å]: **12b**: Br1–B1 1.911(3), B1–N5 1.413(4), B1–N2 1.422(4), N2–C3 1.408(3), Br3–C3 1.872(3), C3–C4 1.332(4), C4–N5 1.410(3); **13b**: Br1–B1 1.915(3), B1–N2 1.421(2), Br2–C3 1.8591(17), N2–C3 1.406(2), N2–C4 1.437(2), C3–C3′ 1.351(3).

the thermodynamically unfavourable formation of Cl_2 as oxidative by-product puts the monochloro-NHB **3e** out of reach.

The marked dependence of the product ratio **11b/12b** on the added amine suggests that the base serves not simply as auxiliary reagent, which captures the by-product (HBr or Br_2), but may also be directly involved as nucleophile in the debromination of the dihaloborenium cation. We therefore thought it worthwhile to search for a reagent that drives the product distribution even further to the side of the monobromo heterocycle and – ideally – avoids formation of **12b** at all. Knowing that triphenylphosphane reacts very rapidly with Br_2, we treated **1b** with the BBr_3–PPh_3 complex. NMR analysis of the crude reaction product revealed a ratio of **11b/12b** of > 98:2, indicating that indeed near quantitative shift of the product ratio had been accomplished, and the product could be isolated in good yield after workup (Scheme 5).



Scheme 5. Reaction of diazadiene **1b** (R = Dipp) with BBr_3–PPh_3.

Initial studies on the reactions of other diazadienes than **1b** with BBr_3 and tertiary amines revealed that formation of mixtures of mono- and dibromo-NHBs is observed as well, and the reaction scheme is thus more general. However, we also noted the appearance of additional side products the structures of which have not yet been fully assigned. Obviously, further optimization is needed to turn this approach into a generally applicable preparative method.

Conclusions

A combined computational and experimental study allowed us to establish a mechanistic picture of the reactions of diazadienes with EX_3 (E = P, B; X = Cl, Br), which can be considered to foster the further development of selective syntheses of N-heterocyclic phosphanes and boranes. The computations suggest that the reactions may proceed by two competing pathways to yield N-heterocyclic compounds featuring either one or two halogeno substituents on the ring. The initial interaction between the diazadiene and EX_3 produces an ion pair containing a cyclic dihalogenophosphonium or -borenium cation as key intermediate. In reactions with phosphorus trihalides, this step represents an oxidative addition, which is closely related to the well-known McCormack reaction.[29] 2-Halogeno-substituted products can then be formed by nucleophilic attack of the halide anion on a covalently bound halogen atom in the cation and concomitant formation of elemental X_2. Alternatively, migration of a halogen from E (E = B, P) to a carbon atom may initiate the formation of 2,4-dihalogenated heterocycles. Our calculations suggest that the former reaction channel is inaccessible for energetic reasons in reactions of diazadienes with ECl_3 and provide thus an explanation for the qualitatively different reactivity of ECl_3 and EBr_3, which is empirically well known.

The experimental studies confirm that the reactions proceed in the absence of any auxiliary reagents, although the presence of a tertiary amine can improve the selectivity and facilitate the workup. The product distribution in reactions with EBr_3 depends strongly on the *N*-substituents, but can also be influenced by the choice of the auxiliary reagent. Even if this diversity implies that reaction conditions need to be optimized for each single target compound and thus impedes the development of a generally applicable synthetic protocol, it was shown that selected target compounds are accessible with comparable or even superior efficiency as compared to established synthetic approaches.

We have further established that tribromo-substituted N-heterocyclic boranes are accessible by bromination of mono- or dibrominated precursors. This reaction seems to be the first example of electrophilic backbone functionalization in an NHB.

Experimental Section

General Conditions: All manipulations were carried out under dry argon in a Schlenk apparatus or a glove box. Solvents were dried according to standard procedures. NMR spectra were recorded with Bruker Avance AV 400 or AV 250 instruments (^{1}H: 400.1/250.0 MHz; ^{13}C: 100.5/62.9 MHz; ^{11}B: 80.2 MHz; ^{31}P: 161.9/101.2 MHz). Chemical shifts were referenced to ext. TMS (^{1}H, ^{13}C), $BF_3{\cdot}(OEt_2)$ (^{11}B; Ξ = 32.083974 MHz), 85% H_3PO_4 (^{31}P; Ξ = 40.480747 MHz). Coupling constants are given as absolute values. Elemental analyses were carried out with an Elementar Micro Cube. Melting points were determined with a Büchi B-545 melting point apparatus in sealed capillaries. Diazabutadienes[30] and Ph_3P–BBr_3[31] were synthesized as described. Et_3N–BBr_3 was prepared in analogy to Et_3N–BCl_3.[32] Both BBr_3 adducts were synthesized under Schlenk conditions at 0 °C. Crude products were filtered off and washed with dry pentane.

Syntheses

Reactions of 1,4-Diazabutadienes with PBr_3: The appropriate 1,4-diazabutadiene (1.3 mmol), Et_3N (0.74 mL, 5.3 mmol), and (if appropriate) cyclohexene (0.9 mL, 9 mmol) were dissolved in CH_2Cl_2 (25 mL). PBr_3 (0.13 mL, 1.3 mmol) was added dropwise within 10 min under the conditions stated in the text. The mixture was stirred for 1 h and then analyzed by ^{31}P{^{1}H} NMR spectroscopy. The product distribution was determined by spectral deconvolution.

2-Bromo-1,3-dicyclohexyl-1,3,2-diazaphospholene (6a): PBr_3 (0.76 mL, 8.0 mmol) was added dropwise within 10 min to a cooled (0 °C) solution of diazabutadiene **1a** (2.00 g, 9.10 mmol) in THF (40 mL). The mixture was stirred at room temp. for 4 d. Crystallization at +7 °C produced colorless needles of **6a**, which were collected by filtration and dried in vacuo. Yield 1.20 g (3.6 mmol, 45%). ^{1}H NMR ($CDCl_3$): δ = 7.31 (s, 2 H, =CH), 4.00 (m, 2 H, NCH), 2.46–1.07 (m, 20 H, CH_2) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 120.9 (d, $^2J_{PC}$ = 8.9 Hz, =CH), 57.9 (d, $^2J_{PC}$ = 10.6 Hz, NCH),

33.3 (d, $^3J_{PC}$ = 9.3 Hz, $NCCH_2$), 25.3 (s, $NCCCH_2$), 25.2 (s, $NCCCCH_2$) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 193.5 ppm. $C_{14}H_{24}BrN_2P$ (331.23): calcd. C 50.77, H 7.30, N 8.46; found C 50.40, H 7.56, N 7.89.

2-Bromo-1,3-dicyclohexyl-1,3,2-diazaphospholene (6a) and 2,4-Dibromo-1,3-dicyclohexyl-1,3,2-diazaphospholene (8a): Diazabutadiene **1a** (500 mg, 2.30 mmol) and Et_3N (2.50 mL, 16.6 mmol) were dissolved in toluene (10 mL). PBr_3 (0.19 mL, 2.2 mmol) was added in one batch. The mixture was stirred for 10 min. Hexane (50 mL) was added, and precipitated solids were filtered off. Storage of the filtrate at +7 °C produced a small amount of colourless crystals. Characterization by ^1H and ^{31}P NMR spectroscopy and a single-crystal X-ray diffraction study allowed to identify the product as a 1:1 mixture of **6a/8a**. **8a:** ^1H NMR ($CDCl_3$): δ = 6.17 (s, 1 H, =CH), 3.60 (m, 1 H, NCH), 3.26 (m, 1 H, NCH), 2.46–1.07 (m, 20 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, data from ^1H,^{13}C HSQC and HMBC spectra; signals of the CH_2 carbon atoms in the cyclohexyl substituents could not be unambiguously assigned): δ = 119.5 (=CH), 105.8 (=CBr), 59.2 (NCH), 57.8 (NCH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 171.4 ppm.

2-Bromo-1,3-bis(2,2-diisopropylphenyl)-1,3,2-diazaphospholene (6b): Et_3N (3.55 mL, 25.6 mmol) was added to a solution of diazabutadiene **1b** (3.84 g, 10.2 mmol) in toluene (50 mL). Subsequently, PBr_3 (0.95 mL, 10.2 mmol) was added dropwise. The resulting yellow solution was stirred for 15 min until it became slightly cloudy. Addition of hexane (50 mL) induced formation of an off-white precipitate, which was removed by filtration. The filtrate was concentrated to dryness under reduced pressure. Recrystallization from toluene/hexane (1:1) or THF at –20 °C afforded a light yellow, crsystalline product (yield 4.46 g, 9.2 mmol, 90%) of m.p. 150 °C (dec.). ^1H NMR (C_6D_6): δ = 7.20–6.97 (m, 6 H, C_6H_3), 6.17 (2 H, NCH), 3.57 [sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH_3)$_2$], 1.31 [d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.08 [d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): 147.5 (d, $^2J_{PC}$ = 4.5 Hz, *i*-C_6H_3), 133.5 (d, $^3J_{PC}$ = 9.0 Hz, *o*-C_6H_3), 129.5 (d, $^5J_{PC}$ = 2.0 Hz, *p*-C_6H_3), 124.8 (s, *m*-C_6H_3), 122.5 (d, $^2J_{PC}$ = 8.5 Hz, =CH), 29.0 [d, $^4J_{PC}$ = 2.0 Hz, *C*H(CH_3)$_2$], 25.3 [s, CH(*C*H$_3$)$_2$], 24.6 [d, $^5J_{PC}$ = 2.0 Hz, CH(*C*H$_3$)$_2$] ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 161.4 (s) ppm. $C_{26}H_{36}N_2PBr{\cdot}C_4H_8O$ (559.56) calcd. C 64.39, H 7.93, N 5.01; found C 63.88, H 7.89, N 4.95.

Reaction of 1,4-Bis(2,6-diisopropylphenyl)-1,4-diazabutadiene with BBr_3: A solution of BBr_3 (0.25 mL, 2.65 mmol) in hexane (10 mL) was added dropwise to a solution of diazabutadiene **1b** (1.00 g, 2.65 mmol) in hexane (40 mL) at room temp. The yellow solution instantly turned red and, after the addition was complete, back to yellow. A colourless precipitate formed, which was filtered off. The filtrate was concentrated to dryness. Both the precipitate and the residue of the filtrate were dissolved in $CDCl_3$ and characterized by ^1H and ^{11}B NMR spectroscopy. As the spectra indicated the presence of a product mixture, no further analyses and determination of the yield were carried out.

2-Bromo-1,3-bis(2,2-diisopropylphenyl)-1,3,2-diazaborole (11b). (a) With Hünig's Base: A solution of BBr_3 (130 µL, 1.33 mmol) in hexane (5 mL) was added dropwise to a solution of ethyldiisopropylamine (230 µL, 1.33 mmol) in hexane (10 mL). The mixture was stirred at room temp. for 30 min during which a yellowish oil separated. Diazabutadiene **1b** (500 mg, 1.33 mmol) was added, and the mixture stirred at 50 °C for 48 h to give a dark brown solution. Solvents and volatiles were removed under reduced pressure. The solid was extracted with hexane (25 mL) and the resulting suspension filtered through Celite. The filtrate was concentrated under reduced pressure to a quarter of the original volume and stored at –20 °C. The crystalline precipitate was collected by filtration and recrystallized from hexane to give 115 mg (246 µmol, 18%) of a brownish crystalline solid. **(b) With PPh_3–BBr_3 (Small Scale):** A mixture of diazabutadiene **1b** (3.60 g, 9.56 mmol) and Ph_3P–BBr_3 (4.90 g, 9.56 mmol) in Et_2O (50 mL) was refluxed for 12 h to give an orange solution and a white precipitate. Solvents were removed under reduced pressure. The residue was dispersed in pentane (80 mL) and insoluble Ph_3PBr_2 removed by filtration through Celite. The filtrate was concentrated under reduced pressure to a quarter of the original volume and the residual solution stored at –20 °C to yield 3.20 g (6.84 mmol, 72%) of product in the form of pale orange crystals. **(c) With PPh_3–BBr_3 (Large Scale):** A mixture of diazabutadiene **1b** (35.0 g, 92.9 mmol) and Ph_3P–BBr_3 (38.4 g, 74.9 mmol) in Et_2O (600 mL) was refluxed for 48 h to give a red solution and a white precipitate. Solvents were removed under reduced pressure, and the residue was dissolved in pentane (600 mL). The insoluble Ph_3PBr_2 was removed by filtration and extracted with hexane (300 mL). The combined filtrates were concentrated under reduced pressure to a quarter of the original volume, and the remaining solution was stored at –20 °C to yield 30.6 g (65.5 mmol, 71%) of a yellow, microcrystalline powder. ^1H NMR ($CDCl_3$): δ = 7.30–7.09 (m, 6 H, ArH), 6.33 (s, 2 H, =CH), 2.98 [sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH_3)$_2$], 1.23 [d, $^3J_{HH}$ = 6.8 Hz, 24 H, CH(C*H*$_3$)$_2$] ppm. $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ = 20.3 (br.) ppm.

2,4-Dibromo-1,3,2-bis(2,6-diisopropylphenyl)-1,3-diazaborole (12b): A mixture of diazabutadiene **1b** (2.00 g, 5.31 mmol) and Et_3N–BBr_3 (1.87 g, 5.31 mmol) in pentane (20 mL) was stirred at room temp. for 12 h. Precipitated $NEt_3{\cdot}HCl$ was removed by filtration through Celite. The yellow filtrate was concentrated under reduced pressure to a quarter of the original volume and the remaining solution stored at –20 °C to give 0.95 g (1.74 mmol, 33%) of **12b** as colourless crystals of m.p. 120 °C (dec.). ^1H NMR (C_6D_6): δ = 7.27–7.07 (m, 6 H, C_6H_3), 6.20 (s, 1 H, =CH), 3.11 [sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH_3)$_2$], 3.09 [sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*(CH_3)$_2$], 1.32 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.30 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.29 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.14 [d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 146.8 (s, *i*-C_6H_3), 145.9 (s, *i*-C_6H_3), 136.4 (s, *o*-C_6H_3), 134.6 (s, *o*-C_6H_3), 128.9 (s, *p*-C_6H_3), 128.4 (s, *p*-C_6H_3), 123.61 (s, *m*-C_6H_3), 123.57 (s, *m*-C_6H_3), 119.4 (s, =*C*H), 103.5 (s, =*C*Br), 28.9 [s, *C*H(CH_3)$_2$], 28.6 [s, *C*H(CH_3)$_2$], 24.0 [s, CH(*C*H$_3$)$_2$], 23.9 [s, CH(*C*H$_3$)$_2$], 23.8 [s, CH(*C*H$_3$)$_2$], 23.4 [s, CH(*C*H$_3$)$_2$] ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 20.5 (br.) ppm. $C_{26}H_{35}BBr_2N_2$ (546.20): calcd. C 57.17, H 6.46, N 5.13; found C 57.42, H 6.49, N 5.16.

2,4,5-Tribromo-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaborole (13b): Br_2 (0.50 mL, 9.8 mmol) was added to a solution of **11b** (2.00 g, 4.28 mmol) in pentane (60 mL). The solution turned red, and a white precipitate formed. The mixture was then stirred for 24 h during which a clear red solution formed. Ethyldiisopropylamine (2.00 mL, 11.8 mmol) was added and the mixture stirred for further 30 min. The solution turned orange, and *i*$Pr_2EtN{\cdot}HBr$ precipitated as a colourless solid. Volatiles were removed under reduced pressure, and the residue was redissolved in pentane (60 mL). An insoluble fraction was removed by filtration through Celite. The filtrate was concentrated under reduced pressure to a quarter of the original volume and the remaining solution stored at –20 °C to give 1.74 g (2.78 mmol, 65%) of **13b** as colourless crystalline solid of m.p. 120 °C (dec.). Analytically pure crystals suitable for a single-crystal X-ray diffraction study were obtained by recrystallization from pentane. ^1H NMR (C_6D_6): δ = 7.24–7.09 (m, 6 H, C_6H_3), 3.05 [sept, $^3J_{HH}$ = 6.9 Hz, 4 H, C*H*(CH_3)$_2$], 1.30 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$], 1.24 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)

$_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 146.6 (s, *o*-C_6H_3), 134.8 (s, *ipso*-C_6H_3), 129.1 (s, *p*-C_6H_3), 123.7 (s, *m*-C_6H_3), 28.9 [s, *C*H(CH_3)$_2$], 24.0 [s, CH(*C*H$_3$)], 23.3 [s, CH(*C*H$_3$)$_2$] ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 20.5 (br.) ppm. $C_{26}H_{34}BBr_3N_2$ (625.09): calcd. C 49.96, H 5.48, N 4.48; found C 49.84, H 5.51, N 4.46.

Crystal-Structure Determinations: Diffraction studies were carried out with a Bruker diffractometer equipped with a Kappa APEX II Duo CCD detector and a KRYO-FLEX cooling device with Mo-K_α radiation (λ = 0.71073 Å) at T = 100 K (**6b**, **12b**–**13b**) or 110 K (**6a/8a**). The structures were solved by direct methods (SHELXS-97[33]) and refined with a full-matrix least-squares scheme on F^2 (SHELXL-2014 and SHELXL-97[33]). Semiempirical absorption corrections were applied for all structures. Non-hydrogen atoms were refined anisotropically, and H atoms with a riding model, on F^2. The Br1 atom in **6a/8a** was disordered over two positions (relative occupations Br1/Br1a = 90:10) and was refined isotropically. A high calculated residual electron density (2.10 e Å^{-3}) at a distance of approx. 1.72 Å from C3 is attributed to partial halogenation of the carbon atom (either by Cl or Br, approx. 5–6%). A solvent molecule in **6a/8a** and **13b** is disordered. CCDC-1059566 (**13b**), -1059567 (**12b**), 1059568 (**6a/8a**), 1059569 (**6b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. **6a and 8a:** Colourless crystals, $C_{15.75}H_{25.50}Br_{1.50}N_2P$, M = 393.71 g mol^{-1}, crystal size 0.35 × 0.27 × 0.13 mm, triclinic, space group $P\bar{1}$, a = 9.2158(6) Å, b = 12.4233(8) Å, c = 15.2820(11) Å, α = 82.943(4)°, β = 88.153(4)°, γ = 87.297(3)°, V = 1733.8(2) Å^3, Z = 4, ρ(calcd.) = 1.508 Mg m^3, F(000) = 806, θ_{max} = 28.49°, μ = 3.61 mm^{-1}, numerical absorption correction, max./min. transmission 0.8098/0.4748, 74382 reflections measured, 8655 unique reflections (R_{int} = 0.0499) for structure solution and refinement with 385 parameters and 50 restraints, $R1$ [$I > 2\sigma(I)$] = 0.0517, $wR2$ = 0.1300, GooF on F^2 1.060, largest diff. peak/hole 2.302/–1.766 e Å^{-3}. **6b:** Colourless crystals, $C_{26}H_{36}N_2PBr$, M = 487.45 g mol^{-1}, crystal size 0.45 × 0.19 × 0.16 mm, orthorhombic, space group $P2_12_12_1$, a = 8.2051(4) Å, b = 13.6053(8) Å, c = 22.8176(15) Å, V = 2547.2(3) A^3, Z = 4, ρ(calcd.) = 1.271 Mg m^{-3}, F(000) = 1024, θ_{max} = 28.28°, μ = 1.69 mm^{-1}, 22458 reflections measured, 6256 unique reflections (R_{int} = 0.0614) for structure solution and refinement with 271 parameters, numerical absorption correction, max./min. transmission 0.7889/0.5316, $R1$ [$I > 2\sigma(I)$] = 0.0384, $wR2$ = 0.0594, GooF on F^2 0.955, absolute structure parameter –0.003(6), largest diff. peak/hole 0.497/–0.315 e Å^{-3}. **12b:** Colourless crystals, $C_{26}H_{35}BBr_2N_2$, M = 546.19 g mol^{-1}, crystal size: 0.15 × 0.14 × 0.13 mm, monoclinic, space group $P2_1/c$, a = 8.5088(5) Å, b = 17.2086(11) Å, c = 17.9580(11) Å, β = 91.221(4)°, V = 2628.9(3) A^3, Z = 4, ρ(calcd.) = 1.380 Mg m^{-3}, F(000) = 1120, θ_{max} = 26.41°, μ = 3.10 mm^{-1}, semi-empirical absorption correction from equivalents, max./min. transmission 0.7350/0.6718, 39706 reflections measured, 5399 unique reflections (R_{int} = 0.0957) for structure solution and refinement with 280 parameters, $R1$ [$I > 2\sigma(I)$] = 0.038, $wR2$ = 0.064, GooF on F^2 1.001, largest diff. peak/hole 0.465/–0.426 e Å^{-3}. **13b:** Colourless crystals, $C_{26}H_{34}BBr_3N_2$/pentane, M = 697.24 g mol^{-1}, crystal size 0.47 × 0.26 × 0.25 mm, monoclinic, space group $C2/c$, a = 22.3719(19) Å, b = 9.5588(6) Å, c = 17.6750(15) Å, β = 117.195(6)°, V = 3361.9(5) A^3, Z = 4, ρ(calcd.) = 1.378 Mg m^3, F(000) = 1424, θ_{max} = 28.36°, μ = 3.62 mm^{-1}, numerical absorption correction, max./min. transmission 0.7028/0.4498, 33878 reflections measured, 4183 unique reflections (R_{int} = 0.0379) for structure solution and refinement with 166 parameters and 16 restraints, $R1$ [$I > 2\sigma(I)$] = 0. 0251, $wR2$ = 0.0617, GooF on F^2 1.048, largest diff. peak/hole 0.553/–0.473 e Å^{-3}.

Computational Studies: Computational studies were performed with the Gaussian 03[34] suite of programs by using def2-tzvp basis sets[35] (obtained from the basis set exchange home page[36,37]) on model compounds featuring *N*-Me instead of the larger *N*-alkyl or *N*-Dipp substituents. Solvent effects were included by using a PCM model as implemented in the Gaussian package (SCRF = CH_2Cl_2). Molecular structures were first energy-optimized without symmetry constraints. Calculations of harmonic vibrational frequencies were carried out in order to ensure that all stationary points located were local minima on the energy hypersurface. Computed (free) reaction energies were corrected for BSSE by using the counterpoise method where appropriate. The NBO analysis[38] was performed with the NBO 3.1 program as implemented in the Gaussian package. MOLDEN[39] was used for visualization.

Acknowledgments

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