From activation to stabilization

Different applications of a frustrated Lewis pair

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Chapter 3

New Insights in Frustrated Lewis Pair Chemistry with Azides

Abstract: The geminal FLP $t$Bu$_2$PCH$_2$BPh$_2$ (1) reacts with phenyl-, mesityl- and tert-butyl azide affording, respectively, a six, five, and four-membered ring as isolable product. DFT calculations revealed that the formation of all products proceeds via a six-membered ring structure, which is thermally stable with an N-phenyl group, but rearranges when MesN$_3$ and $t$BuN$_3$ are used. The reaction of 1 with TMS-N$_3$ is believed to follow the same course, yet subsequent N$_2$ elimination occurs to afford a four-membered heterocycle (5), which can be considered as a FLP–trimethylsilylnitrene adduct. Product 5 reacts with hydrochloric acid or tetramethylammonium fluoride and showed frustrated Lewis pair reactivity towards phenylisocyanate.

Manuscript: In preparation
3.1 Introduction

During the past few decades a vast amount of research has been conducted on small molecule activation utilizing solely main-group species as viable alternative to the well-established transition metal complexes. For example, cyclic alkyl amino carbenes (CAACs) can cleave strong covalent bonds, such as H–H, N–H, P–H, B–C and B–H bonds,\cite{1, 2, 3} and can capture CO and catecholborane.\cite{4, 5} As ubiquitous small molecule, organic azides are key building blocks in, e.g., the Staudinger reaction, which is the reaction of a phosphine with an azide to form a phosphazene after elimination of dinitrogen.\cite{6} Interestingly, the reaction between N-heterocyclic carbenes (NHCs) and azides offers the opportunity to trap reaction intermediates by an “interrupted Staudinger” reaction\cite{7, 8} forming the stabilized triazene moiety A (Figure 1)\cite{9, 10} that can be functionalized and gives access to highly colored materials (B), which may find new applications in nonlinear optics.\cite{11} Utilizing TMS-N3 as substrate leads to the facile elimination of dinitrogen and formation of nitrene adduct C that by subsequent cleavage of the TMS group affords interesting anionic imidazolin-2-iminato ligands, which can coordinate to almost any metal and be utilized in homogeneous catalysis.\cite{12}

![Figure 1. Examples of NHC adducts with azides (top) and FLP adducts with azides (bottom)](image-url)
Related is the reactivity of frustrated Lewis pairs (FLPs)\textsuperscript{[13]} towards organic azides, but in this case multiple Staudinger intermediates have been isolated. Phosphorus/boron-based FLPs have been shown to add to the α-nitrogen of the azide forming coordination mode D (Figure 1)\textsuperscript{[14]} and, in one case, it was found that upon irradiation this species rearranges to α,β-nitrogen adduct E.\textsuperscript{[15]} The unique α,γ-nitrogen coordination mode F was found by treating a geminal FLP with mesityl azide.\textsuperscript{[16,17]} In analogy to the reactivity of NHCs (C; Figure 1), also dinitrogen elimination occurs when TMS azide was reacted with a P/Al-based FLP affording nitrene adduct G,\textsuperscript{[18]} yet in this case no follow-up chemistry has been investigated.

Because of the diverse reactivity of frustrated Lewis pairs with organic azides, we were keen to unravel the mechanistic details of this chemistry as well as to elucidate if all three coordination modes (D, E, F) are interconnected on the potential energy surface. We discovered that by using the geminal phosphorus/boron-based FLP \textit{t}Bu\textsubscript{2}PCH\textsubscript{2}BPh\textsubscript{2} (1)\textsuperscript{[19]} and differently substituted azides all coordination modes can be obtained by formation of the corresponding four, five and six-membered heterocycles (Scheme 1). In addition, we were keen to investigate the reaction of 1 with Me\textsubscript{3}Si-N\textsubscript{3} and explored the reactivity of the resulting nitrene adduct 5.

\begin{center}
\textbf{Scheme 1.} Reactivity of FLP 1 with phenyl azide (2\textsubscript{Ph}), tert-butyl azide (3\textsubscript{tBu}) and mesityl azide (3\textsubscript{Mes}, 4\textsubscript{Mes}) and trimethylsilyl azide (5).
\end{center}
3.2 Results and Discussion

Treatment of FLP tBu2PCH2BPh2 (1) with 1 equivalent of Ph-N3 in THF at –10 °C and subsequent warming to room temperature resulted in the immediate conversion to 2Ph, which after workup was isolated as a yellow powder in 98% yield ($\delta^{31}P\{^1H\} = 31.8$ ppm; $\delta^{11}B\{^1H\} = –6.8$ ppm). The molecular structure of 2Ph, determined by a single-crystal X-ray diffraction analysis, established unequivocally the formation of a six-membered heterocycle (Figure 2) with characteristic P1–N1 (1.687(2) Å), B1–N3 (1.597(3) Å) and N2–N3 (1.323(3) Å) single bonds and a N1–N2 (1.290(3) Å) double bond. Interestingly, 2Ph displays much more localized N–N bonds compared to F (N1–N2 1.304(3) Å, N2–N3 1.306(3) Å; Figure 1), which might be the result of the reduced Lewis acidity of the borane in 2Ph. In order to verify if 2Ph is the result of an interrupted Staudinger reaction, we resorted to DFT calculations at the wB97X-D/6-31G* level of theory and found an alternative, viable reaction path. Instead of nucleophilic attack of the phosphine to the azide (TS3Ph $\Delta E^{\ddagger} = 9.6$ kcal/mol, $\Delta G^{\ddagger} = 16.6$ kcal/mol), which is the first step in the Staudinger reaction, nucleophilic attack of the azide to the boron moiety of the FLP is preferred, which leads to INT1Ph ($\Delta E = 5.2$, $\Delta E^{\ddagger} = 8.0$ kcal/mol) by formation of a boron–γ-nitrogen bond (Scheme 2). Note that this reaction path is well documented for the related transition metal chemistry, yet poorly described for main-group systems. Subsequent ring-closure of Lewis adduct via TS2Ph affords the product 2ph ($\Delta E = –32.1$, $\Delta E^{\ddagger} = 8.3$ kcal/mol).
Scheme 2. Energy and (Gibbs free energy) profile in kcal/mol for the formation of 2$_{ph}$ via the Staudinger reaction versus the formation of Lewis adduct INT1$_{ph}$ as intermediate.

Next, we treated FLP 1 with tBu-N$_3$ and Mes-N$_3$ and found that in these cases the reaction rate is significantly lower. After addition of 1 equiv of tBu-N$_3$ or Mes-N$_3$ to a solution of 1 in THF at 0 °C at least one hour stirring at room temperature was required for full conversion to product 3$_{tBu}$ or 3$_{Mes}$, respectively (3$_{tBu}$: $\delta^{31}P\{^1H\} = 98.1$ ppm; $\delta^{11}B\{^1H\} = 3.8$ ppm, 3$_{Mes}$: $\delta^{31}P\{^1H\} = 95.5$ ppm; $\delta^{11}B\{^1H\} = 2.8$ ppm; Scheme 1). The molecular structures of 3$_{tBu}$ and 3$_{Mes}$, determined by single-crystal X-ray diffraction analyses, revealed in both cases the formation of a four-membered heterocycle in which both the donor and acceptor site of FLP 1 are attached to the α-nitrogen of the corresponding azide. The azide fragment in 3$_{tBu}$ and 3$_{Mes}$ is attached to 1 with a cis conformation of the P and N3 moieties (3$_{tBu}$: P1–N1–N2–N3 1.66(19) Å, 3$_{Mes}$: P1–N1–N2–N3 0.000(1) Å; Figure 2). The N1–N2 bond lengths (3$_{tBu}$: 1.3573(16) Å, 3$_{Mes}$: 1.342(3) Å) are typical for a N–N single bond and the shorter N2–N3 distance (3$_{tBu}$: 1.2502(17) Å, 3$_{Mes}$: 1.259(3) Å) resembles a N= N double bond, which matches well with the related adducts D. Monitoring of the reaction of 1 with
tBu-N₃ and Mes-N₃ by variable temperature NMR spectroscopy revealed the presence of an intermediate during the reaction with comparable ³¹P{¹H} and ¹¹B{¹H} NMR signals as observed for 2ₚₜ (2ₚₜ: δ³¹P{¹H} = 27.0 ppm; δ¹¹B{¹H} = −7.0 ppm, 2ₚₚ: δ³¹P{¹H} = 40.5 ppm; δ¹¹B{¹H} = −6.7 ppm), suggesting that the six-membered heterocycle is an intermediate in the formation of 3ₜₕ and 3ₘₑₕ.

Figure 2. Molecular structures of 2ₚₚ, 3ₜₕ, 3ₘₑₕ and 4ₘₑₕ (ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°] for 2ₚₚ: P1–N1 1.687(2), N1–N2 1.290(3), N2–N3 1.323(3), N3–B1 1.597(3). 3ₜₕ: P1–N1 1.6675(12), N1–N2 1.357(3), N2–N3 1.2502(17), N3–B1 1.6066(19); P1–N1–N2–N3 1.66(19). 3ₘₑₕ: P1–N1 1.6838(19), N1–N2 1.342(3), N2–N3 1.259(3), N3–B1 1.613(3); P1–N1–N2–N3 0.000(1). 4ₘₑₕ: P1–N1 1.6592(13), N1–N2 1.3364(17), N2–N3 1.2733(17), N2–B1 1.668(2); P1–N1–N2–N3 −176.26(11).

DFT calculations indeed confirmed this hypotheses and we found that upon reacting 1 with tBu-N₃ and Mes-N₃ the six-membered intermediates 2ₜₕ and 2ₘₑₕ are easily accessible by B-N Lewis adduct formation (INT₁ₜₕ ΔE = 7.4, ΔE‡ = 8.4; INT₁ₘₑₕ ΔE = 7.4, ΔE‡ = 8.2), and subsequent ring closure (2ₜₕ ΔE = −25.9, ΔE‡ = 9.2; 2ₘₑₕ ΔE = 9.3, ΔE‡ = −23.6); this pathway is again preferred over the interrupted Staudinger reaction that is a 2.0–4.2 kcal/mol higher energy process (tBu-N₃ ΔE‡ = 13.4 kcal/mol, Mes-N₃ ΔE‡ = 11.3 kcal/mol). In the case of phenyl azide, the six-membered heterocycle 2ₚₚ is the kinetic and
thermodynamic product ($\Delta G_{6\text{-ring}} = -21.6$ vs. $\Delta G_{4\text{-ring}} = -19.7$ kcal/mol; see Figure 3), while with tert-butyl and mesityl substituents this heterocycle is only the kinetic product that can rearrange to the four-membered heterocycles $3_{\text{Bu}}$ and $3_{\text{Mes}}$. $\omega$B97X–D/6-31G* calculations showed that indeed the six-membered intermediate $2_{\text{Bu}}$ ($2_{\text{Bu}}$, Scheme 3) can ring open by breaking the B–γ-N bond to form a phosphazide ($\text{INT2}_{\text{Bu}}$, $\Delta E = 21.9$, $\Delta E^\ddagger = 22.5$) which is the first intermediate of a Staudinger reaction. Subsequent rotation around the P–N σ-bond perfectly aligns the α-nitrogen ($\text{INT3}_{\text{Bu}}$, $\Delta E = 21.6$) for a barrierless ring closing to the α,α-nitrogen coordinated four-membered heterocycle, which is the thermodynamic product. We also located a transition state for the direct formation of $\text{INT2}_{\text{Bu}}$ from 1 and tBu-N3 via the Staudinger reaction ($\Delta E^\ddagger = 13.4$ kcal/mol, $\Delta G^\ddagger = 19.7$ kcal/mol). Although this process is lower in energy than ring opening of $2_{\text{Bu}}$ to $\text{INT2}_{\text{Bu}}$ ($\Delta E^\ddagger = 22.5$ kcal/mol, $\Delta G^\ddagger = 21.3$ kcal/mol), the irreversible formation of $2_{\text{Bu}}$ as intermediate from 1 and tBu-N3 through nucleophilic attack of the azide is still favored ($\Delta E^\ddagger = 9.2$ kcal/mol, $\Delta G^\ddagger = 17.0$ kcal/mol) and therefore the preferred pathway. This process is also the preferred path for the rearrangement of $2_{\text{Mes}}$ into $3_{\text{Mes}}$ ($\Delta E = -0.7$, $\Delta E^\ddagger = 21.8$ kcal/mol).[26]

Interestingly, computational analysis[27] revealed that for the reaction with mesityl azide the four-membered heterocycle $3_{\text{Mes}}$ is not the most stable conformer. Indeed, heating a solution of $3_{\text{Mes}}$ in toluene at 75 °C for 3 days resulted in the formation of the thermodynamic

![Scheme 3: Energy profile in kcal/mol for the rearrangement of a six-membered ring to a four-membered ring.](image-url)
product 4_Mes (δ^1^H{1^H} = 91.6 ppm; δ^1^B{1^H} = 5.9 ppm; Scheme 1), which is favored over 3_Mes by 1.5 kcal/mol (ΔG, Figure 3) and most likely proceeds via the endothermic ring opening of 4_Mes to INT3_Mes (ΔE = 22.5 kcal/mol, ΔG = 23.5 kcal/mol). Single-crystal X-ray structure determination provided the molecular structure of 4_Mes (Figure 2) which shows a five-membered heterocycle in which the FLP is attached to the α- and β-nitrogen of the azide, which is only the second example of such coordination mode for the reaction of an intramolecular frustrated Lewis pair with an organic azide^1^ and highlights that for mesityl azide all three possible coordination modes are accessible. The P1–N1 and B1–N2 bond lengths (1.6592(13), 1.668(2) Å, resp.) represent typical single bonds, and, similar to 3_tBu and 3_Mes, the N1–N2 bond length is elongated (1.3364(17) Å) compared to 2_Ph, and the N2–N3 bond is shortened (1.2733(17) Å), suggesting that resonance structure III (Figure 3) has a major contribution in this structure.

![Chemical structures](image)

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**Figure 3.** Four different conformations of FLP-azide adducts (top) and their corresponding Gibbs free energy of formation of the adducts in kcal/mol (bottom). Conformations lowest in energy are highlighted.

Next we investigated the reactivity of FLP tBu2PCH2BPh2 (1) with trimethylsilyl azide. Treatment of 1 with 1.1 equiv of TMS-N3 at room temperature afforded after six days complete conversion to product 5, which was isolated as a colorless solid in 89% yield.
(δ^{31}P{^1}H} = 84.3 ppm; δ^{11}B{^1}H} = 3.2 ppm; Scheme 4). The molecular structure of 5 revealed the formation of a four-membered heterocycle akin to G with only one azide N atom present (Scheme 4), and 5 can be regarded as a non-fluorinated analogue of the PCBN heterocycle reported by Stephan and co-workers that is derived via a different route.\[28] in 5, the B1–N1 distance of 1.6802(18) Å is noticeable longer compared to the four-membered heterocycles 3^{t}Bu and 3^{Mes}, indicating a weaker B1–N1 bond, likely due to sterical hindrance. The P1–N1 is slightly shorter (1.6366(11) Å) and the nitrogen has a planar environment (Σ = 359°), which suggest a pronounced phosphazene character of the P1–N1 bond. As 5 is obtained after elimination of dinitrogen, we were interested to find out how it is formed. During the reaction, one intermediate was observed by $^{31}$P and $^{11}$B NMR spectroscopy with similar chemical shifts as observed for 2 (R = Ph, $^{t}$Bu, Mes) (δ^{31}P{^1}H} = 26.7 ppm; δ^{11}B{^1}H} = –9.9 ppm), therefore we postulate that the six-membered heterocycle 2^{TMS} is an intermediate in the formation of 5. DFT calculations support this notion and revealed that the formation of 2^{TMS} via INT1^{TMS} is a low barrier process (ΔE = –24.2 kcal/mol, ΔE^‡ = 9.8 kcal/mol, which is in good agreement with our spectroscopic findings.\[26]

![Scheme 4](image)

**Scheme 4.** The reaction of 1 with TMS-N$_3$ (top) and the molecular structure of 5 (bottom; ellipsoids at 50% probability, hydrogens are omitted for clarity). Selected bond lengths [Å] and angles [°] for 5: P1–N1 1.6366(11), B1–N1 1.6802(18), N1–Si1 1.7348(12), P1–N1–B1 90.96(7), B1–N1–Si1 132.33(8), Si1–N1–P1 135.66(7).
In order to investigate the follow-up chemistry of the formal FLP-nitrene adduct 5, we first targeted removal of the TMS group, in analogy to the related carbene-nitrene adducts C (Figure 1).

Unfortunately, treatment of 5 with 1 equivalent of ethanol resulted in the formation of multiple unidentifiable products. More successful was the reaction of 5 with 1 equivalent of HCl at −78 °C, which led to the selective formation of a new product 6, which shows only a marginally difference in the $^{31}$P{¹H} and $^{11}$B{¹H} NMR spectrum ($\delta^{31}$P{¹H} = 78.1 ppm; $\delta^{11}$B{¹H} = 2.4 ppm) compared to 5, and an additional doublet for a N–H proton in the ¹H NMR spectrum ($\delta^1$H = 4.68 ppm, $^2J_{H,P}$ = 12.6 Hz). We postulate 5 to behave as a “masked FLP” capturing HCl by ring opening, comparable to the P/Al and P/B FLPs reported by Uhl and Erker,¹⁹,²⁰ which leads to protonation of the phosphazene moiety and chloride addition to the borane giving compound 6 (Scheme 5). The formation of 6 is further supported by the detection of the [6–Cl]$^+$ cation by high-resolution mass spectroscopy.

To investigate the ring opening behavior of 5 in more detail, we reacted 5 with an equimolar amount of anhydrous tetramethylammonium fluoride in MeCN/THF at 0 °C, which afforded the ring-opened product 7. The $^{31}$P{¹H} NMR spectrum displayed a singlet at 38.2 ppm, and the $^{11}$B{¹H} NMR spectrum showed a characteristic doublet due to a $^1J$ boron–fluorine coupling ($\delta^{11}$B{¹H} = 2.35, $^1J_{B,F}$ = 48.6 Hz) indicating that the fluoride is directly attached to the borane moiety. As final proof, single-crystal X-ray structure determination confirmed the molecular structure of 7, which displays a slightly shortened P1–N1 bond (1.543(3) Å) compared to 5 and an almost linear orientation of the P1–N1–Si1 bond angle (171.5(2)° Å), which is relatively large for such P=N–Si motif, but observed previously for electron rich phosphines.³¹
Scheme 5. The reaction of 5 with HCl and TMAF (top) and the molecular structure of 7 (bottom; ellipsoids at 50% probability, hydrogens Me₄N cation and a second ion pair of 7 are omitted for clarity). Selected bond lengths [Å] and angles [°] for 7: P1–N1 1.543(3), B1–F1 1.470(4), N1–Si1 1.653(3), P1–C1–B1 131.9 (2), P1–N1–Si1 171.5 (2), Σ(CB1C) 331.2.

To further probe the reactivity of 5 as a “masked” frustrated Lewis pair, ωB97X–D/6-31G* calculations revealed that the dissociation of the boron–nitrogen bond creating iminophosphorane/borane based FLP 5’ is only slightly uphill (ΔG = 5.4 kcal/mol, ΔE = 9.5 kcal/mol; Scheme 6) and is comparable to the energy required for ring opening of the P/B FLP reported by Erker and co-workers (ΔE = ca. 7 kcal/mol).[30] We found that 5 is indeed susceptible to undergo reactions with typical FLP substrates, such as isocyanides.
Scheme 6. The equilibrium between the open ($5'$) and closed form of $5$ and the corresponding energies.

Treatment of $6$ with an excess (14.4 equiv) of phenylisocyanate in THF at 60 °C for three days resulted in the formation of insertion product $8$ ($\delta^{31}$P{\text{H}} = 57.1 ppm; $\delta^{11}$B{\text{H}} = –3.1 ppm; Scheme 7),[14a,e,16,19a,32] which is, to the best of our knowledge, unprecedented reactivity of an FLP using a iminophosphorane as Lewis base. Next to the formation of $8$, full NMR analysis of the product revealed the formation of a second product in a 55:45 ratio ($8$: $9$), which was characterized as the cyclo-trimerization product $9$. Although the cyclo-oligomerization of isocyanates is known to be catalyzed by Lewis bases, such as NHC’s,[33] amines,[34] Verkade’s bases,[35] and phosphines,[16] or phosphides,[37] this represents the first example of catalytic cyclo-oligomerization of phenylisocyanate using a (masked) frustrated Lewis pair.

Scheme 7. The reaction of nitrene adduct $5$ with an excess phenylisocyanate.

3.3 Conclusion

We have shown that FLP $\text{tBu}_2\text{PCH}_2\text{BPh}_2$ (1) reacts with $\text{tBu-N}_3$, $\text{Mes-N}_3$ and $\text{Ph-N}_3$ giving four-, five-, and six-membered heterocycles, respectively. The mechanism was studied by DFT calculations, which revealed a new mechanism where, instead of a Staudinger reaction,
the reaction starts with formation of a B-N Lewis acid/base adduct (INT1), followed by ring closure to form the six-membered heterocycle 2. In case of $t$Bu-N$_3$ and Mes-N$_3$, this intermediate can subsequently rearrange to the thermodynamically most stable conformation. DFT calculations and NMR spectroscopy suggest that reaction of 1 with TMS-N$_3$ follows the same mechanism, yet no intermediate could be isolated and full conversion towards the nitrene adduct 5 was observed. Compound 5 still is reactive was found to ring open upon treatment with hydrochloric acid or tetramethylammonium fluoride. Additionally, 5 also showed retained FLP-type reactivity when reacted with phenylisocyanate, resulting in PhNCO addition creating a new six-membered heterocycle. At the same time, 5 also functions as catalyst in the cyclo-trimerization of phenylisocyanate.

3.4 Experimental Details

All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques, and were performed in the dark as a precaution to prevent decomposition. Solvents were purified, dried, and degassed according to standard procedures. $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker Avance 400 spectrometer and internally referenced to the residual solvent resonances (THF-$d_8$: $^1$H δ 3.58, 1.72, $^{13}$C{$^1$H} δ 67.2, 25.3; CD$_2$Cl$_2$: $^1$H δ 5.32, $^{13}$C{$^1$H} δ 53.8). $^{31}$P{$^1$H} and $^{11}$B{$^1$H} NMR spectra were recorded on a Bruker Avance 400 spectrometer and externally referenced (85% H$_3$PO$_4$, BF$_3$·OEt$_2$, respectively). $^{19}$F NMR spectra were recorded on a Bruker AV300-II and externally referenced (CFCl$_3$). Chemical shifts are reported in ppm. Melting points were measured on a Büchi M-565 melting point apparatus in sealed capillaries and are uncorrected. High resolution mass spectra were recorded on a Bruker MicroTOF with ESI nebulizer (ESI), or on an AccuTOF GC v 4g, JMS-T100GCV, Mass spectrometer (JEOL, Japan) with a LiFDi probe (FD/FI) equipped with a FD Emitter, Linden CMS GmbH (Germany), FD 13 μm. Current rate 51.2 mA/min over 1.2 min and typical measurement conditions are: counter electrode -10kV, ion source 37V. Trimethylsilyl azide (TMS-N$_3$), hydrochlorid acid 2M in diethyl ether (HCl/Et$_2$O) and phenyl isocyanate (PhNCO) were purchased from commercial resources. TMS-N$_3$ and PhNCO were stored over molecular sieves (4 Å), and HCl/Et$_2$O (2M)
was used as received. \( tBu-N_3 \)\(^{38} \) Ph-N_3\(^{39} \) Mes-N_3\(^{40} \) anhydrous tetramethylammonium fluoride (TMAF)\(^{41} \) and \( tBu_2PCH_2BPh_2 \)\(^{19a} \) were prepared following literature procedures.

**Preparation of FLP-phenyl azide adduct 2_{\text{Ph}}:**

Phenyl azide (0.074 g, 0.617 mmol, 1.0 equiv) was added to a solution of \( tBu_2PCH_2BPh_2 \) (1; 0.200 g, 0.617 mmol, 1.0 equiv) in THF (10 mL) at \(-10 \) °C. After addition, the reaction mixture was stirred for 10 minutes at \(-10 \) °C, after which it was allowed to warm to room temperature and stirred for another 10 minutes. Removal of the solvent and subsequent washing with \( n \)-pentane (3 x 10 mL) gave 2_{\text{Ph}} as a yellow solid (0.267 g, 98%). X-ray quality crystals were grown at room temperature from a THF/toluene solvent mixture layered with \( n \)-pentane.

**Melting point (nitrogen, sealed capillary):** 121 °C (decomposition).

\(^1H\) NMR (400.1 MHz, THF-\( d_8 \), 293 K): \( \delta \) 7.26 (d, \( ^3J_{H,H} = 6.9 \) Hz, 4H; \( o \)-BC\(_6\)H\(_5\)), 7.09 (d, \( ^3J_{H,H} = 7.3 \) Hz, 2H; \( o \)-NC\(_6\)H\(_5\)), 7.04 (t, \( ^3J_{H,H} = 7.4 \) Hz, 4H; \( m \)-BC\(_6\)H\(_5\)), 6.95–6.84 (m, 5H; \( m \)-NC\(_6\)H\(_5\), \( p \)-BC\(_6\)H\(_5\), and \( p \)-NC\(_6\)H\(_5\)), 1.81 (d, \( ^2J_{H,P} = 12.0 \) Hz, 2H; \( PCH_2B \)), 1.22 (d, \( ^2J_{H,P} = 14.3 \) Hz, 18H; \( PC(CH_3)_3 \)).

\(^{13}C\)\(^{1}H\) NMR (100.6 MHz, THF-\( d_8 \), 293 K): \( \delta \) 153.2 (only observed in the HMBC spectrum, \( ^2J_{C,H} \) coupling with \( o \)-BC\(_6\)H\(_5\), \( ^3J_{C,H} \) coupling with \( m \)-BC\(_6\)H\(_5\) and \( PCH_2B \); \textit{ipso-} BC\(_6\)H\(_5\)), 150.0 (s; \textit{ipso-}NC\(_6\)H\(_5\)), 134.8, (s; \( o \)-BC\(_6\)H\(_5\)), 127.5 (s; \( m \)-BC\(_6\)H\(_5\)), 127.4 (s; \( m \)-NC\(_6\)H\(_5\)), 125.3 (s; \( p \)-NC\(_6\)H\(_5\)), 125.2 and 125.1 (2x s; \( p \)-BC\(_6\)H\(_5\) and \( o \)-NC\(_6\)H\(_5\)), 36.0 (d, \( ^1J_{C,P} = 50.5 \) Hz; \( PC(CH_3)_3 \)), 26.6 (s; \( PC(CH_3)_3 \)), 12.7 (only observed in the HSQC spectrum, \( ^1J_{C,H} \) coupling with \( PCH_2B \); \( PCH_2B \)).

\(^{31}P\)\(^{1}H\) NMR (162.0 MHz, THF-\( d_8 \), 294 K): \( \delta \) 31.8 (s).

\(^{11}B\)\(^{1}H\) NMR (128.4 MHz, THF-\( d_8 \), 294 K): \( \delta \) –6.8 (s).

**HR–MS (ESI):** 482.2309 [2_{\text{Ph}}+K]\(^+\), calc. for C\(_{27}\)H\(_{35}\)BN\(_3\)PK\(^+\) 482.2293.

**Preparation of FLP-\( tert \)-butyl azide adduct 3_{\text{Bu}}:**

\( tert \)-butyl azide (0.081 g, 0.817 mmol, 1.1 equiv) was added to a solution of \( tBu_2PCH_2BPh_2 \) (1; 0.241 g, 0.743 mmol, 1.0 equiv) in THF (10 mL) at 0 °C. After addition, the reaction mixture was allowed to warm to room temperature after which it was stirred overnight. Removal of the solvent and subsequent washing with \( n \)-pentane (3 x 8 mL) gave 3_{\text{Bu}} as a
colorless solid (0.221 g, 70%). X-ray quality crystals were grown at room temperature by vapor diffusion of n-pentane into a solution of 3_{Bu} in THF.

Melting point (nitrogen, sealed capillary): 126 °C (decomposition).

$^1$H NMR (400.1 MHz, THF-$d_8$, 297 K): $\delta$ 7.49 (d, $^3J_{H,\text{H}} = 7.3$ Hz, 4H; o-C$_6$H$_5$), 7.00 (t, $^3J_{H,\text{H}} = 7.4$ Hz, 4H; m-C$_6$H$_5$), 6.84 (t, $^3J_{H,\text{H}} = 7.3$ Hz, 2H; p-C$_6$H$_5$), 1.44 (d, $^3J_{H,\text{P}} = 11.0$ Hz, 2H; PCH$_2$B), 1.34 (s, 9H; NC(CH$_3$)$_3$), 1.24 (d, $^3J_{H,\text{P}} = 15.3$ Hz, 18H; PC(CH$_3$)$_3$).

$^{13}$C{$^1$H} NMR (100.6 MHz, THF-$d_8$, 297 K): $\delta$ 156.5 (only observed in the HMBC spectrum, $^2J_{\text{C,H}}$ coupling with o-C$_6$H$_5$, $^3J_{\text{C,H}}$ coupling with m-C$_6$H$_5$ and PCH$_2$B; ipso-C$_6$H$_5$), 131.5 (s; o-C$_6$H$_5$), 127.0 (s; m-C$_6$H$_5$), 124.1 (s; p-C$_6$H$_5$), 61.7 (s; NC(CH$_3$)$_3$), 37.6 (d, $^1J_{\text{C,P}} = 25.6$ Hz; PC(CH$_3$)$_3$), 28.7 (s; NC(CH$_3$)$_3$), 28.1 (d, $^2J_{H,L} = 2.7$ Hz, 18H; PC(CH$_3$)$_3$), 6.7 (only observed in the HSQC spectrum, $^1J_{\text{C,H}}$ coupling with PCH$_2$B; PCH$_2$B).

$^{31}$P{$^1$H} NMR (162.0 MHz, THF-$d_8$, 293 K): $\delta$ 95.5 (s).

$^{11}$B{$^1$H} NMR (128.4 MHz, THF-$d_8$, 294 K): $\delta$ 2.9 (s).

HR–MS (ESI): 424.3044 [3_{Bu}+H]$^+$, calc. for C$_{25}$H$_{40}$BN$_3$P$^+$ 424.3047; 462.2611 [3+K]$^+$, calc. for C$_{25}$H$_{39}$BN$_3$PK$^+$ 462.2606

Preparation of FLP-mesityl azide adduct 3$_{\text{Mes}}$:

Mesitylazide (0.133 g, 0.823 mmol, 1.0 equiv) was added to a solution of tBu$_2$PCH$_2$BPh$_2$ (1; 0.267 g, 0.823 mmol, 1.0 equiv) in THF (12 mL) at 0 °C. After addition, the reaction mixture was allowed to warm to room temperature after which it was stirred for 1 hour. Removal of the solvent and subsequent washing with n-pentane (3 x 3 mL) gave 3$_{\text{Mes}}$ as a pale white solid in 80% yield (0.320 g, 0.659 mmol). X-ray quality crystals were grown at room temperature from a solution of 3$_{\text{Mes}}$ in THF layered with n-pentane.

Melting point (nitrogen, sealed capillary): 175 °C (decomposition).

$^1$H NMR (400.1 MHz, THF-$d_8$, 297 K): $\delta$ 7.53 (d, $^3J_{H,\text{H}} = 7.3$ Hz, 4H; o-C$_6$H$_5$), 7.01 (t, $^3J_{H,\text{H}} = 7.4$ Hz, 4H; m-C$_6$H$_5$), 6.88 (s, 2H; m-MesH), 6.86 (t, $^3J_{H,\text{H}} = 7.3$ Hz, 2H; p-C$_6$H$_5$), 2.27 (s, 3H; p-MesCH$_3$), 2.25 (s, 6H; o-MesCH$_3$), 1.62 (d, $^2J_{H,L} = 11.0$ Hz, 2H; PCH$_2$B), 1.35 (d, $^3J_{H,\text{P}} = 15.4$ Hz, 18H, PC(CH$_3$)$_3$).

$^{13}$C{$^1$H} NMR (100.6 MHz, THF-$d_8$, 297 K): $\delta$ 156.0 (only observed in the HMBC spectrum, $^2J_{\text{C,H}}$ coupling with o-C$_6$H$_5$, $^3J_{\text{C,H}}$ coupling with m-C$_6$H$_5$ and PCH$_2$B; ipso-C$_6$H$_5$), 147.5 (s; ipso-MesC), 135.4 (s; p-MesC), 131.7 (s; o-C$_6$H$_5$), 130.3 (s; o-MesC), 129.9 (s; m-
MesC), 127.1 (s; m-C₆H₅), 124.2 (s; p-C₆H₅), 37.9 (d, ²J_{C,P} = 24.9 Hz; PC(CH₃)₃), 28.0 (d, ²J_{C,P} = 1.8 Hz; PC(CH₃)₃), 20.7 (s; p-MesCH₃), 19.8 (s; o-MesCH₃), 6.50 (only observed in the HSQC spectrum, ¹J_{C,H} coupling with PCH₂B; PCH₂B)

³¹P{¹H} NMR (162.0 MHz, THF-d₈, 297 K): δ 98.3 (s).

¹¹B{¹H} NMR (128.4 MHz, THF-d₈, 297 K): δ 3.8 (s).


Rearrangement of FLP-mesityl azide adduct 3_{Mes} to 4_{Mes}:

Mesitylazide–FLP adduct 3_{Mes} (0.043 g, 0.089 mmol) was dissolved in toluene (10 mL), heated to 75 °C and stirred for 66 hours at this reaction temperature. Subsequently, the solvent was removed in vacuo and the product was dissolved a mixture of n-pentane (8 mL) and THF (1 mL). The solution was filtered and stored at –20 °C for 4 days and then 1 day at –80 °C, after which crystals had formed. The mother liquor was filtered off and after removal of the solvent 4_{Mes} was obtained as a colorless solid (0.031 g, 73%). X-ray quality crystals were grown by cooling a saturated solution of 4_{Mes} in a THF/n-pentane mixture to –20 °C.

Melting point (nitrogen, sealed capillary): 203 °C (decomposition).

¹H NMR (400.1 MHz, THF-d₈, 297 K): δ 7.66 (d, ³J_{H,H} = 7.4 Hz, 4H; o-C₆H₅), 7.07 (t, ³J_{H,H} = 7.4 Hz, 4H; m-C₆H₅), 6.96 (t, ³J_{H,H} = 7.2 Hz, 2H; p-C₆H₅), 6.74 (s, 2H; m-MesH), 2.21 (s, 3H; p-MesCH₃), 2.00 (d, ²J_{H,P} = 11.9 Hz, 2H; PCH₂B), 1.90 (s, 6H; o-MesCH₃), 1.20 (d, ³J_{H,P} = 14.4 Hz, 18H, PC(CH₃)₃).

¹³C{¹H} NMR (100.6 MHz, THF-d₈, 297 K): δ 152.5 (only observed in the HMBC spectrum, ²J_{C,H} coupling with o-C₆H₅, ³J_{C,H} coupling with m-C₆H₅ and PCH₂B; ipso-C₆H₅), 147.5 (s; ipso-MesC), 134.1 (s; p-MesC), 133.0 (s; o-C₆H₅), 128.8 (s; m-MesC), 128.6 (s; o-MesC), 126.9 (s; m-C₆H₅), 125.3 (s; p-C₆H₅), 35.5 (d, ¹J_{C,P} = 49.0 Hz; PC(CH₃)₃), 26.9 (s; PC(CH₃)₃), 20.8 (s; p-MeCH₃), 18.7 (s; o-MeCH₃), 7.70 (only observed in the HSQC spectrum, ¹J_{C,H} coupling with PCH₂B; PCH₂B).

³¹P{¹H} NMR (162.0 MHz, THF-d₈, 297 K): δ 91.6 (s).

¹¹B{¹H} NMR (128.4 MHz, THF-d₈, 297 K): δ 6.1 (s).
Preparation of FLP-trimethylsilyl nitrene adduct 5:

Trimethylsilyl azide (0.088 g, 0.101 mL, 0.763 mmol, 1.1 equiv) was added to a solution of tBu₂PCH₂BPH₂ (1; 0.225 g, 0.694 mmol, 1.0 equiv) in THF (12 mL) at 0 °C. After addition, the reaction mixture allowed to warm to room temperature after which it was stirred for 6 days. Removal of the solvent in vacuo gave 5 as a colorless solid (0.271 g, 89%). If necessary, the product could be washed with cold n-pentane (0 °C) to remove impurities. X-ray quality crystals were grown by cooling a saturated solution of 5 in n-pentane to –20 °C.

Melting point (nitrogen, sealed capillary): 94 °C (decomposition)

\[ ^1H \text{NMR (400.1 MHz, THF-}d_8, \text{ 293 K)}: \delta 7.36 (d, J_{H,H} = 7.3 \text{ Hz, 4H; } o-C₆H₅), 7.02 (t, J_{H,H} = 7.4 \text{ Hz, 4H; } m-C₆H₅), 6.91 (t, J_{H,H} = 7.2 \text{ Hz, 2H; } p-C₆H₅), 1.52 (d, J_{H,P} = 11.7 \text{ Hz, 2H; PCH₂B}), 1.33 (d, J_{H,P} = 14.3 \text{ Hz, 18H; PC(CH₃)₃}), 0.23 (s, 9H; Si(CH₃)₃). \]

\[ ^{13}C\{^1H\} \text{NMR (100.6 MHz, THF-}d_8, \text{ 293 K)}: \delta 156.1 (\text{only observed in the HMBC} \text{ spectrum, } J_{C,H} \text{ coupling with } o-C₆H₅, J_{C,H} \text{ coupling with } m-C₆H₅ \text{ and } PCH₂B; ipso-C₆H₅), 133.9 (s; o-C₆H₅), 126.5 (s; m-C₆H₅), 124.5 (s; p-C₆H₅), 38.0 (d, J_{C,P} = 33.1 \text{ Hz; PC(CH₃)₃}), 28.2 (d, J_{C,P} = 2.7 \text{ Hz; PC(CH₃)₃}), 10.3 (\text{only observed in the HSQC spectrum, } J_{C,H} \text{ coupling with } PCH₂B; PCH₂B), 5.1 (s; Si(CH₃)₃). \]

\[ ^{31}P\{^1H\} \text{NMR (162.0 MHz, THF-}d_8, \text{ 293 K)}: \delta 84.3 (s). \]

\[ ^{11}B\{^1H\} \text{NMR (128.4 MHz, THF-}d_8, \text{ 294 K)}: \delta 3.2 (s). \]


Reaction of 5 with HCl; preparation of compound 6:

A solution of HCl (2M in Et₂O, 0.26 mL, 0.52 mmol, 1.0 equiv) was added dropwise to a solution of 5 in THF (8 mL) at –78 °C. After addition, the mixture was stirred for 5 minutes at –78 °C and was subsequently warmed to room temperature. The solvent was removed in vacuo to afford a colorless solid that was washed with n-pentane (3 x 4 mL) and subsequently dried in vacuo to yield 6 as a colorless solid (0.189 g, 81%).


\[ ^1H \text{NMR (400.1 MHz, CD₂Cl₂, 298 K)}: \delta 7.46 (d, J_{H,H} = 7.5 \text{ Hz, 4H; } o-C₆H₅), 7.16 (t, J_{H,H} = 7.4 \text{ Hz, 4H; } m-C₆H₅), 7.05 (t, J_{H,H} = 7.2 \text{ Hz, 2H; } p-C₆H₅), 4.68 (d, J_{H,P} = 12.7 \text{ Hz, 1H; NH}), 1.86 (d, J_{H,P} = 11.1 \text{ Hz, 2H; PCH₂B}), 1.23 (d, J_{H,P} = 14.7 \text{ Hz, 18H; PC(CH₃)₃}), 0.28 (s, 9H; Si(CH₃)₃). \]
HR‒MS (ESI): 19 11 31

A solution of anhydrous tetramethylammonium fluoride (0.0454 g, 0.487 mmol, 1.0 equiv) in MeCN (10 mL) was added to a solution of 5 (0.200 g, 0.486 mmol, 1.0 equiv) in THF (15 mL) at 0 °C. After addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. Removal of the solvent and subsequent washing with n-pentane (3 x 8 mL) gave 7 as a white solid, which was subsequently washed with benzene (3 x 8 mL) to afford 7 as a pure, colorless solid (0.178 g, 73%). X-ray quality crystals were grown at room temperature from a solution of 7 in THF layered with n-pentane.

Melting point (nitrogen, sealed capillary): 118 °C (decomposition).

13C {1H} NMR (100.6 MHz, CD2Cl2, 300 K): δ 133.2 (s; o-C6H5), 127.1 (s; m-C6H5), 125.1 (s; p-C6H5), 36.5 (d, 1J_{C,P} = 49.0 Hz; PC(CH3)3), 27.6 (s; PC(CH3)3), 14.8 (only observed in the HSQC spectrum, 1J_{C,H} coupling with PCH2B; PCH2B), 2.27 (d, 3J_{C,P} = 1.4 Hz; Si(CH3)3), the signal for ipso-C6H5 is unresolved.

31P {1H} NMR (162.0 MHz, CD2Cl2, 298 K): δ 78.1 (s).

11B {1H} NMR (128.4 MHz, CD2Cl2, 299 K): δ 2.4 (s).

HR‒MS (LiFDi): 412.2750 [6–Cl]+, calc. for C24H40BNPSi+ 412.2755.

Reaction of 5 with TMAF; preparation of compound 7:

A solution of anhydrous tetramethylammonium fluoride (0.0454 g, 0.487 mmol, 1.0 equiv) in MeCN (10 mL) was added to a solution of 5 (0.200 g, 0.486 mmol, 1.0 equiv) in THF (15 mL) at 0 °C. After addition, the reaction mixture was warmed to room temperature and stirred for 1 hour. Removal of the solvent and subsequent washing with n-pentane (3 x 8 mL) gave 7 as a white solid, which was subsequently washed with benzene (3 x 8 mL) to afford 7 as a pure, colorless solid (0.178 g, 73%). X-ray quality crystals were grown at room temperature from a solution of 7 in THF layered with n-pentane.

Melting point (nitrogen, sealed capillary): 118 °C (decomposition).

1H NMR (400.1 MHz, CD2Cl2, 298 K): δ 7.57 (d, 3J_{H,H} = 6.9 Hz, 4H; o-C6H5), 7.08 (t, 3J_{H,H} = 7.3 Hz, 4H; m-C6H5), 6.90 (t, 3J_{H,H} = 7.2 Hz, 2H; p-C6H5), 1.31–1.19 (m, 2H; PCH2B), 1.11 (d, 3J_{H,P} = 12.6 Hz, 18H; PC(CH3)3), –0.18 (s, 9H; Si(CH3)3).

13C {1H} NMR (100.6 MHz, CD2Cl2, 300 K): δ 132.2 (d, 3J_{C,F} = 6.7 Hz; o-C6H5), 126.7 (s; m-C6H5), 123.2 (s; p-C6H5), 36.2 (d, 1J_{C,P} = 60.3 Hz; PC(CH3)3), 28.2 (m; PC(CH3)3), 22.9 (only observed in the HSQC spectrum, 1J_{C,H} coupling with PCH2B; PCH2B), 4.9 (s; Si(CH3)3), the signal for ipso-C6H5 is unresolved.

31P {1H} NMR (162.0 MHz, CD2Cl2, 298 K): δ 38.2 (s).

11B {1H} NMR (128.4 MHz, CD2Cl2, 299 K): δ 2.4 (d, 1J_{B,F} = 48.6 Hz).

19F NMR (282.4 MHz, CD2Cl2, 299 K): δ –191.7 (br. s).

Reaction of 5 with PhNCO; preparation of compound 8 and 9:

PhNCO (2.786 g, 2.54 mL, 23.39 mmol, 14.4 equiv) was added to a solution of 5 (0.673 g, 1.636 mmol, 1.0 equiv) in THF (45 mL) at room temperature. After addition, the reaction mixture was warmed to 60 °C and stirred for 3 days at this temperature. The solvent and excess PhNCO were removed in vacuo to afford a pale white solid, which was washed at 0 °C with n-pentane (3 x 8 mL). Subsequent drying in vacuo afforded a pale white solid that consists of a mixture of the product (8) and phenyl isocyanurate (9) in 55:45 ratio (0.967 g).

Compound 8:

¹H NMR (400.1 MHz, CD₂Cl₂, 299K): δ 7.33 (d, 3J_H,H = 7.1 Hz, 4H; o-BC₆H₅), 7.06 (t, 3J_H,H = 7.4 Hz, 4H; m-BC₆H₅), 6.96, (t, 3J_H,H = 7.2 Hz, 2H; p-BC₆H₅), 6.88–6.08 (br. m, 4H; o,m-NC₆H₅), 6.77–6.71 (m, 1H; p-NC₆H₅), 1.61 (d, 3J_H,P =10.9 Hz, 2H; PCH₂B), 1.16 (d, 3J_H,P = 14.2 Hz, 18H; P(CH₃)₃, 0.26 (s, 9H; Si(CH₃)₃).

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂, 299K): δ 146.4 (s; ipso-NC₆H₅), 134.4 (s; o-BC₆H₅), 128.0 and 127.0 (s; o-NC₆H₅ and m-NC₆H₅), 126.8 (s; m-BC₆H₅), 124.4 (s; p-BC₆H₅), 123.5 (s; p-NC₆H₅), 35.8 (d, 1J_C,P = 57.3 Hz; PC(CH₃)₃), 26.8 (s; PC(CH₃)₃), 14.6 (only observed in the HSQC spectrum, 1J_C,H coupling with PCH₂B; PCH₂B), 0.71 (s; Si(CH₃)₃), the signals for ipso-BC₆H₅ and NCO are unresolved.

³¹P{¹H} NMR (162.0 MHz, CD₂Cl₂, 298K): δ 56.5 (s).

¹¹B{¹H} NMR (128.4 MHz, CD₂Cl₂, 298K): δ –3.4 (s).


Compound 9:

¹H NMR (400.1 MHz, CD₂Cl₂, 299K): δ 7.58–7.47 (m, 9H; m,p-C₆H₅), 7.41 (d, 3J_H,H = 7.6 Hz, 6H; o-C₆H₅).

¹³C{¹H} NMR (100.6 MHz, CD₂Cl₂, 299K): δ 149.1 (s; ipso-C₆H₅), 134.4 (s; CO), 129.84, (s; m-C₆H₅), 129.79 (s; p-C₆H₅), 128.9 (s; o-C₆H₅).

Computational details:

All structures were optimized at the ωB97X–D level of theory,[⁴²] using Gaussian 09, Revision D01.[⁴³] Geometry optimizations were performed using the 6-31G* basis set,[⁴⁴,⁴⁵] and the nature of each stationary point was confirmed by frequency calculations.
Calculated reaction paths for 1 with azides to form a six-membered heterocycle

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<th>INT1</th>
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Scheme 8. Formation of a six-membered ring product via a Lewis adduct intermediate and the corresponding energies, Gibbs free energies and overall barriers in kcal/mol.
Scheme 9. Staudinger reaction of 1 with azides to form cis-products with boron in coordination sphere.
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Scheme 10. Staudinger reaction of 1 with azides to form cis-products with boron out of the coordination sphere.
\[ 1 + R-N_3^{0.0} \]

![Diagram of the reaction involving \( 1 \) and \( R-N_3 \) with the transition state (TS6) and intermediates (INT5).](image)

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<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta E )</td>
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<td>-9.40</td>
<td>30.7</td>
<td>-14.5</td>
<td>40.1</td>
</tr>
<tr>
<td>( \Delta G )</td>
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<td>4.26</td>
<td>44.9</td>
<td>2.91</td>
<td>44.9</td>
</tr>
<tr>
<td>( Mes-N_3 )</td>
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<tr>
<td>( \Delta E )</td>
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<td>-12.7</td>
<td>*</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>( \Delta G )</td>
<td>0.0</td>
<td>1.43</td>
<td>*</td>
<td>*</td>
<td>-</td>
</tr>
<tr>
<td>( TMS-N_3 )</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta E )</td>
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<td>39.6</td>
<td>-4.07</td>
<td>49.2</td>
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<tr>
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<td>6.01</td>
<td>55.5</td>
<td>14.6</td>
<td>55.5</td>
</tr>
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</table>

* The corresponding structure could not be located on the potential energy surface.

**Scheme 11.** Staudinger reaction of \( 1 \) with azides to form \( trans \)-products with boron in coordination sphere.
<table>
<thead>
<tr>
<th></th>
<th>(1 + R)-N(_3)</th>
<th>VdW</th>
<th>TS7</th>
<th>INT6</th>
<th>overall barrier</th>
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<td></td>
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<td>-11.6</td>
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<td>4.48</td>
<td>46.8</td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>-15.2</td>
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<td>1.49</td>
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<td>17.8</td>
<td>55.9</td>
</tr>
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</table>

**Scheme 12.** Staudinger reaction of 1 with azides to form *trans*-products with boron out of the coordination sphere.
Scheme 13. Rearrangement from a six- to a four-membered heterocycle for the tBu-N₃ and Mes-N₃ adduct.

<table>
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<th></th>
<th>2</th>
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<th>INT3</th>
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<td>5.39</td>
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<tr>
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<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>ΔE</td>
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<td>-1.56</td>
<td>2.96</td>
<td>-20.5</td>
<td>18.1</td>
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</table>

X-ray structure determination for 2Ph, 3tBu, 3Mes, 4Mes, 5, 6 and 7:
The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Kα radiation (λ = 1.54178 Å) (2Ph), or Bruker D8 Venture diffractometer with PhotonII CPAD detector at 123(2) K using Cu-Kα radiation (λ = 1.54178 Å) (7) or Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Kα radiation (λ = 0.71073 Å) (3tBu, 3Mes, 4Mes, 5). Direct Methods (SHELXS-97)\textsuperscript{[46]} (for 2Ph, 3tBu, 3Mes, 4Mes, 5) and Duel space methods (SHELXT)\textsuperscript{[47]} (for 7) were used for structure solution and refinement was carried out using SHELXT-
2013/2014 (full-matrix least-squares on \(F^2\)).\(^{[48]}\) Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. \(2_{\text{Ph}}\) and \(7\) were refined as an inversion twin. For \(3_{\text{Bu}}\) and \(4_{\text{Mes}}\) an extinction correction was applied.

\(2_{\text{Ph}}\): colorless crystals, \(C_{27}H_{35}BN_3P\), \(M_r = 443.36\), crystal size 0.20 x 0.10 x 0.06 mm, orthorhombic, space group \(Pca2_1\) (no.29), \(a = 20.3505(5)\) Å, \(b = 18.8682(5)\) Å, \(c = 12.8093(3)\) Å, \(V = 4918.5(2)\) Å\(^3\), \(Z = 8\), \(\rho = 1.197\) Mg/m\(^3\), \(\mu(\text{Mo-K\(\alpha\)}) = 1.12\) mm\(^{-1}\), \(F(000) = 1624\), \(2\theta_{\text{max}} = 144^\circ\), 36741 reflections, of which 9434 were independent \((R_{\text{int}} = 0.039)\), 578 parameters, \(R_1 = 0.034\) (for 8901 I > 2σ(I)), \(wR_2 = 0.086\) (all data), \(S = 1.03\), largest diff. peak / hole = 0.30 / -0.22 e Å\(^{-3}\).

\(3_{\text{Bu}}\): colorless crystals, \(C_{25}H_{39}BN_3P\), \(M_r = 423.37\), crystal size 0.22 x 0.08 x 0.06 mm, monoclinic, space group \(P2_1/n\) (no.14), \(a = 8.8381(6)\) Å, \(b = 14.9452(9)\) Å, \(c = 19.3839(12)\) Å, \(\beta = 102.622(2)^\circ\), \(V = 2498.5(3)\) Å\(^3\), \(Z = 4\), \(\rho = 1.126\) Mg/m\(^3\), \(\mu(\text{Mo-K\(\alpha\)}) = 0.13\) mm\(^{-1}\), \(F(000) = 920\), \(2\theta_{\text{max}} = 55.2^\circ\), 49835 reflections, of which 5768 were independent \((R_{\text{int}} = 0.040)\), 272 parameters, \(R_1 = 0.045\) (for 4845 I > 2σ(I)), \(wR_2 = 0.113\) (all data), \(S = 1.05\), largest diff. peak / hole = 0.89 / -0.38 e Å\(^{-3}\).

\(3_{\text{Mes}}\): colorless crystals, \(C_{30}H_{41}BN_3P\), \(M_r = 485.44\), crystal size 0.40 x 0.20 x 0.06 mm, orthorhombic, space group \(Cmc2_1\) (no.36), \(a = 16.5487(6)\) Å, \(b = 8.6092(4)\) Å, \(c = 19.6231(8)\) Å, \(V = 2795.7(2)\) Å\(^3\), \(Z = 4\), \(\rho = 1.153\) Mg/m\(^3\), \(\mu(\text{Mo-K\(\alpha\)}) = 0.12\) mm\(^{-1}\), \(F(000) = 1048\), \(2\theta_{\text{max}} = 55^\circ\), 30510 reflections, of which 3318 were independent \((R_{\text{int}} = 0.033)\), 174 parameters, \(R_1 = 0.027\) (for 3209 I > 2σ(I)), \(wR_2 = 0.071\) (all data), \(S = 1.05\), largest diff. peak / hole = 0.23 / -0.20 e Å\(^{-3}\).

\(4_{\text{Mes}}\): colorless crystals, \(C_{30}H_{41}BN_3P\), \(M_r = 485.44\), crystal size 0.40 x 0.30 x 0.20 mm, monoclinic, space group \(P2_1/n\) (no.14), \(a = 11.2998(5)\) Å, \(b = 34.1311(14)\) Å, \(c = 14.9127(6)\) Å, \(\beta = 99.415(2)^\circ\), \(V = 5674.0(4)\) Å\(^3\), \(Z = 8\), \(\rho = 1.137\) Mg/m\(^3\), \(\mu(\text{Mo-K\(\alpha\)}) = 0.12\) mm\(^{-1}\), \(F(000) = 2096\), \(2\theta_{\text{max}} = 55.2^\circ\), 88690 reflections, of which 13092 were independent \((R_{\text{int}} = 0.039)\),
638 parameters, $R_1 = 0.048$ (for 10823 $I > 2\sigma(I)$), $wR_2 = 0.114$ (all data), $S = 1.06$, largest diff. peak / hole = 0.43 / -0.34 e Å$^{-3}$.

5: colorless crystals, $C_{24}H_{39}BNPSi$, $M_r = 411.43$, crystal size 0.55 x 0.40 x 0.25 mm, triclinic, space group $P-1$ (no.2), $a = 9.2355(8)$ Å, $b = 9.7839(9)$ Å, $c = 14.8260(15)$ Å, $\alpha = 73.617(3)^{\circ}$, $\beta = 73.528(3)^{\circ}$, $\gamma = 76.448(3)^{\circ}$, $V = 1215.1(2)$ Å$^3$, $Z = 2$, $\rho = 1.125 \text{Mg/m}^3$, $\mu$(Mo-K$\alpha$) = 0.17 mm$^{-1}$, $F(000) = 448$, $2\theta_{\text{max}} = 55.2^{\circ}$, 23381 reflections, of which 5576 were independent ($R_{\text{int}} = 0.048$), 253 parameters, $R_1 = 0.041$ (for 4947 $I > 2\sigma(I)$), $wR_2 = 0.110$ (all data), $S = 1.05$, largest diff. peak / hole = 0.44 / -0.40 e Å$^{-3}$.

7: colorless crystals, $C_{24}H_{39}BFNPSi \cdot C_4H_{12}N$, $M_r = 504.57$, crystal size 0.20 x 0.08 x 0.03 mm, orthorhombic, $Pca2_1$ (no.29), $a = 17.3700(5)$ Å, $b = 15.5606(5)$ Å, $c = 22.4527(7)$ Å, $V = 6068.7(3)$ Å$^3$, $Z = 8$, $\rho = 1.105 \text{Mg/m}^3$, $\mu$(Mo-K$\alpha$) = 1.36 mm$^{-1}$, $F(000) = 2208$, $2\theta_{\text{max}} = 144.4^{\circ}$, 67557 reflections, of which 10540 were independent ($R_{\text{int}} = 0.037$), 609 parameters, $R_1 = 0.047$ (for 10177 $I > 2\sigma(I)$), $wR_2 = 0.124$ (all data), $S = 1.04$, largest diff. peak / hole = 1.36 / -0.35 e Å$^{-3}$.

### 3.5 References


[20] Compound 2m, 3m, 3mα and 4mα showed decomposition when solutions were handled in the presence of light and therefore all reactions were performed in the absence of light.


[25] A broad $^{31}$P {$^{[1]}$H} NMR signal was observed for 3mα at room temperature ($\nu_{1/2}$ ~ 235 Hz), which upon cooling to 223 K split into a pair of signals at $\delta$ + 98.6 and +89.4 in a 97 : 7 ratio. The structure of these isomers is still to be determined. For comparison, see reference 12a.

[26] The computational details for all mechanisms with Ph-N₃, tBu-N₃, Mes-N₃ and TMS-N₃ can be found in the supporting information.

[27] See the supporting information.


