New Insights in Frustrated Lewis Pair Chemistry with Azides


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Abstract: The geminal frustrated Lewis pair (FLP) tBuPCH3BPH3 (1) reacts with phenyl-, mesityl-, and tert-butyl azide affording, respectively, six, five, and four-membered rings as isolable products. DFT calculations revealed that the formation of all products proceeds via the six-membered ring structure, which is thermally stable with an N-phenyl group, but rearranges when sterically more encumbered Mes–N, and tBu–N are used. The reaction of 1 with Me3Si–N3 is believed to follow the same course, yet subsequent N2 elimination occurs to afford a four-membered heterocycle (5), which can be considered as a formal FLP-trimethylsilylnitrene adduct. Compound 5 reacts with hydrochloric acid or tetramethylammonium fluoride and showed frustrated Lewis pair reactivity towards phenylisocyanate.

Introduction
During the past two decades a vast amount of research has been conducted on small-molecule activation utilizing main-group species as viable alternatives to the well-established transition-metal complexes. For example, cyclic (alkyl)(amino)-carbenes (CAACs) can cleave the strong covalent H–H, N–H, P–H, B–C, and B–H bonds, and can capture CO and catecholborane. Organic azides are common organic molecules and are used. The reaction of 1 with Me3Si–N3 is believed to follow the same course, yet subsequent N2 elimination occurs to afford a four-membered heterocycle (5), which can be considered as a formal FLP-trimethylsilylnitrene adduct. Compound 5 reacts with hydrochloric acid or tetramethylammonium fluoride and showed frustrated Lewis pair reactivity towards phenylisocyanate.

Results and Discussion
Treatment of tBuPCH3BPH3 (1) with 1 equiv of Ph–N3 in THF at −10 °C and subsequent warming to room temperature resulted in the immediate conversion to 2ν, which after workup was isolated as a yellow powder in 98% yield (δ13CPh(H) = 31.8; δ31P(H12) = −6.8 ppm; Scheme 1).20 The molecular structure of 2ν, determined by a single-crystal X-ray diffraction analysis, established unequivocally the formation of a six-membered heterocycle (Figure 2, top left) with P1–N1 (1.687(2), 1.686(2) Å).
Molecular structures of $2_{\text{ph}}$, tert-butyl azide (3$_{\text{Bu}}$), and mesityl azide (3$_{\text{Mes}}$) and trimethylsilyl azide (5).

and B1–N3 (1.597(3) [1.603(3)] Å) bonds (the numbers in brackets refer to the bond metrics of a second crystallographically independent molecule in the asymmetric unit). Interestingly, $2_{\text{ph}}$ displays much more localized N–N bonds (N1–N2: 1.290(3) [1.291(3)], N2–N3: 1.323(3) [1.329(3)] Å) compared with F (N1–N2: 1.304(3), N2–N3: 1.306(3) Å; Figure 1)[16] which is likely due to the more electron-rich phosphorus center in $2_{\text{ph}}$.

We wanted to explore the mechanism for the formation of $2_{\text{ph}}$, and considered two options that differ according to the initial interaction of the azide with the FLP. DFT calculations at the ωB97X-D/6-31G* level of theory showed that the nucleophilic attack of the phosphine to the azide (TS3$_{\text{ph}}$, $\Delta \varepsilon = 9.6$ kcal mol$^{-1}$), which is the first step in the Staudinger reaction[21] is disfavored, and instead nucleophilic attack of the azide to the boron moiety of the FLP is preferred, which leads to INT1$_{\text{ph}}$ ($\Delta \varepsilon = 5.2$, $\Delta \varepsilon = 8.0$ kcal mol$^{-1}$) by formation of a boron–γ-nitrogen bond (Scheme 2). Note that this reaction path is well documented for the related transition metal chemistry with azides[22, 23] yet poorly described for main-group systems.[24] Subsequent ring closure of this Lewis adduct, 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 γ-nitrogen of the cor...

![Scheme 1](image1.png)

**Scheme 1.** Reactivity of FLP 1 with phenyl azide (2$_{\text{ph}}$), tert-butyl azide (3$_{\text{Bu}}$), and mesityl azide (3$_{\text{Mes}}$) and trimethylsilyl azide (5).

![Scheme 2](image2.png)

**Scheme 2.** Complete energy profile ($\Delta \varepsilon$) in kcal mol$^{-1}$ for the formation of $2_{\text{ph}}$ (blue), $3_{\text{Bu}}$ (red) and $3_{\text{Mes}}$ (green) through initial P–N bond formation (interrupted Staudinger reaction, shown in red) versus initial B–N bond formation and rearrangement to heterocycle 3. *TS4$_{\text{ph}}$ could not be located.*
responding azide. The azide fragment in 3_{Bu} and 3_{Mes} is attached to 1 with a s-Z conformation of the P1 and N3 moieties (3_{Bu}: P1-N1-N2-N3 = 1.66(19); 3_{Mes}: P1-N1-N2-N3 = 0.00(1); Figure 2). The N1–N2 bond lengths (3_{Bu}: 1.3573(16), 3_{Mes}: 1.342(3) Å) are typical for a N–N single bond and the shorter N2–N3 distance (3_{Bu}: 1.2502(17), 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–N1 and Mes–N1 by variable-temperature NMR spectroscopy revealed the presence of an intermediate during the reaction with comparable 1^{39}P[H] and 1^{31}B[H] NMR signals as observed for 2_{Bu} (2_{Bu}: δ(1{^39}P[H]) = 27.0; δ(1^{31}B[H]) = −7.0, 2_{Mes}: δ(1{^39}P[H]) = 40.5; δ(1^{31}B[H]) = −6.7 ppm), suggesting that the six-membered heterocycle is an intermediate in the formation of 3_{Bu} and 3_{Mes}.

DFT calculations indeed supported this hypothesis and we found that upon reacting 1 with tBu–N1 and Mes–N1 the six-membered intermediates 2_{Bu} and 2_{Mes} are easily accessible by B–N Lewis adduct formation and subsequent ring closure with maximum barriers of 9.2 and 9.4 kcal mol$^{-1}$ (ΔE), respectively. All of the systems show a preference for initial B–N interaction over the Staudinger pathway that is a 1.9–4.2 kcal mol$^{-1}$ higher energy process (tBu–N1, ΔE = 13.4, Mes–N1, ΔE = 11.3 kcal mol$^{-1}$), but due to the small energetic differences it is possible that the initial P–N formation is also a minor competing process. In the case of phenyl azide, the six-membered heterocycle 2_{Ph} is the kinetically and thermodynamic product (ΔG$_{ring}$ = −21.6 vs. ΔG$_{ring}$ = −19.7 kcal mol$^{-1}$; see Figure 3 and Table 1), whereas with tert-butyl and mesityl substituents this heterocycle is only the kinetic product that can rearrange to the four-membered heterocycles 3_{Bu} and 3_{Mes}. When the steric bulk on the azide was reduced in silico (R = H, Table 1), more insight in the preference in ring formation was obtained: the formation of a 6-membered ring is most favored (ΔG$_{ring}$ = −23.7 kcal mol$^{-1}$), and the smaller the ring becomes, the less favored the formation is (ΔG$_{ring}$ = −18.2 (see below) vs. ΔG$_{ring}$ = −15.8 kcal mol$^{-1}$).

![Figure 3](image-url) Four different isomers of FLP–azide adducts (R = H, Ph, tBu, Mes, and TMS, see Table 1).

For the follow up reaction, DFT calculations (ωB97X-D/6-31G*) showed that indeed the six-membered intermediate 2_{Bu} (Scheme 2) can ring open by breaking the B–N bond to form a phosphazide, INT2$_{Bu}$ (25) which is the first intermediate of a Staudinger reaction. Subsequent rotation around the P–N o-bond perfectly aligns the α-nitrogen of INT3$_{Bu}$ for a barrierless ring closing to the α,α-nitrogen-coordinated four-membered heterocycle 3_{Bu} (Scheme 2), which is the thermodynamic product. It should be noted that INT2$_{Bu}$ can be formed directly from 1 and tBu–N1 through the Staudinger reaction, but the barrier for this process (ΔE = 13.4 kcal mol$^{-1}$) is higher than the barrier for the initial formation of 2_{Bu} (ΔE = 9.2 kcal mol$^{-1}$), and thus the six-membered heterocycle is computed to be a likely intermediate in this transformation, consistent with the aforementioned NMR spectroscopic data. This process is also the preferred path for the rearrangement of 2_{Mes} into 3_{Mes}.

Interestingly, our computational analysis (26) revealed that for the reaction with mesityl azide the four-membered heterocycle 3_{Mes} is not the most stable isomer (Table 1). Indeed, heating a solution of 3_{Mes} in toluene at 75 °C for 3 days resulted in the formation of the thermodynamic product 4_{Mes} (δ(1{^39}P[H]) = 91.6; δ(1^{31}B[H]) = 5.99 ppm; Scheme 1), which is favored over 3_{Mes} by ΔG = −1.5 kcal mol$^{-1}$ (Figure 3) and most likely proceeds through the endothermic ring opening of 3_{Mes} to INT3$_{Mes}$ (ΔE = 22.5 kcal mol$^{-1}$). Single-crystal X-ray structure determination provided the molecular structure of 4_{Mes} (Figure 2, bottom right) 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 (15) and highlights that for mesityl azide all three possible coordination modes are synthetically accessible. The P1–N1 and B1–N2 bond lengths (1.6592(13) [1.6557(13)], 1.6682(2) [1.6552(2)] Å, respectively) represent typical single bonds, and, similar to 3_{Bu} and 3_{Mes} the N1–N2 bond is elongated (1.3364(17) [1.3397(17)] Å) compared with 2_{Mes} and the N2–N3 bond is shortened (1.2733(17) [1.2695] Å), suggesting that resonance structure 3 (Figure 3) has a major contribution in this structure.

Next, we investigated the reactivity of tBu_PCH_3BP_3 (1) with trimethylsilyl azide. Treatment of 1 with 1.1 equiv of TMS–N3 at room temperature afforded complete conversion after six days to product 5, which was isolated as a colorless solid in 89% yield (δ(1{^39}P[H]) = 84.3; δ(1^{31}B[H]) = 3.2 ppm; Scheme 3). The molecular structure of 5 revealed the formation of a four-membered heterocycle akin to G with only one azide N atom present; note that 5 can be regarded as a non-fluorinated analogue of the PCBN heterocycle reported by Stephan and coworkers, which is obtained from the reaction between a lithiated iminophosphorane and a chloroborane. (29) In 5, the B1–N1 distance of 1.6802(18) Å is notably longer compared to the four-membered heterocycles 3_{Bu} and 3_{Mes} indicating a weaker B1–N1 bond, likely due to steric hindrance. The P1–N1 distance 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 $^{19}$B NMR spectroscopy with similar chemical shifts as observed for 2 (R = Ph, rBu, Mes) ($\delta^{(31)}$P(H)) = 26.7; $\delta^{(19)}$B(H)) = −9.9 ppm), therefore we postulate that the six-membered heterocycle $2_{\text{MS}}$ is an intermediate in the formation of 5. DFT calculations support this notion and revealed that the formation of $2_{\text{MS}}$ via INT1$_{\text{MS}}$ is a low-energy process ($\Delta E^* = 9.8$, $\Delta E = −24.2$ kcal mol$^{-1}$), which is in good agreement with our spectroscopic findings.\(^{[26]}\) We were able to locate a transition state for direct N$_2$ elimination from INT1$_{\text{MS}}$, which is comparable to the thermal elimination of N$_2$ from diarylazido-boranes (see page S72, Supporting Information).\(^{[30]}\) However, this process is too high in energy ($\Delta E^* = 37.3$, $\Delta G^* = 44.2$ kcal mol$^{-1}$) to proceed at room temperature and was therefore regarded as unfeasible. We postulate that the elimination of N$_2$ proceeds through ring opening of $2_{\text{MS}}$ by breaking the B–N bond that affords intermediate INT2$_{\text{MS}}$, which eliminates dinitrogen through a classical Staudinger mechanism to form the corresponding iminophosphorane followed by ring closure to form 5 (Scheme 3), yet the transition states for this process could not be located on the potential-energy surface. Alternatively, Schulz and co-workers found that elimination of N$_2$ could proceed via a structure comparable to INT1.\(^{[24c]}\) However, such mechanism would presumably lead to a different product than 5.\(^{[31]}\) Related compounds have been referred to as formal FLP adducts of nitrenes.\(^{[32]}\) Based on this finding of N$_2$ loss in the TMS–N$_2$ reactions, we explored the possibility of similar N$_2$ extrusion for the Ph-, rBu- and Mes-substituted azide products; according to DFT calculations, N$_2$ loss is thermodynamically favorable in all cases (see Table S1 in the Supporting Information). However, 3$_{\text{Bu}}$ and 4$_{\text{Mes}}$ were both thermally stable up to 100 °C when dissolved in toluene, whereas 2$_{\text{Ph}}$ decomposes unsselectively to a range of products.

To investigate the follow-up chemistry of 5, we first targeted removal of the TMS group, in analogy to the related carbene-nitrene adducts C (Figure 1).\(^{[11]}\) Unfortunately, treatment of 5 with 1 equiv of ethanol resulted in the formation of multiple unidentifiable products. More successful was the reaction of 5 with 1 equiv of HCl (2 M in Et$_2$O) at −78 °C, which led to the selective formation of a new product 6, which shows only marginally different signals in the $^{31}$P(H) and $^{19}$B(H) NMR spectrum ($\delta^{(31)}$P(H)) = 78.1; $\delta^{(19)}$B(H)) = 2.4 ppm) compared to 5, and an additional doublet for a N–H proton in the $^1$H NMR spectrum ($\delta$(H)) = 4.68 ppm, $J_{HF}$ = 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 UhI and Erker,\(^{[32, 33]}\) which leads to protonation of the phosphazene moiety and chloride addition to the borane giving compound 6 (Scheme 4). The formation of 6 is further supported by the detection of the 6–Cl$^+$ cation by high-resolution mass spectrometry.

To investigate the ring-opening behavior of 5 in more detail, we reacted 5 with an equimolar amount of anhydrous tetramethylammonium fluoride (TMAF) in MeCN/THF at 0 °C, which afforded the ring-opened product 7. The $^{31}$P(H) NMR spectrum displayed a singlet at 38.2 ppm, and the $^{19}$B(H) NMR spectrum showed a characteristic doublet due to a $J_{HF}$ coupling at $\delta^{(19)}$B(H)) = 2.35 ppm with $J_{HF}$ = 48.6 Hz indicating that the fluoride is directly attached to the borane moiety. As final proof, a single-crystal X-ray structure determination confirmed the molecular structure of 7, which displays a slightly shortened P–N bond (1.543(3) [1.545(3)] Å) compared with 5 and an almost linear orientation of the P–N–Si bond angle (171.5(2)° [174.6(2)] ; Scheme 4), which is relatively large for such P–N–Si motif, but observed previously for electron rich phosphines.\(^{[34]}\)
To further probe the reactivity of 5 as a “masked” frustrated Lewis pair, α-B97X-D/6-31G* calculations revealed that the splitting of the boron–nitrogen bond creating iminophosphorane/borane based FLP 5 is only slightly uphill (ΔG = 5.53, ΔE = 9.48 kcal mol⁻¹; Scheme 5) and is comparable to the energy required for ring opening of the four-membered heterocyclic P/B FLP reported by Erker and co-workers (ΔE ≈ 7 kcal mol⁻¹). We found that 5 is indeed susceptible to undergo reactions with typical FLP substrates, such as isocyanates.

\[
\begin{align*}
\text{PhNCO} & \rightarrow \text{PhNC} = \text{N} \\
\text{Mes} & \rightarrow \text{PhNC} = \text{N} \\
\text{Mes} & \rightarrow \text{PhNC} = \text{N}
\end{align*}
\]

Scheme 5. The equilibrium between the open (5') and closed form of 5 and the corresponding energies.

Specifically, treatment of 6 with an excess (14.4 equiv) of phenylisocyanate in THF at 60 °C for three days resulted in the formation of insertional product 8 (δ(1H)(Ph) = 5.71; δ(13C)(H)) = −3.1 ppm; Scheme 6), which represents a rare case of an FLP using a iminophosphorane as Lewis base.[36] 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 NHCl,[15] amines,[40] Verkade’s bases[30] and phosphines,[40] or phosphoranes,[41] this represents to our knowledge the first example of cyclo-oligomerization of phenylisocyanate in which a (masked) frustrated Lewis pair is involved.

\[
\begin{align*}
\text{PhNCO} & \rightarrow \text{PhNC} = \text{N} \\
\text{Mes} & \rightarrow \text{PhNC} = \text{N} \\
\text{Mes} & \rightarrow \text{PhNC} = \text{N}
\end{align*}
\]

Scheme 6. The reaction of 5 with phenylisocyanate.

Conclusions

We have shown that the phosphorus/boron-based FLP rBu₄PH₂BN₂Bu₄ (1) reacts with rBu-N₃, Mes-N₃ and Ph-N₃ giving four-, five-, and six-membered heterocycles, respectively. The mechanism was studied by DFT calculations, which revealed that instead of a Staudinger reaction, the reaction starts with formation of a B–N Lewis adduct (INT1), which ring closes to form the six-membered heterocycle 2. In case of the bulkier rBu-N₃ and Mes-N₃, 2 is the kinetic product that can subsequently rearrange to the thermodynamically most stable isomer. DFT calculations and NMR spectroscopy suggest that reaction of 1 with TMS–N₃ follows the same mechanism, however the six-membered intermediate is unstable and rapid extrusion of dinitrogen results in full conversion towards the four-membered heterocycle 5. Compound 5 is reactive, and was found to ring open upon treatment with hydrochloric acid or tetramethyammonium fluoride. Additionally, 5 also retained FLP reactivity when reacted with phenylisocyanate, resulting in PhNCO addition creating a new six-membered heterocycle. At the same time, 5 can promote the cyclo-trimerization of phenylisocyanate to the corresponding isocyanurate.

**Experimental Section**

**General methods and materials**

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. ¹H and ¹³C(¹H) NMR spectra were recorded on a Bruker Avance 400 spectrometer and internally referenced to the residual solvent resonances (D₂O/THF: ¹H: δ = 3.58, 1.72, ¹³C(¹H): δ = 67.2, 25.3; CDCl₃: ¹H: δ = 5.32, ¹³C(¹H): δ = 5.38 ppm). ¹⁹F(¹H) and ¹³B(¹H) NMR spectra were recorded on a Bruker Avance 400 spectrometer and externally referenced (85% H₂PO₄, BF₃·OEt₂, respectively). ¹⁹F NMR spectra were recorded on a Bruker AV300-II and externally referenced (CFCl₃). 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 4 g JMS-T100GCV, Mass spectrometer (JEOL, Japan) with a LIFDI probe (FD/FI) equipped with a FD Emitter, Linden CMS GmbH (Germany), FD 13 mm. Current range 51.2 mA/min to 1.2 min and typical measurement conditions are: counter electrode −10 kV, ion source 37 V. Trimethylsilyl azide (TMS–N₃), hydrochloric acid 2 M in diethyl ether (HCl/Et₂O) and phenyl isocyanate (PhNCO) were purchased from commercial resources. TMS–N₃ and PhNCO were stored over molecular sieves (4 Å), and HCl/Et₂O (2 M) was used as received. rBu–N₃,[42] Ph–N₃,[43] Mes–N₃,[44] anhydrous tetramethyammonium fluoride (TM AF)[45] and rBu₄PH₂BN₂Bu₄,[19] were prepared following literature procedures.

**Synthesis and characterization**

**Synthesis of 2ₚₙ:** Phenyl azide (0.074 g, 0.617 mmol, 1.0 equiv) was added to a solution of rBu₄PH₂BN₂Bu₄ (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 × 10 mL) gave 2ₚₙ 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. M.p. (nitrogen, sealed capillary): 121 °C (decomp); ¹H NMR (400.1 MHz, D₂O/THF: 293 K): δ = 7.26 (d, Jₓᵧᵧₜ = 6.9 Hz, 4H; o-BC₆H₄), 7.09 (d, Jₓᵧᵧₜ = 7.3 Hz, 2H; o-NC₆H₄), 7.04 (t, Jₓᵧᵧₜ = 7.4 Hz, 4H; m-BC₆H₄), 6.95–6.84 (m, 5H; m-NC₆H₄), p-BC₆H₄, and p-NC₆H₄), 1.81 (d, Jₓᵧᵧₜ = 12.0 Hz, 2H; PCH₃(B)), 1.22 ppm (d, Jₓᵧᵧₜ = 14.3 Hz, 18H; PC(CH₃)₂); ¹³C(¹H) NMR (100.6 MHz, D₂O/THF, 293 K): δ = 153.2 (only observed in the HMBC spectrum, Jₓᵧᵧₜ coupling with o-BC₆H₄, Jₓᵧᵧₜ coupling with m-BC₆H₄, and PCH₃(B), 150.0 (s; ipso-NC₆H₄), 134.8, (s; o-BC₆H₄), 130.0 (s; o-BC₆H₄), 121.8 (s; m-BC₆H₄), 113.6 (s; ipso-NC₆H₄), 113.1 (s; o-BC₆H₄), 52.5 (s; NCH₃), 52.4 (s; NCH₃), 38.6 (s; NCH₃), 21.2 (s; NCH₃), 20.4 (s; NCH₃).

Synthesis of 3m: tert-Butyl azide (0.081 g, 0.817 mmol, 1.1 equiv) was added to a solution of tBuCH2CH2Ph, (1.025 g, 0.473 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 × 8 mL) gave 3m 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 3m in THF. M.p. (nitrogen, sealed capillary): 126 °C (decomp); ‘H NMR (400.1 MHz, [D6]THF, 297 K): δ = 7.49 (d, 2JCH = 7.3 Hz, 4H; c-CH3), 7.00 (t, 2JCH = 7.4 Hz, 4H; m-CH3), 6.84 (t, 2JCH = 7.3 Hz, 2H; p-CH3), 4.40 (d, 2JCH = 11.0 Hz, 2H; PCH3); 13C NMR (100.6 MHz, [D6]THF, 297 K): δ = 156.5 (only observed in the HMBC spectrum, 1JCN coupling with p-CH3, 1JCN coupling with c-CH3, and PCH3-B); 11C[N] NMR (100.6 MHz, [D6]THF, 297 K): δ = 156.5 (only observed in the HMBC spectrum, 1JCN coupling with p-CH3, 1JCN coupling with c-CH3, and PCH3-B); 31P[19] F NMR (162.0 MHz, [D6]THF, 293 K): δ = 95.5 ppm (s); 31P[20] B NMR (128.4 MHz, [D6]THF, 294 K): δ = -2.9 ppm (s); HR ESI-MS: calc for C10H12N2P+ (M+K) 462.2293, found 462.2309.

Synthesis of 3n: Mesitylazide (0.133 g, 0.823 mmol, 1.0 equiv) was added to a solution of tBuCH2CH2Ph, (1.025 g, 0.473 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 × 8 mL) gave 3n 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 3n in THF layered with n-pentane. M.p. (nitrogen, sealed capillary): 175 °C (decomp); ‘H NMR (400.1 MHz, [D6]THF, 297 K): δ = 7.53 (d, 2JCH = 7.3 Hz, 4H; c-CH3), 7.01 (t, 2JCH = 7.4 Hz, 4H; m-CH3), 6.88 (s, 2H; m-CH3), 6.86 (t, 2JCH = 7.3 Hz, 2H; p-CH3), 2.27 (s, 3H; p-MesCH3), 2.25 (s, 6H; o- MesCH3), 1.62 (d, 2JCH = 11.0 Hz, 2H; PCH3); 13C NMR (100.6 MHz, [D6]THF, 297 K): δ = 156.0 (only observed in the HMBC spectrum, 2JCH coupling with o-Me, 2JCH coupling with p-CH3, and PCH3-B); 11C[N] NMR (100.6 MHz, [D6]THF, 297 K): δ = 156.1 (only observed in the HMBC spectrum, 2JCH coupling with o-Me, 2JCH coupling with p-CH3, and PCH3-B); 31P[19] F NMR (162.0 MHz, [D6]THF, 293 K): δ = 84.3 ppm (s); 31P[20] B NMR (128.4 MHz, [D6]THF, 294 K): δ = 3.2 ppm (s); HR ESI-MS: calc for C12H14N2P+ (M+H) 412.2755, found 412.2786.

Synthesis of 3o: A solution of HCl (2 mL in EtOH, 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 × 4 mL) and subsequently dried in vacuo to yield 6 as a colorless solid (0.189 g, 81%). M.p. (nitrogen, sealed capillary): 93 °C (decomp); ‘H NMR (400.1 MHz, CDCl3, 298 K): δ = 7.46 (d, 2JCH = 7.5 Hz, 4H; c-CH3), 7.16 (t, 2JCH = 7.4 Hz, 4H; m-CH3), 7.05 (t, 2JCH = 7.2 Hz, 2H; p-CH3), 4.68 (d, 2JCH = 12.7 Hz, 1H; CHE), 1.86 (d, 2JCH = 11.1 Hz, 2H; PCH3), 1.23 (d, 2JCH = 14.7 Hz, 18H; PC(CH3)2), 0.28 ppm (s, 9H; Si(CH3)3); 11C[N] NMR (100.6 MHz, CDCl3, 300 K): δ = 133.2 (s, c-CH3), 127.1 (s, m-CH3), 125.1 (s, p- CH3), 28.2 (d, 2JCH = 27.7 Hz, 2H; PCH3), 7.6 (s); HR LiDIA-MS: calc for C10H12N2PSi+ (M–Cl) 412.2755, found 412.2750.
and subsequent washing with n-pentane (3 × 8 mL) gave 7 as a white solid, which was subsequently washed with benzene (3 × 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 THF layered with n-pentane. M.p. (nitrogen, sealed capillary): 118 °C (decomp); 1H NMR (400.1 MHz, CDCl₃, 298 K): δ = 7.57 (d, Jsub = 6.9 Hz, 4H; o-C₆H₄), 7.08 (t, Jsub = 7.3 Hz, 4H; m-C₆H₄), 6.90 (t, Jsub = 7.2 Hz, 2H; p-C₆H₄), 1.31–1.19 (m, 2H; PCH₃B), 1.11 (d, Jsub = 12.6 Hz, 18H; PCH(CH₃)₂), −0.18 ppm (s, 9H; Si(CH₃)₃); 13C(NMR (100.6 MHz, CDCl₃, 300 K): δ = 132.2 (d, Jsub = 6.7 Hz; o-C₆H₄), 126.7 (s; m-C₆H₄), 123.2 (s; p-C₆H₄), 36.2 (d, Jsub = 60.3 Hz; PCH₂(CH₃)₂), 28.2 (m; PCH(CH₃)₂), 22.9 (only observed in the HSQC spectrum, Jcoupl coupling with PCH₂B; PCH₃B), 4.9 ppm (s; Si(CH₃)₃), the signal for ipso-CH₃ is unresolved; 19F(NMR (162.0 MHz, CDCl₃, 298 K): δ = −38.2 ppm (s); 19BF₃(NMR (128.4 MHz, CDCl₃, 299 K): δ = 2.4 ppm (d, Jsub = 48.6 Hz); 19F(NMR (282.4 MHz, CDCl₃, 294 K): δ = −191.7 ppm (br. s); HR ESI-MS: calc. for C₈H₂₀BF₃N₃Si(3-Me,Me) 430.6272, found 430.6273.

**Synthesis of 8 and 9:** PhNCO (2.786 g, 2.54 mL, 23.39 mmol, 1.0 equiv) was added to a solution of 5 (0.673 g, 1.663 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 × 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, CDCl₃, 298 K): δ = 7.33 (d, Jsub = 7.1 Hz, 4H; o-B(C₆H₄), 7.06 (t, Jsub = 7.4 Hz, 4H; m-B(C₆H₄)), 6.96, (t, Jsub = 7.2 Hz, 2H; p-B(C₆H₄)), 6.88–6.08 (br. m, 4H; o-Br(C₆H₄)), 6.77–6.71 (m, 1H; p-Br(C₆H₄)), 1.61 (d, Jsub = 10.9 Hz, 2H; PCH₂B), 1.16 (d, Jsub = 14.2 Hz, 18H; PCH(CH₃)₂) 0.26 ppm (s, 9H; Si(CH₃)₃); 13C(NMR (100.6 MHz, CDCl₃, 299 K): δ = 146.4 (s; ipso-NC₆H₄), 134.4 (s; o-B(C₆H₄)), 128.0 and 127.0 (s; o-NC₆H₄ and m-NC₆H₄), 126.8 (s; m-Br(C₆H₄)), 124.4 (s; p-B(C₆H₄)), 123.5 (s; p-NC₆H₄), 35.8 (d, Jsub = 57.3 Hz; PCH₂B), 26.8 (s; PCH₂(CH₃)₂), 14.6 (only observed in the HSQC spectrum, Jcoupl coupling with PCH₂B; PCH₃B), 0.71 ppm (s; Si(CH₃)₃), the signals for ipso-B(C₆H₄) and NCO are unresolved; 19F(NMR (162.0 MHz, CDCl₃, 298 K): δ = −56.5 ppm (s); 19BF₃(NMR (128.4 MHz, CDCl₃, 298 K): δ = −3.4 ppm (s); HR ESI-MS: calc. for C₈H₂₀BF₃N₃Si 531.3126, found 531.3142. Compound 9: 1H NMR (400.1 MHz, CDCl₃, 298 K): δ = 7.58–7.47 (m, 9H; m-Br(C₆H₄)), 7.41 ppm (d, Jsub = 7.6 Hz, 6H; o-C₆H₄); 13C(NMR (100.6 MHz, CDCl₃, 299 K): δ = 149.1 (s; ipso-C₆H₄); 134.4 (s; CO), 129.84 (s; m-C₆H₄), 129.79 (s; p-C₆H₄), 128.9 ppm (s; o-C₆H₄).

**X-ray crystal structure determinations**

The single-crystal X-ray diffraction studies were carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2)K using Cu-Kα radiation (λ = 1.54187 Å) (1), or Bruker D8 Venture diffractometer with Photon100 detector at 123(2)K using Mo-Kα radiation (λ = 0.71073 Å) (3), with Direct Methods (SHELXS-97)[46] (for 2a) and Dual Space methods (SHELXT)[47] (for 7) were used for structure solution and refinement. (for 7) Hydrogen atoms were localized by difference electron density determination and refined using a riding model. Semi-empirical absorption corrections were applied. 2a and 7 were refined as an inversion twin, for 3a the absolute structure was determined. 

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**Conflict of interest**

The authors declare no conflict of interest.
Keywords: azides · density functional calculations · frustrated Lewis pairs · heterocycles · isocyanates


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


[14] A broad 13C{1H} NMR signal was observed for 3aa at room temperature (δ(C) = 235 Hz), which upon cooling to 223 K splits into two signals at δ = +98.6 and +89.4 ppm in a 93:7 ratio. The structure of these isomers is still to be determined. For comparison, see Ref. [12a].

[15] Note that the geometry of the phenyl analogue of INT2 (INT2<sub>p</sub>) could not be optimized without constraints. For more information see the supporting information.

[16] The computational details for all mechanisms with Ph<sub>p</sub>, Bu<sub>p</sub>, Mes<sub>p</sub>, and TMS<sub>p</sub> can be found in the Supporting Information.

[17] See the Supporting Information.


[36] Only one other example of an iminophosphorane Lewis base in FLP chemistry is reported, see: C. Jiang, D. W. Stephan, Dalton Trans. 2013, 42, 630–637.


[50] CCDC 1896718, 1896719, 1896720, 1896721, 1896722, and 1896723 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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