N-Borane-Substituted Cyclic Phosphine Imides (BCPIs)
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Abstract
Phosphine imides are ubiquitous nucleophiles/Lewis bases in modern organic chemistry. The introduction of unexplored substituents on the phosphine imidoyl nitrogen and/or phosphorus atoms should facilitate the discovery of unprecedented utility for phosphine imides. Herein, we have designed and prepared a novel class of phosphine imides known as N-borane-substituted cyclic phosphine imides (BCPIs). Experimental and theoretical analyses of the electronic structure of BCPIs demonstrate the existence of substantial negative hyperconjugation between the nitrogen and the phosphorus atoms. Given a characteristic nucleophilic/Lewis basic reactivity of BCPIs, we represent the first experimental demonstration that a λ5-oxazaphosphetane species is a key intermediate in the transformation of CO₂ using phosphine imides. Moreover, although it has been previously considered unlikely, the spontaneous heterolysis of a B–Cl bond in a BCPI-coordinated chloroborane has been directly observed, suggesting that such process is a plausible key step in the Lewis acid-promoted generation of borenium species from chloroboranes. These results thus provide evidence of two species that have been missing in contemporary organic chemistry.

Graphical Abstract

Key Words: Phosphine imides; Boron cations; CO₂ transformation; Oxazaphosphetanes; Lewis bases
Introduction

Chemists have conducted much research on the synthesis of molecules that can trigger unprecedented molecular transformations. Moreover, well-designed molecules can provide insight into reaction mechanisms that have so far remained unclear. Indeed, a variety of phosphine imides (R′–NPR₃), also known as iminophosphorananes,¹ have been prepared and used in multiple ways, for example, as nitrogen-based Brønsted bases,² donor ligands for main-group and transition-metal complexes,³ polyphosphazenes,⁴ and organocatalysts.⁵ The multipurpose utility of phosphine imides comes from the characteristic electronic properties of their P–N bonds which have resonance structures including a multiple bond P=N form and a zwitterionic P⁺−N⁻ form (Figure 1A left). Theoretical calculations suggest the predominant contribution from the zwitterionic form that includes a negative hyperconjugation from a lone pair on the N atom to an empty orbital on the P atom.⁶ The reactivity of phosphine imides should be thus designed and modulated based on the manipulation of the aforementioned donor-acceptor interactions via the introduction of appropriate functional groups on the N and P atoms, and/or by the structural constraint (i.e. an acyclic or a cyclic structure) of the molecule.⁷,⁸,¹⁶ In this context, N-boron-substituted phosphine imides, such as B(NPPh₃),⁷ [B(NPBU₃)₂][B(C₆F₅)₃],⁸ and [B₃(NPET₃)₃]Br₂,⁹ have been investigated because the empty π orbitals on the B atoms can regulate the reactivity of the phosphine imides via delocalization.¹⁰ Stephan et al. reported the preparation of acyclic N-boryl phosphine imides (R″₂B–NPR₃), and demonstrated the contribution of a multiple-bond character between the B and N atoms and a zwitterionic P⁺−N⁻ character to the bonding of these molecules (Figure 1B).⁸,¹¹ The corresponding resonance structures were also proposed for the cyclic N-boryl phosphine imides reported by Nöth et al.¹² The synthesis of cyclic/acyclic adducts of the type R₃P(R′)N–BR‴₃ comprising of phosphine imides and boranes (BR‴₃) was also studied by Stephan et al.,¹³ Erker et al.,¹⁴ Bourissou et al.,¹⁵ and Slootweg et al.;¹⁶ however, studies on their reactivity have been limited (Figure 1A). Given this background, we envisioned the synthesis of N-borane-substituted cyclic phosphine imides (BCPIs, Figure 1C) for the exploration of unprecedented molecular transformations utilizing phosphine imides. BCPIs should have sufficient basicity and/or nucleophilicity at their phosphinimidoyl nitrogen atoms due to the absence of the obvious π interaction between the adjacent B atoms, which would clearly distinguish their reactivity, and thus utility from that of N-boryl phosphine imides. The reactivity of BCPIs can be finely tuned via the introduction of appropriate substituents on not only the phosphinimidoyl N/P atoms but also the B atoms. Moreover, the combination of these substituents is a crucial factor in modulating the spatial environment around the phosphinimidoyl moiety.

Herein, we report the synthesis and reactivity of BCPIs, equipped with an imidazolium linker for the construction of the cyclic structure, which can neutralize a formal anionic charge generated on a four-coordinate B atom (Figure 1C). The synthesized BCPIs were successfully
applied to provide evidence for two species that were previously missing from contemporary organic chemistry; i.e. a \( \lambda^5 \)-oxazaphosphetane species that is generated via a formal [2+2] cycloaddition between BCPIs and \( \text{CO}_2 \), and a borenium species with a chloride counterion that is generated via the spontaneous heterolysis of the B–Cl bond in a BCPI-coordinated chloroborane even in the absence of an external halophile.

Figure 1. (A) Resonance structures for phosphine imides and classical Lewis adducts with tricoordinate boranes (BR\(^3\)). (B) \( N \)-Boryl phosphine imides. (C) \( N \)-Borane-substituted cyclic phosphine imides (BCPIs), reported in this work. Cat = catecholato (\( \text{C}_6\text{H}_4\text{O}_2^{2-} \)).

Results and Discussion

The synthesis of BCPIs 3 was attempted via the Staudinger reaction between \( N \)-phosphanyl-substituted imidazolylidene 1, bearing a 2,6-diisopropylphenyl group (Dipp),\(^{17}\) and a boryl azide (Figure 2A), which was designed based on our previous synthesis of \( N \)-phosphine-imide-substituted imidazolylidene (PimImS).\(^{18}\) Treatment of 1 with 9-azido-9-borafluorene (N\(_3\)-B\(_f\), where B\(_f\) is a 9-borafluorenyl group)\(^{19}\) in toluene resulted in the formation of carbene–borane adduct 2a, which was isolated in 71% yield. Then, we synthesized 3a by heating a toluene solution of 2a at 100 °C and 3a was isolated in 90% yield. BCPI 3a was also obtained from the reaction between 1 and N\(_3\)-B\(_f\) without the isolation of 2a in 76% yield. Similarly, we also prepared 3b in 95% yield using bis(pentafluorophenyl)boryl azide (N\(_3\)-B(C\(_6\)F\(_5\))\(_2\)),\(^{20}\) where the formation of both the C–B and N=\( P \) bonds proceeded at room temperature. We were not able to confirm the
generation of a carbene–borane adduct even though we monitored the formation of 3b using NMR spectroscopy. Compounds 2a, 3a, and 3b were unambiguously characterized using multinuclear NMR spectroscopy as well as single-crystal X-ray diffraction (SC-XRD) analysis. In the $^{31}$P NMR spectrum of 3a, a resonance showing the formation of the phosphinimidoyl moiety is observed at $\delta$ 69.9, which is significantly upfield shifted compared to 2a ($\delta$ 95.2). A nearly identical chemical shift was observed in the case of 3b ($\delta$ 70.2), which is clearly different from that of (C$_6$F$_5$)$_2$B–NPtBu$_3$ ($\delta$ 43.6), thus demonstrating the difference in the electronic structures around the P atoms of BCPIs and N-boryl phosphine imides. For comparison, we prepared 5, a silane analogue of BCPIs, using B(C$_6$F$_5$)$_3$ for the methyl abstraction from PimIm 4 bearing a N-trimethylsilyl group (Figure 2B). Compound 5 demonstrates a resonance at $\delta$ 83.5, downfield shifted in comparison with 3a and 3b. These results manifest the critical roles that both the substituents on the N atom (i.e. borane, silyl, or boryl group) and the cyclic structure play in determining the electronic and steric properties of the phosphinimidoyl moieties. In the $^{11}$B NMR spectra, the resonance that supports the generation of a four-coordinate boron species is observed for 3a at $\delta_B$ -1.6 and for 3b at $\delta_B$ -5.9.
The molecular structures of 2a and 3a determined by SC-XRD analysis are shown in Figure 2C and 2D, respectively, demonstrating that the framework of BCPI is constructed via the formation of the carbene–boron bond before the formation of the N=P bond. The molecular structure of the cationic species in 5 is also given in Figure 2E. The geometrical parameters of 3a and 3b (Figure S3) are nearly identical (with the exception of the parameters that are derived from each B-diaryl substituent), and the following discussions thus use those for 3a unless otherwise noted. In 3a and 5, the imidazolium and the C1-N2-P-N3-X (X = B for 3a; X = Si for 5) rings are almost coplanar, i.e. the angles between the two five-membered rings are 3.5° in 3a and 0.8° in 5. The C1–B bond length in 3a (1.671(3) Å) is almost identical to those reported for known carbene–borane adducts (ca. 1.66–1.70 Å) that mediate, via regeneration of frustrated Lewis pairs, the heterolytic cleavage of H; at room temperature or under heating conditions. The N=P bond lengths commonly fall in the range 1.53–1.62 Å, and little difference was found for 3a (1.541(2) Å), 3b (1.536(2) Å), 5 (1.557(3) Å), and (CdF)₂B–NPBu₃ (1.560(3) Å), despite the obvious differences in the chemical environment surrounding the phosphinimidoyl nitrogen atoms.

To gain a deeper insight into the electronic structures of 3a and 3b, a topological analysis of the electron density, ρ (e × r̃_{Bohr}⁻³), was performed using the quantum theory of atoms in molecules (AIM) method based on the results of density-functional theory (DFT) calculations conducted at the PBE0/6-311G(d,p)/ωB97X-D/6-31G(d) level of theory. The following discussions are focused on the results for 3a, shown in Figure 3A, as almost identical conclusions were confirmed with 3b (Figure S13). Figure 3A depicts the bond paths (solid lines connecting...
atoms), bond critical points (BCPs; green dots), and the contour plots of the Laplacian of $\rho$, $\nabla^2\rho$ ($e \times r_{\text{Bohr}}^{-5}$), through a plane defined by the C1, B, and N3 atoms. For BCP1 to BCP8, values of $\rho$, $\nabla^2\rho$, the delocalization indices $\delta(\text{BCP})$, and energy densities $H_{\rho}(E_h \times r_{\text{Bohr}}^{-3})$ are also shown. It should be noted that $H_{\rho}$ represents a total energy density given as the sum of $G_{\rho}$ and $V_{\rho}$, where $G_{\rho}$ is the kinetic energy density and $V_{\rho}$ is the potential energy density. In general, a negative value of $H_{\rho}$ is expected at a BCP included in a covalent bond. Moreover, increased covalency tends to give a value of $G_{\rho}/\rho < 1$ at a BCP, while a value of $G_{\rho}/\rho \geq 1$ is expected for an ionic or a donor-acceptor interaction. This is also consistent with the fact that the C1–B bond in 3a should be classified as a covalent bond, albeit the partial contribution of a donor-acceptor interaction should be involved ($\nabla^2\rho \approx 0; H_{\rho} = -0.11; G_{\rho}/\rho = 0.99$). Similarly, the N2–P and B–N3 bonds have substantial covalency, but they are rather polarized compared to the C1–B bond due to differences in the electronegativity of the B, N, and P atoms (for BCP2: $\nabla^2\rho = 0.27$, $H_{\rho} = -0.12$, $G_{\rho}/\rho = 1.28$; for BCP4: $\nabla^2\rho = 0.12$, $H_{\rho} = -0.11$, $G_{\rho}/\rho = 1.05$). In contrast, the increased $\nabla^2\rho$ and $G_{\rho}/\rho$ values of 0.90 and 1.89, respectively, at BCP3 clearly demonstrate the participation of both covalent and donor-acceptor interactions between the N3 and P atoms. This multiple-bond character can also be rationalized based on the $\delta(\text{BCP})$ values which show the average number of electrons (based on the self-consistent field densities) shared at a BCP, and hence give an insight into the bond order. In fact, the value of $\delta(\text{BCP3})$ is 1.07 and is almost identical to values calculated for BCP5 (1.13) and BCP6 (1.09) involved in the C1–N2 and C2–N2 bonds, respectively, both of which are widely acknowledged to have multiple-bond character through delocalization of electrons over the imidazolium ring. Consequently, the $\delta(\text{BCP})$ values calculated for BCP1 (0.39), BCP2 (0.44), BCP4 (0.54), and BCP8 (0.47) are consistent with single-bond character as the values are nearly half of those calculated for BCP3, BCP5, and BCP6. These results demonstrate that resonance structures shown in Figure 1C would be taken in account for BCPs synthesized in this work, which is also consistent with the results obtained from a natural bond orbital (NBO) analysis (Figures S19).
Figure 3. (A) The quantum theory of AIM bond paths (white lines) and bond critical points (BCPs, green dots) with overlaid contour plots of $\nabla^2 \rho (e \times r_{\text{Bohr}}^{-5})$ through the plane defined by the C1, B, and N3 atoms ($\nabla^2 \rho < 0$ shown in blue; $\nabla^2 \rho > 0$ shown in red) in 3a. Selected atoms are shown for clarity. Values of electron density $\rho (e \times r_{\text{Bohr}}^{-3})$, delocalization indices $\delta (\text{BCP})$, energy densities $H_\rho (E_h \times r_{\text{Bohr}}^{-3})$ and $G_\rho (E_h \times r_{\text{Bohr}}^{-3})$ at the selected BCPs are summarized. (B) Comparison of the energy levels (eV) for selected molecular orbitals in 3a, 3b and 5' (the cationic species in 5). Energy levels for orbitals including the contribution of the lone pair of the phosphinimidoyl nitrogen atom are highlighted in blue. The HOMO and HOMO−2 of 3a are also shown.

Next, we analyzed the frontier molecular orbitals (FMOs) of 3a. The energy levels (eV) of the selected orbitals are given in Figure 3B. The contribution of the lone pair on the N3 atom is confirmed in several of the FMOs, including the HOMO and HOMO−2. An in-phase overlap that forms a $\pi$-bond between the N3 and P atoms is also found in the HOMO−2, which is consistent with the increased electron densities around the N3 atom found in the AIM analysis (Figure 3A). Molecular orbitals that include the lone pair of the phosphinimidoyl nitrogen (such as N3 in 3a) are also found in the FMOs of 3b (e.g. the HOMO and the molecular orbitals between
the HOMO–2 and HOMO–5, Figure S21) and the cationic species in 5 (denoting as 5′ in Figure 3B) (e.g. the HOMO and HOMO–3, Figure S22). A comparison of the energy levels of the FMOs of 3a and 3b shows that the substituents on the B atom would influence the nucleophilicity/Lewis basicity of the N-borane-substituted phosphinimidoyl groups (Figure 3B). Moreover, the replacement of these N-borane moieties with an N-silyl substituent results in a decrease in the corresponding nucleophilicity/Lewis basicity. Thus, the nucleophilicity and/or Lewis basicity would decrease as follows: 3a > 3b >> 5.

We then explored the nucleophilic reactivity of 3a, 3b and 5 toward CO2 as an electrophile (Figure 4A). It is well-known that phosphine imides react with CO2 to give phosphate oxides (O=PR3) and isocyanates (R′–N=C=O). In such reactions, λ5-oxazaphosphetane species have been proposed as a key intermediate. However, there have been no reports on the direct observation and isolation of a λ5-oxazaphosphetane species from the reaction of a phosphine imide and CO2 (or other heterocumulenes). Thus, demonstrating direct evidence for such species in the transformation of CO2 is valuable for the fundamental understanding of the corresponding reaction mechanism.

Treatment of 3a with CO2 (5 atm) at room temperature resulted in the quantitative formation of λ5-oxazaphosphetane 6a within 20 minutes, which was isolated in >99% yield. When 3b was subjected to the identical conditions, 6b was quantitatively obtained after a period of 1 h, and was also isolated in 95% yield. No reaction occurred between 5 and CO2 even at 60 °C after a period of 3 days. In these reactions, we used α,α,α-trifluorotoluene (TFT) as a solvent because 3a is sufficiently soluble in TFT, but the formation of 6a and 6b also proceeded in C6D6 and CD2Cl2. Compounds 6a and 6b were unambiguously characterized using multinuclear NMR spectroscopy as well as by SC-XRD analysis. The 31P NMR spectra show the characteristic chemical shifts of δP –18.5 and –16.8 for 6a and 6b, respectively, and are consistent with the formation of penta-coordinate phosphorus species. The molecular structure of 6a is shown in Figure 4B. The construction of the P-N3-C4-O1 ring is confirmed and the phosphorus atom adopts a distorted trigonal bipyramidal geometry that has the N2 and O1 atoms at the axial positions (N2–P–O1 = 158.3(1)°) and the N3 atom and two C atoms in the trigonal plane. The N3–P (1.673(3) Å) and N2–P (1.899(2) Å) bonds in 6a are notably elongated compared with those in 3a, suggesting a decrease in their bond orders. In contrast, the length of the B1–N3 bond remains almost unchanged (ca. 1.56 Å) through the transformation from 3a to 6a.

λ5-Oxazaphosphetane 6a gradually decomposed to yield N-phosphinoyl isocyanate 7 along with the concomitant formation of 8a at room temperature. These results thus demonstrate the direct observation of a λ5-oxazaphosphetane species as the intermediate in the transformation of CO2 using phosphine imides. Given that the thermolysis of 6a would be promoted by the formation of the thermodynamically favorable P=O bond, we then explored the cleavage of P–
O1 bond in 6a. The reaction between 6a and HB(C₆F₅)₄ afforded 9a in 97% yield (Figure 4A) through the coordination of the carboxylate moiety to the borane (O2–B2 = 1.518(4) Å, Figure 4C). Accordingly, reconfiguration of the geometry around the phosphorus center to form a distorted tetrahedron occurs along with the shortening of the N2–P bond (1.720(3) Å) and the elongation of the B1–N3 bond (1.608(5) Å). The N3–P bond length was almost unchanged at 1.642(3) Å in comparison with that of 6a and thus significantly longer than in 3a. NMR analyses also gave an insight into the electronic state of the P atom in 9a. The resonance at δ 59.9 indicates that the electron density on the P atom in 9a is nearly identical with 3a, although that of 9a should be slightly higher. Based on these experimental data, we conclude that the electron delocalization between the N3 atom and the adjacent carbonyl group partially weakens the negative hyperconjugation between the N3 and P atoms, while the increased π-donation from the imidazolium unit to the P atom eventually compensates for the loss of electron density on the P atom. Results of the AIM analyses also support this conclusion, as exemplified by increased values of ρ (0.16), ∇²ρ (0.30), and G/ρ (1.30) in 9a (Figures S15). It should be noted that no BCP was found between the P and O2 atoms from calculations at the current level of theory.

**Figure 4.** (A) Synthesis of 6a and 6b and transformations of 6a. Yield of isolated products is given. “Based on the molar amount of the loading 6a. TFT = α,α,α-trifluorotoluene. (B) Molecular...
structure of 6a, drawn with thermal ellipsoids at 30% probability; H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N2 1.341(4), C1–B1 1.626(4), N2–P 1.899(2), P–N3 1.673(3), N3–B1 1.556(4), P–O1 1.831(2), O1–C2 1.334(5), C4–O2 1.212(4), C4–N3 1.371(3); B1–C1–N2 117.6(2), C1–N2–P 114.2(2), N2–P–N3 84.6(1), P–N3–B1 128.1(2), N3–B1–C1 94.7(2), N3–P–O1 73.7(1), P–O1–C4 89.2(2), O1–C4–N3 102.2(2), C4–N3–P 94.8(2), N2–P–O1 158.3(1). (C) Molecular structure of 9a, drawn with thermal ellipsoids at 30% probability; H atoms (except B2–H) are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N2 1.367(5), C1–B1 1.624(5), N2–P 1.720(3), P–N3 1.642(3), N3–B1 1.608(5), N3–C4 1.397(4), O2–C4 1.228(5), C4–O1 1.291(4), O1–B2 1.518(4); B1–C1–N2 116.2(3), C1–N2–P 114.7(3), N2–P–N3 92.7(2), P–N3–B1 119.8(2), N3–B1–C1 96.2(3), B1–N3–C4 122.8(3), N3–C4–O2 120.5(3), C4–O1–B2 122.7(3).

We also explored the reaction between 3a and CatBCl (Cat = catecholato, C₆H₄O₂⁺) to examine whether the exchange of the B⁺ unit with a CatB unit could proceed or not. However, the quantitative formation of a borenium species 10a including a Cl⁻ counterion was unexpectedly observed (Figure 5B). This borenium 10a was isolated in 83% yield, and its molecular structure was unambiguously confirmed by NMR and SC-XRD analyses (vide infra).

It is well-known that borenium species II are furnished via the formal substitution of a leaving group (X⁻) with an external nucleophile (Nu) in the presence of a Lewis acid (LA) (Figure 5A). Two mechanisms have been commonly proposed for the formation of II following the generation of a classical Lewis acid–base adduct (CLA). Path A involves a stepwise mechanism that proceeds via B–X heterolysis to yield borenium species I followed by the subsequent capture of X⁻ by LA. In path B, these steps proceed in a concerted manner. Previous studies have suggested that path A would only be plausible when the leaving groups X⁻ are sufficiently stable and spontaneously dissociate from the CLA, such as X = I, OTf, and NTf₂ (where Tf is trifluoromethanesulfonyl). Conversely, the reaction that proceeds via the cleavage of the relatively strong B–Cl bonds is believed to take place through path B (or an analogous associated transition state), given the addition of LA is predominantly required to abstract the Cl⁻ from the boron atoms. To date, there has been no report on either the direct isolation of a borenium species including the Cl⁻ counterion via the reaction between a chloroborane and Nu in the absence of LA, nor has there been one that provides direct evidence of the interconversion between borenium species with Cl⁻ and [Cl⁻–LA]+ counterions.

In the ¹H NMR spectrum of 10a, the resonance of H1 (the atomic labelling is shown in Figure 5C) is observed at δ = 10.4, which suggests the formation of a hydrogen bonding interaction with Cl⁻ in CD₂Cl₂. This result is consistent with the results from the SC-XRD analysis that show the participation of a hydrogen bonding interaction between these atoms (H1⋯Cl⁻ = 2.47 Å,
Figure 5C). In addition, the AIM analysis also showed the participation of several non-covalent interactions between the Cl\(^-\) and P-\(^5\)Bu \(^8\)groups (Figure S16). In the \(^{31}\)P NMR spectrum, the resonance is observed at \(\delta = 106.5\), demonstrating a substantial decrease in the electron density on the P atom via the formation of a \(\pi\)-bonding interaction between the lone pair on the N3 atom and the empty p orbital on the B2 atom. In the \(^{11}\)B NMR spectrum, two independent resonances for the tetracoordinate B1 and tricoordinate B2 atoms are observed at \(\delta = 0.7\) and 25.0, respectively. For comparison, comparable chemical shifts were reported for Et\(_2\)P=N(BCat)[B(C\(_8\)F\(_5\))\(_3\)] at \(\delta = 6.4\) and 28.0.\(^{13b}\) These results establish that the solvated structure of 10a is nearly identical with the structure corroborated by the SC-XRD analysis shown in Figure 5C. The structural parameters of the 3a moieties in 9a and in 10a, with the exception of the B1–N3 bond lengths (1.608(5) in 9a vs 1.660(4) Å in 10a), are comparable.

Subsequently, we explored the reactivity of 10a toward an external Lewis acid. The reaction between 10a and CatBCl (1.1 equiv.) quantitatively afforded borenium species 11a with a [CatBCl\(_2\)]\(^-\) counterion (Figure 5B). Compound 11a could also be prepared via treatment of 3a with 2.0 equivalents of CatBCl. The molecular structure of 11a was confirmed by NMR and SC-XRD analyses (Figure S10). We also confirmed the quantitative regeneration of 10a by mixing 11a and 3a (1.1 equiv.). Although we could not experimentally confirm the generation of a CLA species under the present reaction conditions, the molecular structure of 3a–B(Cat)Cl was optimized theoretically. Three isomers (CLA1 with a B1-N3-B2-Cl angle of 53.1°, CLA2 with a B1-N3-B2-Cl angle of 273.1°, and CLA3 with a B1-N3-B2-Cl angle of 144.3°) are predicted at the \(\omega\)B97X-D/6-311+G(d,p)/\(\omega\)B97X-D/6-31G(d)/PCM(CH\(_2\)Cl\(_2\)) level of theory. The structure of CLA1 is given in Figure 5D, and those of CLA2 and CLA3 are given in Figure S23. The relative Gibbs energies of these CLAs are found to be \(-28.2 \sim -28.8\) kcal mol\(^{-1}\) with respect to [3a + CatBCl] (\(+0.0\) kcal mol\(^{-1}\)), which shows that the formation of the CLAs is thermodynamically favorable. The heterolysis of the B–Cl bond in CLA1 and CLA2 was theoretically predicted to be essentially barrierless. For example, Int1 (\(-29.3\) kcal mol\(^{-1}\)) was furnished from CLA1 via TS1 (\(-26.7\) kcal mol\(^{-1}\)) and would yield 10a (\(-39.3\) kcal mol\(^{-1}\)) with ease (Figure 5D; for details of the reaction from CLA2, see Figure S23). Importantly, these results suggest that borenium I (cf. 10a) is an intermediate in the formation of borenium II (cf. 11a) from a Nu (cf. 3a) and CatBCl (2.0 equiv.), demonstrating that path A shown in Figure 5A would be plausible even for chloroboranes.
Figure 5. (A) A Lewis acid-promoted generation of borenium species via the cleavage of B–X bonds. Nu: neutral or anionic nucleophiles; LA: Lewis acids. (B) Syntheses of 10a and 11a from 3a and CatBCl (Cat = catecholato, C₆H₄O₂⁻). NMR yields are given. Yield of isolated products is given in parenthesis. (C) Molecular structure of 10a, depicted with thermal ellipsoids at 30% probability; H atoms except H1 are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N2 1.365(3), C1–B1 1.608(3), N2–P 1.710(2), P–N3 1.632(2), N3–B1 1.660(4), N3–B2 1.426(3); B1–C1–N2 116.3(2), C1–N2–P 114.4(2), N2–P–N3 95.5(1), P–N3–B1 115.8(1), N3–B1–C1 97.7(2), B1–N3–B2 116.7(2). (D) Theoretical studies of the formation of 10a via 3a–B(Cat)Cl, calculated at the oB97X-D/6-311+G(d,p)//oB97X-D/6-31G(d)/PCM(CH₂Cl₂) level of theory. Relative Gibbs energies (kcal mol⁻¹) are given with respect to [3a + CatBCl] (+0.0 kcal mol⁻¹). Optimized structures for CLA1, TS1, and Int1 are also shown.
Conclusions

N-Borane-substituted cyclic phosphine imides (BCPIs) have been synthesized via the Staudinger reaction between an N-phosphanyl-substituted imidazolylidene and boryl azides. Based on both experimental and theoretical analyses, the presented BCPIs are found to involve negative hyperconjugation between the phosphine imidoyl nitrogen and the phosphorus atoms. The reactivity of BCPIs was also explored using CO$_2$ and CatBCl. In a reaction with CO$_2$, a $\lambda^2$-oxazaphosphetane species was isolated and demonstrated to be a key intermediate in the transformation of CO$_2$ using phosphine imides. Moreover, in a reaction with CatBCl, the spontaneous heterolysis of the B–Cl bond in the BCPI-coordinated chloroborane was directly observed. This process would be thus viable as a key step in the Lewis acid-promoted generation of borenium species from chloroboranes. These results successfully provide evidence for two species that have been missing in contemporary organic chemistry. Further research on the application of BCPIs in the fields of organic and organometallic chemistry are ongoing in our group.

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Competing interests

The authors declare there are no competing interests.

Author contributions

Y.H. conceived and directed this project. S.N. and T.H. performed the experiments. Y.H. performed theoretical calculations. Y.H. prepared this manuscript with feedbacks from all authors.

Data availability

Data generated or analyzed during this study are provided in full within the published article and its supplementary materials.

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Chemistry of \((\text{Di-}t\text{-butylphosphanyl})\text{imino})-\text{(2,2,6,6-tetramethylpiperidino)borane}.


28. We also carried out a reaction between 6a and HSiEt$_3$; however, only thermal decomposition of 6a to 7 and 8a was observed.


Vedejs *et. al.* proposed that a boronopyridinium salt is the preferred classification of the π-conjugated borenium analogue, as it allows the contribution of a canonical structure including the carbene–borenium adduct to be considered. In this context, a boron-substituted pyridinium chloride might be also involved in the π-conjugated borenium analogues.

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\begin{align*}
\text{B(OH)}_2 & \quad \text{N} \quad \text{H} \quad \text{Cl}^- \\
\text{N} \quad \text{H} \quad \text{Cl}^- & \quad \text{B(OH)}_2 \\
\end{align*}
\]