

Review

Triphenylborane in Metal-Free Catalysis

Suresh Mummadi ^{1,*}  and Clemens Krempner ^{2,*}¹ Department of Natural Sciences, The University of Virginia's College, Wise, VA 24293-4400, USA² Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA

* Correspondence: svm3se@uvawise.edu (S.M.); clemens.krempner@ttu.edu (C.K.)

Abstract: The development and application of new organoboron reagents as Lewis acids in synthesis and metal-free catalysis have dramatically expanded over the past 20 years. In this context, we will show the recent uses of the simple and relatively weak Lewis acid BPh₃—discovered 100 years ago—as a metal-free catalyst for various organic transformations. The first part will highlight catalytic applications in polymer synthesis such as the copolymerization of epoxides with CO₂, isocyanate, and organic anhydrides to various polycarbonate copolymers and controlled diblock copolymers as well as alternating polyurethanes. This is followed by a discussion of BPh₃ as a Lewis acid component in the frustrated Lewis pair (FLP) mediated cleavage of hydrogen and hydrogenation catalysis. In addition, BPh₃-catalyzed reductive N-methylations and C-methylations with CO₂ and silane to value-added organic products will be covered as well along with BPh₃-catalyzed cycloadditions and insertion reactions. Collectively, this mini-review showcases the underexplored potential of commercially available BPh₃ in metal-free catalysis.

Keywords: triphenyl borane; metal-free catalysis; Lewis acid; frustrated Lewis pair; cycloaddition; hydrogenation; hydrosilylation; polymerization; carbon dioxide

1. Introduction

Last year marked the 100th anniversary of the discovery of triphenyl borane, BPh₃, the first isolated triaryl borane by E. Krause and R. Nitsche [1]. The authors obtained BPh₃ as a crystalline solid through the treatment of BF₃ with excess phenyl magnesium bromide followed by distillation under vacuum. About 50 years later, its solid-state structure was determined by single crystal X-ray crystallography [2]. The results revealed a trigonal planar coordination environment for boron with the three phenyl rings being tilted by about 30° toward the plane.

BPh₃ has found widespread application as a promoter in the hydrocyanation of olefins in the presence of Ni complexes and is used industrially by Du Pont for its hydrocyanation of butadiene to adiponitrile, a nylon intermediate [3]. In addition, BPh₃ has been employed extensively as a diphenyl boryl transfer agent in the synthesis of boron-containing heterocyclic materials with remarkable photophysical properties, such as electro- and photoluminescence and aggregation-induced emission (AIE) [4–17]. BPh₃ is a relatively weak Lewis acid that forms Lewis acid–base adducts with pyridine and a wide variety of aliphatic amines [18]. These stable adducts have found use as catalysts for the polymerization of acrylic esters [3], as antifouling reagents in marine environments [19–21] and as agrochemical fungicides [22–24].

Despite its early discovery and structural simplicity, BPh₃ has not risen to the same prominence amongst scientists in academia as has its ingenious perfluorinated and highly Lewis acidic counterpart, B(C₆F₅)₃, first reported in 1963 [25]. Perhaps one major factor that has caused BPh₃ to lag behind B(C₆F₅)₃, particularly in the emerging field of metal-free Lewis acid catalysis, is its comparably low Lewis acidity [26]. As high Lewis acidity is often key to the activation and rapid catalytic transformation of organic substrates, it is not a surprise that B(C₆F₅)₃ has been at the forefront of current research in metal-free



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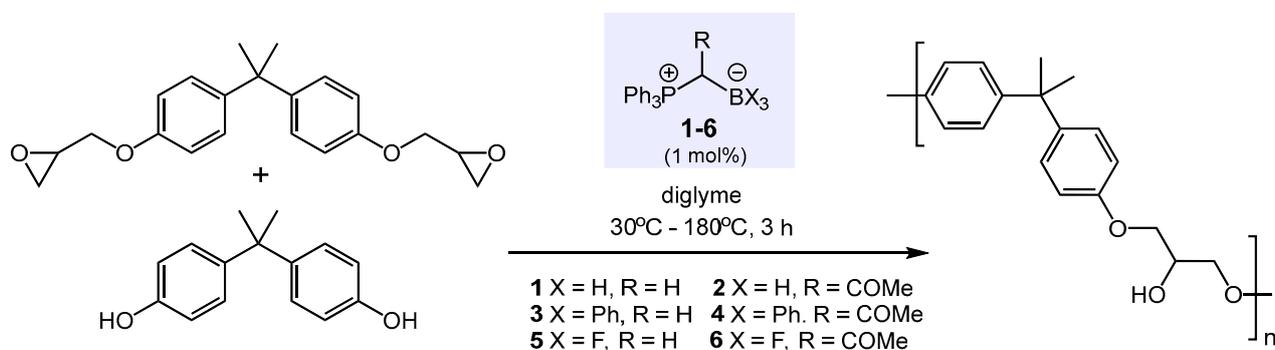
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catalysis [27–36]. However, as the development and application of new boron Lewis acids have expanded at an amazing pace over the past 20 years, it has also become apparent that tuning the Lewis acidity of the catalyst can be an important factor in achieving new modes of substrate activation and selectivity. A prime example of this development has been the application of frustrated Lewis pairs (FLPs) [37–39] in catalytic hydrogenations of unsaturated organic molecules. Work from various groups has shown that weaker Lewis acid components may exhibit better performances, improved functional group tolerances, or different selectivities [40–45].

In this context, this mini-review aims to showcase the underexplored potential of commercially available and weakly Lewis-acidic BPh_3 in metal-free catalysis. Particular emphasis is given to the role of BPh_3 as a catalyst in polymer synthesis, in frustrated Lewis pair (FLP) mediated hydrogen cleavage, and hydrogenation catalysis as well as transformations of CO_2 to value-added organic products and Lewis acid catalyzed cycloadditions and insertion reactions.

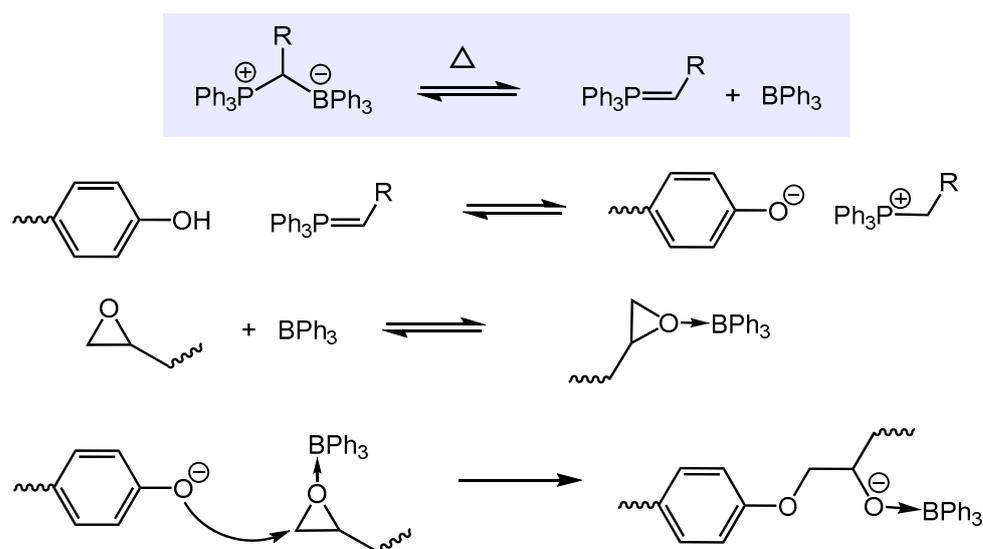
2. BPh_3 in Polymerization Catalysis

In developing effective “latent catalysts” for the curing of epoxy resins that overcome issues associated with previously utilized systems, such as poor solubility and hygroscopicity, Endo and co-workers studied Lewis pairs of general formula $\text{Ph}_3\text{P}^+\text{CHR}^-\text{BX}_3$, where $\text{X} = \text{H}, \text{Ph}, \text{F}$ (Scheme 1) [46,47]. Most of these air- and moisture-stable zwitterionic phosphonium borates **1–6**, derived from reactions of the respective boranes with phosphonium ylides, proved to be active pre-catalysts in the co-polymerization of bisphenol A and bisphenol A diglycidyl ether at high temperatures (Scheme 1). The pre-catalyst activity at 120°C was found to be in the following order: **4** > **2** > **1** > **3** > **5** > **6**. The fact that BPh_3 -adduct **4** and BH_3 -adduct **2** converted the bisphenol A diglycidyl ether within 3 h to ca. 90% and 70%, respectively, whereas BF_3 -adduct **6** was essentially inactive, impressively shows the importance of steric and electronic parameters in the design of Lewis pairs as active polymerization catalysts.



Scheme 1. Catalytic copolymerization of bisphenol A and bisphenol A diglycidyl ether.

The key to the catalytic activity of the phosphonium borate catalysts **1–6** was assumed to be their thermally induced dissociation to BX_3 and $\text{Ph}_3\text{P}=\text{CHR}$, with the degree of dissociation being a sensitive function of temperature as well as the strength of the C-B bond (Scheme 2). The significantly better performances of the BPh_3 -ylide and BH_3 -ylide adducts **4** and **2** compared to the BF_3 -ylides **5** and **6** have been attributed to their weaker B-C bonds due to the lower Lewis acidity of BPh_3 and BH_3 . Upon dissociation of the adduct, the resulting phosphonium ylide serves as an initiator deprotonating the phenolic OH group of bisphenol A to generate a phenoxide anion. BX_3 activates, as a Lewis acid, the epoxide functionality, facilitating its ring-opening via nucleophilic attack of the phenoxide anion. Whether BX_3 remains to be intact as a catalyst during the course of the reaction is questionable given the harsh conditions and the Bronsted acidity of bisphenol A.



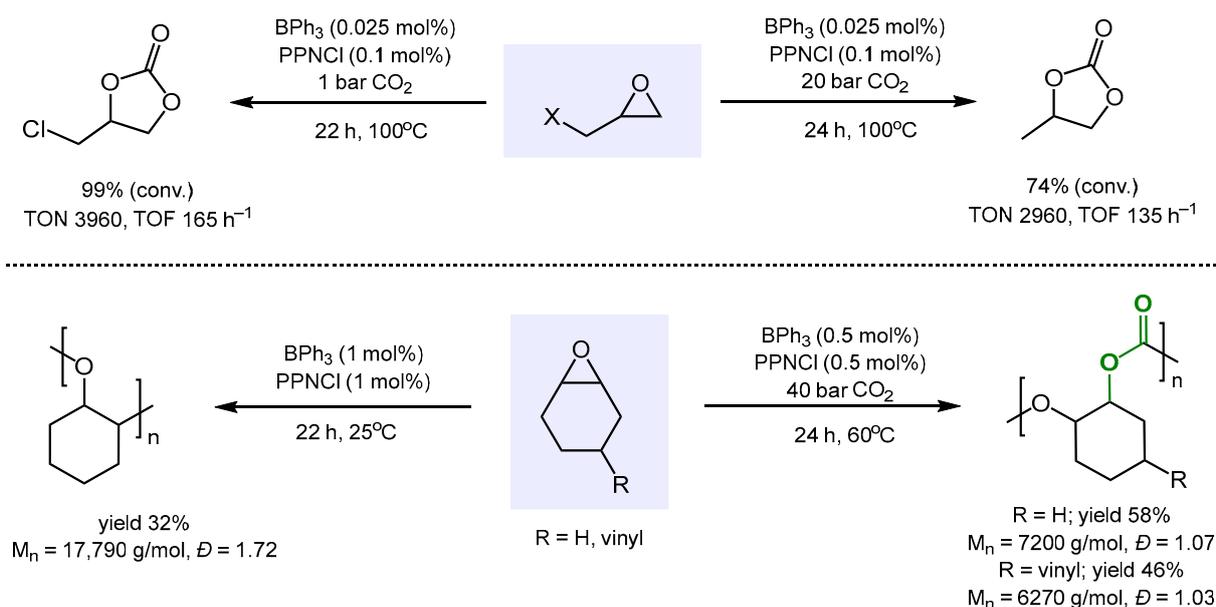
Scheme 2. Proposed mechanistic steps of the catalytic copolymerization of bisphenol A and bisphenol A diglycidyl ether.

The past decade has witnessed increasing interest in the metal-free catalyzed formation of cyclic organic carbonates and polycarbonates from epoxide monomers and CO_2 as an alternative to metal-based catalysts [48–51]. Recent reports from Feng [50] and Darenbourg [51] demonstrated that metal-free Lewis pairs can be utilized as effective catalysts in the copolymerizing of propylene oxide (PO) with CO_2 or carbonyl sulfide (COS). The catalyst systems comprised triethyl borane as a Lewis acid, and amines, onium salts, or alkoxides as Lewis bases.

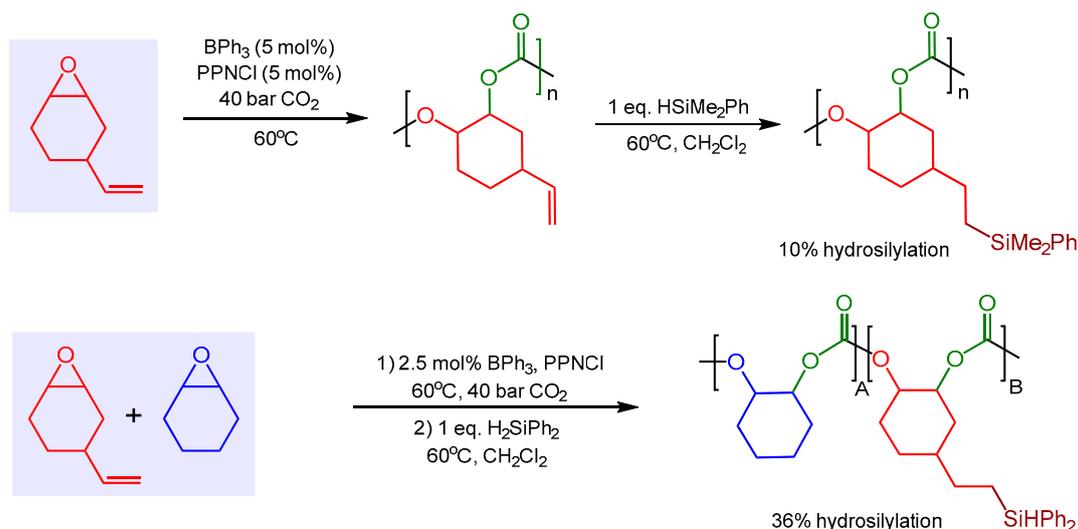
The Kerton group investigated the activity of BPh_3 and $\text{B}(\text{C}_6\text{F}_5)_3$ as catalysts and bis(triphenylphosphine)iminium chloride (PPNCl) as a co-catalyst for the reaction of propylene oxide (PO) and CO_2 at 100°C (Scheme 3) [52]. Both were active catalysts in generating propylene carbonate under identical conditions. These findings were in stark contrast with previous work using triethyl borane as the catalyst, which produced poly(propylene carbonate) [50]. It is worthwhile noting that based on initial rate measurements, the catalyst system BPh_3 /PPNCl was more than five times faster than $\text{B}(\text{C}_6\text{F}_5)_3$ /PPNCl. This is most likely due to the significantly higher Lewis acidity of $\text{B}(\text{C}_6\text{F}_5)_3$, which binds much more strongly to the Cl^- anion of co-catalyst PPNCl than BPh_3 does. Consistent with kinetic studies revealing that lowering the CO_2 pressure increases the reaction rate, BPh_3 catalyzed the reaction of epichlorohydrin with CO_2 , even under atmospheric CO_2 pressure, to give the respective cyclic carbonate as the sole product.

In addition, BPh_3 was found to catalyze the copolymerization of CO_2 with cyclohexene oxide (CHO) and vinyl cyclohexene oxide (VCHO), respectively, at low catalyst loadings. Polycarbonates with high numbers of averaged molecular weights and excellent polydispersities were obtained. In the absence of CO_2 , BPh_3 catalyzed the ring opening of CHO to give the epoxide homopolymer (Scheme 3).

In a follow-up study, Kerton and co-workers investigated the ability of BPh_3 to catalyze the addition of Si–H groups onto a vinyl-substituted polycarbonate [53]. In a ‘one-pot’ sequence, BPh_3 catalyzed both reactions: the copolymerization of VCHO and CO_2 to polycarbonate followed by the hydrosilylation of the vinyl groups in the polymer with phenyl dimethyl silane to give side-chain silylated polycarbonate (Scheme 4). Perhaps for steric reasons, the degree of hydrosilylation of polycarbonate was only 10%. However, when using a polycarbonate terpolymer derived from CHO, VCHO, and CO_2 , the degree of hydrosilylation could be increased to 36%, in this case with H_2SiPh_2 as the hydrosilylation reagent.



Scheme 3. BPh₃-catalyzed formation of cyclic carbonates and polycarbonates.



Scheme 4. Sequential BPh₃-catalyzed copolymerization and hydrosilylation.

In 2021, Kerton et al. disclosed the BPh₃/PPNCI catalyzed copolymerization of organic anhydrides and epoxides [54]. Cyclohexene oxide (CHO), vinyl cyclohexene oxide (VCHO) and also limonene oxide (LO) could be polymerized with phthalic anhydride (PAH) and *cis*-4-cyclohexene-1,2-dicarboxylic anhydride (CDA), respectively, to give perfectly alternating copolymers with excellent polydispersities (Figure 1).

In addition, the authors discovered that these perfectly alternating co-polymers can be further polymerized to form controlled diblock copolymers using BPh₃/PPNCI as the catalyst system. For example, PAH was first allowed to react with excess CHO to generate copolymer I. Once the full conversion of PAH was achieved, the second anhydride, CDA, was added and allowed to react to completion, resulting in the selective formation of controlled diblock copolymer II (Scheme 5). Similarly, by sequentially adding CO₂ to the in situ generated copolymer I, controlled diblock copolymer III could be obtained again with high selectivity and excellent polydispersities. It is worthwhile noting that the markedly stronger Lewis acid B(C₆F₅)₃ was not an active catalyst either for epoxide/anhydride copolymerization or for epoxide/anhydride/CO₂ block copolymerizations. However, it

was found that when $B(C_6F_5)_3$ was added to diblock copolymer III, the carbonate block of the polymer was depolymerized to give the respective cyclic carbonate.

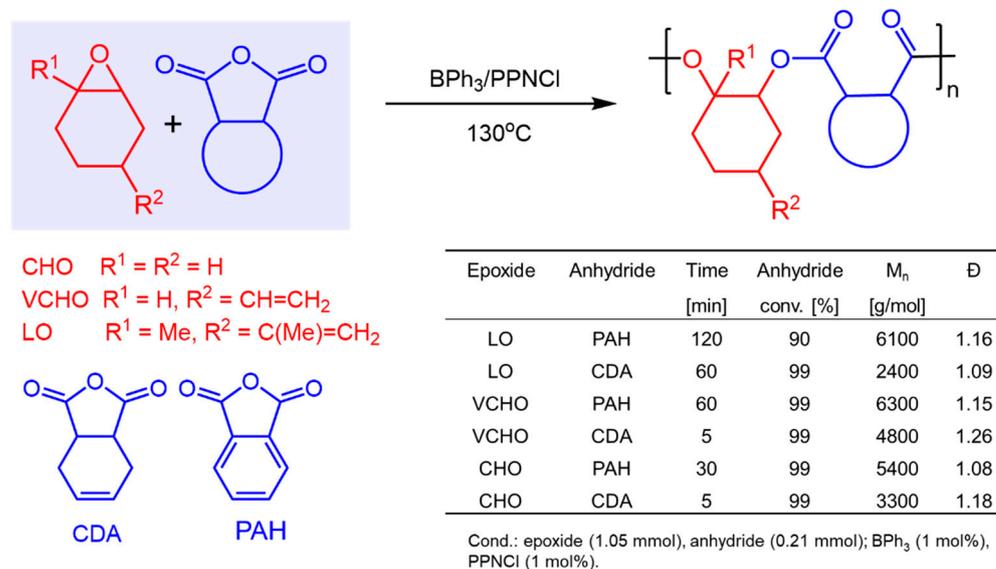
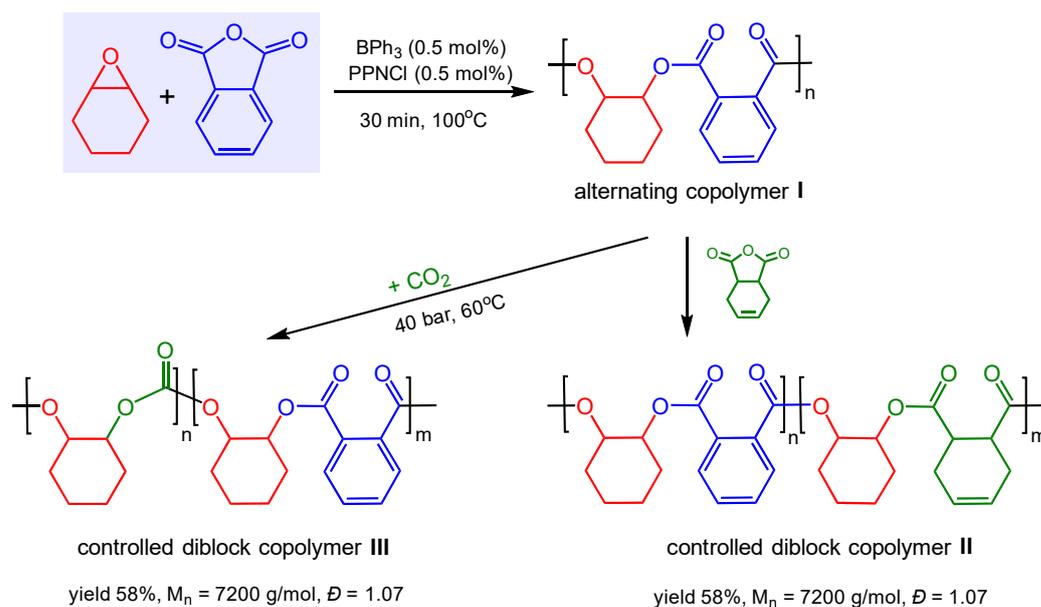


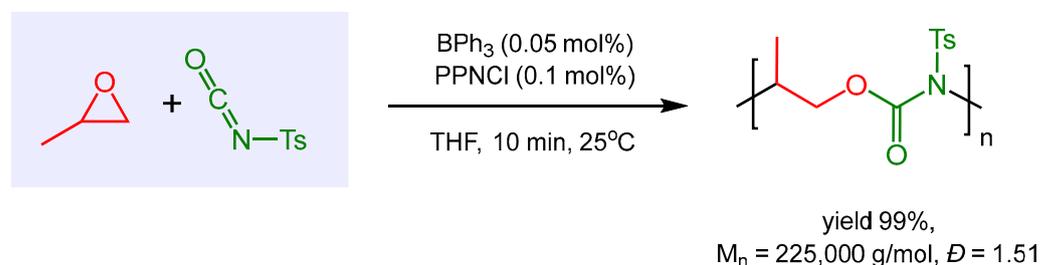
Figure 1. BPh_3 -catalyzed copolymerization of organic anhydrides and epoxides.



Scheme 5. BPh_3 -catalyzed copolymerization to alternating copolymers and controlled diblock copolymers.

Gnanou, Feng, and co-workers investigated triethyl borane (BEt_3) catalyzed copolymerizations of epoxides with organic isocyanates to polyurethanes [55], challenging transformations due to the propensity of most isocyanates to undergo side-reactions such as homopolymerization, cyclotrimerization and [2 + 3] cycloaddition with epoxides. Strongly electron-withdrawing p-tosyl isocyanate (TSI) was found to be the most suitable substrate selectively undergoing copolymerization with a range of epoxides to form almost perfectly alternating polyurethanes (less than 1% ether linkages in the polymer) in high yields and purities. Interestingly, when investigating the impact of the Lewis acidity of the borane catalyst on the rate of propylene oxide/TSI copolymerization, it was found that with BPh_3 , a stronger Lewis acid than BEt_3 , the reaction occurred explosively with the release of large amounts of heat. Astonishingly, with very low catalyst loadings of 0.05 mol% BPh_3 and

0.1 mol% PPNCI, complete polymerization was accomplished within 10 min with turnover frequencies of over $10,000 \text{ h}^{-1}$, and a remarkably high number of averaged molecular weight ($M_n = 225,000 \text{ g/mol}$), exclusively alternating polyurethane structure and a polydispersity of 1.51. Unfortunately, a substrate scope with this highly active and selective catalyst system was not investigated (Scheme 6).



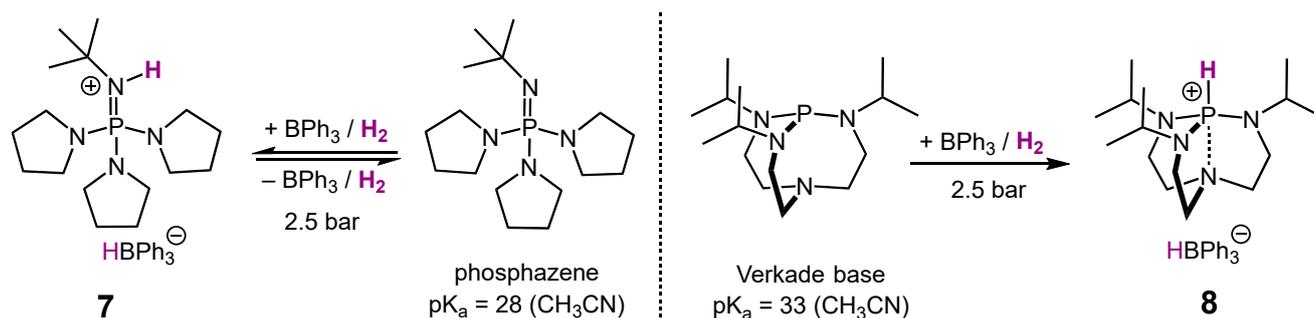
Scheme 6. BPh₃-catalyzed copolymerization of propylene oxide (PO) and p-tosyl isocyanate (TSI).

3. BPh₃ as an FLP Component in Hydrogenation Catalysis

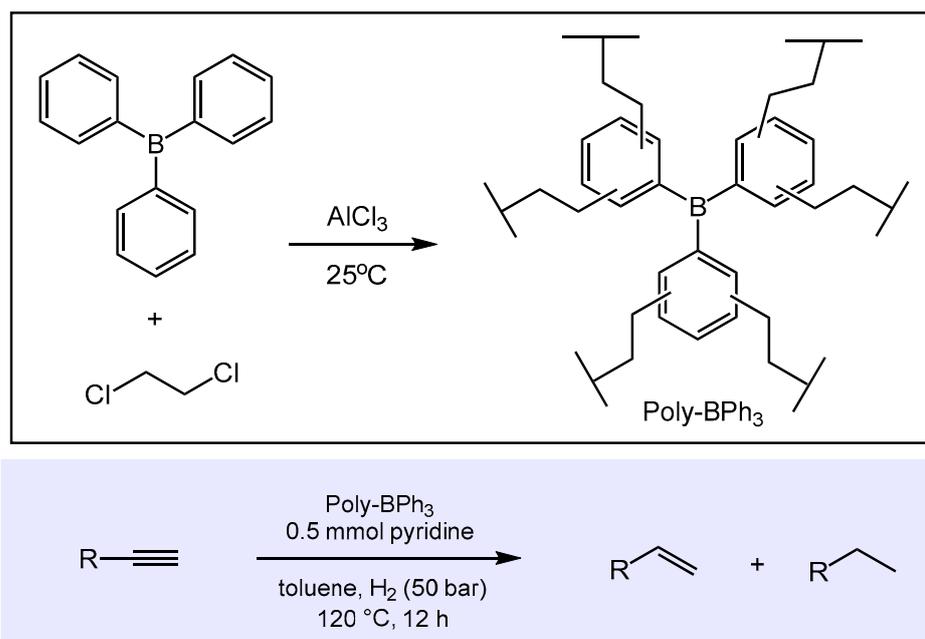
Stephan and co-workers' discovery that Lewis acidic boranes can actively participate in the heterolytic cleavage of H₂ via a frustrated Lewis pair (FLP) approach [37–39] opened the door to the design of metal-free catalysts for the hydrogenation of unsaturated organic substrates [56–60]. Briefly, FLPs comprise sterically encumbered Lewis acid–base pairs, unable to form Lewis acid–base adducts due to unfavorable steric interactions. As a result, Lewis acidity and basicity of the individual FLP components remain unquenched, thus enabling the heterolytic cleavage of H₂, a key step in catalytic hydrogenation reactions [41–45]. Typically, active FLP catalysts are comprised of strongly Lewis acidic, often highly fluorinated or chlorinated aryl boranes coupled with relatively weak N- or P-containing Lewis bases. Theoretical studies concerning the thermodynamic feasibility of the FLP-mediated H₂ cleavage, however, suggested that weak Lewis acids could be active as well, provided that a sufficiently strong base is present [61]. In this context, it is worthwhile noting that Stephan, in one of his seminal papers [38], disclosed the stoichiometric H₂ cleavage utilizing the FLPs B(C₆F₅)₃/P(Bu^t)₃ and BPh₃/P(Bu^t)₃. The former FLP with B(C₆F₅)₃ ($\Delta H_{\text{HA}} = -112 \text{ kcal/mol}$) quickly and quantitatively generated the phosphonium borate salt [HB(C₆F₅)₃][HP(Bu^t)₃] at room temperature, whereas with less acidic BPh₃ ($\Delta H_{\text{HA}} = -74.4 \text{ kcal/mol}$) salt [HBPh₃][HP(Bu^t)₃] was formed in only 33% yields after 24 h. However, theoretical calculations by Papai and co-workers appear to contradict the effectiveness of BPh₃/P(Bu^t)₃ to cleave H₂ as the reaction was calculated to be endergonic ($\Delta G_{\text{R}} = +18.2 \text{ kcal/mol}$), while for B(C₆F₅)₃/P(Bu^t)₃ the reaction with H₂ was exergonic ($\Delta G_{\text{R}} = -14.7 \text{ kcal/mol}$) [61].

Building on these and other results [62,63], Krempner et al. employed the bulky organosuperbases Verkade base ($\text{p}K_{\text{a}} = \sim 33$ in CH₃CN) and phosphazene ($\text{p}K_{\text{a}} \sim 28$ in CH₃CN) in combination with BPh₃ (Scheme 7) [64]. Upon exposure to H₂, both FLPs instantly generated the corresponding borate salts **7** and **8** in yields of 71% and 85%, resp. Solutions of **8** appeared to be thermally stable, while **7** in solution quickly released H₂ when heated to 60 °C, indicating reversibility of heterolytic hydrogen cleavage, which is key to the development of effective hydrogenation catalysts. In fact, BPh₃/phosphazene was demonstrated to be an active FLP catalyst system in the quantitative hydrogenation of the N-benzylidene aniline to N-benzyl aniline in THF as solvent.

An interesting extension of this concept was recently introduced by Hu and co-workers for the FLP-catalyzed hydrogenation of alkynes [65]. Because the molecular FLP BPh₃/pyridine thermally degraded during hydrogenation of phenylacetylene (conversion 12% after 12 h at 120 °C and 50 bar H₂), the group developed a polymeric Lewis acid based on BPh₃. The synthesis is illustrated in Scheme 8 and involves a classical Friedel–Crafts reaction of BPh₃ with 1,2-dichloroethane in the presence of AlCl₃.



Scheme 7. FLP-mediated stochiometric H₂-cleavage and catalytic hydrogenation of N-benzylidene aniline.

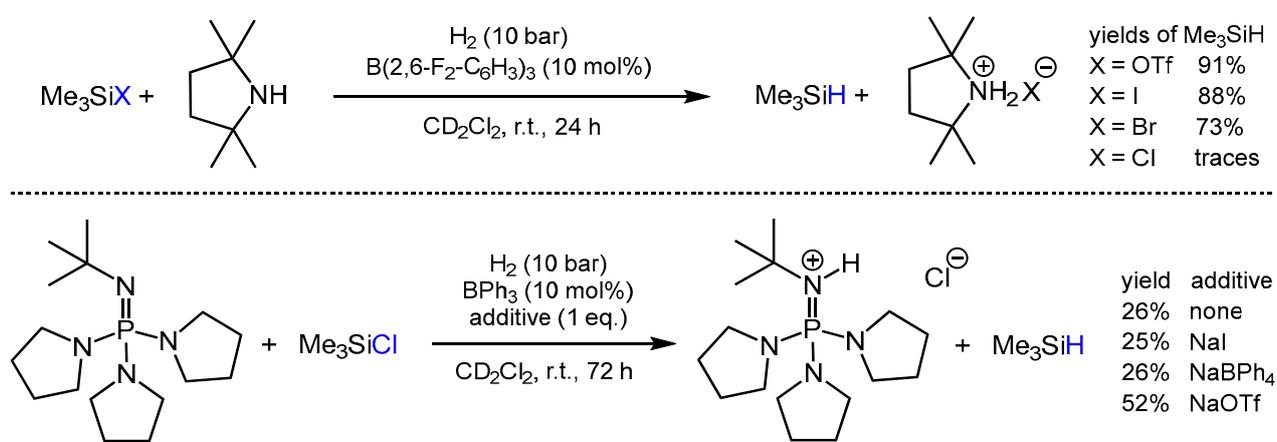


Scheme 8. Synthesis and catalytic activity of Poly-BPh₃ in the FLP-mediated semi-hydrogenation of alkynes to alkenes.

This polymeric Lewis acid, Poly-BPh₃, combined with pyridine as the Lewis base was shown to be active in the semi-hydrogenation of a variety of aliphatic and aromatic terminal alkynes at 120 °C to preferentially give the corresponding alkenes. The Lewis acid component of this FLP, Poly-BPh₃, is reusable without loss of catalytic activity after being recovered from the reaction mixture, and appears to be thermally and hydrolytically remarkably stable.

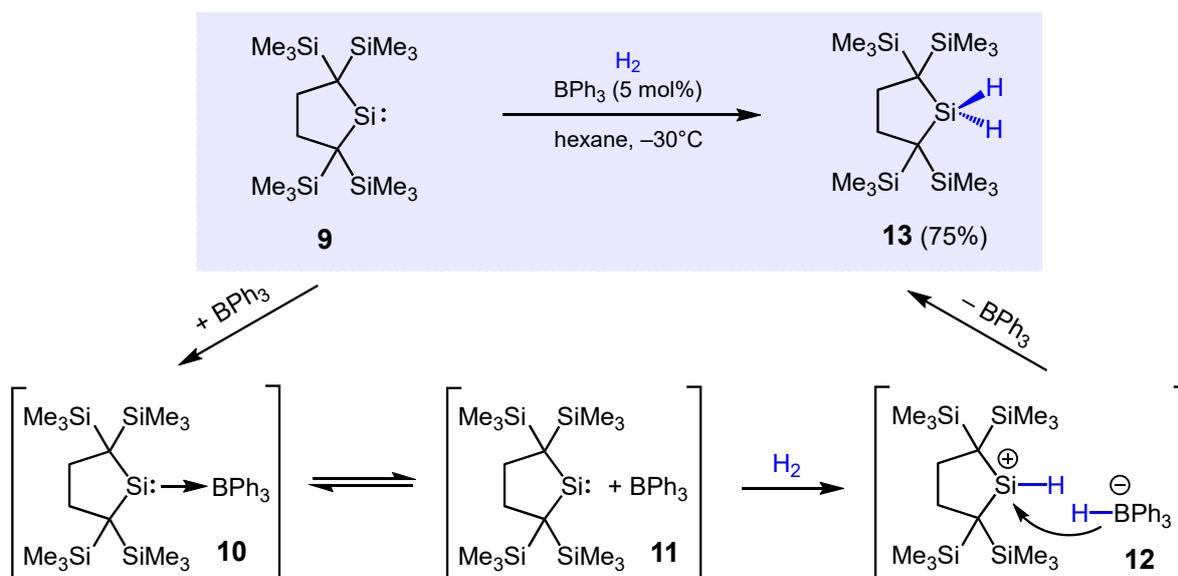
Recent developments concerning iridium- and ruthenium-catalyzed hydrogenations of organosilicon compounds [66–70] motivated the Cantat group to design FLP catalysts for the metal-free hydrogenation of various organosilanes with Si-X bonds (X = OTf, I, Br, Cl) [71]. After extensive screening, B(2,6-F₂-C₆H₃)₃ as the Lewis acid combined with stoichiometric amounts of 2,2,6,6-tetramethylpiperidine (TMP) as the base was identified as

the most effective FLP catalyst for the hydrogenation of Me_3SiX ($\text{X} = \text{OTf}, \text{I}, \text{Br}$) to Me_3SiH (Scheme 9). Employing the same FLP catalyst, Et_3SiOTf , Ph_3SiOTf , and $(\text{Pr}^i)_2\text{Si}(\text{OTf})_2$ could be hydrogenated to the corresponding hydrosilanes in good yields as well. However, irrespective of the base used, $\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$ was not able to convert the more challenging substrate Me_3SiCl to Me_3SiH , primarily because of the comparably stronger Si-Cl bond and lower hydricity of the respective borohydride anion, $\text{HB}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3^-$, formed upon H_2 -splitting. Building on the idea of favoring the thermodynamics by increasing the hydricity of the borohydride, less Lewis acidic BPh_3 was tested in combination with stronger base phosphazene to ensure H_2 -cleavage. With this FLP in hand, 28% of Me_3SiCl were converted after 72 h to Me_3SiH in yields of 26%. Moreover, upon adding the chloride abstracting additive NaOTf , the yields of Me_3SiH were further increased to a respectable 52% (Scheme 9).



Scheme 9. FLP-catalyzed hydrogenation of Me_3SiX to Me_3SiH .

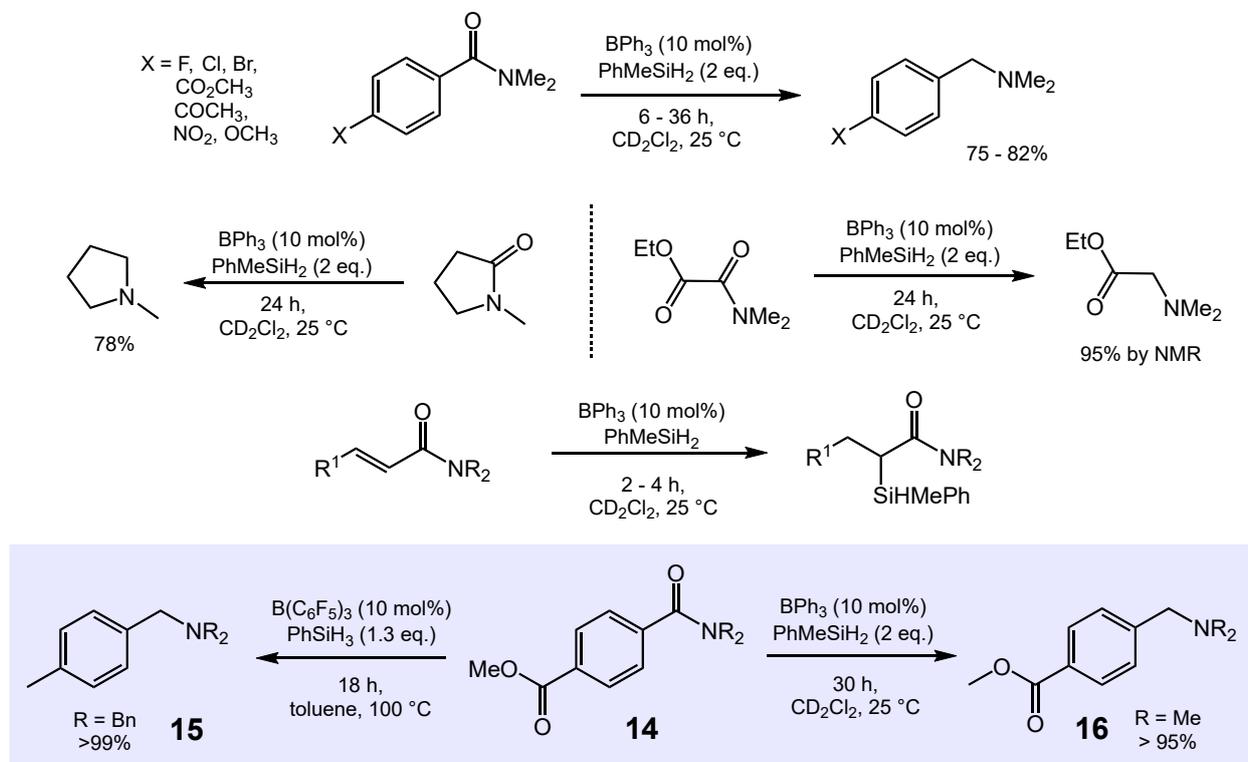
Silylenes, divalent silicon species of general formula $\text{R}^1\text{R}^2\text{Si}$, are known to exhibit amphoteric behavior, capable of serving either as Lewis acids or Lewis bases. In this respect, Kira, Mueller, and co-workers investigated the potential of sterically overcrowded silylene **9** to be an active component in the heterolytic cleavage of H_2 via an FLP approach (Scheme 10) [72]. It was found that **9** not only actively engaged in H_2 splitting, it was also fully hydrogenated to hydrosilane **13** in isolated yields ranging from 75–84% with catalytic amounts of either Lewis base (PPh_3 , NPh_3 , PEt_3 , and NEt_3) or Lewis acids such as BEt_3 and BPh_3 . NMR spectroscopic investigations in solution showed that neither PPh_3 nor BPh_3 forms a classical Lewis acid–base adduct, indicative of FLP formation in both cases. Nonetheless, when H_2 was introduced into the solution, rapid formation of hydrosilane **13** occurred. Based on DFT calculations, a mechanism was proposed in which BPh_3 initially forms the weak complex **10** with the silylene, which is stabilized by ca. -7 kcal/mol compared to the starting materials. Subsequent heterolytic cleavage of H_2 leads to the formation of silylium borate **12**; its formation is slightly endothermic ($+14$ kcal/mol). Finally, the hydride is transferred from the borohydride to the silylium cation to give the final product **2**, a strongly exothermic process (-37 kcal/mol). It should be noted that strong Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ was not capable of hydrogenating silylene **9**, instead, degradation occurred.



Scheme 10. BPh_3 -catalyzed hydrogenation of a silylene and proposed mechanism of formation.

4. Hydrosilylation Catalysis

Arguably, one of the most challenging metal-free catalyzed reductive transformations represents the reduction of organic amides to amines [73–75]. In 2016, Okuda and co-workers reported the highly selective hydrosilylation of a variety of aromatic and aliphatic tertiary amides to the corresponding amines with 10 mol% BPh_3 as the catalyst system and 2 eq. of PhMeSiH_2 as the reducing agent (Scheme 11) [76].

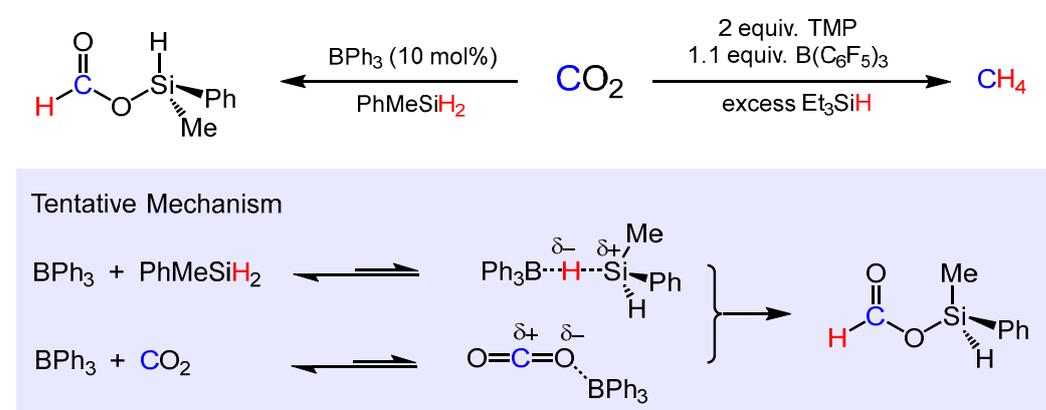


Scheme 11. Catalytic hydrosilylation of organic amides to amines.

Aromatic and aliphatic tertiary amines were obtained in good to excellent isolated yields. In contrast, α,β -unsaturated amides underwent hydrosilylation of the olefinic

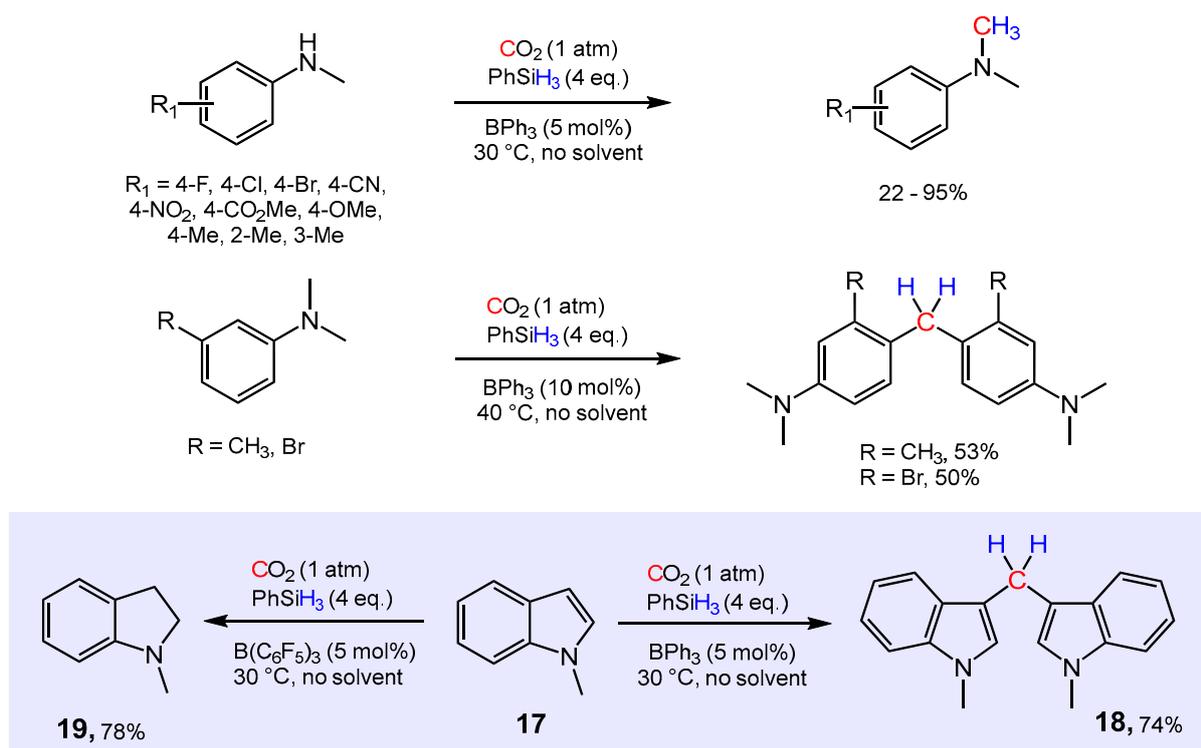
groups (C=C) to give the respective α -silylated amides. In addition, this process showed a good functional group tolerance with additives such as acetophenone, ethyl acetate, N-benzylidene aniline, *tert*-butyl isocyanate, and thiophene not inhibiting the activity of the catalyst. Only in the case of benzaldehyde and ethanol, hydrosilylation and dehydrosilylation, respectively, occurred prior to amide reduction. The addition of pyridine deactivated the catalyst due to irreversible Lewis acid–base adduct formation with BPh₃. The BPh₃-catalyzed amide hydrosilylations described by Okuda's group appear to be superior in terms of both functional group tolerance and chemo-selectivity when compared with other metal-free catalysts reported in the literature [74,75]. For example, B(C₆F₅)₃ catalyzes the reduction of both functional groups of **14**, the ester as well as the amide, to give benzylamine **15**. In contrast, BPh₃ reduces the amide group while keeping the ester group intact leading to the selective formation of the ester-functionalized benzylamine **16** (Scheme 11) [74].

The same group reported the BPh₃-catalyzed hydrosilylation of CO₂ (Scheme 12) [77]. This approach enabled the highly selective formation of silyl formates with various hydro silanes such as PhSiH₃, PhMeSiH₂ or Et₃SiH in polar solvents such as acetonitrile, nitromethane and propylene carbonate. No turnover was observed in less polar and non-polar solvents such as benzene, toluene, tetrahydrofuran (THF) and CH₂Cl₂. Mechanistically the BPh₃-catalyzed hydrosilylation of CO₂ is suggested to proceed via the dual activation of CO₂ and organosilane by BPh₃, where polar solvents with high dielectric constants stabilize the partially charged transient species (Scheme 11). Note that strongly Lewis acidic B(C₆F₅)₃ itself was not capable of catalyzing the hydrosilylation of CO₂, while as the FLP component in combination with tetramethyl piperidine (TMP) as a Lewis base and with an excess of triethylsilane CO₂ was quantitatively reduced to give CH₄ [78].



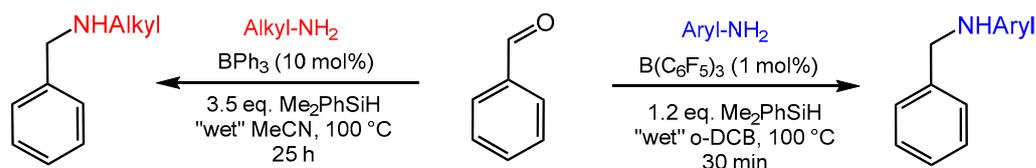
Scheme 12. Lewis acid catalyzed hydrosilylation of CO₂ and proposed mechanism of silyl formate formation (TMP = 2,2,6,6-tetramethylpiperidine).

More recently, Ema and co-workers reported the utilization of CO₂ as C1-feedstock for the reductive methylation of *secondary* and tertiary aromatic amines derivatives, employing PhSiH₃ as a reducing agent and BPh₃ as the catalyst (Scheme 13) [79,80]. The N-methylation of *sec*-amines was achieved with 1 atm of CO₂, 4.0 equivalents of PhSiH₃ and 5 mol% of BPh₃ under solvent-free conditions at 30 °C. The process tolerates various functional groups such as halides, nitrile, nitro, ester and alkoxy groups. On the other hand, C-methylenation was observed with tertiary aromatic amines to give the corresponding diarylmethanes in moderate yields at 40 °C. Note that B(C₆F₅)₃ was inactive even at higher temperatures in any of these transformations, probably due to irreversible Lewis acid–base adduct formation. Similar to what was seen for the reaction of tertiary aromatic amines, 1-methylindole at 30 °C converted to 3,3'-methylenebis(1-methylindole) **18** in good yields. On the contrary, B(C₆F₅)₃ catalyzed the formal hydrogenation of the olefinic bond of N-methyl indole to selectively give N-methyl dihydroindole **19**.



Scheme 13. BPh₃-catalyzed N-methylation and C-methylenation of secondary and tertiary aromatic amines.

Motivated by the moderate water tolerance of B(C₆F₅)₃ in catalytic hydrogenation reactions [81], Ingleson and co-workers disclosed the triaryl borane catalyzed reductive aminations of aldehydes to aromatic and aliphatic amines using Me₂PhSiH as the reducing agent [82,83]. Notably, the employed catalysts BPh₃ and B(C₆F₅)₃ showed strikingly different selectivities for aliphatic and aromatic amine substrates (Scheme 14). With B(C₆F₅)₃ as the catalyst, the amine substrates were limited to aryl amines (pK_a of the conjugate acid ≤ 12), while with weaker Lewis acidic BPh₃, the more basic alkyl amines (pK_a of the conjugate acid ≥ 16) performed well with excellent conversions and yields. These findings were attributed to the different interactions of the amine base with the intermediately formed water adducts H₂O→BPh₃, and H₂O→B(C₆F₅)₃. Thus, with more basic alkyl amines, irreversible deprotonation of the highly acidic adduct H₂O→B(C₆F₅)₃ (pK_a = 8.4 in CH₃CN) occurred, resulting in the degradation of the catalyst. BPh₃, on the other hand, undergoes rapid protodeboronation in the presence of the more acidic aryl amines. It is worth noting that the in situ generated Lewis acid B(3,5-Cl₂-C₆H₃)₃, whose Lewis acidity is in between B(C₆F₅)₃ and BPh₃, was capable of catalyzing the reductive amination with both aryl and alkyl amines. However, a detailed substrate scope was not explored with B(3,5-Cl₂-C₆H₃)₃ as the catalyst.

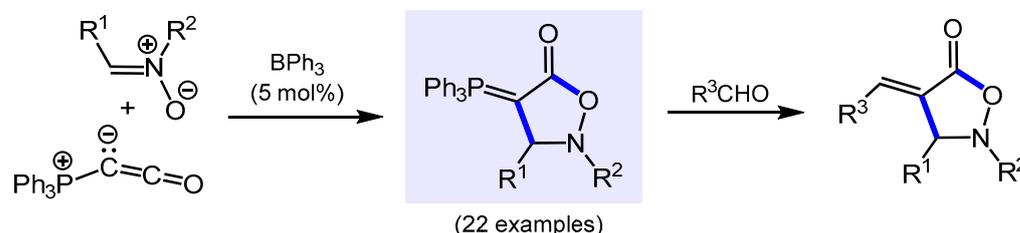


Scheme 14. Triaryl borane catalyzed reductive amination of aldehydes.

5. Miscellaneous

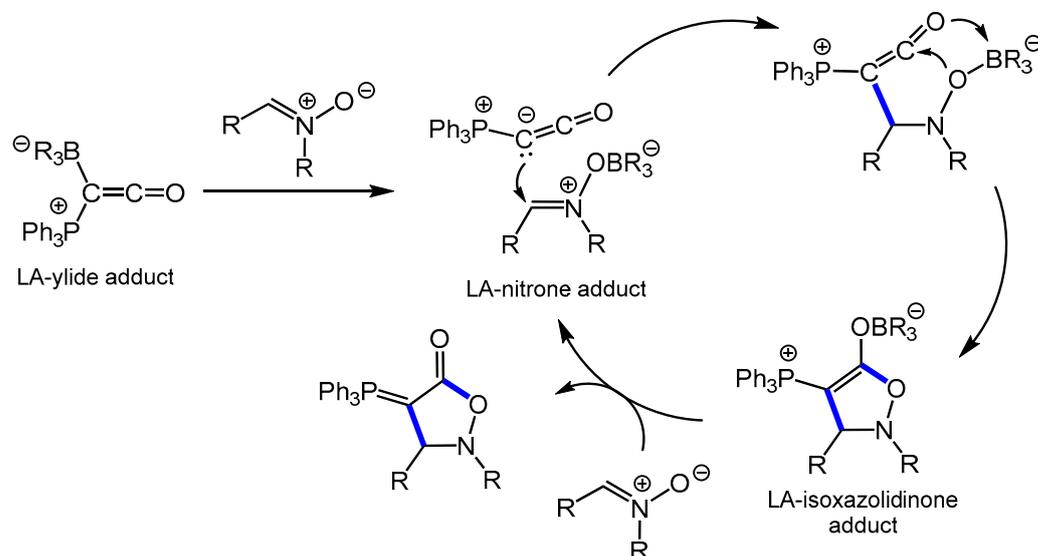
Krempner and co-worker reported the Lewis acid catalyzed [2 + 3] cycloaddition of Bestmann's ylide, Ph₃P=C=C=O, with nitrones to produce a variety of previously unknown

5-isoxazolidinones with exocyclic phosphonium ylide functionality in excellent isolated yields [84]. Subsequent quenching with reactive aldehydes via a classical Wittig reaction gave access to 5-isoxazolidinones with exocyclic double bonds (Scheme 15).



Scheme 15. BPh₃-catalyzed formal [2 + 3] cycloaddition of Ph₃PCCO with nitrones to 5-isoxazolidinone with exocyclic phosphonium ylide moiety and their Wittig reaction.

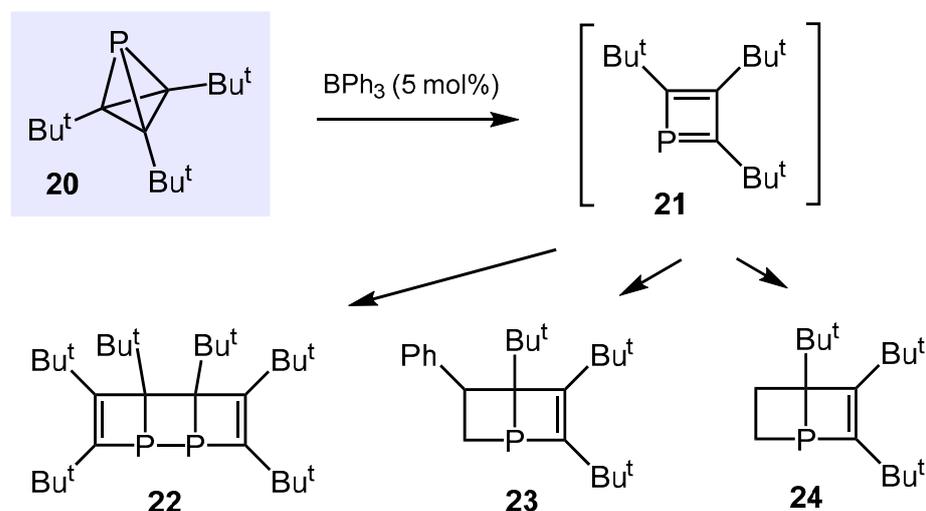
Of the boron-containing Lewis acid catalysts tested, BPh₃ proved to be most effective in providing the cycloaddition product in almost quantitative yields within 8 h at room temperature. Weaker Lewis acids such as BEt₃, BMe₃ and B(OMe)₃ were inactive even at elevated temperatures, while B(C₆F₅)₃, the strongest amongst the Lewis acids studied, required 80 °C and 16 h to quantitatively produce the cycloaddition product. The authors proposed a mechanism (Scheme 16) in which the borane catalyst activates the nitronium via Lewis acid–base interactions, which facilitates the nucleophilic attack of the ylidic carbon of Ph₃PCCO resulting in the cyclized borane–5-isoxazolidinone adduct from which the 5-isoxazolidinone is liberated via borane–nitronium adduct formation. The higher activity of the BPh₃ over its more acidic counterpart B(C₆F₅)₃ is attributed to the latter forming stable adducts with both Ph₃PCCO and the nitronium, while BPh₃ does not [85].



Scheme 16. Proposed mechanism of the BPh₃-catalyzed formal [2 + 3] cycloaddition of Ph₃PCCO with nitrones (LA = Lewis acid).

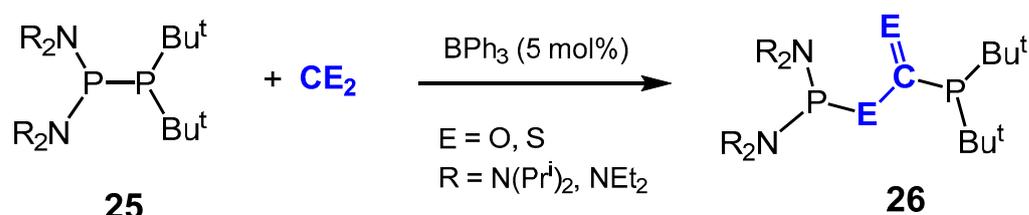
Recently, Cummins and co-workers disclosed the synthesis and reaction behavior of highly strained tri-*tert*-butylphosphatetrahedrane **20** (Scheme 17) [86]. Thus, upon the addition of BPh₃ (20 mol%), **20** underwent rapid dimerization to form the bicyclic structure **22** in 72% yield. To trap potential intermediates, tetrahedrane **20** was treated with a 20-fold excess of styrene, which in the presence of BPh₃ (20 mol%) furnished the cycloaddition product **23** in a yield of 88%. Similarly, BPh₃ catalyzed the cycloaddition of **20** with 1 atm of ethylene to give the corresponding bicyclic structure **24** in yields of 74%. Quantum chemical calculations revealed BPh₃ to mediate C–P bond cleavage to give intermediately tri-*tert*-

butyl-phospatcyclobutadiene **21**, which subsequently either dimerizes to **22** or undergoes a formal [2 + 4] cycloaddition with styrene and ethylene to yield **23** and **24**, respectively.



Scheme 17. BPh₃-catalyzed reactions of tri-*tert*-butylphosphatetrahedrane.

Finally, Grubba et al. demonstrated the ability of BPh₃ to act as an efficient Lewis acid catalyst in the diphosphination of CO₂ and CS₂ (Scheme 18) [87]. BPh₃-catalyzed insertion of CO₂ and CS₂ into the P-P bond of unsymmetrical diphosphines **25** led to the selective formation of products **26** of the general formula (R₂N)₂P-E-C(=E)-P(Bu^t)₂, where the central carbon of CE₂ binds to the more nucleophilic P(Bu^t)₂ moiety. In elucidating the reaction mechanism, it was found that neither CO₂ nor the bulky diphosphines reacted with BPh₃ individually to form the Lewis acid–base adducts, respectively, suggesting FLP-type behavior. It was proposed that the FLP diphosphine/BPh₃ synergistically interacts with CO₂ resulting in rapid P-P bond insertion.



Scheme 18. BPh₃-catalyzed insertion of CE₂ (E = O, S) into diphosphines.

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