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Frustrated Lewis Pairs: From Concept to Catalysis

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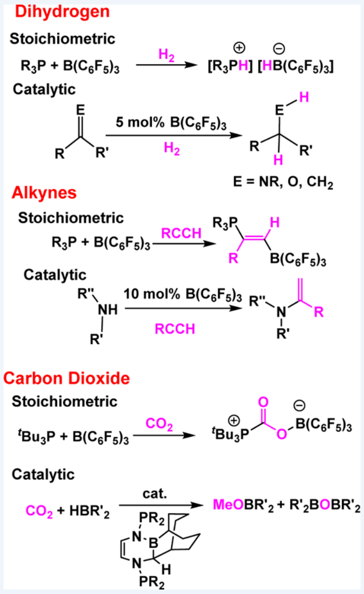

CONSPECTUS: Frustrated Lewis pair (FLP) chemistry has emerged in the past decade as a strategy that enables main-group compounds to activate small molecules. This concept is based on the notion that combinations of Lewis acids and bases that are sterically prevented from forming classical Lewis acid−base adducts have Lewis acidity and basicity available for interaction with a third molecule. This concept has been applied to stoichiometric reactivity and then extended to catalysis. This Account describes three examples of such developments: hydrogenation, hydroamination, and CO_2 reduction.

The most dramatic finding from FLP chemistry was the discovery that FLPs can activate H_2, thus countering the long-existing dogma that metals are required for such activation. This finding of stoichiometric reactivity was subsequently evolved to employ simple main-group species as catalysts in hydrogenations. While the initial studies focused on imines, subsequent studies uncovered FLP catalysts for a variety of organic substrates, including enamines, silyl enol ethers, olefins, and alkynes. Moreover, FLP reductions of aromatic anilines and N-heterocycles have been developed, while very recent extensions have uncovered the utility of FLP catalysts for ketone reductions.

FLPs have also been shown to undergo stoichiometric reactivity with terminal alkynes. Typically, either deprotonation or FLP addition reaction products are observed, depending largely on the basicity of the Lewis base. While a variety of acid/base combinations have been exploited to afford a variety of zwitterionic products, this reactivity can also be extended to catalysis. When secondary aryl amines are employed, hydroamination of alkynes can be performed catalytically, providing a facile, metal-free route to enamines.

In a similar fashion, initial studies of FLPs with CO_2 demonstrated their ability to capture this greenhouse gas. Again, modification of the constituents of the FLP led to the discovery of reaction systems that demonstrated stoichiometric reduction of CO_2 to either methanol or CO. Further modification led to the development of catalytic systems for the reduction of CO_2 by hydrosilylation and hydroboration or deoxygenation.

As each of these areas of FLP chemistry has advanced from the observation of unusual stoichiometric reactions to catalytic processes, it is clear that the concept of FLPs provides a new strategy for the design and application of main-group chemistry and the development of new metal-free catalytic processes.

■ INTRODUCTION

"*To be effective, the two functional groups must be so disposed that they can interact simultaneously with a hydrogen molecule, but at the same time are prevented from interacting with (neutralizing) each other.*"[1]

This quote from Halpern provided insight in 1959 and seems prophetic in light of modern bifunctional transition-metal catalysis.[2] Moreover these words foreshadow the notion of *frustrated Lewis pairs* (FLPs), which are Lewis acids and bases that are sterically prevented from interaction and yet can act cooperatively to activate H_2 and other small molecules.[3,4] Interestingly, early reports by Brown,[5] Wittig,[6] and Tochtermann[7] showed that steric demands can preclude Lewis acid−base adduct formation and precipitate unexpected reactivity. Most closely related to the notion of FLPs is seminal work by Piers[8] in which $B(C_6F_5)_3$ and imine or ketone act concurrently on Si−H bonds to effect hydrosilylation catalysis. Despite these precedents, the articulation of the concept of FLPs sparked a flurry of studies that have been the subject of symposia, monographs,[9,10] and reviews.[11−16] This Account focuses on FLP chemistry of H_2, alkynes, and CO_2, each of which has evolved from stoichiometric reactions to metal-free catalytic processes.

■ STOICHIOMETRIC HETEROLYTIC H_2 ACTIVATION

The concept of FLPs emerged from our studies in which sterically bulky phosphines and $B(C_6F_5)_3$ were shown to activate H_2 (Scheme 1).[3,4] This metal-free activation of H_2 prompted a number of studies focusing on the impact of the nature of the FLP. While Erker's group reported and developed the intramolecular FLP $Mes_2PCH_2CH_2B(C_6F_5)_2$,[17] which rapidly and reversibly activates H_2 (Scheme 2), we probed systems employing ferrocenyl-based phosphines[18] and sterically bulky N-heterocyclic carbenes (NHCs)[19−21] with $B(C_6F_5)_3$, demonstrating that both systems gave FLPs that activated H_2 to afford the corresponding zwitterions (Scheme 2).

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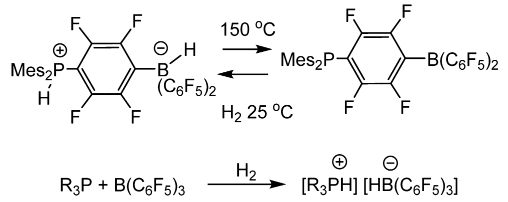
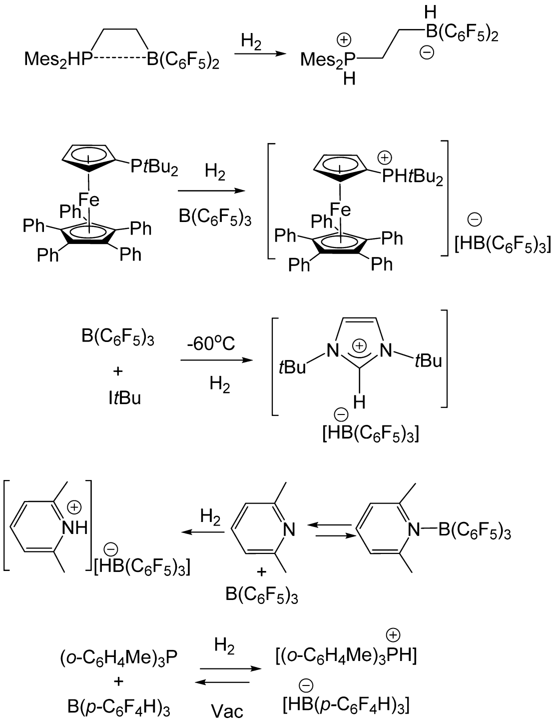
Scheme 1. Reactions of FLPs with H_2



Scheme 2. FLP Activation of H_2



The use of nitrogen bases in FLP activation of H_2 was a logical extension, and indeed, bulky pyridines are effective bases in the FLP activation of H_2.[22,23] The lutidine/$B(C_6F_5)_3$ combination focused attention on the fact that despite an equilibrium involving free Lewis acid and base with the corresponding adduct, such combinations still provide access to FLP chemistry.[22,23] Thus, while the adduct was isolated, exposure of a solution of lutidine/$B(C_6F_5)_3$ to H_2 yielded $[2,6\text{-}Me_2C_5H_3NH][HB(C_6F_5)_3]$ (Scheme 2).[22,23]

The seemingly trivial variation of the Lewis acid to $B(p\text{-}C_6F_4H)_3$[24,25] was targeted to preclude substitution at the *para* carbon by the Lewis base, thus providing a broader range of FLPs that activate H_2 (Scheme 2). The slightly reduced Lewis acidity in $B(p\text{-}C_6F_4H)_3$ compared with $B(p\text{-}C_6F_5)_3$ allows $[(o\text{-}C_6H_4Me)_3PH][HB(p\text{-}C_6F_4H)_3]$ to release H_2 under vacuum at 25 °C (Scheme 2).[24,25]

The heterolytic cleavage of H_2 by FLPs has subsequently been generalized to a wide variety of acid/base combinations derived from boranes, alanes, Lewis acidic transition metals, and even C- and Si-based acids in combination with a range of sterically hindered donors (vide infra).[12,13,16]

Computational studies of the mechanism of H_2 activation showed that the process is initiated by generation of an "encounter complex" (Figure 1) in which the Lewis acid and base are in close proximity yet stop short of adduct formation. However, Papai[26,27] computed a linear $B{-}H_2{-}P$ vector, while Grimme's model[28] provides H_2 in a "side-on" interaction with B and an "end-on" interaction with P. This latter orientation allows σ donation from the H−H bond to B with P donation to the H_2 σ^* orbital.

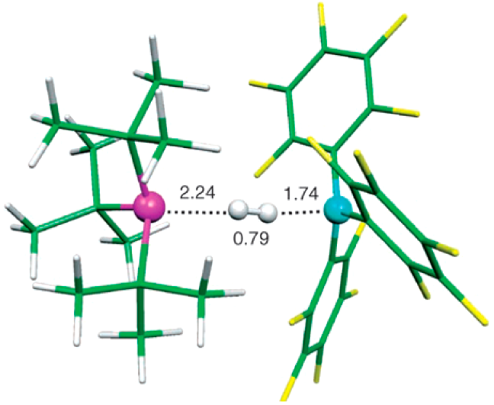
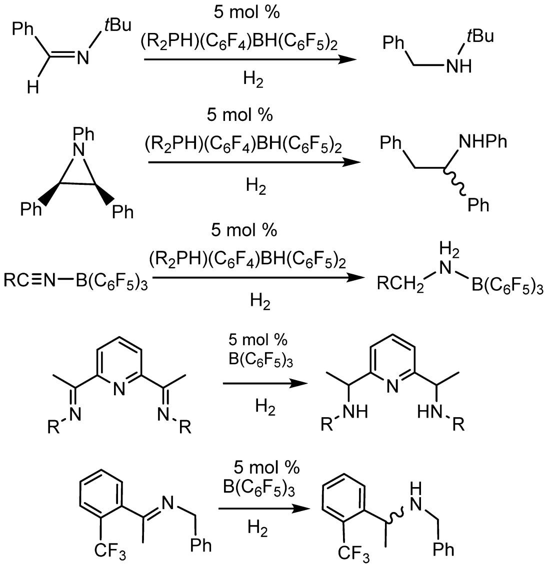


Figure 1. "Encounter complex" between tBu_3P and $B(C_6F_5)_3$.

CATALYTIC HYDROGENATIONS

Heterolytic cleavage of H_2 by FLPs prompted us to query metal-free catalytic hydrogenations. In our initial report, sterically demanding aldimines, protected nitriles, and an aziridine were effectively hydrogenated in the presence of 5 mol % $(R_2PH)(C_6F_4)BH(C_6F_5)_2$ (R = Mes, *t*Bu) at 80−120 °C under 1−5 atm H_2 in reaction times ranging from 1 to 48 h (Scheme 3).[29] Subsequently, we recognized that imine substrates could act as the FLP base, and thus, imine reductions proceed under H_2 using $B(C_6F_5)_3$ as the catalyst.[30] Mechanistically, these reductions proceed by protonation of the imine and subsequent hydride transfer from the hydridoborate to the iminium carbon,[29] regenerating free borane. Such reductions have been extended to reduce diimines, pyridyldiimines (Scheme 3), and imine precursors for herbicides, antidepressants, and anticancer drugs.[31]

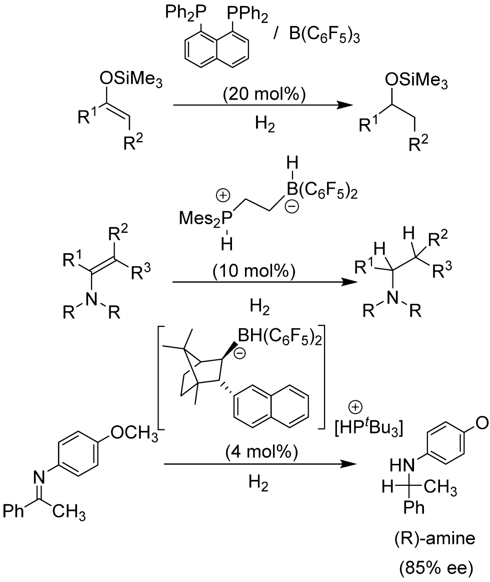
Scheme 3. FLP Hydrogenations



While the first-generation FLP catalysts tolerate sensitive organometallic substrates,[32,33] they exhibit limited tolerance to polar, sterically unencumbered donors.[31] Interestingly, sensitivity to trace water can be overcome by the use of a scrubbing agent such as $i\mathrm{Bu_3Al}$ or $\mathrm{Et_3SiH}$.[34] Imine reductions were optimized to use as little as 0.1 mol % catalyst at 130 °C and 120 atm H_2.[31]

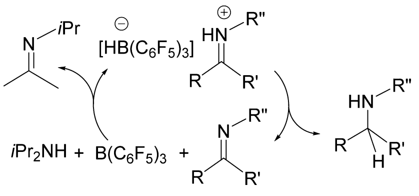
Subsequent studies uncovered other FLP catalysts or broadened the substrate scope. For example, Repo and Rieger[35,36] prepared intramolecular amine−borane-based catalysts, while the Erker group expanded the substrate scope to include silyl enol ethers[37,38] and enamines (Scheme 4).[17] In a further elegant extension, Klankermayer and co-workers[39,40] designed asymmetric borane catalysts, achieving enantiomeric excesses as high as 85% for ketamine reductions (Scheme 4). More recently, Liu and Du developed a chiral catalyst derived from hydroboration of chiral dienes.[41]

Scheme 4. Silyl Enol Ether, Enamine, and Asymmetric FLP Hydrogenations



Another strategy for hydrogenations involves the use of a surrogate source of H_2. As $B(C_6F_5)_3$ is known to abstract hydride from the α-carbon of amines,[42,43] it effects the racemization of chiral amines[44] allowing $i\mathrm{Pr_2NH}$ to be used as a source of H_2 for $B(C_6F_5)_3$-catalyzed transfer hydrogenation of imines (Scheme 5), enamines, quinolines, and aziridines.

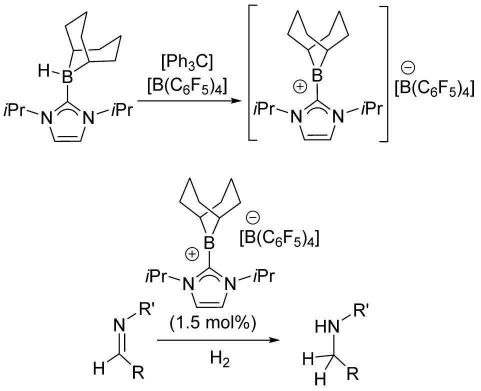
Scheme 5. FLP-Catalyzed Transfer Hydrogenation



Erker's group also reported the analogous transfer hydrogenation of the enamine $\mathrm{PhNC_5H_{10}C{=}CH_2}$ using ammonia−borane as the H_2 source and $\mathrm{Mes_2PCH{=}CMeB(C_6F_5)_2}$ as the catalyst.[45]

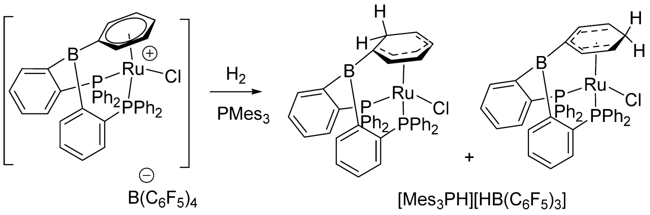
To target a readily accessible catalyst, electrophilic borenium cations[46] were prepared via hydride abstraction from carbene−borane adducts by $[\mathrm{Ph_3C}][B(C_6F_5)_4]$. Judicious choice of the carbene showed that $[(\mathrm{I}i\mathrm{Pr_2})(\mathrm{BC_8H_{14}})][B(C_6F_5)_4]$ generates an FLP with $\mathrm{P}t\mathrm{Bu_3}$ that is capable of H_2 activation (Scheme 6).[47] Moreover, a 1−5 mol % loading of this species proved to be effective in mediating the hydrogenation of imines and enamines at room temperature under 100 atm H_2, typically in 2−4 h. This catalyst offers greater tolerance of functional groups while the borane−carbene adduct precursor is air-stable, thus representing a significant advance over the earlier FLP catalysts.

Scheme 6. Hydrogenation Catalysis by a Borenium Cation



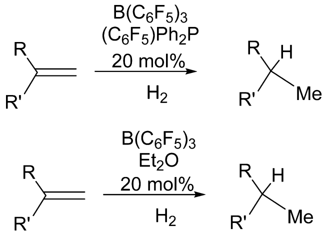
Another, perhaps unusual, approach to FLP catalysts was uncovered when the species $[((\mathrm{Ph_2PC_6H_4})_2\mathrm{B}(\eta^6\text{-Ph}))\mathrm{RuCl}][B(C_6F_5)_4]$[48] was shown not to react with sterically encumbered phosphines, generating an FLP. Addition of H_2 resulted in a 2:1 mixture of the *ortho*- and *para*-substituted isomers of $[(\mathrm{Ph_2PC_6H_4})_2\mathrm{B}(\eta^5\text{-}\mathrm{C_6H_6})\mathrm{PRuCl}]$ (Scheme 7) and $[\mathrm{Mes_3PH}][\mathrm{HB}(C_6F_5)_3]$. Moreover, this FLP is an effective catalyst for the hydrogenation of aldimines at 25 °C. The Lewis acidic carbon of the π-bound arene in the Ru cation provides an interesting situation where the metal center plays an ancillary role.

Scheme 7. H_2 Activation by an FLP Containing an Ancillary Metal Center



Seeking to broaden the scope of FLP hydrogenations to include olefins, we recognized that protonation of the olefin required a weak base in the FLP heterolytic cleavage of H_2. The electron-deficient phosphine $(C_6F_5)\mathrm{Ph_2P}$ and $B(C_6F_5)_3$ showed no evidence of reaction with H_2 at 25 °C, but at −80 °C the formation of the phosphonium species $[(C_6F_5)\mathrm{Ph_2PH}]^+$ was observed. The remarkably low barrier to reversible activation of H_2 results from the generation of the highly acidic cation.[49] This acidity prompts the protonation of 1,1-disubstituted olefins by protonation of the olefin, and subsequent hydride capture by the generated carbocation effects hydrogenation. While initial trials employed 20 mol % P/B FLP catalyst (Scheme 8), the use of $p\mathrm{Tol_2NMe}$ as the base allowed the catalyst loading to be reduced to 5 mol %.[49] A subsequent study

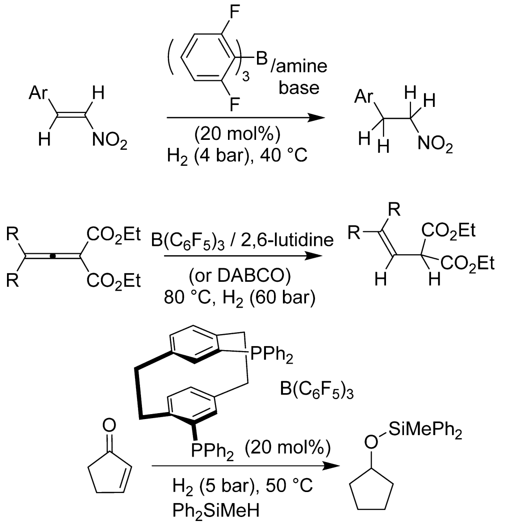
Scheme 8. Catalytic Hydrogenation of Olefins



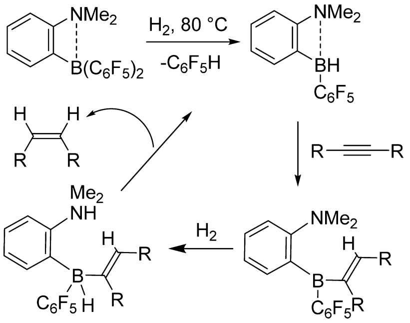
uncovered the ability of Et_2O and $B(C_6F_5)_3$ to effect heterolytic H_2 cleavage by HD scrambling experiments and showed that this system can catalyze the hydrogenation of 1,1-disubstituted olefins despite the formation of an ether−borane adduct[50] (Scheme 8).

In efforts to further broaden the substrate scope, Paradies and co-workers[51] extended FLP reductions to include *β*-nitrostyrenes using $(2,6\text{-}C_6H_3F_2)_3B$/2,6-lutidine at 40 °C (Scheme 9), while Alcarazo and co-workers[52] showed that $B(C_6F_5)_3$ with either (1,4)-diazabicyclo[2.2.2]octane (DABCO) or 2,6-lutidine (10−15 mol %) can catalytically hydrogenate allenic esters (Scheme 9). Similarly, enones were reduced in a combined hydrogenation/hydrosilylation using [2,2]-bis(phosphino)paracyclophane/$B(C_6F_5)_3$ catalysts (Scheme 9).[53] While the ynone PhC≡CC(O)*t*Bu was stoichiometrically reduced with $R(R')C{=}C(C_6F_5)B(C_6F_5)_2$ and tBu_3P under H_2 to afford the *cis*-enone product,[54] the use of DABCO permitted catalytic reduction, although the *trans*-enone was obtained. Repo and co-workers[55] further broadened the substrate scope, effecting selective hydrogenation of nonfunctionalized internal alkynes to give *cis*-alkenes using the intramolecular FLP $C_6H_4(NMe_2)B(C_6F_5)_2$ under H_2 at 80 °C. Interestingly, activation of H_2 liberates C_6F_5H and generates $C_6H_4(NMe_2)BH(C_6F_5)$ (Scheme 10), which effects hydroboration of the alkyne, while subsequent activation of H_2 prompts protonolysis to afford the *cis*-alkene and regenerate the catalyst.[55]

Scheme 9. Catalytic Olefin, Allene−Ester, and Enone Hydrogenation

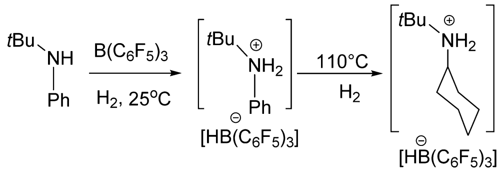


Scheme 10. Catalytic Hydrogenation of Alkynes



Activation of H_2 by *t*BuNHPh/$B(C_6F_5)_3$ at 25 °C afforded $[tBuNH_2Ph][HB(C_6F_5)_3]$,[56] but prolonged heating at 110 °C for 96 h under H_2 gave $[tBuNH_2Cy][HB(C_6F_5)_3]$ (Scheme 11). The reduction of the N-bound arene ring was subsequently generalized for a series of bulky secondary anilines, yielding the corresponding cyclohexylammonium salts in high yields. The corresponding treatment of *cis*-1,2,3-triphenylaziridine or the imines PhN=CMePh and $(Me_2C{=}N)_2C_6H_4$ led to either reductive aziridine ring opening or imine hydrogenation followed by exclusive reduction of the N-bound arene to a cyclohexyl ring.

Scheme 11. Reduction of Anilines to Cyclohexylammonium Salts



These arene reductions consume 4 equiv of H_2 before sequestration of the borane by precipitation of the ammonium hydridoborate. Computational studies showed that the FLP activation of H_2 by amine and borane is reversible at elevated temperatures, allowing amine rotation to attain a van der Waals complex in which the *para*-arene carbon is proximal to boron (Figure 2). Subsequent activation of H_2 occurs with a further barrier of 8.7 kcal/mol to give an enthalpy of activation of 23.8 kcal/mol. The aromaticity of the phenyl ring is disrupted in the transient product $[tBuNHC_6H_6][HB(C_6F_5)_3]$, allowing for a thermodynamically downhill pathway to the cyclohexyl product.[56]

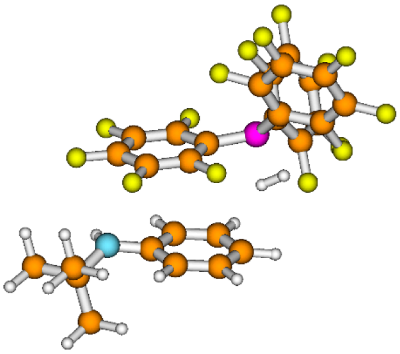
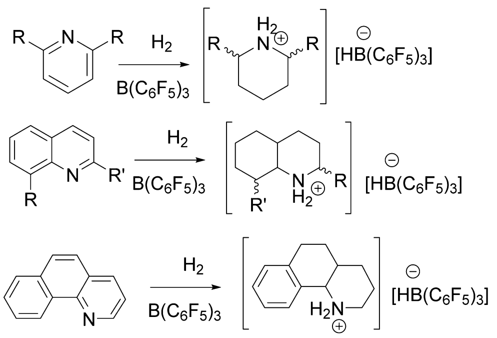


Figure 2. Calculated van der Waals complex involving $tBuNHC_6H_5$/$B(C_6F_5)_3$/H_2.

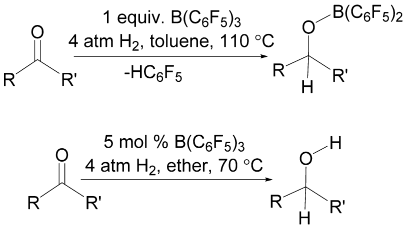
Such FLP aromatic reductions were extended to N-heterocycles, including hindered pyridines, quinolines, acridines, and quinoxalines.[57] In these cases, treatment with $B(C_6F_5)_3$ and H_2 at 110 °C for 16−60 h resulted in the corresponding saturated species. Interestingly, the nominal "pyridine" and "aniline" rings of benzoquinoline are reduced while the remote ring remains untouched (Scheme 12).

Scheme 12. FLP Hydrogenations of N-Heterocycles

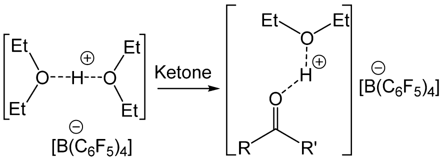


Reactions of FLPs, H_2, and benzaldehyde resulted in the stoichiometric formation of phosphonium alkoxyborates.[58] More recently, stoichiometric reactions of ketones and $B(C_6F_5)_3$ in the presence of H_2 in toluene generated C_6F_5H and borinic esters $ROB(C_6F_5)_2$ (Scheme 13). Interestingly, when ether[59] or dioxane[60] was used as the solvent, catalytic reduction of ketones in the presence of H_2 using 5 mol % $B(C_6F_5)_3$ at 70 °C was achieved for a series of ketones (Scheme 13). The dramatic solvent effect is consistent with a mechanism initiated by ketone/borane heterolytic cleavage of H_2. In toluene, the protonated ketone cleaves a B−C bond, liberating C_6F_5H, while in ether the protonated ketone forms hydrogen bonds with the solvent, allowing hydride transfer from the hydridoborate to the carbonyl carbon. Such H-bonding is supported by the isolation and crystallographic characterization of $[Et_2OH(OCPr_2)][B(C_6F_5)_4]$ in which ether and the ketone are H-bonded in the cation (Scheme 14).[59]

Scheme 13. Ketone Reductions in Toluene and Ether



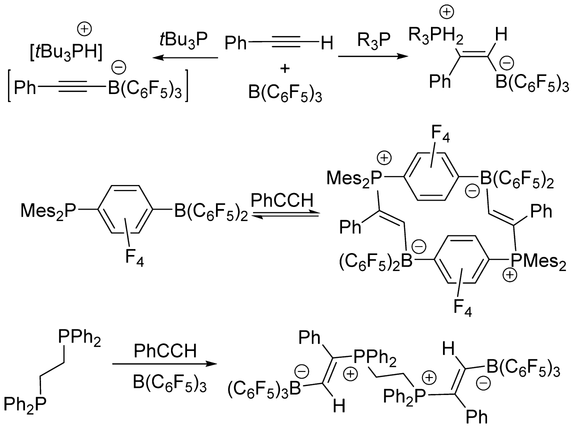
Scheme 14. Synthesis of a Model of the Intermediate in FLP Ketone Hydrogenation



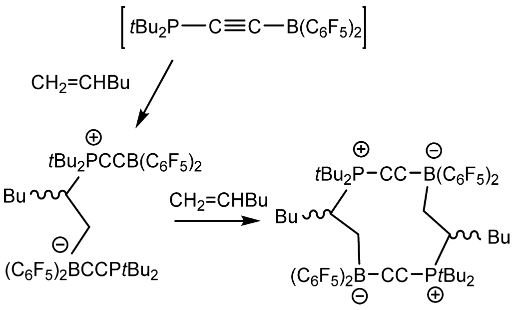
■ STOICHIOMETRIC FLP REACTIONS WITH ALKYNES

In 2008 studies, FLPs were shown to react with alkynes via two pathways dependent on the nature of the Lewis base.[61,62] Reactions of $B(C_6F_5)_3$, tBu_3P, and $PhC{\equiv}CH$ resulted in deprotonation of the alkyne, while use of the less basic phosphine $(o\text{-}C_6H_4Me)_3P$ gave the 1,2-addition product (Scheme 15). These pathways proved quite general with a variety of terminal alkynes. Reactions employing a variety of less basic phosphines[63] and polyphosphines[64] gave the corresponding addition products, while the macrocyclic and chain-like species $[(H)C{=}C(Ph)Mes_2PC_6F_4B(C_6F_5)_2]_2$ and *trans*-$(CH_2PPh_2(Ph)C{=}C(H)B(C_6F_5)_3)_2$, respectively, could also be constructed (Scheme 15).[62] The related chain and macrocyclic systems, $(tBu_2PC{\equiv}CB(C_6F_5)_2)_2(BuCH_2CH_2)$[65] and $[(tBu_2PC{\equiv}CB(C_6F_5)_2)(BuCH_2CH_2)]_2$ were derived from the alkynyl-linked phosphine−borane $tBu_2PC{\equiv}CB(C_6F_5)_2$ in reactions with 1-hexene (Scheme 16).

Scheme 15. Reactions of Alkynes with P/B FLPs



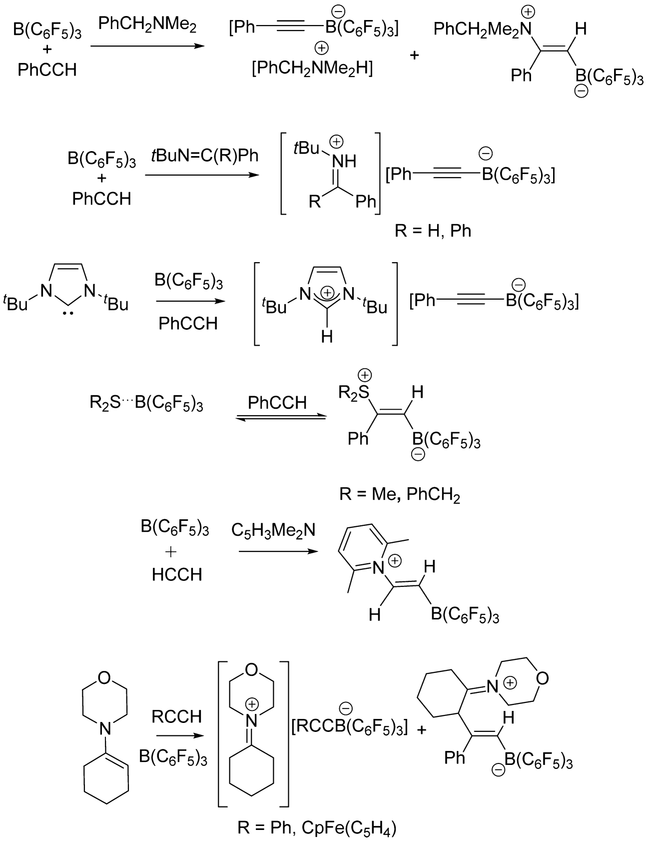
Scheme 16. Reaction of Alkynyl-Linked Phosphine−Borane with Olefin



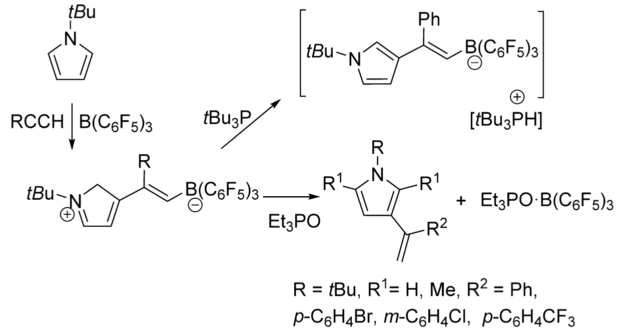
Such reactions with alkynes are limited to B/P FLPs. Amine, borane, and alkyne led to mixtures of deprotonation and addition products, whereas the corresponding reactions of imines, carbenes, or enamines also led exclusively to deprotonation products.[62,66] In contrast, combination of lutidine or S donors with $B(C_6F_5)_3$ with alkyne gave addition products (Scheme 17), suggesting that the product formed is determined by steric and electronic factors.[67]

Pyrrole derivatives that act as C-based nucleophiles afford a strategy for C−C bond formation, as addition to PhCCH and $B(C_6F_5)_3$ gave addition products. The less hindered *N*-methylpyrrole gave a 3:2 mixture of addition products derived from the 2- and 3-substituted pyrroles,[66] while bulky *N-tert*-butylpyrrole gave exclusively the 3-substituted product (Scheme 18). Subsequent deprotonation or thermally induced

Scheme 17. Various Bases in FLP Reactions with Alkynes



Scheme 18. Reactions of Pyrroles with Alkynes and $B(C_6F_5)_3$

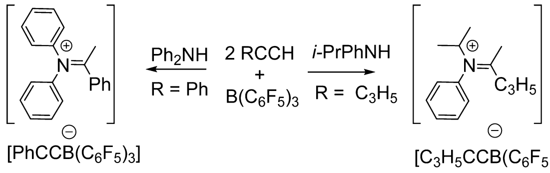


proton migrations afforded routes to the salt $[tBu_3PH][tBuNC_4H_3(PhC{=}C(H)B(C_6F_5)_3)]$, the rearranged species $tBuNC_4H_3(3\text{-}RC{=}C(H)(C_6F_5)B(C_6F_5)_2)$, and a series of vinyl pyrroles (Scheme 18).

Stoichiometric C−N bond formation is achieved via the reaction of *N*-alkylanilines or diarylamines with $B(C_6F_5)_3$ with 2 equiv of PhCCH affording $[Ph_2N{=}C(Me)Ph][PhC{\equiv}CB(C_6F_5)_3]$ (Scheme 19).[68]

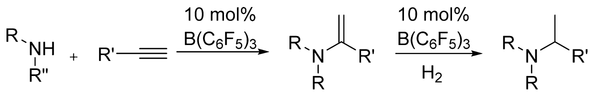
CATALYTIC FLP HYDROAMINATION OF ALKYNES

Scheme 19. Stoichiometric Reactions of Arylamine, Borane, and Alkyne



In these latter reactions, consumption of a second equivalent of alkyne can be avoided by slow addition. Transient generation of the amine−borane addition product with the alkyne generates an ammonium salt that is sufficiently acidic to protonate the *β*-carbon, releasing the enamine,[68] rather than reacting with excess alkyne. In this fashion, catalytic hydroamination of alkynes is achieved, affording a series of aryl enamines in yields between 62 and 84%. Furthermore, tandem hydroamination/hydrogenation provides a one-pot route to the corresponding amines (Scheme 20).[68]

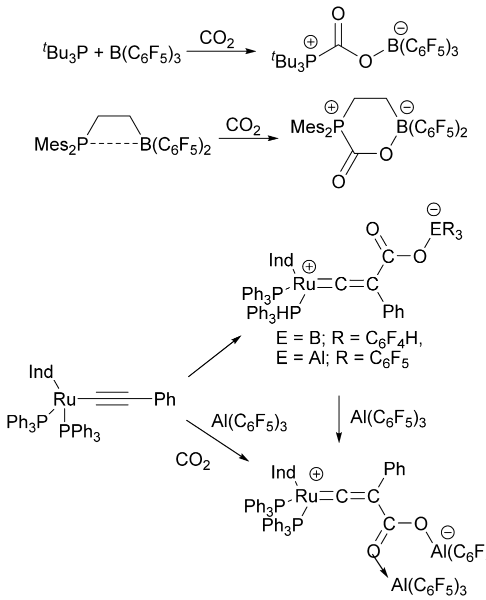
Scheme 20. Catalytic Hydroaminations of Alkynes



STOICHIOMETRIC REACTIONS OF CO_2 WITH FLPS

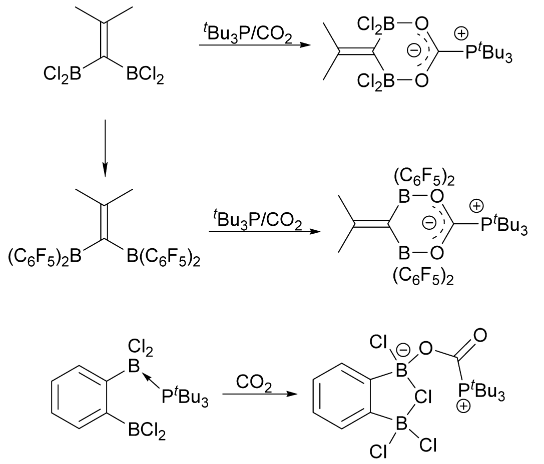
The classic inter- and intramolecular FLPs capture CO_2[69] to give the addition products $tBu_3PCO_2B(C_6F_5)_3$ and $Mes_2P(CH_2)_2B(C_6F_5)_2(CO_2)$ (Scheme 21). The thermodynamics of this capture of CO_2 has been recently determined by microfluidic methods.[70] Similarly, inter- or intramolecular FLP variants derived from B,[71−74] Al,[75−81] Ti,[73] Zr,[82−85] Hf,[86] and Si[87] electrophiles as well as NHC,[88−91] amine,[92−95] phosphinimine,[96] and pyrazole[97] Lewis bases have been exploited for CO_2 capture. In an unusual case, the basic *β*-carbon of a ruthenium acetylide was used as a Lewis base with $B(C_6F_4H)_3$ or $Al(C_6F_5)_3$ to capture CO_2, affording (indenyl)-$Ru(PPh_3)_2({=}C{=}C(Ph)(CO_2ER_3)$ (ER_3 = $B(C_6F_4H)_3$, $Al(C_6F_5)_3$) and (indenyl)$Ru(PPh_3)_2({=}C{=}C(Ph)(C(OAl(C_6F_5)_3)_2)$, respectively (Scheme 21).[98]

Scheme 21. FLP Capture of CO_2



Bis(boranes) were used to isolate $Me_2C{=}C(BCl_2)_2O_2CP^tBu_3$[99] and $Me_2C{=}C(B(C_6F_5)_2)_2O_2CP^tBu_3$ (Scheme 22), both of which exhibit symmetric bidentate binding of CO_2. In contrast, the FLP derived from $C_6H_4(BCl_2)_2/tBu_3P$ captures CO_2 to afford $C_6H_4[BCl_2(Cl)$-

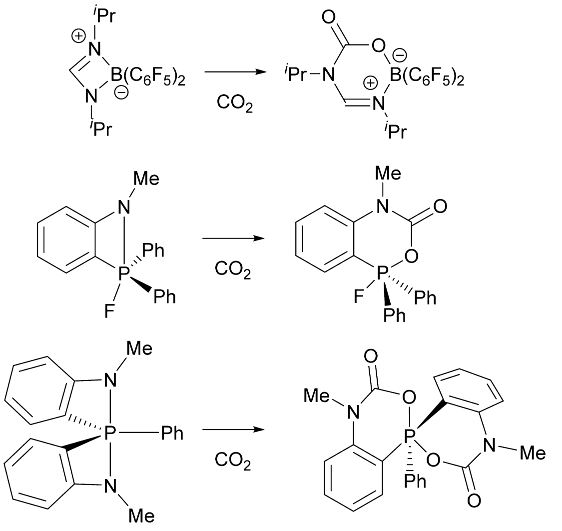
Scheme 22. Reactions of Bis(boranes) with CO_2



$BCl(O_2CP^tBu_3)]$[100] (Scheme 22), in which CO_2 binds to a single boron with a bridging Cl atom between the B centers, generating a more thermally robust product of CO_2 capture.

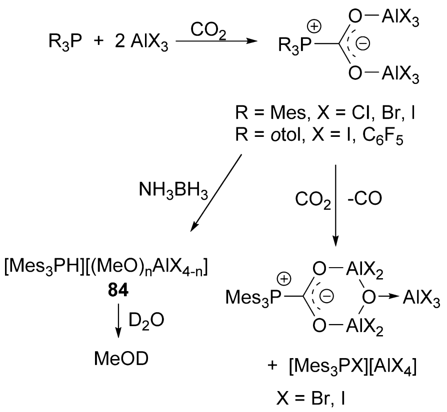
Even in systems where the base and acid of the FLP appear to be quenched, CO_2 can be captured. For example, the four-membered boron amidinate $HC(^iPrN)_2B(C_6F_5)_2$[101] undergoes insertion of CO_2 to give $HC(^iPrN)_2(CO_2)B(C_6F_5)_2$ (Scheme 23). This reaction must proceed via an equilibrium involving an open N/B FLP. In analogous systems, the four-membered rings containing Lewis acidic P(V) centers in $C_6H_4(NMe)PFPh_2$ and $[C_6H_4(NMe)]_2PPh$ were shown to capture CO_2, affording $C_6H_4(NMe)(CO_2)PFPh_2$ and $[C_6H_4NMe(CO_2)]_2PPh$, respectively (Scheme 23).[102]

Scheme 23. Reactions of Four-Membered Rings with CO_2



Beyond CO_2 capture, FLP CO_2 adducts can be exploited for stoichiometric reductions. For example, FLPs derived from $PMes_3/AlX_3$ (X = Cl, Br) generate the species $Mes_3P(CO_2)(AlX_3)_2$ (Scheme 24).[76] While these species are stable toward loss of CO_2 upon heating to 80 °C under vacuum, they react with H_3NBH_3 to give methoxyaluminum species that upon workup afford MeOH. Alternatively, upon prolonged exposure to CO_2, $Mes_3PC(OAlI_3)_2$ reacts to give $Mes_3PC(OAlI_2)_2OAlI_3$, $[Mes_3PI][AlI_4]$, and CO (Scheme 24).[75,78] Mechanistic investigations[75] suggest a series of dissociative equilibria generating AlX_3 and free phosphine. This permits associative insertion of CO_2 into an Al–X bond of Al_2X_6, while subsequent nucleophilic attack by phosphine yields $[Mes_3PI]^+$ and $Mes_3PC(OAlI_2)_2OAlI_3$ and liberates CO. While these stoichiometric reductions of CO_2 are interesting, they suggest that a less oxophilic Lewis acid is necessary for catalysis.

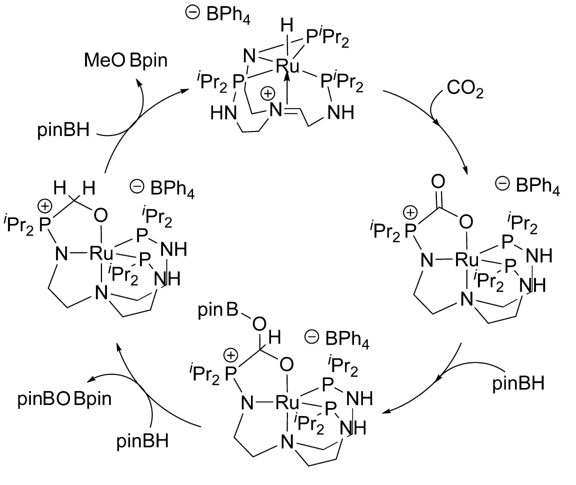
Scheme 24. Stoichiometric Reductions of CO_2 with P/Al FLPs



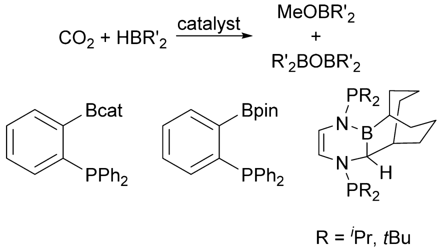
CATALYTIC REDUCTIONS OF CO_2

O'Hare and Ashley[103] described the first evidence of FLP reductions of CO_2 when they combined CO_2 and H_2 in the presence of the FLP tetramethylpiperidine (TMP)/$B(C_6F_5)_3$. This gave $CH_3OB(C_6F_5)_2$ after 6 days at 160 °C. In a related study, Piers and co-workers used Et_3SiH to effect catalytic reduction of CO_2, yielding CH_4 and $(Et_3Si)_2O$.[104] In our efforts, a metal-based FLP derived from a Ru complex with a pendant phosphine moiety, $[(N((CH_2)_2NHP^iPr_2)((CH_2)_2NP^iPr_2)(CHCH_2NHP^iPr_2))RuH][BPh_4]$, was shown to catalyze the hydroboration of CO_2 in the presence of excess pinacolborane (HBpin), catecholborane (HBcat), or 9-borabicyclo[3.3.1]nonane (9-BBN), generating MeOB and BOB species (Scheme 25). Interestingly, crystallographic characterization of CO_2- and aldehyde-capture products supported the proposed mechanism.[105,106] The Fontaine group[107] recently achieved a related borane reduction of CO_2 employing the main-group FLP $Ph_2PC_6H_4B(O_2C_6H_4)$ (Scheme 26), while we reported the related use of

Scheme 25. Catalytic Hydroboration of CO_2 by a Ru/P FLP



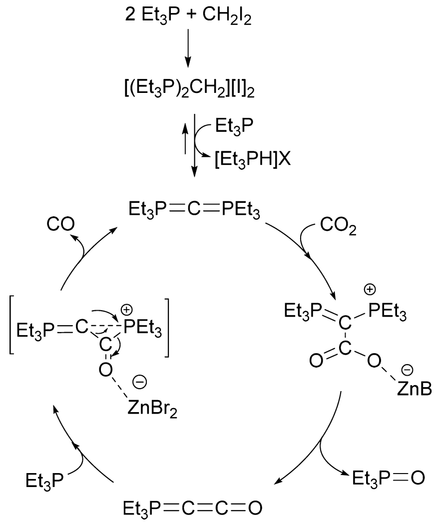
Scheme 26. Catalytic Hydroboration of CO_2 by B/P FLPs



$C_3H_2(NPR_2)_2BC_8H_{14}$, derived from the insertion of $C_3H_2(NPR_2)_2$ into 9-BBN (Scheme 26),[108] to catalyze the hydroboration of CO_2 to methoxyboranes and BOB species.

In addition, we discovered that combining Et_3P and CO_2 in the presence of a catalytic amount of CH_2I_2 and $ZnBr_2$ resulted in catalytic oxidation of the phosphine with liberation of CO (Scheme 27).[109] Mechanistic and computational studies revealed the in situ generation of $[(Et_3P)_2C]$, which acts as the base, in combination with zinc halides to give FLP addition to CO_2, generating $((Et_3P)_2CCO_2)(ZnBr_2)$. Subsequent elimination of Et_3PO affords $Et_3P{=}C{=}C{=}O$, which reacts with the FLP $Et_3P/ZnBr_2$, prompting loss of CO and regeneration of the bis(ylide) catalyst.[109]

Scheme 27. Catalytic Reduction of CO_2 by P/Zn FLPs



CONCLUSION

The advent of the concept of FLPs has provided a new strategy for the activation of small molecules, often but not always exploiting main-group systems. This has led to the discovery of new stoichiometric chemistry, which in some cases has spawned the development of new catalytic processes. In this Account, we have highlighted hydrogenation, hydroamination, and CO_2 reduction as three such avenues in which we contributed to FLP chemistry and advanced the reactivity to new catalysis. These examples illustrate the utility of the concept, and yet each of these areas has much potential for further development. Undoubtedly, as FLP chemistry is a rapidly growing and exciting field, new chemistry and catalysis will emerge in the coming years.

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Notes

The authors declare no competing financial interest.

Biography

Douglas W. Stephan earned his Ph.D. at the University of Western Ontario in 1980. After NATO postdoctoral studies with R. H. Holm at Harvard in 1980–82, he became an Assistant Professor at the University of Windsor, ultimately being appointed Full Professor in 1992. In 2008, he took up a Canada Research Chair and Professorship at the University of Toronto. He has authored 380 scientific articles and 80 patents involving fundamental and innovative technologies for catalysis. He has also received a number of national and international awards and has been named a Fellow of the Royal Societies of Canada and London.

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