Frustrated Lewis Pairs

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Frustrated Lewis Pair Chemistry: Development and Perspectives

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In memory of Michael Lappert

Frustrated Lewis pairs (FLPs) are combinations of Lewis acids and Lewis bases in solution that are deterred from strong adduct formation by steric and/or electronic factors. This opens pathways to novel cooperative reactions with added substrates. Small-molecule binding and activation by FLPs has led to the discovery of a variety of new reactions through unprecedented pathways. Hydrogen activation and subsequent manipulation in metal-free catalytic hydrogenations is a frequently observed feature of many FLPs. The current state of this young but rapidly expanding field is outlined in this Review and the future directions for its broadening sphere of impact are considered.

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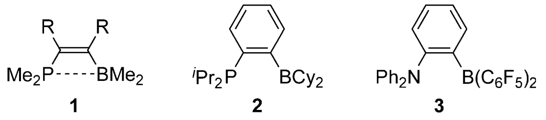
1. Introduction

Lewis acids and Lewis bases usually form strong adducts. This typical behavior of electron-pair-donor and electron-pair-acceptor compounds was described by Gilbert N. Lewis in 1923,[1] who drew the analogy to the H_3O^+/OH^- neutralization reaction in Brønsted acid/base chemistry.[2] Lewis pair adducts (e.g. ammonia borane $H_3B\text{-}NH_3$, formed from $0.5\,B_2H_6$ and NH_3)[3] exhibit chemistry that is distinct from the original components.

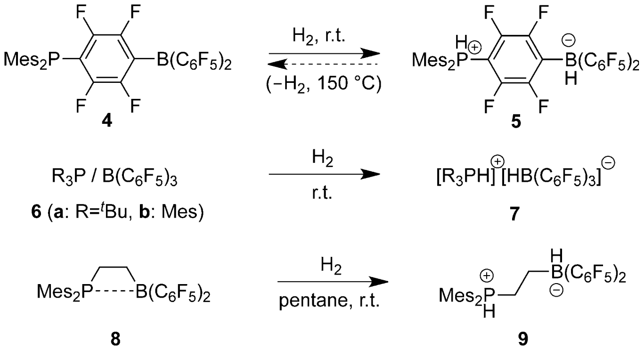
Early on, it was recognized that not all Lewis acid/Lewis base combinations form strong adducts. For example, in 1942 H. C. Brown et al. showed that lutidine formed an adduct with BF_3 but not with the less Lewis acidic and bulkier $B(CH_3)_3$.[4] Subsequently, the Wittig school described 1,2-addition reactions of the PPh_3/BPh_3 pair to in situ-generated benzyne and also showed that the $[CPh_3]^-$ anion/BPh_3 pair adds to butadiene.[5] These latter cases demonstrated that bulky Lewis pairs evade self-quenching by strong adduct formation and thus find an alternate pathway for reactivity.

Several reports have also described the combination of Lewis acid and Lewis base functional groups into single molecules (e.g. Scheme 1). Some such systems (**1**, **2**) have been used as ambiphilic ligands in metal coordination chemistry,[6] while the system **3** was shown to react with a variety of polar reagents (HCl, H_2O, LiH).[7]



Scheme 1. Molecules containing Lewis acid and base sites. Cy = cyclohexyl.

The disclosure by Stephan and co-workers that the intramolecular Lewis acid/Lewis base pair in **4** cleanly cleaves the dihydrogen molecule under ambient conditions (Scheme 2)[8] marked a major development in cooperative Lewis acid/base chemistry. Subsequently, Stephan further demonstrated that combinations of bulky phosphines with $B(C_6F_5)_3$ provided intermolecular systems that also cleaved H_2 to yield the respective phosphonium/hydridoborate salts **7**[9] while the Erker group reported the intramolecular ethylene-bridged phosphine/borane Lewis pair **8** which is also a highly active non-metallic system for the activation of hydrogen.[10]



Scheme 2. First examples of FLP activation of dihydrogen. Mes = mesityl.

These three publications marked the beginning of a remarkably rapid development of new chemistry arising

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from the combination of a bulky Lewis base with a bulky, electrophilic Lewis acid. Such combinations were termed “frustrated Lewis pairs (FLPs) ”.[11] They are not quenched but act cooperatively to heterolytically cleave the strong H−H bond. In this manner, FLPs effect a reaction that is normally attributed to the chemistry of transition-metal surfaces or homogeneous transition-metal complexes.[12]

Theoretical chemists rapidly started analyzing this situation.[13] Although differing in detail, most computational studies now seem to converge on a description that involves concerted pathways of H−H cleavage and formation of the $[\mathrm{PH}]^+$ and $[\mathrm{HB}]^-$ moieties. Many intramolecular FLPs exhibit weak internal Lewis acid/Lewis base interactions and, according to calculations, they usually react from a readily accessible open conformation. In contrast, intermolecular FLPs evade a self-quenching reaction pathway by the interaction of dihydrogen with an “encounter complex” in which the acid and base are held together by van der Waals interactions. Recent experimental studies have determined the thermodynamic and kinetic parameters for FLP hydrogen activation. Autrey et al. determined by reaction calorimetry the reaction enthalpy of the exothermic H_2-splitting reaction of the intramolecular FLP **8** affording the zwitterion **9** as $\Delta H_\mathrm{r} = -7.5 \pm 1.0\,\mathrm{kcal\,mol^{-1}}$.[14] They found that hydrogen activation by the FLP **8** is rate determining in the imine hydrogenation catalyzed by **8**. The second-order rate constant of the **8**+H_2→**9** hydrogen splitting reaction was determined at 295 K as $k_\mathrm{r} = 0.7\,\mathrm{M^{-1}\,s^{-1}}$.[14]

Since 2006, the field of FLP chemistry has expanded enormously. Hydrogen activation rapidly led to the development of metal-free FLP-catalyzed hydrogenations. However, the rapid expansion of FLP chemistry in the following years was also due to the great variability of the cooperative reactions of FLPs with a variety of other substrates, leading to small-molecule binding and activation. FLP chemistry is often experimentally rather simple to perform and it affords the possibility of new reactions as a result of the cooperative action by Lewis acid and Lewis base sites.

We described the early stages of this steep development in our 2010 Review.[15] In the intervening time, several more Reviews about selected aspects of FLP chemistry have appeared.[16] In addition, a two volume set of *Topics in Current Chemistry*[17] and several specific journal issues[18] as well as several international symposia have been devoted to this topic. In this Review we outline some of the principal lines of development that FLP chemistry has taken in recent years and attempt to provide a perspective for future developments for this young but exciting area of chemistry.

2. Hydrogen Splitting and Metal-Free Hydrogenation

The ability of many inter- and intramolecular FLPs to heterolytically cleave the dihydrogen molecule has resulted in the development of a variety of methods for metal-free catalytic hydrogenation processes of various unsaturated organic substrates. In the beginning this was mostly the hydrogenation of bulky imines,[16f,19] but then this route was rapidly extended to enamines[20] and silyl enol ethers.[21] These reactions of electron-rich organic substrates were shown to proceed by initial protonation to generate an iminium ion intermediate that is then reduced by the hydrido-borate component of the FLP-H_2 activated compound. This chemistry has been amply reviewed[16e,h,22] and will therefore not be detailed herein.

The impact of Lewis acid donors on H_2 activation was probed using phosphites.[23] Despite the fact that $\mathrm{P(O\text{-}2,4\text{-}(^tBu_2C_6H_3)_3}$ and $\mathrm{P(O\text{-}2,6\text{-}Me_2C_6H_3)_3}$ generate FLPs with $\mathrm{B(C_6F_5)_3}$, these combinations do not react with H_2. The more basic species $\mathrm{^tBu_2POR}$, (R = Ph; 2,6-$\mathrm{Me_2C_6H_3}$) and $\mathrm{^tBu_2PCl}$ also form FLPs with $\mathrm{B(C_6F_5)_3}$, but these too do not react with H_2. The mixture of $\mathrm{B(OC_6F_5)_3}$ and $\mathrm{P^tBu_3}$ also generates an FLP, but this combination does react with H_2, affording $\mathrm{[HP^tBu_3][B(OC_6F_5)_4]}$, the product of hydrogen activation and borate-substituent redistribution. Boronic esters, such as $\mathrm{(C_6H_4O)_2BC_6F_5}$, $\mathrm{(C_6H_3FO)_2BC_6F_5}$, and $\mathrm{(C_6F_4O)_2BC_6F_5}$, and borate esters $\mathrm{B(OC_6H_3(CF_3)_2)_3}$, $\mathrm{B(OC_6H_2F_3)_3}$, and $\mathrm{B(OC_6H_4CF_3)_3}$ generate FLPs with $\mathrm{^tBu_3P}$ or $\mathrm{Mes_3P}$, although these show no reaction with H_2. Collectively these data suggest that there is a threshold of combined Lewis acidity and basicity that is required to effect the splitting of H_2.[23]

While in the beginning mostly P/B FLPs were employed, this was extended to a larger variety of N/B FLP systems. Wang et al. have proposed a variety of adamantane derived N/B containing frameworks as theoretical FLP designs.[24] The

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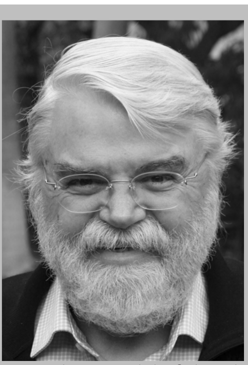
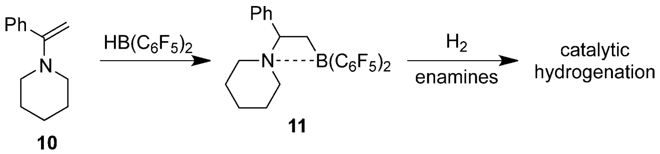


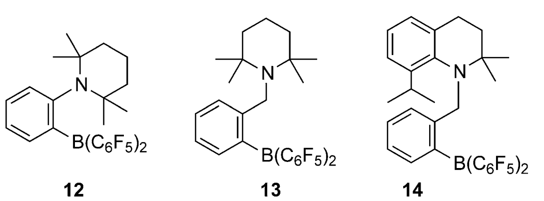
Gerhard Erker (Dr. rer. nat. Universität Bochum 1973) did his habilitation in 1981 followed by a stay at the MPI for Kohlenforschung in Mülheim as a Heisenberg fellow. In 1985 he became a Professor at the Universität Würzburg and then a Full Professor at the Universität Münster in 1990. He was the GDCh president in 2000/1 and a member of the DFG senate (2002–2008). He has received a number of awards, among them the Krupp Preis (1986), the Otto Bayer Award (1995), the Adolf von Baeyer Denkmünze (2009) and the Werner Heisenberg Medal of the Alexander von Humboldt-Stiftung (2011). He is a member of the NRW Academy of Sciences, Humanities and the Arts and of the German National Academy of Sciences Leopoldina.

Erker group has found that vicinal intramolecular N/B FLPs[25] are readily available from hydroboration of enamines with Piers' borane.[26] Many of these systems show features and reactivity similar to the P/B FLP analogues, although they do exhibit a slightly reduced tendency to activate H_2. Nonetheless, some examples, such as compound **11**, cleaved dihydrogen reversibly and served as an active metal-free hydrogenation catalyst (Scheme 3).



Scheme 3. Vicinal N/B FLPs: formation and dihydrogen splitting.

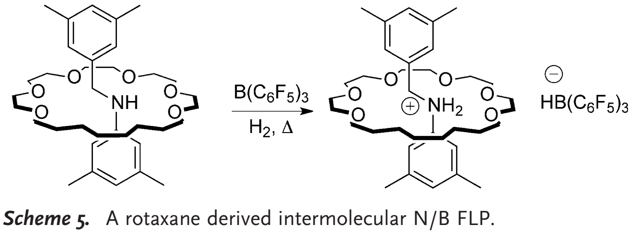
Repo et al.[27] re-investigated Piers' N/B system **3** (Scheme 1) and found that it can be converted into a H_2-activating system by formally exchanging the weak -NPh_2 base component for more Lewis basic alkylamines. The systems **12**–**14** (Scheme 4), among others, cleave dihydrogen efficiently under mild conditions and have served as active catalysts for imine hydrogenation at elevated temperatures (ca. 100 °C).



Scheme 4. Intramolecular amine/borane FLPs.

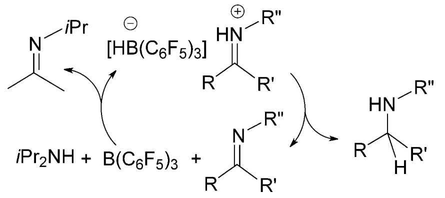
In related work, Berke et al.[28] have used tetramethylpiperidine/$RB(C_6F_5)_2$ pairs for dihydrogen activation. The parent system with $R = C_6F_5$ seems to result in an irreversible H_2 activation; however, using the slightly less Lewis acidic (cyclohexyl)$B(C_6F_5)_2$ results in reversible H_2-splitting at elevated temperature.

An alternative strategy to the incorporation of steric encumbrance was demonstrated with the activation of dihydrogen by the Lewis acid/base combination comprising $B(C_6F_5)_3$ and a secondary amine which is sterically encumbered by inclusion in a rotaxane (Scheme 5).[29]



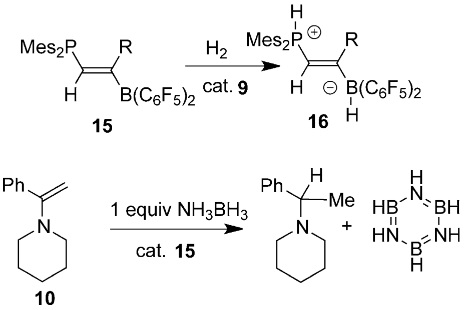
Scheme 5. A rotaxane derived intermolecular N/B FLP.

Transfer hydrogenation using hydrogen-releasing substrates in lieu of dihydrogen itself has been exploited to develop selective transition-metal catalysts for hydrogenation.[30] It is well established that $B(C_6F_5)_3$ is able to abstract hydride from amines in the α-position to nitrogen.[31] Stephan et al.[32] observed that secondary amines undergo racemization upon treatment with the Lewis acid $B(C_6F_5)_3$, and further developed this into a $B(C_6F_5)_3$-catalyzed transfer hydrogenation of imines, enamines, quinolines, and aziridines using diisopropylamine as the hydrogen source (Scheme 6).



Scheme 6. FLP catalyzed transfer hydrogenation.

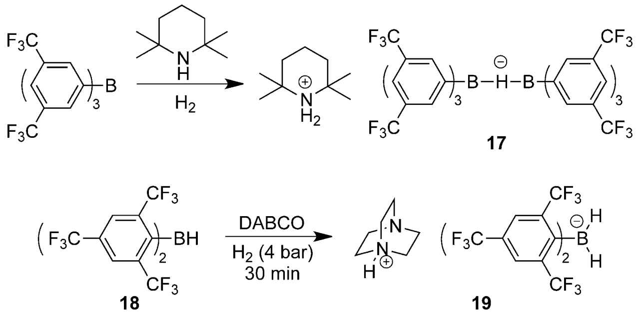
A second example of transfer hydrogenation has been reported for the unsaturated intramolecular FLP $Mes_2PCH{=}CMeB(C_6F_5)_2$ (**15**). Interestingly, this FLP did not activate H_2, however, treatment with a catalytic amount of $Mes_2PCH_2CH_2BH(C_6F_5)_2$ (**9**) facilitated reduction to give $Mes_2PHCH{=}CRBH(C_6F_5)_2$ (**16**; Scheme 7).[20] In addition, 16 mol% of **15** acts as an effective catalyst for the transfer hydrogenation of the enamine $PhNC_5H_{10}C{=}CH_2$ (**10**) using ammonia-borane as the H_2 source, yielding the tertiary amine and borazine (Scheme 7).



Scheme 7. Other FLP catalyzed transfer hydrogenation reactions.

A variety of new frameworks have been employed to link -PR_2/-$B(C_6F_5)_2$ Lewis base/Lewis acid pairs to generate intramolecular FLPs for H_2 splitting. For example, a paracyclophane-based framework[33] and even a calixarene-derived intermolecular two-fold P/B FLP have been reported to be active in dihydrogen splitting.[34]

A variety of new boron Lewis acids were employed for H_2 activation and catalysis. For example, the O'Hare group used tris(2,2',2''-perfluorobiphenyl)borane[35] while Ashley et al.[36] used tris[3,5-bis(trifluoromethyl)phenyl]borane in combination with tetramethylpiperidine for dihydrogen activation. Wang and co-workers[37] reported the related bis[(2,4,6-trifluoromethyl)phenyl]borane **18** which, in combination



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18

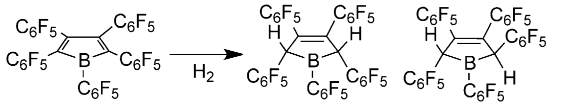
19

Scheme 8. Variation of boron Lewis acids in active FLP dihydrogen-splitting systems. DABCO = 1,4-diazabicyclo[2.2.2]octane.

with the Lewis base DABCO, readily cleaves dihydrogen in what is probably a concerted reaction, to give the salt **19** (Scheme 8).

Repo et al.[38] reported a rare case of B(C$_6$F$_5$)$_3$ mediated reduction of aromatic carbonyl compounds with dihydrogen. At 110°C, a 29% yield of benzylalcohol was obtained after aqueous workup. Benzophenone was apparently reduced to diphenylmethanol under these conditions, although it was not stable and underwent Friedel–Crafts alkylation with the toluene solvent to eventually yield the respective triarylmethane products.

A Lewis acidic borole has been shown to react with dihydrogen even in the absence of an auxiliary Lewis base. Piers' borole **20** (Scheme 9) upon exposure to dihydrogen under near ambient conditions gives a mixture of the *cis*- and *trans*-dihydroborole products **21**. The mechanistic course of the reaction has been investigated.[39] The apparent role of a B–H$_2$ interaction suggest this may be relevant to the mechanism of FLP activation of H$_2$.

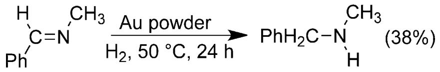


20 *cis*-**21** *trans*-**21**

Scheme 9. Reaction of Piers' borole with dihydrogen.

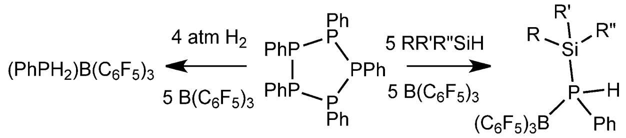
Ashley et al.[40] published an interesting electrochemical study in which they heterolytically split dihydrogen using the intermolecular ^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$ FLP. Subsequent electrochemical oxidation of the borohydride anion took place with a substantial reduction of the overpotential. This effects the formal conversion of H$_2$ into two protons and two electrons, a reaction scheme reminiscent of the conversion of H$_2$ enabled by hydrogenase enzymes.[41]

In an interesting extension of FLP chemistry to heterogeneous catalysis, it was noted that clean gold surfaces are inert to H$_2$. However, combination with imine or nitrile Lewis bases appears to produce a FLP-like situation which effects the activation of dihydrogen and the eventual reduction of the imines to the corresponding saturated amine products (Scheme 10).[42] This interesting study illuminates the potential of FLP chemistry employing active metal surfaces.



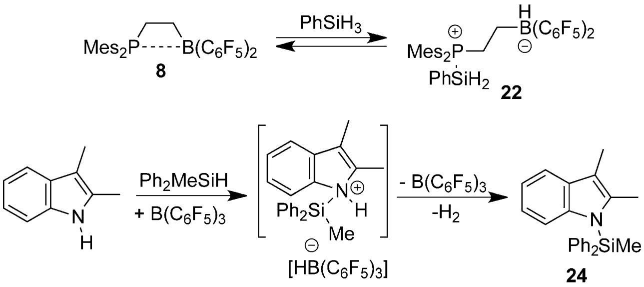
Scheme 10. FLP reaction on a gold surface.

Silanes often behave like activated analogues of dihydrogen. In this regard, Stephan's group showed that H$_2$, R$_3$SiH, or R$_2$SiH$_2$ react with P$_5$Ph$_5$ in the presence of stoichiometric B(C$_6$F$_5$)$_3$ to effect the hydrogenation or hydrosilylation of the P–P single bonds, affording the phosphine-borane adducts (PhPH$_2$)B(C$_6$F$_5$)$_3$, ((R$_3$Si)PhPH)B(C$_6$F$_5$)$_3$, and ((R$_2$SiH)PhPH)B(C$_6$F$_5$)$_3$, respectively, in excellent yields (Scheme 11).[43]



Scheme 11. Borane-induced reductive P–P bond cleavage.

Nikonov and co-workers[44] showed that B(C$_6$F$_5$)$_3$ induces H/D exchange between dihydrogen and various Si–D containing silanes. The borane was first converted into Piers' borane HB(C$_6$F$_5$)$_2$ under the reaction conditions and it was this species that was subsequently responsible for the actual exchange reaction. In a related study, a collaborative effort from the groups of Erker and Oestreich[45] showed that the intramolecular P/B FLP **8** heterolytically splits silanes with formation of the respective silylphosphonium/hydridoborate zwitterions. For example, compound **22** is formed reversibly from **8** and PhSiH$_3$ (Scheme 12).



8 **22** **23** **24**

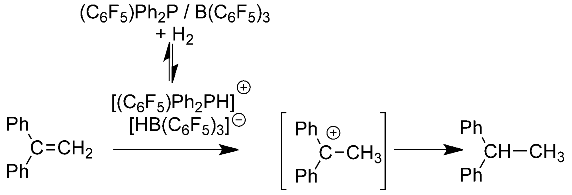
Scheme 12. Formation of silylium-containing FLP systems.

Paradies and co-workers[46] have recently reported the dehydrocoupling of a variety of secondary amines and silanes catalyzed by B(C$_6$F$_5$)$_3$. These reactions are thought to proceed by reactive intermediate silylammonium/hydridoborate ion pairs (e.g. **23**), which eliminate H$_2$ affording the N-silylated products (e.g. **24**) and regenerating the borane catalyst (Scheme 12).

Four specific areas in the field of dihydrogen splitting and hydrogenation with FLPs are discussed in the following Sections. We draw special attention to these advances as they are in our estimation of general importance and are poised for further development in the near future.

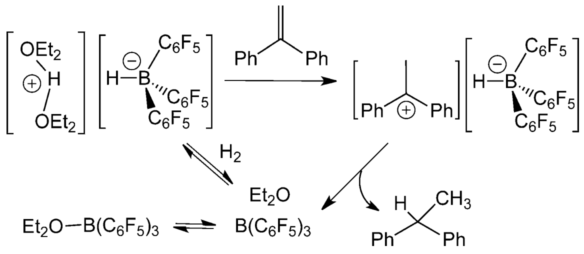
2.1. Hydrogenation of Non-Functionalized Alkenes and Alkynes

The intermolecular FLP $(C_6F_5)Ph_2P/B(C_6F_5)_3$ was shown to activate dihydrogen reversibly at low temperature (below −60 °C). The resulting $[(C_6F_5)Ph_2PH]^+$ phosphonium ion is quite Brønsted acidic and consequently protonates a variety of alkenes, generating substituted tertiary benzylic or allylic carbenium ions which undergo hydride delivery from the hydridoborate anion. Although this effects catalytic hydrogenation for a limited array of substrates, it opened an avenue to FLP hydrogenation of non-functionalized alkenes (Scheme 13).[33b,47]



Scheme 13. FLP hydrogenation through a benzylic cation.

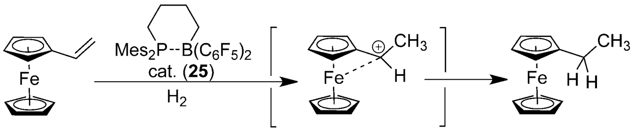
In a related fashion, the activation of dihydrogen by the combination of ether and $B(C_6F_5)_3$ was demonstrated by the redistribution of HD to H_2 and D_2, although the intermediate $[H(OEt_2)_2][HB(C_6F_5)_3]$ was never detected spectroscopically.[48] Nonetheless, this FLP was also shown to effect the catalytic hydrogenation of $Ph_2C{=}CH_2$ (Scheme 14). Computations suggested the role of a second ether molecule in the transient stabilization of the protonated ether cation.



Scheme 14. Hydrogenation with the ether/borane FLP.

More recently, the intramolecular FLP $Mes_2P(CH_2)_4B(C_6F_5)_2$ (**25**) was shown to catalyze the hydrogenation of vinylferrocene to give ethylferrocene. The 1-ferrocenylethyl-cation **26**, the intermediate in the reaction, is subsequently trapped by the borohydride derived from the activation of H_2 by **25** (Scheme 15).[49]

A variety of non-functionalized olefins were hydrogenated with catalytic amounts of Piers' borane $HB(C_6F_5)_2$ under forcing conditions (20 mol % borane, 140 °C, 72–120 h reaction time). These reactions are thought to proceed by initial hydroboration (e.g. **27**) of cyclohexene with $HB(C_6F_5)_2$, followed by σ-bond metathesis with dihydrogen, liberating the alkane and regenerating Piers' borane. The reaction of **27** with H_2 was shown to follow overall second order kinetics, first order in **27** and first order in H_2. DFT calculations revealed a slightly unsymmetric transition state (Scheme 16).[50] Attempts to effect the reductions of ketones showed that these combinations were too reactive, thus precluding catalytic hydrogenations.



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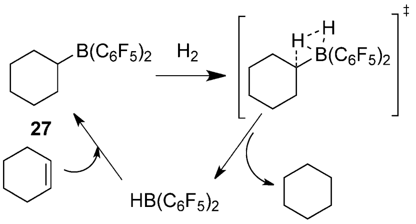
Scheme 15. Hydrogenation of vinylferrocene.



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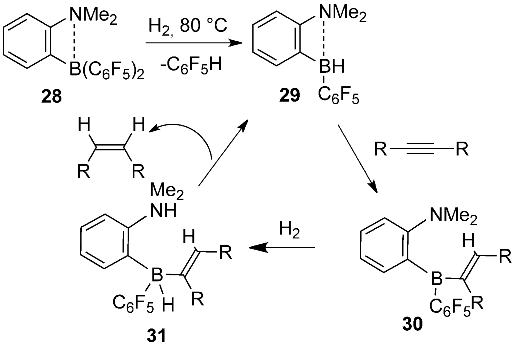
Scheme 16. Alkene hydrogenation with Piers' borane.

Repo et al.[51] reported a conceptually related pathway that resulted in the selective hydrogenation of non-functionalized internal alkynes to give the respective *cis*-alkenes. They showed that the intramolecular N/B FLP **28** (Scheme 17) reacted with dihydrogen at 80 °C to give the [B]-H borane **29** with liberation of pentafluorobenzene. This species was catalytically active, undergoing hydroboration of an alkyne to give **30**, and subsequent FLP activation of dihydrogen to generate **31**. Internal protonolysis liberates the observed *cis*-alkene product and regenerates the active catalyst **29**. This strategy was used to hydrogenate a series of over 20 internal alkynes, demonstrating that FLPs represent an alternative to Lindlar's alkyne reduction catalyst.[51]

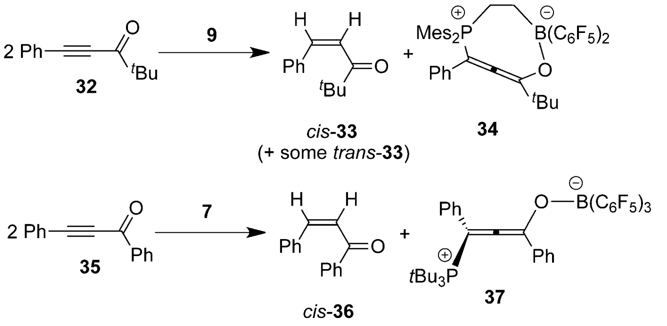


Scheme 17. *cis*-Hydrogenation of an internal alkyne.

2.2. Electron-Poor Alkenes and Alkynes

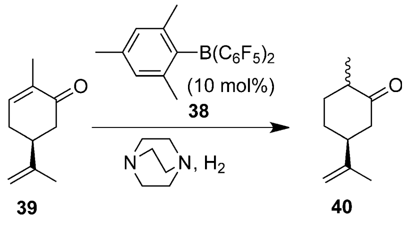
Further efforts to expand the scope of the metal-free catalytic hydrogenation reactions focused on alkenes and alkynes with polar, strongly electron-withdrawing substituents.

The hydrogen-activation product $Mes_2PH(CH_2)_2BH(C_6F_5)_2$ (**9**) reacts readily with conjugated ynones. For example, the stoichiometric reaction of **9** with ynone **32** resulted in the reduction of the carbon–carbon triple bond to yield the *cis*-enone **33** with a small amount of its isomerization product, the *trans*-enone. Even in the presence of dihydrogen, the liberated FLP **8** was very efficiently trapped by a second equivalent of ynone to give the eight-membered heterocycle **34** (Scheme 18). Similarly, reaction of $[^tBu_3PH][HB(C_6F_5)_3]$ (**7**) with the ynone **35** gave predominantly the *cis*-enone **36** and the P/B ynone addition product **37**.[52] Apparently, these FLPs were too reactive towards the unsaturated ketone substrates even in the presence of H_2, thus precluding catalytic hydrogenations.



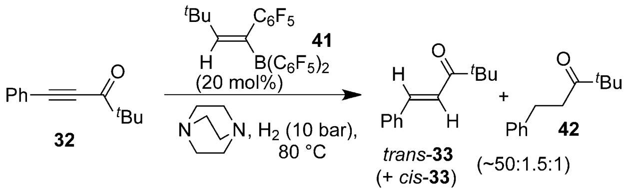
Scheme 18. Stoichiometric FLP hydrogenation of conjugated ynones.

In contrast, Soós et al.[53] found that the electronically and sterically moderated boron Lewis acid $(C_6H_2Me_3)B(C_6F_5)_2$ (**38**) is sufficiently Lewis acidic to activate dihydrogen in the presence of bulky tertiary amines, such as DABCO or quinuclidine, and is sufficiently bulky to effect catalytic imine hydrogenation under mild reaction conditions. Remarkably, this system selectively hydrogenates the carbon–carbon double bond in carvone (**39**) to give the product **40** in 87 % yield (Scheme 19).

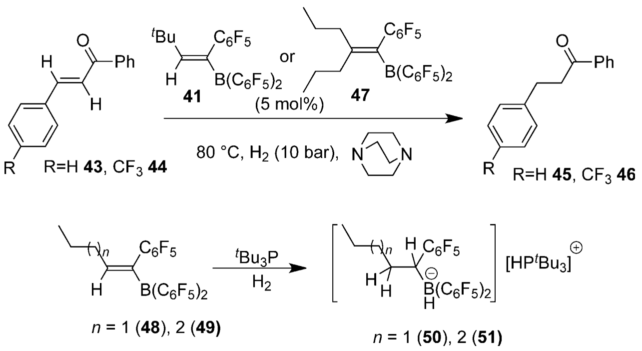


Scheme 19. Metal-free carvone hydrogenation.

In a related fashion, the bulky alkenylborane **41**, which is easily prepared by means of a 1,1-carboboration reaction of ^tBu-acetylene with $B(C_6F_5)_3$,[54] was shown to form an FLP with $^tBu_3P$ or with DABCO. The latter combination proved to be catalytically active, effecting the hydrogenation of the ynone **32** to give predominantly the conjugated enone *trans*-**33** with a small amount of *cis*-**33** and the saturated ketone **42** (Scheme 20).[52a] In this fashion, a small series of conjugated enones was treated with the **41**/DABCO pair under similar metal-free hydrogenation conditions. For example, *trans*-**43** and *trans*-**44** were hydrogenated to the ketone products **45** and **46** by using either of the bulky alkenylboranes **41** or **47** jointly with either Lewis base DABCO or P^tBu_3 (Scheme 21).[55] Alkenyl boranes (**48**, **49**) with less-bulky substituents were catalytically ineffective but instead were themselves hydrogenated to give the phosphonium hydridoborate salts **50** and **51**, respectively.



Scheme 20. Catalytic ynone hydrogenation.

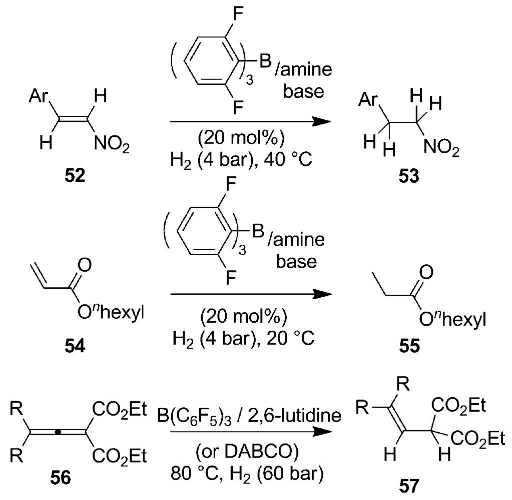


Scheme 21. Catalytic enone and alkenylborane hydrogenation reactions.

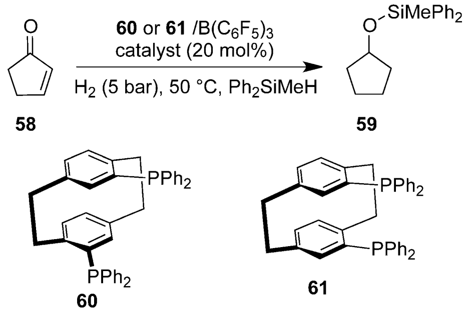
More recently, Paradies and co-workers[56] have demonstrated that β-nitrostyrenes **52** can be hydrogenated using *tris*(2,6-difluorophenyl)borane/amine FLPs at 40 °C. Good conversions were obtained using 2,6-lutidine as the amine base (Scheme 22). In a similar fashion, Alcarazo and co-workers[57] showed that the combination of $B(C_6F_5)_3$ and DABCO or 2,6-lutidine (10–15 mol %) effectively hydrogenated allenic esters, such as **56** to the corresponding esters **57**, respectively (Scheme 22). In a related sense, several enones were completely reduced in a domino hydrogenation/hydrosilylation catalyzed by [2,2]-paracyclophane bisphosphine/$B(C_6F_5)_3$ FLP catalysts (Scheme 23).[33c]

2.3. Arene Hydrogenation

Selective arene hydrogenation by homogeneous transition-metal catalysts is rare but has drawn recent attention.[58] FLP hydrogenations have also recently been shown to be effective for specific arene reductions. Such reductions were

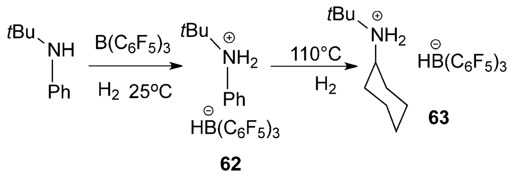


Scheme 22. FLP hydrogenation of electron-poor alkenes.



Scheme 23. Catalytic enone hydrogenation/hydrosilylation.

uncovered initially while examining the activation of H_2 by an FLP comprised of the amine ^{t}BuNHPh and $B(C_6F_5)_3$ at 25 °C which affords the salt [^{t}BuNH$_2$Ph][HB$(C_6F_5)_3$] (**62**).[59] However, on prolonged (96 h) heating to 110 °C, the salt isolated was [^{t}BuNH$_2$Cy][HB$(C_6F_5)_3$] (**63**), demonstrating the hydrogenation of the N-bound arene ring (Scheme 24). Analogous treatment of a series of bulky anilines, imines, and an aziridine were reduced to give the corresponding *N*-arene-hydrogenated products (Table 1).[59]



Scheme 24. Hydrogenation of *tert*-butylaniline.

Table 1: Hydrogenations of aniline.

Aniline	Product cation	*t* [h]	Y [%]
^{t}BuNHPh	[^{t}BuNH$_2$Cy]$^+$	96	30
^{i}PrNHPh	[^{i}PrNH$_2$Cy]$^+$	36	93
CyNHPh	[Cy$_2$NH$_2$]$^+$	36	88
Ph$_2$NH	[Cy$_2$NH$_2$]$^+$	96	65
^{i}PrNH(2-MeC$_6$H$_4$)	[^{i}PrNH$_2$(2-MeC$_6$H$_{10}$)]$^+$	36	77
^{i}PrNH(4-MeC$_6$H$_4$)	[^{i}PrNH$_2$(4-MeC$_6$H$_{10}$)]$^+$	36	73
^{i}PrNH(4-MeOC$_6$H$_4$)	[^{i}PrNH$_2$(4-MeOC$_6$H$_{10}$)]$^+$	36	61
^{i}PrNH(3-MeC$_6$H$_4$)	[^{i}PrNH$_2$(3-MeC$_6$H$_{10}$)]$^+$	36	82
^{i}PrNH(3,5-Me$_2$C$_6$H$_3$)	[^{i}PrNH$_2$(3,5-Me$_2$C$_6$H$_9$)]$^+$	72	48
PhN(C$_2$H$_2$Ph$_2$)	[CyNH$_2$(CH(Ph)CH$_2$Ph)]$^+$	96	50
PhN=C(Me)Ph	[CyNH$_2$CH(Me)Ph]$^+$	96	57
(Me$_2$C=N)$_2$C$_6$H$_4$	[(^{i}PrNH$_2$)$_2$C$_6$H$_{10}$]$^{2+}$	72	64

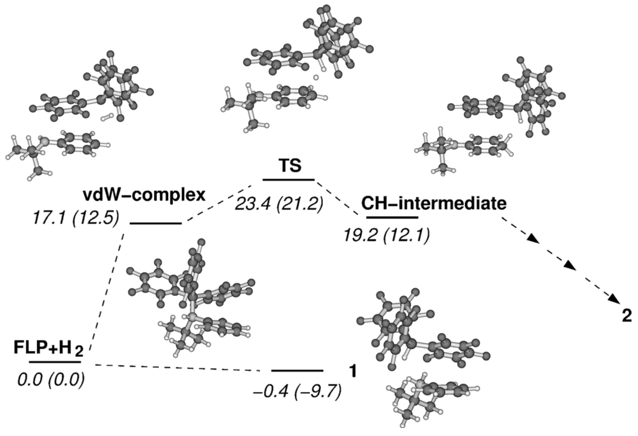
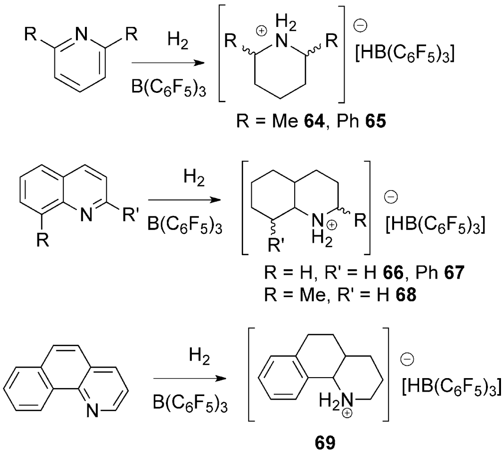


Figure 1. Computed reaction pathway for arene hydrogenation of ^{t}BuNHPh.

Computational studies showed that FLP activation of H_2 by amine ^{t}BuNHPh and borane has an exothermicity of 9.7 kcal mol^{-1} providing access to the FLP at elevated temperatures. This activation allows access to a van der Waals complex between the *para*-carbon of the arene ring and the boron center which has an activation barrier of 8.7 kcal mol^{-1}. Subsequent activation of H_2 disrupts the aromaticity and further hydrogenation to the cyclohexylammonium product is thermodynamically downhill (Figure 1).[59]

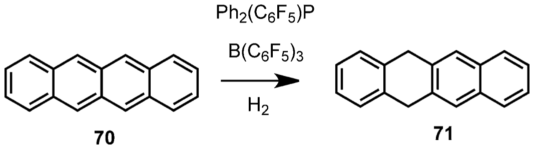
Such aromatic reductions are readily extended to N-heterocycles. For example, several sterically hindered pyridines when treated with $B(C_6F_5)_3$ and H_2 at 110 °C for 16–60 h resulted in the reduction to give the corresponding piperidium salts for example, **64**, **65** (Scheme 25). In a similar



Scheme 25. Examples of hydrogenations of N-heterocycles.

fashion, a series of N-heterocycles including 2-methyl quinoline, 2-phenyl quinoline, 8-methylquinoline, acridine, and 2,3-dimethyl- and 2,3-diphenylquinoxaline are completely reduced to the corresponding saturated heterocyclic ammonium and piperazinium salts (e.g. **66–68**). Interestingly 7,8-benzoquinoline is partial reduced with the "pyridine" and aniline-type rings being reduced but the remote arene ring remaining untouched thus affording $[(C_6H_4)C_7H_{12}NH_2][HB(C_6F_5)_3]$ (**69**). It is noteworthy that these aromatic reductions are stoichiometric reactions in aniline or N-heterocycle and borane. However, 4–8 equivalents of H_2 are consumed in these reductions. Catalytic turnover, however, ceases as the generated amines react with H_2 and borane forming an ammonium salt and thus sequestering the borane from solution. On the other hand, catalytic hydrogenation is observed under mild conditions for sterically congested N-heterocycles, such as 2- or 8-substituted quinolines, although in these cases only the 'pyridine' ring is reduced.[53b,60]

In related work, several polyaromatics including anthracene derivatives, tetracene, and tetraphene were reduced employing 10 mol% of the FLP $B(C_6F_5)_3/Ph_2PC_6F_5$ at 80 °C and 100 atm H_2 pressure.[61] In these cases, only one equivalent of dihydrogen is added to the substrates, for example the tetracene **70** is catalytically converted into dihydrotetracene **71** (Scheme 26).

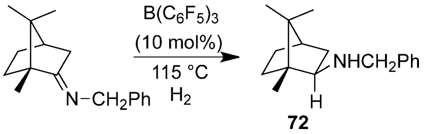


Scheme 26. Arene hydrogenation.

2.4. Asymmetric Hydrogenation

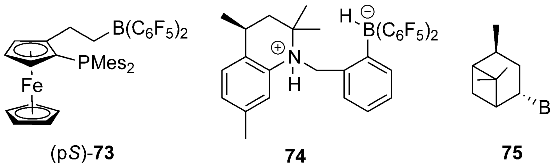
While asymmetric hydrogenation with transition-metal complexes has been of enormous synthetic importance,[30a,62] efforts to adapt FLPs as catalysts for asymmetric hydrogenation are still in their infancy. Nonetheless, such development might become significant in areas where even minimal amounts of noble metal contaminations are not tolerated, such as for some pharmaceutical or materials applications.

Diastereoselective reactions have been described by Stephan et al.[63] A series of imines containing chiral moieties either at nitrogen or at the carbon atom of the C=N unit were hydrogenated with $B(C_6F_5)_3$ as the FLP Lewis acid partner. Typically 10 to 20 mol% of the borane were used. The hydrogenation reactions were typically carried out at elevated temperatures (80 °C to 115 °C) and mostly at a hydrogen pressure of 5 bar. Chiral auxiliaries on the nitrogen side gave generally poor diastereoselectivities whereas those on carbon in some cases led to very high asymmetric inductions (Scheme 27). In contrast, use of typical borohydride reagents, such as $Na[BH_3CN]$ or $Na[BH(OAc)_3]$, gave much lower diastereoselectivities. This observation emphasizes the superiority of the bulkier $[HB(C_6F_5)_3]^-$ ion for chiral discrimination.



Scheme 27. Diastereoselective hydrogenation.

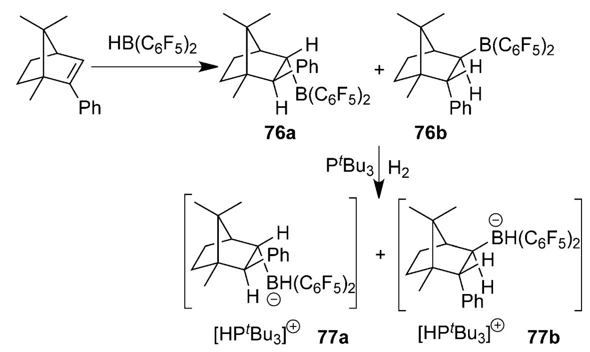
Jäkle et al. have described syntheses of optically active N/B FLPs with planar chirality derived from pyridylferrocene, but to our knowledge, have not reported applications of these potentially interesting systems in asymmetric catalysis.[64] Erker et al. have briefly investigated the catalytic hydrogenation of prochiral bulky imines with the enantiomerically highly enriched chiral ferrocene derivative **73** bearing a borane and a phosphine substituent (Scheme 28) at one Cp ring (Cp = η-C_5H_5) but obtained only rather moderate *ee* values (max. 26%).[49] Repo et al.[27a] reported similar catalytic hydrogenations of imines and a 2-substituted quinoline using the H_2-activation product derived from the intramolecular N/B FLP **74** (Scheme 28) achieving up to 37% *ee*.



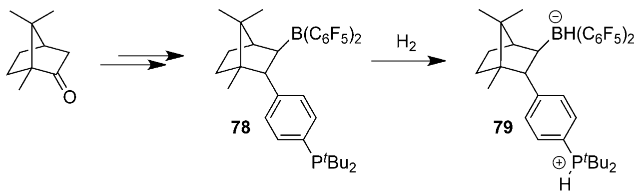
Scheme 28. Chiral FLPs **73** and **74** and the chiral borane **75**.

Klankermeyer et al. made a major contribution to this field with the strongly electrophilic chiral borane **75**. They showed that imines could be hydrogenated induced with asymmetric selectivity but achieved an initial enantiomeric excess of only 13%.[65] Subsequent chiral borane designs were significantly more successful. The enantiomerically pure phenylbornene derivative which is readily made from (1*R*)(+)-camphor, reacts with $HB(C_6F_5)_2$ to give a mixture of the diastereomeric boranes **76a** and **76b**. Reaction with $^tBu_3P$ and dihydrogen gave the respective diastereomeric salts **77a**/**77b** which crystallized as a 1:1 mixture. Asymmetric induction in the catalytic hydrogenation of the ketimine Ph(Me)C=N-Ph gave 20% excess enantiomer of the *S*-amine. However, as the P/B FLPs derived from $^tBu_3P$ with **76a** and **76b** reacted with different reaction rates with dihydrogen, allowing a kinetic resolution.[66] Thus catalytic hydrogenation of the prochiral imine with the pure **77a** gave the *S*-amine Ph(Me)HC-NHPh with 48% *ee*, while the other diastereoisomer **77b** resulted in *R*-amine as the hydrogenation product in excellent yield with 79% *ee* (Scheme 29). Several other imines were also subjected to catalytic hydrogenation with the **77b** catalyst, several giving greater than 80% *ee*.

The related chiral P/B FLP **78** was prepared in a series of steps starting from camphor.[67] It activated dihydrogen to give zwitterion **79** (Scheme 30) and was also used for the enantioselective hydrogenation of a series of bulky prochiral



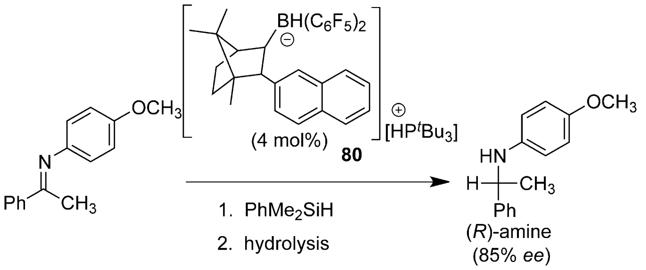
Scheme 29. Chiral P/B FLPs for asymmetric hydrogenation.



Scheme 30. An intramolecular FLP for asymmetric hydrogenation catalysis.

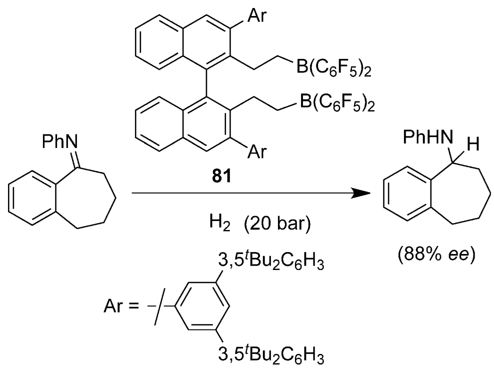
imines. The respective *sec*-amines were invariably obtained enantiomerically enriched with approximately 70% *ee*.

In a related method, a series of imines was catalytically hydrosilylated and subsequently subjected to hydrolysis to give the respective amines. Utilization of the salt **77b** and the related 2-β-naphthyl derivative **80** as the catalyst gave slightly higher enantiomeric excesses of approximately 85% (Scheme 31).[68] Similarly, Oestreich et al. employed a chiral silane as the reductant either with $B(C_6F_5)_3$ or a binaphthyl derived axially chiral borane.[69]



Scheme 31. An asymmetric FLP-catalyzed hydrosilylation/hydrolysis sequence.

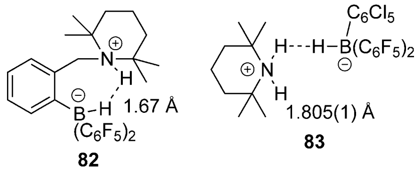
Liu and Du[70] have used a chiral bis-borane which was generated in situ by hydroboration of a substituted divinylbinaphthyl derivative using $HB(C_6F_5)_2$. The best system (**81**) resulted in asymmetric hydrogenation of a series of 19 imines with asymmetric inductions between 74% and 88% *ee* (Scheme 32). Slightly less-bulky *ortho*-substituents on the naphthyl fragment gave the corresponding amines with a considerably lower asymmetric induction.



Scheme 32. Asymmetric imine hydrogenation.

3. Lewis Acid/Lewis Base Interaction

Two hydrogen FLP activation products have been characterized by neutron diffraction. Repo, Rieger et al.[71] described the structure of the products of heterolytic dihydrogen splitting by an intramolecular N/B FLP. The ammonium/hydridoborate zwitterion **82** contains a $N{-}H^+/B{-}H^-$ pair of functionalities, but it still features a $H^+\cdots H^-$ contact inside its framework. In compound **82** this contact is reasonably short at 1.67 Å (Scheme 33).



Scheme 33. Ammonium/hydridoborate zwitterions characterized by neutron diffraction.

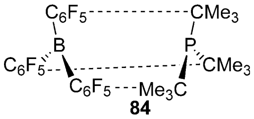
Ashley and O'Hare reported the neutron-diffraction structure of a related compound. The ammonium/hydrido borate contact ion pair **83** was obtained by heterolytic dihydrogen splitting by the tetramethylpiperidine/$B(C_6F_5)_2$-(C_6Cl_5) FLP (Scheme 33). It also contains a residual $H^+\cdots H^-$ interaction (1.805(1) Å), which is less pronounced as in **82**.[28,72]

Both compounds **82** and **83** were obtained from the respective N/B FLPs, posing the question of the Lewis acid/Lewis base interaction in these reactive precursors. How do these systems circumvent termolecularity (i.e. three molecules reacting) in the reaction with H_2 and other small molecules? Since the search for Lewis acid·H_2 minimum structures or even Lewis base·H_2 intermediates has proved fruitless, interest has focused on the description of the nature and/or importance of the Lewis acid/Lewis base interaction in active FLPs.

3.1. Intermolecular FLP Systems

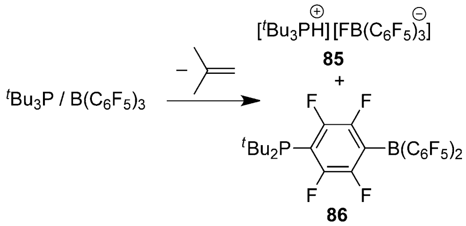
The Lewis acid/Lewis base (LA/LB) interaction in intramolecular FLPs has been studied by quite an array of different methods. Autrey et al.[73] have used calorimetry to determine the association energies of the 2,6-lutidine/B(C_6F_5)$_3$ adduct formation finding $\Delta H = -17.9 \pm 1.0$ kcal mol^{-1} and $\Delta S = -49.2 \pm 2.5$ cal K^{-1} mol^{-1}. A variety of other typical FLP Lewis acid/Lewis base pairs were investigated as well.

Much information on the LA/LB FLP interaction has come from computational chemistry. Early state of the art DFT studies already gave a strong indication that, for example, the ^{t}Bu$_3$P/B(C_6F_5)$_3$ pair reacts from an associated form (**84**) that is formed by non-covalent C_6F_5···^{t}Bu interactions (Scheme 34).[13a,c,74] The actual reaction with H_2 then is essentially a bimolecular reaction between the adduct **84** and dihydrogen. The structure of the ^{t}Bu$_3$P/B(C_6F_5)$_3$ association allows for the H–H molecule to enter the space between P and B. P-mesityl-containing FLPs were suggested to behave similarly.[75] Molecular dynamics simulations have indicated that only a small fraction of the ^{t}Bu$_3$P/B(C_6F_5)$_3$ FLP compounds are associated with each other in solution at any given time (ca. 2 % at room temperature in toluene).[76] The association of the Mes$_3$P/B(C_6F_5)$_3$ pair in solution was studied by NMR spectroscopic techniques although no specific LA/LB orientation was apparent, suggesting association was determined by dispersion forces rather than direct P···B interaction.[77]


84

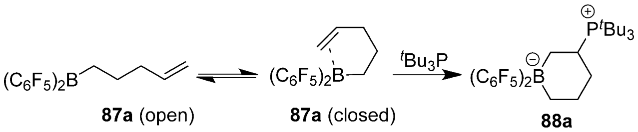
Scheme 34. FLP "encounter complex".

The stability of some FLPs in solution for a prolonged time in the absence of H_2 or other reaction partners has also been probed. A prominent example was described by Piers et al.[78] who observed the formation of isobutylene plus the salt **85** and its co-product **86** (Scheme 35) from the ^{t}Bu$_3$P/B(C_6F_5)$_3$ pair in neat phosphine solution. The potential that these products might be involved in the activation of dihydrogen was also considered as these species appear to be kinetically competent for such reactivity.



Scheme 35. Reaction of ^{t}Bu$_3$P/B(C_6F_5)$_3$ in neat phosphine.

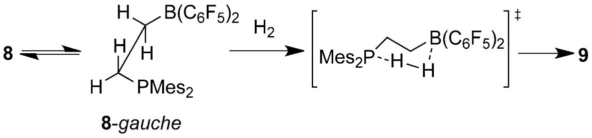
The interaction of FLPs with other small-molecule substrates has also been probed. Stephan et al.[79] found NMR spectroscopic evidence of the formation of an intramolecular borane/alkene van der Waals complex (**87a** closed) at low temperature preceding the formation of the FLP olefin addition product **88a** (Scheme 36).



Scheme 36. Internal alkene/borane interaction.

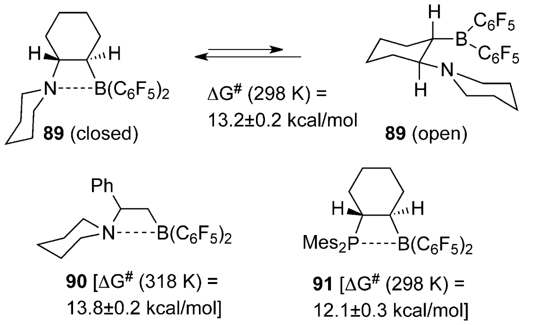
3.2. Intramolecular FLP Systems

Intramolecular FLPs react with added substrates in bimolecular reactions. Nevertheless, their internal Lewis acid/Lewis base interaction might be important for their reaction behavior. The early reported ethylene bridged P/B FLP **8** was calculated by DFT methods to have a closed heterocyclic four-membered-ring structure[13] although the P···B interaction was weak. Calculations showed the presence of two open isomers with different conformations lying only about 7–9 kcal mol^{-1} above the global minimum structure. Consequently, one of them, the open *gauche*-like conformer, was suggested to be the reactive species for dihydrogen activation. This was calculated to proceed by an almost ideal chair-like transition state[13a] (Scheme 37).



Scheme 37. Hydrogen activation by the intramolecular FLP **8**.

For selected examples it was possible to experimentally determine either the activation barrier of the intramolecular Lewis acid/Lewis base dissociation or the thermodynamics of the equilibrium between the open and closed internal FLP forms. For example, the vicinal intramolecular N/B FLP **89** made by hydroboration of the respective enamine, exists as an intramolecular adduct in the solid state with a N–B distance of 1.824(6) Å.[25] The ^{11}B NMR spectrum indicates a closed structure also in solution. Consequently, compound **89** shows two sets of ^{19}F NMR signals for the diastereotopic C_6F_5 substituents at boron. Opening of the N–B bond generates a planar-tricoordinate boron center and consequently, the C_6F_5 substituents become homotopic, thus giving a single set of ^{19}F NMR resonance signals. Monitoring the equilibrium of the closed N/B FLP of **89** with the higher energy open isomer (not directly observed) by temperature dependent NMR spectroscopy revealed a Gibbs activation energy of the N–B dissociation process of $\Delta G^{\#}(298\,\mathrm{K}) = 13.2 \pm 0.2$ kcal mol^{-1} (Scheme 38). The closely related chiral N/B FLP **90** shows the analogous dynamic NMR behavior ($\Delta G^{\#}$(318 K) of N–B rupture $= 13.8 \pm 0.2$ kcal mol^{-1}).[25] Similarly, the vicinal P/B FLP **91** shows a closed structure with a reasonably short P–B



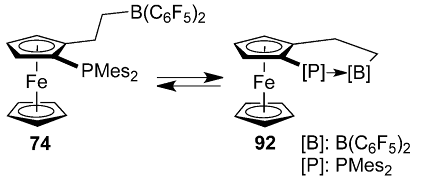
Scheme 38. Activation barriers of ring opening in intramolecular FLPs.

distance in the crystal (P–B: 2.188(5) Å) and an analogous structure in solution ($\delta(^{11}B) = +12.6$ ppm). From the dynamic ^{19}F NMR spectra an activation barrier of internal P–B dissociation of ($\Delta G^{\#}$(298 K) 12.1 ± 0.3 kcal mol^{-1} was determined, a slightly lower value than that found for the N/B FLPs above.[80] These data reveal that the N–B and P–B interactions in these vicinal intramolecular FLPs are rather weak and that dissociation is kinetically rapid, making the open isomers available for reactivity, although they may be thermodynamically disfavored by as much as 10 kcal mol^{-1}.

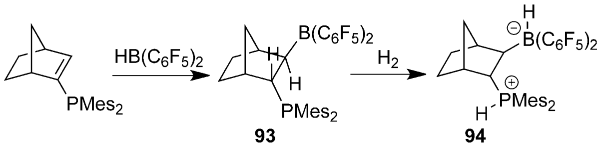
Solid-state NMR spectroscopy is also a useful tool for characterizing FLPs, especially with regard to their internal P/B Lewis base/Lewis acid interaction.[81] The ^{11}B NMR shifts in the solid state and the ^{31}P–^{11}B coupling were compared to those observed in solution. Specifically in the solid-state NMR spectra, the ^{11}B NMR quadrupole coupling constants (C_Q) and the ^{11}B electric field tensors provide information regarding the coordination of boron. Furthermore, P/B distances could be quite accurately determined by ^{31}P decoupled ^{11}B REDOR experiments for a variety of P/B FLP examples and related systems.

In contrast, the C_4-bridged internal P/B FLP **74** shows an open structure in the crystal and in solution. At lower temperature new NMR signals attributable to the closed isomer are observed. This is a rare example where both the internal P/B adduct and the dissociated free P-Lewis base/B-Lewis acid pair can be detected directly.[49] From the appropriate van't Hoff plot, the thermodynamic parameters of the **74**⇄**92** equilibrium were determined at $\Delta H^0 = 4.7 \pm 0.2$ kcal mol^{-1} and $\Delta S^0 = 25.9 \pm 0.2$ cal K^{-1} mol^{-1}, indicating an entropically governed dissociation process as expected (Scheme 39).

The Lewis acid/Lewis base interaction can be "switched off" in intramolecular FLPs by altering the relative orientation of the donor and acceptor sites. The vicinal P/B FLP **93** may serve as a typical example.[82] It has readily been obtained by hydroboration of 2-dimesitylphosphinonorbornene with Piers' borane $HB(C_6F_5)_2$, placing the resulting C–[B] vector selectively on the *exo*-side and the C–[P] vector *endo*-oriented. The resulting P···B separation is large (3.878(1) Å) and consequently, there is no indication of any residual P–B interaction. Solid-state NMR spectroscopy gives a ^{11}B NMR signal at $\delta = 75.2$ ppm and a quadrupolar coupling constant C_Q of 4.7 MHz consistent with the crystallographically observed trigonal-planar boron center. This geometry is retained in solution as evidenced by the ^{11}B NMR resonance signal at $\delta = 75.0$ ppm. Compound **93** is a very reactive FLP, readily cleaving dihydrogen to yield **94** (Scheme 40) and adding to a variety of small unsaturated molecules (see Section 5).

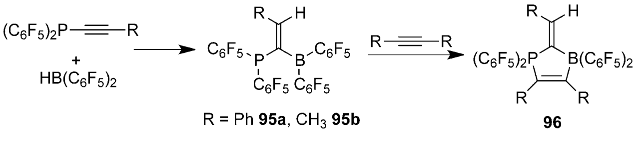


Scheme 39. Internal coordination equilibrium of a ferrocene-derived FLP.



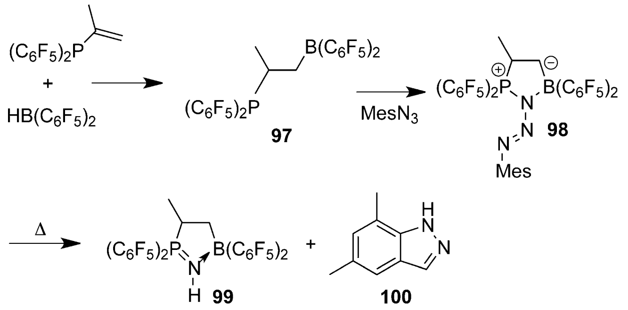
Scheme 40. Dihydrogen cleavage with the non-interacting intramolecular FLP **93**.

The internal P···B interaction becomes unfavorable when the Lewis basicity of the phosphine building block is strongly diminished. The reaction of the $(C_6F_5)_2P$-substituted alkynes with $HB(C_6F_5)_2$ provides the geminal P/B FLP systems **95**. X-ray diffraction data for **95a** revealed no direct P···B contact with a P···B separation of 2.951 Å. Solid-state and solution NMR spectroscopy data are also consistent with the absence of any significant P···B contact.[83] Interestingly while compound **95** is unreactive toward H_2, it readily adds alkynes to give compounds of the form **96** (Scheme 41).



Scheme 41. Geminal FLPs.

The corresponding hydroboration of $(C_6F_5)_2PC(H){=}CHCH_3$ gave the saturated geminal P/B FLP $(C_6F_5)_2PCH(C_2H_5)B(C_6F_5)_2$[84] whereas hydroboration of $(C_6F_5)_2PC(Me){=}CH_2$, produced the vicinal P/B FLP **97**.[85] In contrast to **8**, **97** does not exhibit any significant phosphorus Lewis base/boron Lewis acid interaction as evidenced by NMR spectroscopic data (**97**: ^{11}B $\delta = +67.8$, ^{31}P $\delta = -32.5$). Nonetheless, both compounds **97** and **8** react with mesitylazide. The reaction of **97** affords the 1,1-addition product **98** which on heating, undergoes a Staudinger-type reaction giving the products **99** and **100** (Scheme 42). Anomalous Staudinger oxidation of the mesityl azide addition product of **8** is achieved by photolysis.[85]



Scheme 42. Staudinger reaction of a P/B FLP.

3.3. Hidden FLPs

Sometimes combinations of Lewis acids and bases form seemingly stable "unproductive" Lewis acid/base adducts. However, some such adducts reveal their reversible formation on exposure to reagents that typically react with dissociated FLPs. This notion was initially demonstrated with lutidine/$B(C_6F_5)_3$ which formed both an adduct and yet reacted with H_2 to effect heterolytic cleavage affording $[C_6H_3Me_2NH][HB(C_6F_5)_3]$.[86] A similar seemingly "invisible" FLP was implied in the reactions of boron imidinates with CO_2 and CO (see Section 4).[87]

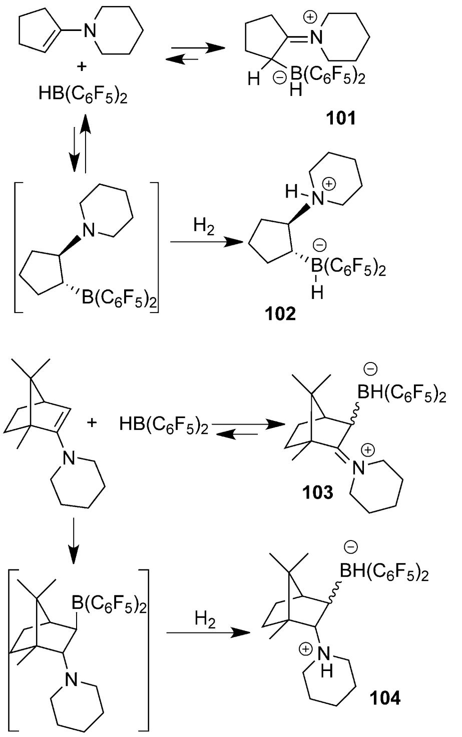
More recent reports have described similar situations. For example, the reaction of the enamine piperidinocyclopentene with $HB(C_6F_5)_2$. The C/B adduct **101** was isolated and characterized including an X-ray diffraction study.[88] Brief exposure of **101** to dihydrogen (2.5 bar, 30 min) cleanly resulted in the formation of the N/B FLP H_2-activation product **102**, inferring that **101** exists in a tautomeric equilibrium which provides access to a transient, intramolecular N/B FLP which reacts with dihydrogen. An analogous situation was encountered in the reaction of the camphor enamine with $HB(C_6F_5)_2$ which gave a mixture of the exo/endo isomers of the C/B adducts **103**. Again, exposure to H_2 or D_2 gave a mixture of the reduced diastereomeric product **104**. Again, this infers the transient generation of an otherwise "invisible" N/B FLP resulting from tautomerization of the iminium-borate in an apparent equilibrium situation (Scheme 43).[89]

4. FLP Chemistry of CO_2, SO_2, and N_2O

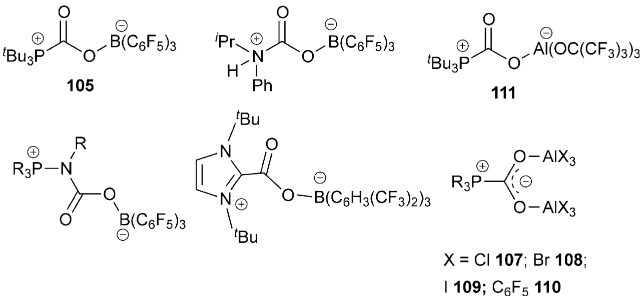
4.1. Capture of CO_2, SO_2, and N_2O

The capture of CO_2 by inter- and intramolecular P/B FLPs was initially demonstrated in 2009.[90] The resulting species $^tBu_3PCO_2B(C_6F_5)_3$ (**105**; Scheme 44) and $Mes_2P(CH_2)_2B(C_6F_5)_2(CO_2)$ (**106**; Scheme 45) liberate CO_2 although in the case of **105** this occurred at 80 °C, whereas **106** loses CO_2 above approximately −20 °C. These observations were consistent with the calculated barriers of approximately 35 and 18 $kcal\,mol^{-1}$, respectively.

Recently the capture of CO_2 by phosphine and borane has been studied by microfluidic methods.[91] Using alternating pulses of solution of $^tBu_3P$ and $B(C_6F_5)_2Cl$ and CO_2 gas bubbles, the gas bubbles were observed to shrink as they flow through the microfluidic channel. This results from the CO_2 capture into the B/P solution. These data enable the determination of the equilibrium constants at different temperatures and thus the fundamental thermodynamics of other gas/liquid reactions.



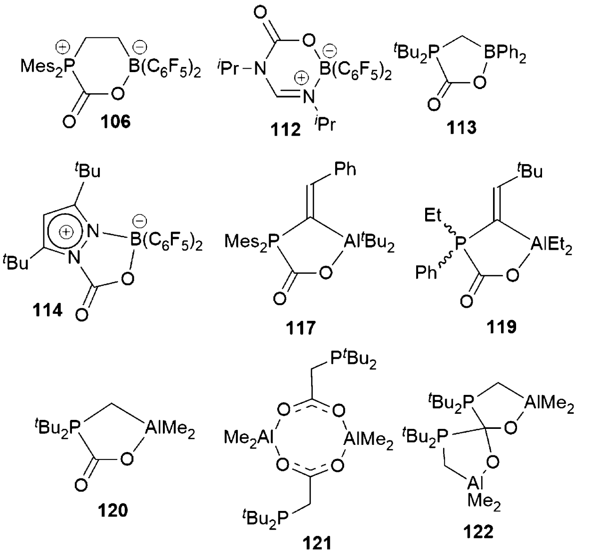
Scheme 43. FLP trapping after tautomerization of conventional enamine Lewis base/borane Lewis acid adducts.



Scheme 44. Examples of CO_2 capture by intermolecular FLPs.

A variety of closely related intermolecular FLP derivatives in which either the borane Lewis acid or the phosphine base were modified, were subsequently prepared and characterized.[92,93] Similarly, the base can be replaced by primary and secondary amines,[94] or N-heterocyclic carbenes (NHCs).[95] These NHC FLP products are significantly more stable thermodynamically than the simple carbene/CO_2 adducts. Sterically hindered phosphinimines[96] can also be employed to capture CO_2 although on heating to 60 °C for 30 min, the FLP/CO_2 adducts are converted into the phosphine-oxide-borane adduct and isocyanate.[97]

Use of aluminum-based Lewis acids in intermolecular FLPs for CO_2 capture has also been explored. For example



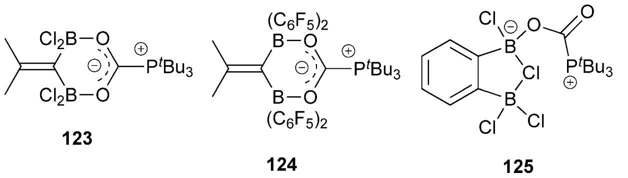
Scheme 45. Examples of intramolecular FLP/CO_2 adducts.

sterically less-demanding alanes also bind CO_2 affording the species $Mes_3P(CO_2)(AlX_3)_2$ (X = Cl (**107**), Br (**108**), I (**109**), and $(o\text{-tol})_3PC(OAl(C_6F_5)_3)_2$ (**110**)).[98] Using a bulkier alane, the species $R_3P(CO_2)Al(OC(CF_3)_3)_3$ (**111**)[98] was isolated in a straightforward manner.

Intramolecular FLP binding of CO_2 has also been expanded. For example, despite the fact that the B-amidinate, $HC(^iPrN)_2B(C_6F_5)_2$ exists as a four-membered ring, it behaves as a hidden FLP and reacts with CO_2 to give $HC(^iPrN)_2(CO_2)B(C_6F_5)_2$ (**112**),[87] presumably via a transient ring-opened N/B FLP (Scheme 45).

Lammertsma and co-workers[99] prepared the geminal phosphine-borane species $^tBu_2PCH_2BPh_2$ and demonstrated the formation of the CO_2 adduct $^tBu_2PCH_2BPh_2(CO_2)$ (**113**; Scheme 45) despite the dramatic reduction in Lewis acidity. Tamm and co-workers[100] prepared the intramolecular N/B FLP based on the pyrazolyl-borane $(C_3H^tBu_2N_2)B(C_6F_5)_2$ and showed binding of CO_2 to give, in a strongly exothermic reaction, $(C_3H^tBu_2N_2)B(C_6F_5)_2(CO_2)$ (**114**).

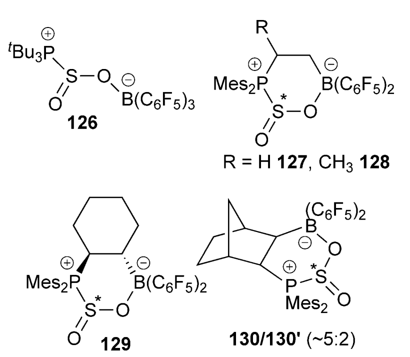
The Uhl group has also prepared intramolecular Al/P systems for CO_2 capture by hydroalumination of the alkynyl phosphine by R_2AlH affording $Mes_2PC(CHR')AlR_2$ ($R' = {}^tBu$, $R = CH_2{}^tBu$ (**115**), $R' = Ph$, $R = {}^tBu$ (**116**)). Subsequent reaction of **116** with CO_2 affords the five-membered-ring species $Mes_2PC(CHPh)Al^tBu_2(CO_2)$ (**117**).[101] The analogous cyclic dimer $(EtPhPC(CH^tBu)AlEt_2)_2$ (**118**) also reacts with CO_2 to give $(EtPhPC(CH^tBu)AlEt_2)(CO_2)$ (**119**).[102] Fontaine and co-workers reported the related species $^tBu_2PCH_2AlMe_2(CO_2)$ (**120**), the carboxylate bridged dimer $(^tBu_2PCH_2CO_2AlMe_2)_2$ (**121**), as well as the spirocyclic species $(^tBu_2PCH_2AlMe_2)_2(CO_2)$ (**122**; Scheme 45).[103]



Scheme 46. Bis-borane in FLP/CO_2 adducts.

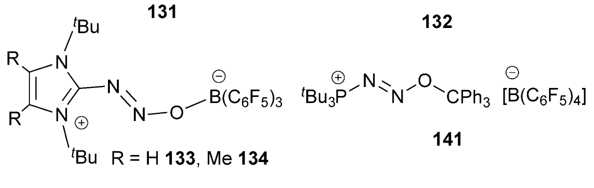
The corresponding reactions of bis-boranes and phosphines with CO_2 was also probed. The species $Me_2C{=}C(BX_2)_2O_2CP^tBu_3$ (X = Cl (**123**), C_6F_5 (**124**))[104] are heterocyclic species in which both oxygen atoms of CO_2 are boron bound (Scheme 46). In contrast, the analogous reaction of the bis-borane $C_6H_4(BCl_2)_2$ shows binding of CO_2 to give **125** in which a single boron center with a Cl bridges to the second B center. Interestingly **125** is thermally robust (80 °C for over 24 h).[103]

The analogous reactions of FLPs with SO_2 afford the inter- and intramolecular FLP adducts $^tBu_3PSO_2B(C_6F_5)_3$ (**126**) and $Mes_2P(CH_2)_2B(C_6F_5)_2(SO_2)$ (**127**).[105] While the connectivity is similar to that of the CO_2 adducts, these species exhibit a pseudo-pyramidal geometry and thus a center of chirality at the S atom. Analogues incorporating substituents on the intramolecular FLP are also accessible and thus the diastereomeric species $Mes_2PCH(Me)CH_2B(C_6F_5)_2(SO_2)$ (**128**) and $Mes_2P(C_6H_{10})B(C_6F_5)_2$ (SO_2) (**129**) have been prepared (Scheme 47). In these cases, two diastereomeric products were observed in 3:1 and 86:14 ratios, respectively.[105] The related reaction of the norbornene-linked FLP gave a mixture of diastereomers of the species $Mes_2P(C_7H_{10})B(C_6F_5)_2(SO_2)$ (**130**) in a 5:2 ratio.[80a]



Scheme 47. FLP/SO_2 adducts.

Intermolecular FLPs have also been employed to capture N_2O. The species $^tBu_3P(N_2O)B(C_6F_5)_3$ (**131**; Scheme 48) contains inequivalent N atoms consistent with the PNNOB linkage which was confirmed crystallographically.[106] The phosphine and $OB(C_6F_5)_3$ fragments are *trans* with respect to the N=N bond, presumably a result of the steric demands.



Scheme 48. Examples of FLP/N_2O adducts.

Indeed this geometry is consistent with the observation that use of smaller and less-basic phosphines results in facile oxidation of the phosphine and liberation of N_2. The species **131** is stable but will evolve N_2 on heating to 135 °C for 2 days or on photolysis for 5 min, suggesting that isomerization about the N=N bond is required for N_2 liberation. The analogous species ^{t}Bu$_3$P(N$_2$O)Al(C$_6$F$_5$)$_3$ (**132**) was also prepared in a similar fashion, although careful attention to the stoichiometry was required.[107]

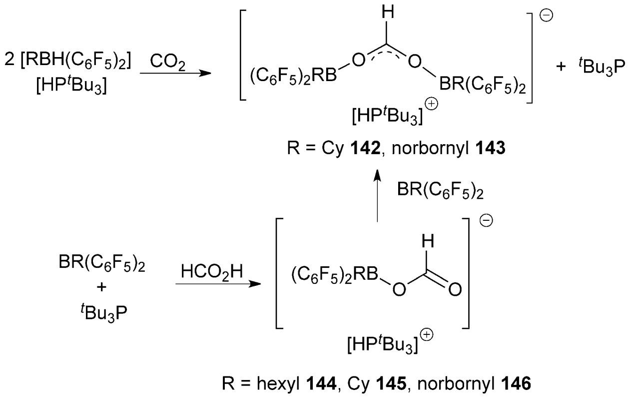
Carbenes are strong donors and thus carbene-based FLPs will also capture N_2O, affording the species (C$_3$R$_2$-(N^{t}Bu)$_2$)N$_2$OB(C$_6$F$_5$)$_3$ (R = H (**133**), Me (**134**); Scheme 48).[95d] However, it is interesting to note that Severin and co-workers have shown that carbene reacts with N_2O in the absence of borane to oxidize the carbene to the corresponding urea derivative,[108] whereas the use of an FLP captures N_2O intact.[95d]

The formation of FLP/N_2O adducts does tolerate the use of significantly weaker Lewis acids, and thus ^{t}Bu$_3$P(N$_2$O)B-(C$_6$F$_5$)$_2$Ph (**135**) was also obtained.[109] Similarly, the species ^{t}Bu$_3$P(N$_2$O)B(C$_6$H$_4$F)$_3$ (**136**) was prepared and used in Lewis acid exchange reactions to give a variety of analogues including the exchange of the weak Lewis acid for other more electrophilic boranes.[109] For example, treatment with a variety of boranes gave ^{t}Bu$_3$P(N$_2$O)BR$_2$R′ (R = C$_6$F$_5$, R′ = Mes (**137**); R = C$_6$F$_5$, R′ = OC$_6$F$_5$ (**138**); R = R′ = C$_6$F$_4$-*p*-H (**139**)) and the bis-borane derivative ^{t}Bu$_3$P(N$_2$O)B(C$_6$F$_5$)$_2$C$_6$F$_4$(C$_6$F$_5$)$_2$B(ON$_2$)P^{t}Bu$_3$ (**140**).[109] This exchange route is also effective beyond B-based Lewis acids affording access to the trityl derivative [^{t}Bu$_3$P(N$_2$O)CPh$_3$][B(C$_6$F$_5$)$_4$] (**141**; Scheme 48).

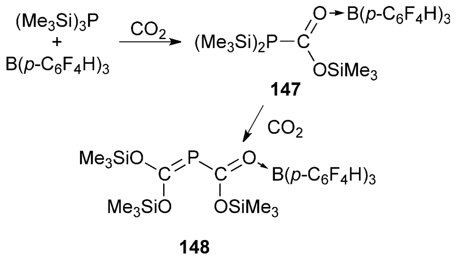
4.2. CO_2 Reductions

In a seminal paper in 2009, O'Hare and Ashley[110] described experiments that demonstrated the possibility of FLP reduction of CO_2. Using a 1:1 mixture of the FLP tetramethylpiperidine (TMP)/B(C$_6$F$_5$)$_3$ under a H_2 atmosphere, CO_2 was quantitatively converted into CH$_3$OB(C$_6$F$_5$)$_2$ after 6 days at 160 °C and indeed methanol was actually isolated in 17–25 % yield. Subsequently, Piers and co-workers[111] showed that with TMP/B(C$_6$F$_5$)$_3$ the hydrosilylation of CO_2 proceeds via a silyl carbamate and [TMPH][HB(C$_6$F$_5$)$_3$] which was transformed to the formate derivative [TMPH]-[HCO$_2$B(C$_6$F$_5$)$_3$]. Excess B(C$_6$F$_5$)$_3$ and triethylsilane resulted in the catalytic hydrosilylation of formatosilane to CH_4 and (Et$_3$Si)$_2$O.[111] Independent reactions involving the salts [^{t}Bu$_3$PH][RBH(C$_6$F$_5$)$_2$] (R = Cy, norbornyl) were shown to give the species [^{t}Bu$_3$PH][((C$_6$F$_5$)$_2$BR)$_2$(μ-HCO$_2$)] (R = Cy (**142**), norbornyl (**143**)), while the related species [^{t}Bu$_3$PH]-[(C$_6$F$_5$)$_2$BR(O$_2$CH)] (R = hexyl (**144**), Cy (**145**), norbornyl (**146**); Scheme 49) were obtained from the reactions of the FLPs and formic acid. Addition of further borane to **142** or **143** provides a second synthetic route to bis-borane-formate species.

In a related stoichiometric reduction of CO_2, the FLP (Me$_3$Si)$_3$P/B(*p*-C$_6$F$_4$H)$_3$ reacts in pentane with CO_2 to silylate CO_2 affording ((Me$_3$Si)$_2$PC(OSiMe$_3$)O)B(*p*-C$_6$F$_4$H)$_3$ (**147**).[112] The corresponding reaction in CH$_2$Cl$_2$ affords further reaction with CO_2 to give the bis-insertion product ((Me$_3$SiO)$_2$C=P-C(OSiMe$_3$)=O)B(*p*-C$_6$F$_4$H)$_3$ (**148**; Scheme 50). These products are thought to be formed by initial FLP capture of CO_2 and subsequent silyl-group migration.

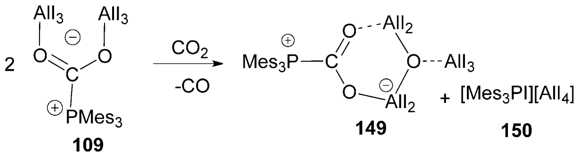


Scheme 49. Reactions of phosphonium borate salts with CO_2.



Scheme 50. Reaction of (Me$_3$Si)$_3$P with CO_2 and borane.

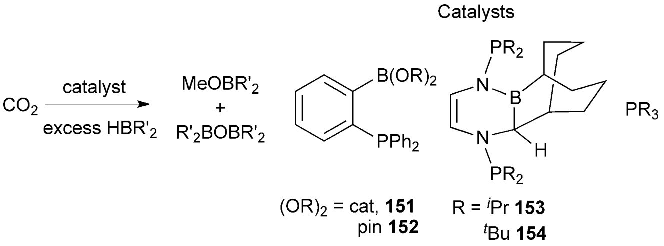
Reaction of Mes$_3$P(CO$_2$)(AlX$_3$)$_2$ (X = Cl (**107**); Br (**108**); I (**109**))[113] with H$_3$NBH$_3$ took place in less than 15 min to generate a mixture of products which on hydrolysis afforded methanol. ^{13}C NMR spectroscopy and labelling studies confirmed the consumption of CO_2 and the generation of Al-methoxy species.[114] Interestingly, **109** was shown to react further on exposure to CO_2 for 16 h to give the products Mes$_3$PC(OAlI$_2$)$_2$OAlI$_3$ (**149**) and [Mes$_3$PI][AlI$_4$] (**150**) with the simultaneous liberation of CO (Scheme 51).[98,115] The mechanism of this reaction was probed and shown to be first order in **109** and CO_2. The reduction of CO_2 is thus thought to proceed by a dissociative process in which solvent complexation of AlX$_3$ initiates reduction of CO_2 to CO. This view is supported by additional experimental evidence including the enhanced reaction rate in the presence of [Mes$_3$PMe][AlI$_4$].



Scheme 51. Reaction of **109** with CO_2.

Nucleophilic attack by phosphine mediates liberation of CO in a barrierless process.

In recent work, Fontaine and co-workers[6f] have carried out the reduction of CO_2 in the presence of $HB(O_2C_2Me_4)$ employing 1 mol % of the P/B FLP catalyst $Ph_2PC_6H_4B(O_2C_6H_4)$ (**151**) affording $MeOB(O_2C_2Me_4)$ and $O(B(O_2C_2Me_4))_2$ with a turnover frequency (TOF) of 973 h^{-1} and turnover numbers (TONs) as high as 2950 at 70 °C. They noted that no adduct between the catalyst and CO_2 was observed, inferring that the ambiphilic catalyst interacts weakly with CO_2 yet this prompts reaction with boranes. In addition the species $Ph_2PC_6H_4B(O_2C_2Me_4)$ (**152**) in the presence of $BH_3{\cdot}SMe_2$ was also shown to be an effective catalyst for the CO_2 reduction (Scheme 52).[6f]



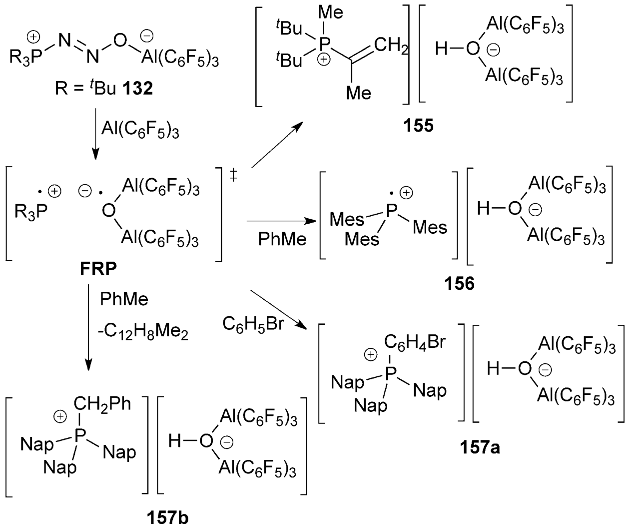
Scheme 52. Catalytic reduction–hydroboration of CO_2.

In a related study the reduction of CO_2 in the presence of the boranes HBpin, HBcat, and $BH_3{\cdot}SMe_2$ to give methoxyboranes and B-O-B species was achieved employing the B/P species $C_3H_3(NPR_2)_2BC_8H_{14}$ [R = ^{i}Pr (**153**), ^{t}Bu (**154**)] (Scheme 52).[116] These catalysts were derived from the reaction of the NHC $C_3H_2(NPR_2)_2$ with 9-BBN prompting hydride migration, carbene-ring opening, and B−C bond cleavage with subsequent formation of B−N and C−C bonds.

Most recently, Wang and Stephan[117] have also demonstrated that the reduction of CO_2 by 9-BBN is catalyzed by phosphine. For example, using as little as 0.02 mol % of ^{t}Bu$_3$P, CO_2 is reduced to a mixture of $MeOB(C_8H_{14})$ and $O(B(C_8H_{14}))_2$ in 98 % yield at 60 °C with TON of almost 5500 and a TOF of 170 h^{-1}. Stoichiometric reactions afford the compounds $(R_3PCH_2O)(HC(O)O)B(C_8H_{14})$ which are thought to be intermediates in the reduction process.

4.3. N_2O and C−H Bond Activation

Addition of an additional equivalent of alane to ^{t}Bu$_3$P$(N_2O)Al(C_6F_5)_3$ (**132**)[107] resulted in N_2 liberation and the generation of the transient “frustrated radical pair (FRP)” $[R_3P{\cdot}]^+[(\mu\text{-}O{\cdot})(Al(C_6F_5)_3)_2]^-$ which effects either alkyl and aryl C−H bond activations. In the case of exposure of a 1:2 ratio of ^{t}Bu$_3$P and $Al(C_6F_5)_3{\cdot}$tol to N_2O, the species $[^t\text{Bu}_2PMe(C(CH_2)Me)][(\mu\text{-}OH)(Al(C_6F_5)_3)_2]$ (**155**) was formed (Scheme 53).[107] In this case the transient FRP activates the C−H bond of one of the *tert*-butyl groups on P affording the hydroxy-bridged anion. Methyl migration yields the resulting cation.



Scheme 53. C−H activation by transient FRPs.

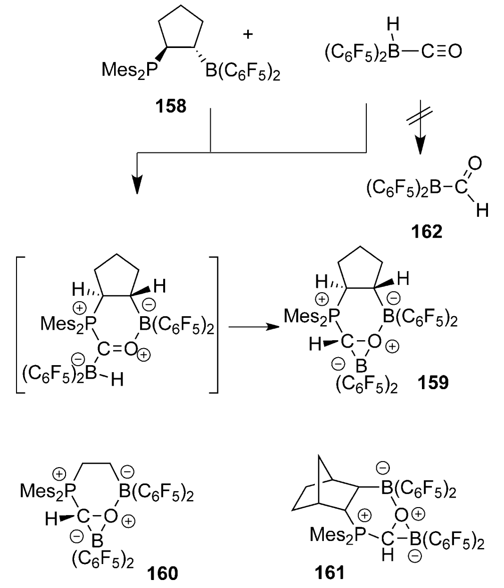
The use of Mes_3P and $Al(C_6F_5)_3{\cdot}$tol in the analogous reaction with N_2O afforded the deep purple species $[Mes_3P{\cdot}][(\mu\text{-}HO)(Al(C_6F_5)_3)_2]$ (**156**; Scheme 53).[107] The presence of the radical cation was confirmed by EPR spectroscopy and X-ray crystallography. The origin of the H atom in the diamagnetic anion was identified as the solvent toluene as the products of toluene radical coupling was evident in the GC-MS analyses.

Use of $(Nap)_3P$, $Al(C_6F_5)_3{\cdot}$tol, and N_2O resulted in the isolation of the product $[(Nap)_3PCH_2Ph][(\mu\text{-}OH)(Al(C_6F_5)_3)_2]$ (**157b**) derived from reaction of the FRP and toluene. On the other hand, performing the reaction in C_6H_5Br gave the species $[(Nap)_3PC_6H_4Br][(\mu\text{-}HO)(Al(C_6F_5)_3)_2]$ (**157a**) where the aryl C−H bond of bromobenzene was activated (Scheme 53).[107]

5. CO Reduction

Trialkylboranes react with carbon monoxide under insertion into the B−C bond. This reaction has been used for the synthesis of alcohols and, with variations, of ketones and aldehydes.[118] In contrast, [B]-H boranes do not reduce carbon monoxide. As early as 1937 Schlesinger and Burg[119] reported the formation of borane carbonyl $[BH_3{\cdot}CO]$ upon treatment of B_2H_6 with CO. Borane carbonyl does not rearrange to give a boron-bound formyl group, rather this low-boiling liquid dissociates on warming.

FLP chemistry can fundamentally change this situation. Erker et al. found that Piers’ borane $[HB(C_6F_5)_2]$ reacts with CO to form the respective borane carbonyl adduct $[(C_6F_5)_2BH{\cdot}CO]$. It was isolated and characterized by an X-ray crystal structure analysis.[120] However, when a $HB(C_6F_5)_2$/CO mixture was treated with, for example, the in situ generated FLP **158**, CO was cleanly reduced to formyl which is side-on coordinated to boron. The “η^2-formylborane” is also C-O-bound to the phosphine Lewis base/borane Lewis acid pair of the FLP in **159** (Scheme 54). The P/B FLPs



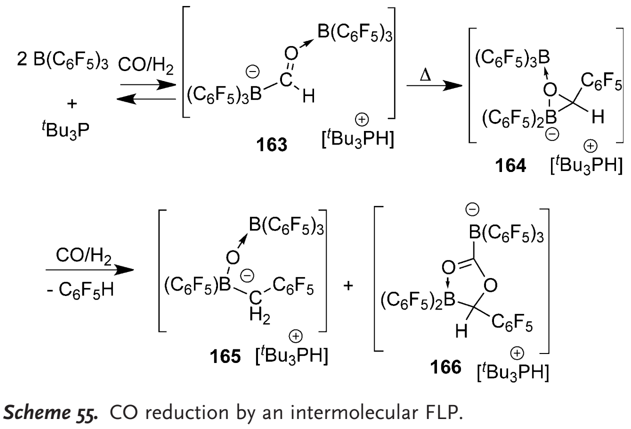
Scheme 54. Reduction of CO to formyl by borane and FLP.

8 and **93** react analogously to give **160** and **161**.[121] A thorough DFT analysis revealed that the formation of the simple formylborane **162** from $[(C_6F_5)_2BH{\cdot}CO]$ would be markedly endothermic. This thermodynamic restriction can, however, efficiently be circumvented by attaching the system to the P/B FLP framework and the overall formation of the (η^2-formyl)borane CO reduction product (e.g. **159**) is strongly exothermic.

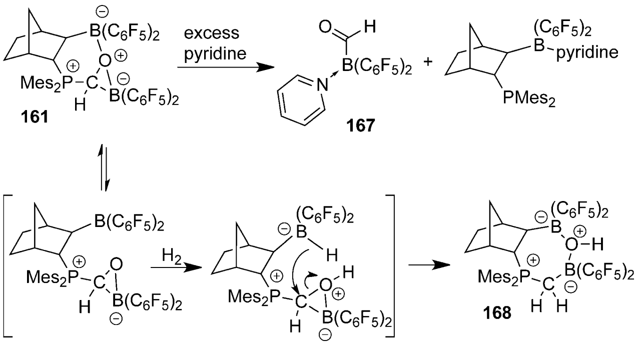
A related system started from $B(C_6F_5)_3/{}^tBu_3P$, carbon monoxide, and hydrogen. At room temperature this system gave the formylborate salt **163**. Upon heating to 90°C it rearranged to the (η^2-pentafluorobenzaldehyde)borate system **164**, which subsequently reacted with syn-gas (CO/H_2) to give the products **165** and **166** in an approximately 2:3 ratio. Compound **165** is formed by hydrogenation of **164** whereas **166** was formed by carbonylation (Scheme 55).[122]

The elusive formylborane **162** was removed from the FLP template of compound **161** by treatment with excess pyridine and the stable pyridine adduct **167** was isolated and characterized by X-ray diffraction (Scheme 56). This adduct **167** undergoes a variety of typical carbaldehyde reactions, such as Wittig olefination or chromate(VI) oxidation to the corresponding vinylborane or borane carboxylic acid, respectively. Both products were obtained as the pyridine adducts.[120] The (η^2-formylborane)FLP complex **161** also reacts with dihydrogen, resulting in a further reduction of the formyl group with cleavage of the C−O bond to give the product **168**. It is likely that the boron–oxygen bond to the borataoxirane moiety in compound **161** is reversibly opened generating an O/B FLP which effects the heterolytic cleavage of dihydrogen while subsequent opening of the oxonium activated borataoxirane by borohydride yields the observed product **168**.[120]

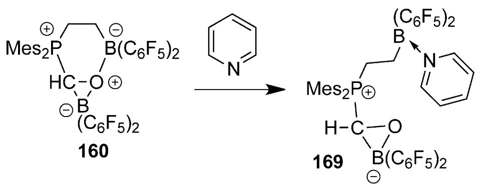
This suggested pathway is supported by the observation that diethyl ether forms a FLP with $B(C_6F_5)_3$ that cleaves dihydrogen under mild conditions.[48] It was also shown that the parent (η^2-formylborane) FLP adduct **160** reacts with one equivalent of pyridine to give the respective product of B−O bond cleavage **169** (Scheme 57).[120]



Scheme 55. CO reduction by an intermolecular FLP.



Scheme 56. Formylborane formation and reduction.



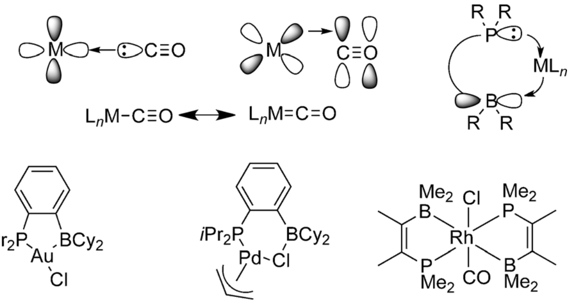
Scheme 57. Reaction of the (η^2-formylborane) FLP adduct **160** with pyridine.

6. New Cooperative FLP Reactions

The simultaneous presence of Lewis acids and Lewis bases in the same solution generates situations for new cooperative reactivity. Heterolytic splitting of dihydrogen by FLPs is the most prominent example but there have been examples of other types of new cooperative FLP reactions emerging. Below, we present a few of these new developments.

6.1. Transition-Metal Reminiscent Behavior of FLPs

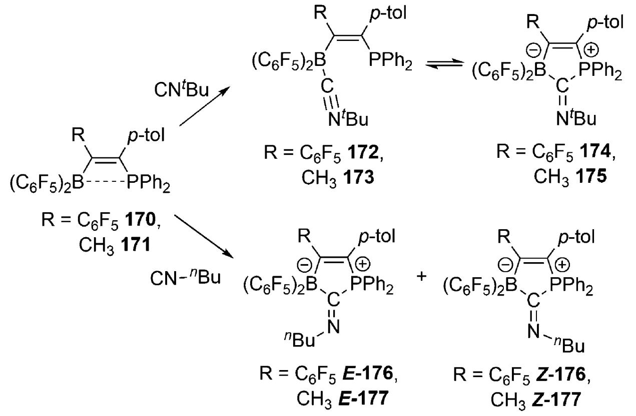
Coordination of small ligands such as CO or isonitriles to transition-metal centers can be described by the Dewar–Chatt–Duncanson model.[123] The overall bonding is then



Scheme 58. Ambiphilic behavior of P/B systems.

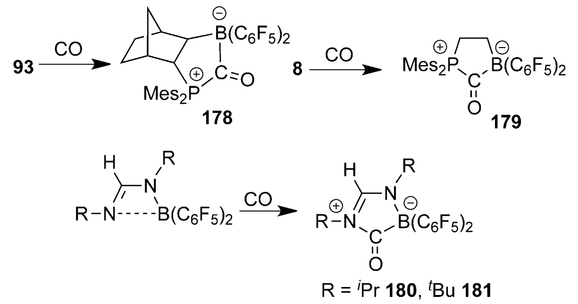
composed of a dative bond by the lone pair at carbon to an empty metal d orbital, which is augmented by back bonding from a filled metal d orbital to the antibonding ligand π* orbital (Scheme 58). It has long been recognized that mixed borane/phosphine ligands can bind to d-metals in a related way. The phosphine donor and the borane acceptor interact similarly with the empty and filled metal d-orbitals, respectively. However in this case, the donor and acceptor functions are located on separate atoms. Such ambiphilic donor/acceptor chelate ligands have been used in transition–metal coordination chemistry.[6] Some typical examples are depicted in Scheme 58.

The donor/acceptor properties of FLPs suggest the possibility of behavior towards small molecules that is analogous to metal centers. This notion was investigated by treating a small series of unsaturated vicinal P/B FLPs with isocyanides. The compounds **170** and **171** were synthesized by 1,1-carboboration reactions (Scheme 59).[124] These FLPs readily add *tert*-butylisocyanide to give the crystalline borane-^{t}BuNC adducts **172** and **173**. However, in solution these species are in equilibrium with the starting materials and the isomers **174** and **175**, respectively. These isomeric species were formed by cooperative P/B addition to the isonitrile. Using the less-sterically encumbered *n*-butylisocyanide afforded the exclusive formation of the cooperative addition products **176** and **177**, obtained as mixtures of the *E*/*Z*-isomers. The *E*-isomers were characterized by X-ray diffraction.[125]



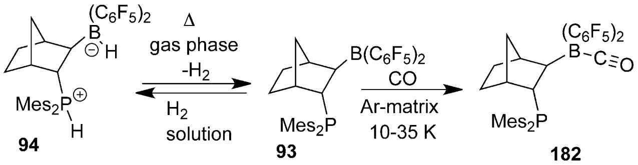
Scheme 59. Cooperative P/B FLP addition to isocyanides.

Some saturated vicinal P/B and N/B FLPs exhibit similar behavior toward carbon monoxide. For example, both the FLPs **93**, **8**[126] and boron-imidinates $HC(NR)_2B(C_6F_5)_2$[87] (R = ^{i}Pr, ^{t}Bu) reacted with CO by cooperative P/B addition to form the bridged carbonyl adducts **178**–**181**, respectively (Scheme 60). These compounds were characterized by X-ray diffraction and spectroscopy (**178**–**181**: IR: $\tilde{\nu}$(CO) = 1791, 1714, 1713 cm^{-1}).



Scheme 60. Cooperative FLP addition to carbon monoxide.

While the simple borane carbonyl adduct was not seen in solution, using the H_2-addition product **94** as a protected FLP, the intact FLP **93** was transported through the gas phase into a CO doped argon matrix[126a] affording the borane/CO adduct **182** at 10 to 35 K (IR: $\tilde{\nu}$(CO) = 2196 cm^{-1}; cf. free CO: 2143 cm^{-1}). Computations showed that **94** is less stable in the gas phase than in the solution and rapidly loses H_2 upon sublimation (Scheme 61).

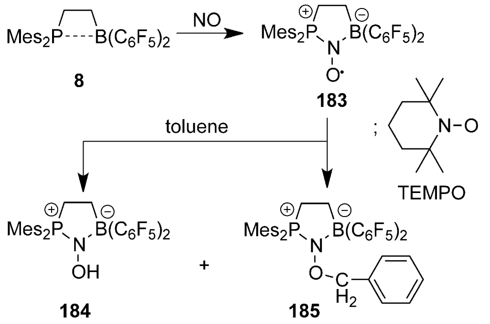


Scheme 61. Formation of an FLP carbonyl adduct in a low-temperature argon matrix.

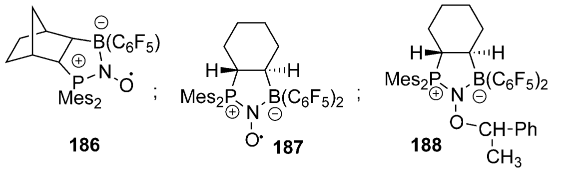
6.2. FLP Reactions with NO: Persistent Nitroxide Radicals

The conceptual relationship between metal carbonyl and metal nitrosyl complexes suggests that some intramolecular FLPs might cooperatively add nitric oxide (NO). Indeed, the ethylene-bridged P/B FLP **8** reacts readily with NO to form the new five-membered heterocyclic FLP-NO radical **183** (Scheme 62).[127] The persistent nitroxide radical **183** was characterized by X-ray diffraction (d(N–O) 1.296(2) Å vs. 1.151 Å in free NO) and by ESR spectroscopy (A(^{14}N) = 18.5 MHz vs 43.5 MHz in TEMPO). This species is a reactive, oxygen-centered radical like TEMPO, reacting readily with a variety of substrates by H-atom abstraction. For example, **183** reacts with toluene to give the diamagnetic FLP/NOH **184** and FLP/NO-benzyl **185** products.

A variety of FLP/NO radicals are readily available from saturated vicinal P/B FLPs and NO (Scheme 63).[127] The



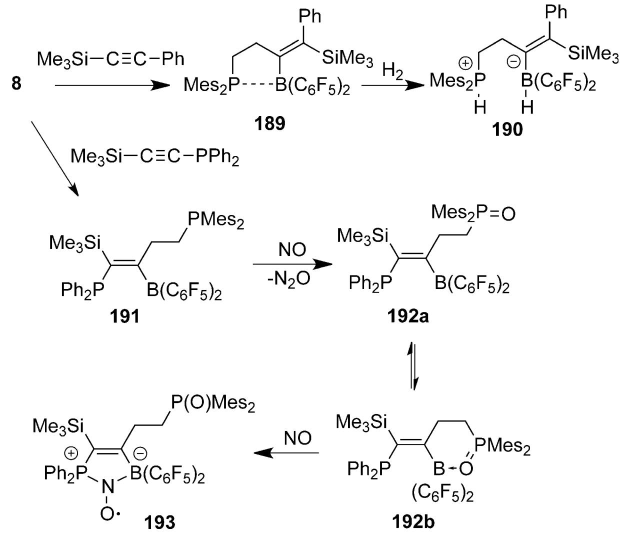
Scheme 62. Formation and reactions of a persistent FLP/NO radical.



Scheme 63. FLP/NO nitroxide radicals and benzylic derivative.

kinetics and the mechanistic path of the formation of the FLP/NO system **186** was studied in quite some detail.[128] The species **187** and its benzylic derivative **188** were employed in the nitroxide-mediated polymerization of styrene.[127]

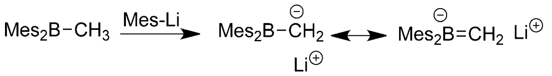
The 1,1-carboboration reaction is very well suited to modifying intramolecular FLP systems. The ring-enlargement reaction of **8** with trimethylsilylphenylacetylene is a typical example affording the C_3-bridged derivative **189**. While this compound splits dihydrogen under mild conditions to give **190** (Scheme 64),[129] the analogous 1,1-carboboration product **191** derived from the reaction of **8** with trimethylsilyl(diphenylphosphino)acetylene cooperatively binds NO, triggered by initial phosphine oxide formation[130] to give **192** and subsequently the FLP/NO radical **193** (Scheme 64). In contrast, **189** did not react with NO.



Scheme 64. FLPs formed by 1,1-carboboration.

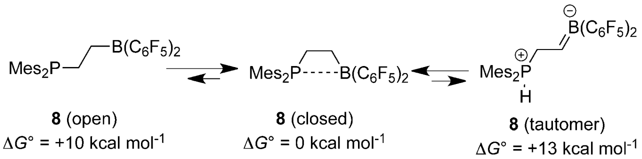
6.3. FLP Routes to Borata Alkenes

Borata-alkenes are resonance forms of α-boryl carbanions that can only be made by direct deprotonation of boranes in special cases because of the high Lewis acidity of the borane (Scheme 65).[131] These species can be viewed as FLPs with adjacent donor and acceptor sites. Recently this class of compounds has received some attention.[132]

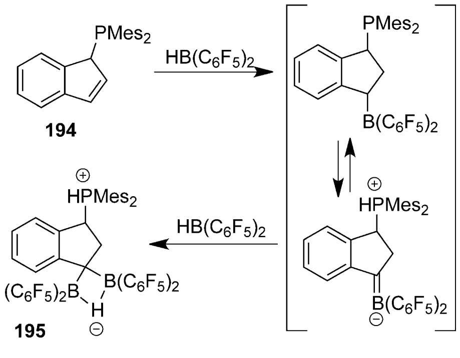


Scheme 65. Formation of an α-boryl carbanion.

The pK_a values of a variety of $RCH_2B(C_6F_5)_2$ boranes have recently been determined to be in the same range as cyclopentadienes. Although these systems are quite acidic, in the case of most FLPs this is not sufficient to assume any participation of the $[PH]^+$/[borata-alkene]$^-$ tautomer (Scheme 66). However, there may be exceptions if additional carbanionic stability factors come into play. Treatment of the phosphanyl-indene system **194** with excess $[HB(C_6F_5)_2]$ resulted in the formation of the product **195**. Its formation was rationalized by the intermediate formation of the stabilized phosphonium/borata-alkene zwitterion that is trapped by an additional equivalent of the hydroboration reagent (Scheme 67).[133]

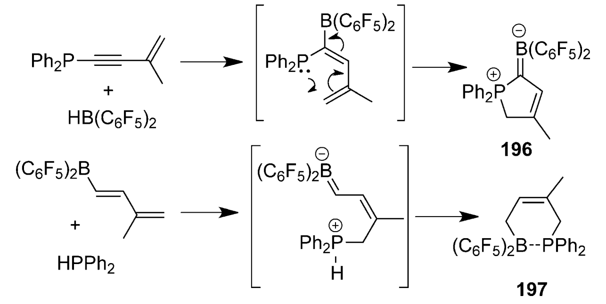


Scheme 66. Equilibria for **8** involving borata-alkene/phosphonium tautomer (Gibbs energy values were derived from DFT calculations).



Scheme 67. Formation of **195**.

Zwitterionic phosphonium/borata-alkenes can also be prepared by internal phosphine addition to conjugated dienylborane moieties. For example, the reaction of an in situ generated geminal P/B FLP gives the zwitterionic



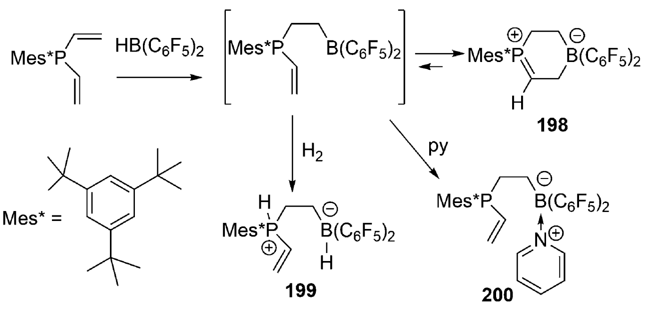
Scheme 68. Phosphine addition to conjugated boryldienes.

phosphonium borata-alkene product **196** (Scheme 68).[134] The related uncatalyzed selective 1,4-hydrophosphination of dienylboranes to give **197** represents an analogous intermolecular example of this reaction (Scheme 68).[133]

6.4. The FLP Route to Methylene Phosphonium Systems

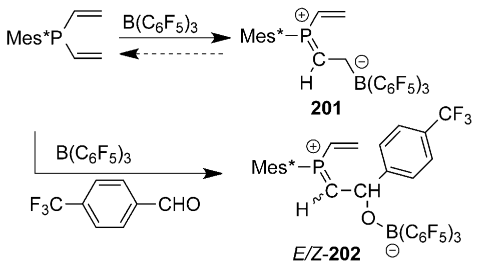
Methylene phosphonium compounds are the phosphorus analogues of the ubiquitous iminium ions. The "phospha-iminium" cations are rarely encountered as they are quite reactive and thus isolated only in special circumstances. Most of the isolated examples of methylene phosphonium compounds bear bulky substituents.[135] Frustrated Lewis pair chemistry proved useful to extend the availability of methylene phosphonium systems and to find new reactions involving them as intermediates.

Many FLPs readily undergo 1,2-addition reactions to olefins.[11,136] An intramolecular version of this reaction was probed by bridged vinylphosphine/borane systems generated in situ by $HB(C_6F_5)_2$ hydroboration of the aryldivinylphosphine bearing the bulky 2,4,6-tri-*tert*-butylphenyl ("supermesityl") substituent. Interestingly, the simple hydroboration product was not observed, rather the heterocyclic, intramolecular zwitterionic methylenephosphonium derivative **198** is obtained (Scheme 69).[137] The ^{31}P NMR spectroscopy signal at $\delta = +148$ ppm is characteristic of a methylene phosphonium fragment and X-ray diffraction data showed a P=CH bond of 1.64 Å with a trigonal planar phosphorus coordination geometry. Equilibration of **198** with the (unobserved) vinylphosphine isomer is inferred as the vinylphosphine species is trapped by reactions with dihydrogen or pyridine, giving **199** or **200**, respectively (Scheme 69).[137]



Scheme 69. FLP route to a methylenephosphonium borate.

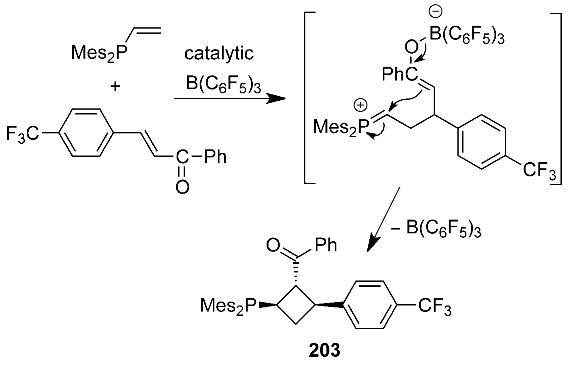
This is not a singular example. The aryldivinylphosphine reversibly adds the Lewis acid $B(C_6F_5)_3$ to the vinyl substituent yielding the corresponding methylene phosphonium system **201** (Scheme 70).[137] This species has a similar P=C bond of 1.695(5) Å and gives rise to a ^{31}P NMR resonance signal at $\delta = +126.6$ ppm.



Scheme 70. C–C coupling products from enphosphine reaction.

Enamines react with a variety of electrophiles as carbon nucleophiles (Stork reaction).[138] In an analogous fashion the divinylphosphine or "enphosphine" reacts with electrophiles in the presence of $B(C_6F_5)_3$. For example, the reaction with *p*-trifluoromethylbenzaldehyde gave a 0.75:1.0 mixture of the diastereomeric methylene phosphonium C–C coupling products *E*-/*Z*-**202** (Scheme 70).[137b]

This reaction type could even be developed into a catalytic version of the new "phospha-Stork reaction". Treatment of the "enphosphine" dimesitylvinylphosphine with the α,β-unsaturated ketone in the presence of catalytic amounts of the Lewis acid $B(C_6F_5)_3$ gave the trisubstituted cyclobutane product **203**. This species is thought to arise from an intramolecular reaction of a reactive methylene phosphonium with the adjacent boron enolate. In this manner, the formation of **203** liberates the $B(C_6F_5)_3$ catalyst (Scheme 71).[137]

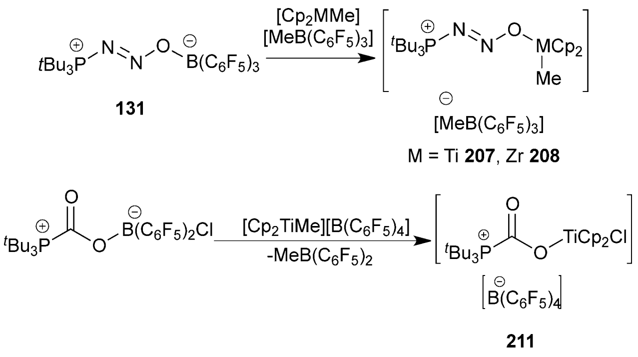


Scheme 71. $B(C_6F_5)_3$-catalyzed phospha-Stork reaction.

7. Transition-Metal FLPs

7.1. Group 4 Derived FLPs

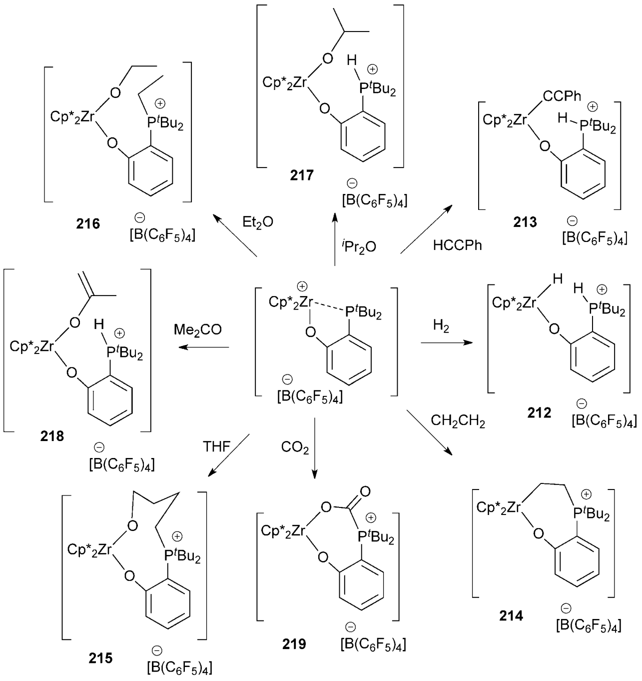
Early suggestions that transition metals might be amenable to FLP reactions were derived from exchange reactions of N_2O species.[109] For example, reaction of $^{t}Bu_3P(N_2O)B(C_6H_4F)_3$ with $Zn(C_6F_5)_2$ afforded a series of Zn derivatives including $[^{t}Bu_3PN_2OZn(C_6F_5)_2]_2$ (**204**), $(^{t}Bu_3PN_2OZn(C_6F_5)_2)_2Zn(C_6F_5)_2$ (**205**), and $^{t}Bu_3PN_2O(Zn(C_6F_5)_2)_2$ (**206**).[139] Similarly, exchange with early-transition-metal-based Lewis acids $[Cp_2MMe][MeB(C_6F_5)_3]$ (M = Ti, Zr) provides a route to the complexes $[^{t}Bu_3P(N_2O)MCp_2Me][MeB(C_6F_5)_3]$ (M = Ti (**207**), Zr (**208**)); Scheme 72).[109] The mechanism of these exchange reactions was suggested on the basis of NMR experiments to proceed by a weakened B–O linkage prior to binding of the incoming Lewis acid.



Scheme 72. Exchange reactions affording transition-metal FLP complexes. Cp = cyclopentadienyl.

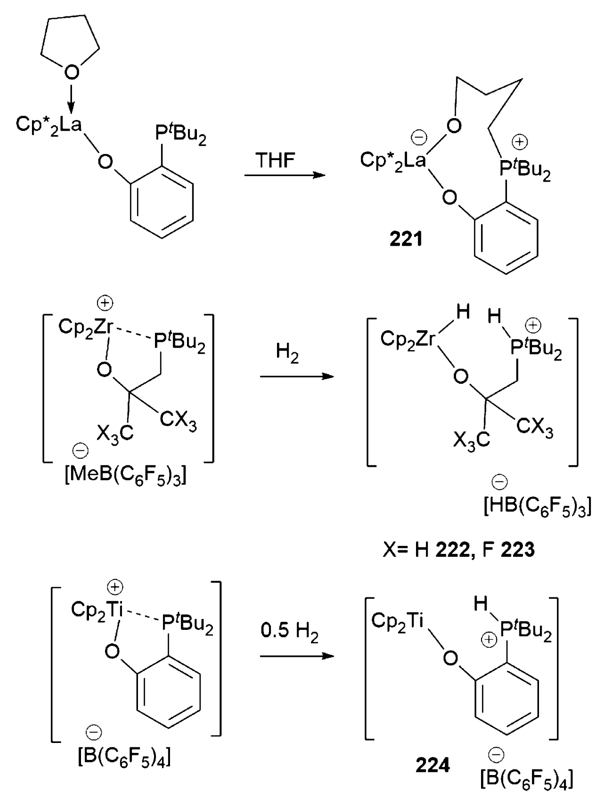
Initial efforts to employ a transition-metal species directly as the Lewis acid component of an FLP were not successful, as the combination of $[Cp_2ZrMe][MeB(C_6F_5)_3]$ with phosphine failed to capture N_2O. However, combination of $[Cp^*_2Zr(OMe)][B(C_6F_5)_4]$, phosphine, and N_2O afforded the product $[^{t}Bu_3P(N_2O)ZrCp^*_2(OMe)][B(C_6F_5)_4]$ (**210**)[109] demonstrating this was a viable approach for sufficiently bulky systems. In a similar sense, an exchange reaction of $^{t}Bu_3P(CO_2)B(C_6F_5)_2Cl$ with the cationic complex $[Cp_2TiMe][B(C_6F_5)_4]$ provides access to the metal-based FLP/CO_2 species $[^{t}Bu_3P(CO_2)TiCp_2Cl][B(C_6F_5)_4]$ (**211**; Scheme 72).[93]

While the above reactivity suggested the possibility, it was Wass and co-workers[140] and subsequently the Erker group,[141] who demonstrated the generation and reactivity of FLPs incorporating transition-metal Lewis acids directly. In the original work of Wass et al.[140a] the metal-based FLP species $[Cp_2ZrOC_6H_4P^{t}Bu_2][B(C_6F_5)_4]$ and $[Cp^*_2ZrOC_6H_4P^{t}Bu_2][B(C_6F_5)_4]$ were developed. The steric demands about the P center generate a weak interaction with the Lewis acidic Zr cation and thus it acts as an intramolecular FLP. As a result the intramolecular FLP species reacts with H_2 to effect heterolytic cleavage affording $[Cp^*_2ZrH(OC_6H_4PH^{t}Bu_2)][B(C_6F_5)_4]$ (**212**; Scheme 73). These species were also shown to efficiently catalyze the dehydrogenation of amino-borane by a mechanism that involves a transient role of the FLP capture and subsequent release of H_2.



Scheme 73. Reactions of transition-metal-based FLPs. Cp* = pentamethylcyclopentadienyl.

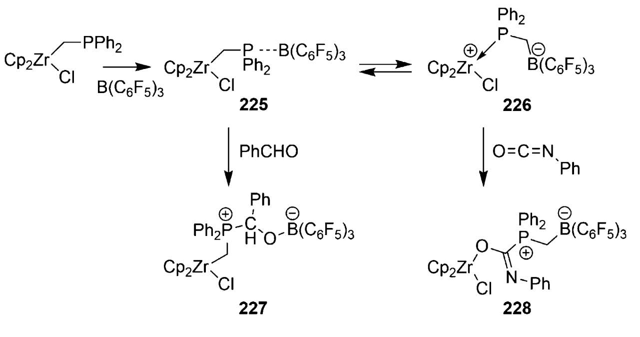
Subsequently Wass and co-workers[140b] showed that this class of FLPs could be broadened to include $[Cp^*_2ZrOC_6H_4PR_2][B(C_6F_5)_4]$ (R = Mes, ^{i}Pr) and $[Cp(Cp^*)ZrOC_6H_4P^{t}Bu_2][B(C_6F_5)_4]$, all of which react with H_2 in a fashion similar to that described above. In the case of $[Cp^*_2ZrOC_6H_4PMes_2][B(C_6F_5)_4]$, the room-temperature activation of H_2 is readily reversed by the application of vacuum at 60 °C. These species were also shown to effect the activation of phenylacetylene and ethylene affording species of the form $[Cp'_2Zr(CCPh)OC_6H_4PHR_2][B(C_6F_5)_4]$ (**213**; R = ^{t}Bu, Cp′ = Cp, Cp*; R = Mes, Cp′ = Cp*) and $[Cp^*_2Zr(CH_2CH_2)OC_6H_4P^{t}Bu_2][B(C_6F_5)_4]$ (**214**), respectively. These species also react with alkyl halides leading to alkylation of the P atom and halide capture by Zr (X = Cl, F). In the case of ^{t}BuCl, the analogous reaction prompts loss of isobutylene and protonation of P. These metal-based FLPs were also shown to effect the ring-opening of THF affording $[Cp'_2Zr(O(CH_2)_4)OC_6H_4P^{t}Bu_2][B(C_6F_5)_4]$ (**215**) (Cp′ = Cp, Cp*). Reactions with Et_2O prompts C–O bond cleavage to give $[Cp^*_2Zr(OEt)OC_6H_4PEt^{t}Bu_2][B(C_6F_5)_4]$ (**216**), while the analogous reaction with $^{i}Pr_2O$ yields $[Cp^*_2Zr(O^{i}Pr)OC_6H_4PH^{t}Bu_2][B(C_6F_5)_4]$ (**217**), with loss of propene. Similarly, acetone is deprotonated to give the enolate-phosphonium salt $[Cp^*_2Zr(OCMe{=}CH_2)OC_6H_4PH^{t}Bu_2][B(C_6F_5)_4]$ (**218**). In addition it binds CO_2 to give the species $[Cp^*_2ZrOC_6H_4P^{t}Bu_2CO_2][B(C_6F_5)_4]$ (**219**; Scheme 73). In a fashion similar to metal-free FLPs, this species binds CO_2 between the phosphine and the oxophilic Zr center. Also similar to metal-free systems the product of H_2 activation $[Cp^*_2ZrHOC_6H_4PH^{t}Bu_2][B(C_6F_5)_4]$ (**212**) also reacts with CO_2 affording the formate species $[Cp^*_2Zr(O_2CH)OC_6H_4PH^{t}Bu_2][B(C_6F_5)_4]$ (**220**).



Scheme 74. Further examples of transition-metal FLPs.

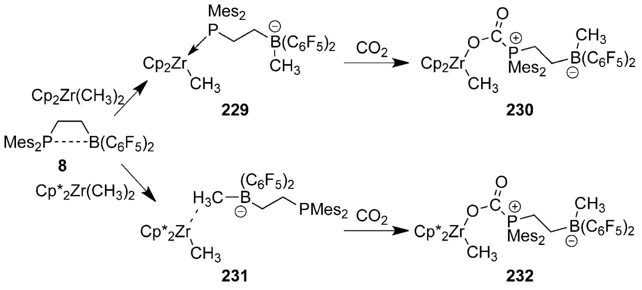
In a further extension, Wass et al. showed that this strategy could be extended to La^{III}, demonstrating that [Cp*$_2$LaOC$_6$H$_4$P^{t}Bu$_2$] effects the ring-opening of THF to give [Cp*$_2$La(O(CH$_2$)$_4$)OC$_6$H$_4$P^{t}Bu$_2$] (**221**; Scheme 74).[140b] In addition Zr analogues of the form [Cp$_2$Zr(OC(CX$_3$)$_2$CH$_2$P^{t}Bu$_2$][MeB(C$_6$F$_5$)$_3$] (X = H, F) react with H$_2$ to effect the loss of methane affording [Cp$_2$ZrH(OC(CX$_3$)$_2$CH$_2$PH^{t}Bu$_2$][HB(C$_6$F$_5$)$_3$] (X = H (**222**), F (**223**; Scheme 74).[142] The Ti analogue [Cp$_2$TiOC$_6$H$_4$P^{t}Bu$_2$][B(C$_6$F$_5$)$_4$] reacts with H$_2$ by the reduction of Ti^{IV} to Ti^{III} to give [Cp$_2$TiOC$_6$H$_4$PH^{t}Bu$_2$][B(C$_6$F$_5$)$_4$] (**224**) which was shown to catalyze the dehydrogenation of Me$_2$HN·BH$_3$.[143]

Erker et al.[144] treated B(C$_6$F$_5$)$_3$ with Shore's (diphenylphosphinomethyl)zirconocene chloride complex. This system affords two different FLP systems, namely the conventional P/B FLP **225** and/or the P/Zr$^+$ FLP **226** (Scheme 75). Compound **226** can be formed by abstraction of the σ-alkyl ligand at zirconium by B(C$_6$F$_5$)$_3$, a variant of the frequently used activation reaction in homogeneous Group 4 metallocene Ziegler–Natta olefin polymerization catalysis.[145] Under specific reaction conditions benzaldehyde was observed to yield the product **227** while under slightly different conditions, addition of phenylisocyanate gave **228** (Scheme 75). The characterization of these two species was consistent with an equilibrium between **225** and **226**.[144]



Scheme 75. Zirconocene derived FLPs.

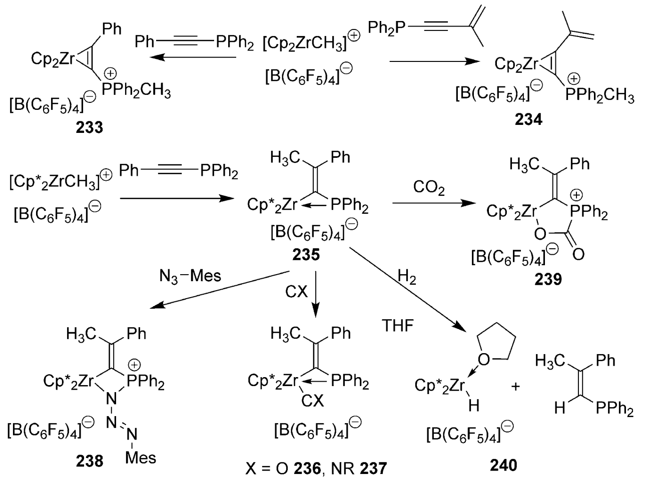
Treatment of [Cp$_2$Zr(CH$_3$)$_2$] with the FLP **8** resulted in the usual abstraction of a methyl anion equivalent by the borane Lewis acid to give **229** (Scheme 76) in which the phosphine fragment is coordinated to zirconium. Nevertheless, compound **229** reacted rapidly with a variety of reagents, including carbon dioxide affording the product **230**. Analogous reaction of **8** with [Cp*$_2$Zr(CH$_3$)$_2$] complex gave a tight ion pair structure **231** in which the methyl-borate binds to the Zr center. Nonetheless, reaction with CO$_2$ gave the species **232** (Scheme 76) which exhibits a structure similar to **230**.[146]



Scheme 76. FLPs derived from the P/B system **8** and zirconium alkyl complexes.

The reactions of the preformed methylzirconocene cations with diphenylphosphino-substituted acetylenes opened another pathway for generating active P/Zr$^+$ FLPs. As these cations contain a residual Zr–C σ-bond, they are quite Lewis acidic. Diphenylphosphino-alkynes remarkably abstracted a methyl cation from [Cp$_2$ZrCH$_3$]$^+$ to give the organometallic phosphonium salt **233**, thus providing a novel method of generating Zr(II) acetylene complexes.[147] The analogous reaction of the phosphinoenyne with [Cp$_2$ZrCH$_3$]$^+$ afforded the phosphonium salt **234** (Scheme 77). The more bulky [Cp*$_2$ZrCH$_3$]$^+$ ion reacts differently. In this case regioselective insertion of the donor-functionalized alkyne reagent into the Zr–CH$_3$ unit is favored yielding the unsaturated geminal P/Zr$^+$ FLP **235** (Scheme 77).[148]

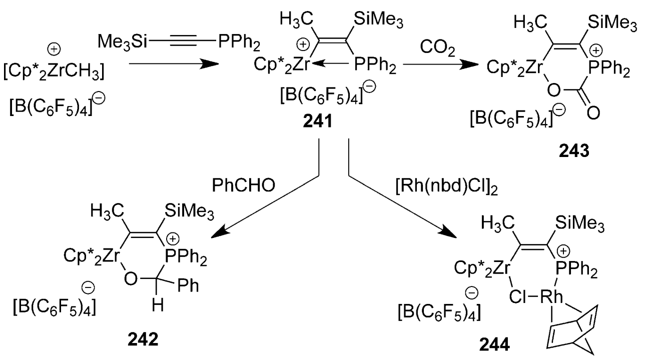
Compound **235** shows a dichotomic behavior. The small strong-donor molecules CO and CNR coordinate to the cationic early-transition-metal center affording **236** and **237**, respectively. However, **235** reacts as a typical P/Zr$^+$ FLP with a variety of other reagents, among them mesitylazide to give **238**, or with carbon dioxide to give **239**.[141] The P/Zr$^+$ FLP even reacts with dihydrogen.[141] The H$_2$ molecule is cleaved heterolytically with the probably resulting phosphonium Brønsted acid subsequently cleaving the reactive Zr–C σ bond to eventually give the product pair **240** (Scheme 77).



Scheme 77. Formation of Zr$^+$/P FLPs.

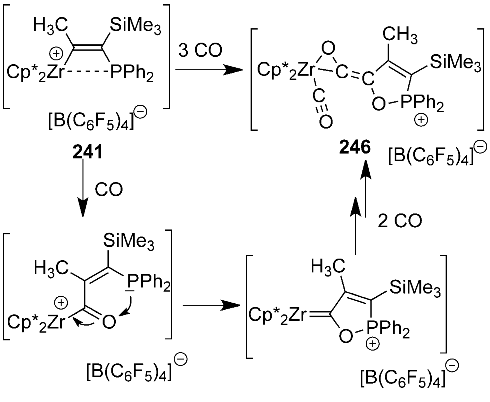
Complex **235** could also be used as an active hydrogenation catalyst for a few alkenes and alkynes.[141]

The $[Cp^*_2ZrCH_3]^+$ ion reacts in a different way with diphenylphosphino(trimethylsilyl)acetylene as this alkyne contains a $SiMe_3$ group which readily migrates. Indeed an unprecedented 1,1-carbozirconation is seen affording the unsaturated intramolecular vicinal P/Zr$^+$ FLP **241**.[149] The new P/Zr$^+$ FLP **241** reacts in a typical FLP fashion with aldehyde or CO_2 to give **242** and **243**, respectively (Scheme 78) and even adds in a typical bifunctional way to (norbornadiene)rhodium chloride affording **244**.



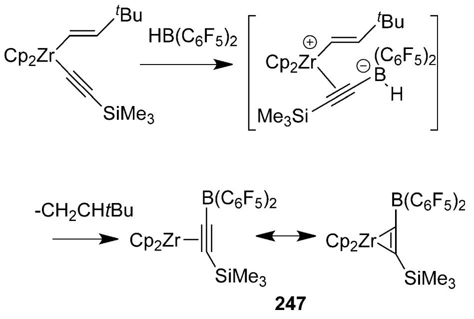
Scheme 78. FLP reactions of complex **241**. nbd = Norbornadiene.

The P/Zr$^+$ FLP **241** undergoes an unusual reaction with carbon monoxide. It takes up three equivalents of CO to yield the product **246**.[149] It is assumed that the reaction sequence is initiated by the usual CO insertion into the Zr–C σ bond. Subsequent rearrangement using the cooperative Zr$^+$/P activation then generates a transient reactive Zr carbene complex intermediate which is trapped by additional carbon monoxide yielding the (η^2-ketene)zirconium carbonyl product **246** (Scheme 79).



Scheme 79. Reaction of the metal-containing FLP **241** with carbon monoxide.

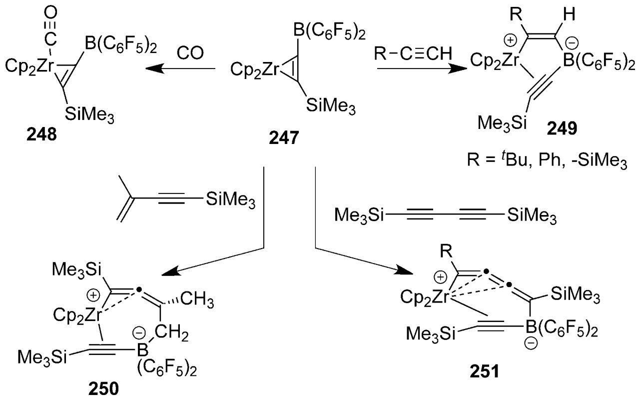
Erker et al.[150] described an unusual (borylalkyne)zirconocene complex **247** that behaved as a unique Zr/B FLP system toward a variety of selected reagents. The system was formed by treatment of the precursor (σ-alkenyl, σ-alkynyl)zirconocene complex with $HB(C_6F_5)_2$. In this case hydroboration is strongly disfavored as the borane serves as a Lewis acid abstracting the σ-alkynyl substituent from the bent metallocene. The resulting reactive intermediate is thought to transfer hydride from boron to zirconium prompting reductive elimination of *tert*-butylethene to eventually give the Zr/B product **247** (Scheme 80). The X-ray crystal structure analysis revealed η^2-coordination of the boryl, silyl-substituted acetylene to the Group 4 bent metallocene, which has a pronounced metallacyclopropene character.[147] While the Si substituent is markedly bent away from Zr, the B substituent is bent slightly towards the metal atom. This arrangement, together with the rather short C–B bond infers some α-boryl carbanion character.[131,133,134]



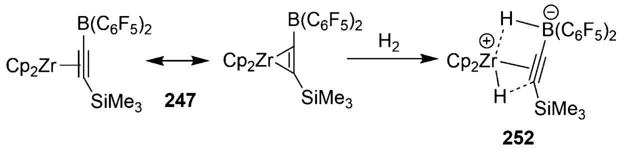
Scheme 80. Formation of the (borylalkyne)zirconium complex **247**.

Complex **247** also shows dichotomic behavior. Toward small donor ligands (e.g. CO, ^{t}BuNC, ^{t}BuCN, THF) it behaves as a coordinatively unsaturated (η^2-alkyne)$ZrCp_2$ system coordinating these ligands to form the corresponding pseudotetrahedral zirconocene complexes (e.g. the carbonyl complex **248**). However, the system **247** shows some typical FLP behavior toward several monosubstituted terminal alkynes which results in 1,2-addition to give the products **249**. With the conjugated enynes or a conjugated diyne, **247** reacts to undergo 1,4-additions affording **250** and **251**, respectively (Scheme 81).[151]

These reactions of **247** demonstrate FLP behavior in which the zirconium center serves as the metal Lewis base[152]



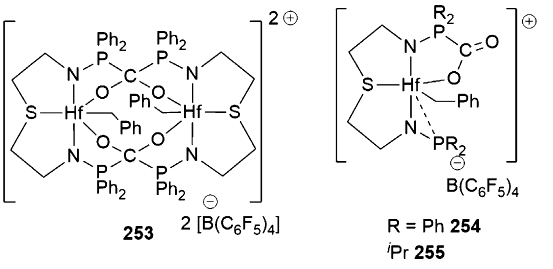
Scheme 81. Reactions of the (borylalkyne)zirconium complex **247**.



Scheme 82. Reaction of the Zr/B FLP with dihydrogen.

with the adjacent boron Lewis acid. Thus not surprisingly, **247** reacts with dihydrogen under mild conditions to give product **252** (Scheme 82).[150,151] This organometallic dihydrogen activation product was also shown to serve as an active hydrogenation catalyst.

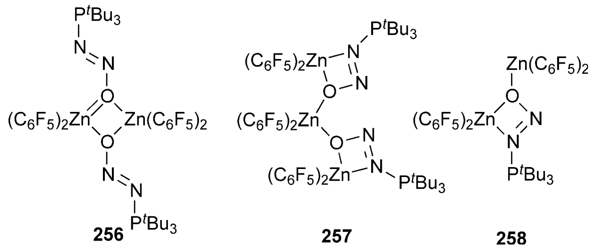
In other developments, the complex $[S(CH_2CH_2NPPh_2)_2Hf(CH_2Ph)_2]$ has been shown to react with $[Ph_3C][B(C_6F_5)_4]$ to generate the corresponding cationic species $[S(CH_2CH_2NPPh_2)_2Hf(CH_2Ph)][B(C_6F_5)_4]$.[153] This species is an intramolecular FLP composed of the pendant phosphine Lewis base and the Lewis acidic Hf cation. Indeed this FLP reacts with CO_2 to give the twofold symmetric bimetallic species $[S(CH_2CH_2NPPh_2)_2Hf(CH_2Ph)(CO_2)]_2[B(C_6F_5)_4]_2$ (**253**; Scheme 83)[153] in which the CO_2 molecules are bound between the phosphine and Hf centers. This species is a monomer in solution and takes up an additional equivalent of CO_2 in THF to generate $[S(CH_2CH_2NPPh_2)_2(CO_2)_2Hf(CH_2Ph)][B(C_6F_5)_4]$. The corresponding reaction of $[S(CH_2CH_2NP^{i}Pr_2)_2Hf(CH_2Ph)_2]$ with $[Ph_3C][B(C_6F_5)_4]$ and CO_2 yields the analogue $[S(CH_2CH_2NP^{i}Pr_2)_2(CO_2)Hf(CH_2Ph)][B(C_6F_5)_4]$ (**255**; Scheme 83).[153]



Scheme 83. Hafnium/phosphine-based FLPs bind CO_2.

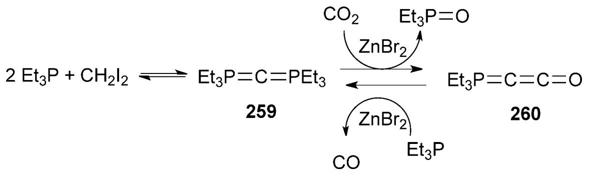
7.2. Late-Transition-Metal-Based FLPs

An early route to late-transition-metal-based FLP systems was derived from exchange reactions. Thus, reactions of $^{t}Bu_3P(N_2O)B(C_6H_4F)_3$ with $[Zn(C_6F_5)_2]$ were shown to give several species depending on the stoichiometry. In this fashion, the species $[^{t}Bu_3P(N_2O)Zn(C_6F_5)_2]_2$ (**256**), $[\{^{t}Bu_3PN_2OZn(C_6F_5)_2\}_2Zn(C_6F_5)_2]$ (**257**) and $[^{t}Bu_3PN_2O(Zn(C_6F_5)_2)_2]$ (**258**) were isolated (Scheme 84).[139] These compounds represent the first metal complexes for which the binding mode of N_2O was unambiguously established.



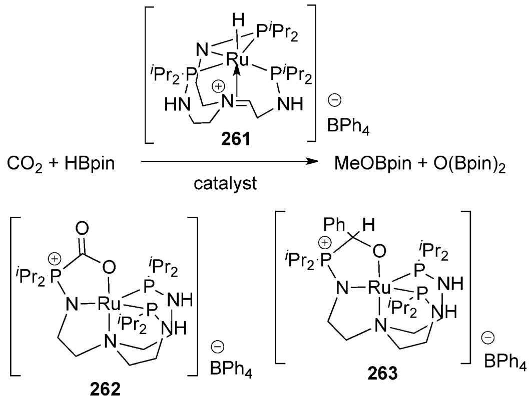
Scheme 84. Products of exchange of P/B-N_2O complexes and $[Zn(C_6F_5)_2]$.

The lower oxophilicity of Zn was also attractive in the development of a catalytic system for the reduction of CO_2. Thus combining Et_3P, CO_2 in the presence of a catalytic amount of CH_2I_2, and $ZnBr_2$ proved to be a viable catalytic avenue for the oxidation of the phosphine and liberation of CO.[154] Mechanistically, this reaction is thought to proceed by the initial generation of a mixture containing $[(Et_3P)_2C]$ (**259**). This bis-ylide reacts with CO_2 to generate a phosphaketene **260** with the liberation of phosphine oxide (Scheme 85). The phosphaketene is then attacked in a FLP-type addition of Et_3P and $ZnBr_2$, prompting loss of CO and regeneration of the bis-ylide. The participation of Zn in the process is supported by the isolation of $[Et_3P{=}CH(PEt_3)(COZnBr_3)]$. Further support for this mechanism was provided by DFT calculations.[154]

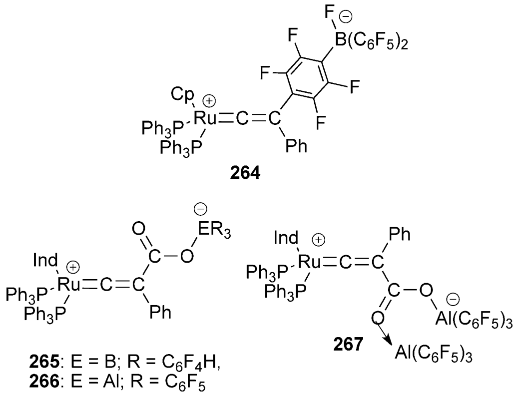


Scheme 85. Catalytic reduction of CO_2 to CO and Et_3PO.

An alternative approach to the use of late-transition-metals in FLP-type reactivity has been based on an amidophosphine ligand at a ruthenium center. The complex $[N((CH_2)_2NHP^{i}Pr_2)((CH_2)_2NP^{i}Pr_2)(CHCH_2NHP^{i}Pr_2))RuH][BPh_4]$ (**261**) provides a pendent phosphine donor in addition to a vacant, Lewis acidic coordination site on Ru. Thus reaction with CO_2 results in capture affording $[(N((CH_2)_2NHP^{i}Pr_2)_2((CH_2)_2NP(CO_2)^{i}Pr_2))Ru][BPh_4]$ (**262**; Scheme 86).[155] This species is thermally robust, on heating



Scheme 86. Catalytic reduction of CO_2 by **261** and isolated intermediates **262** and **263**. HBpin = pinacolborane.



Scheme 87. Products of ruthenium acetylides as bases in FLP reactions with CO_2. Ind = indolyl.

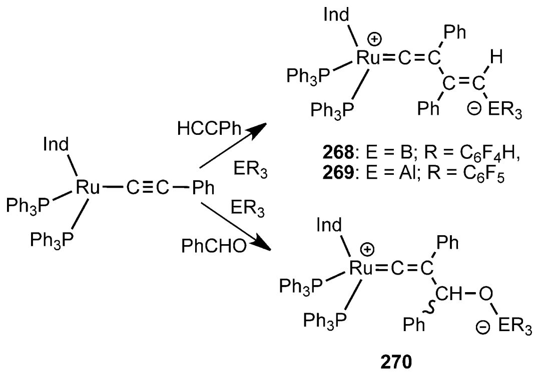
to 80 °C for over a week and yet it mediates the catalytic reduction of CO_2. In the presence of excess HBpin, the products MeOBpin and $O(Bpin)_2$ are formed (Scheme 86) while HBcat or 9-BBN led to the corresponding products of reduction, MeOBcat and $O(Bcat)_2$, or MeOBBN and $O(BBN)_2$, respectively. Mechanistically, successive hydroboration of the CO_2 is supported by spectral evidence. In addition, the proposed formaldehyde intermediate has been independently modeled by the isolation of a benzaldehyde derivative $[(N((CH_2)_2NHP^iPr_2)_2((CH_2)_2NP(PhCHO)^iPr_2))Ru][BPh_4]$ (**263**; Scheme 86).

7.3. FLPs with Ancillary Metal Centers

Another class of FLPs containing transition-metal centers are ones in which the metal does not play an active role in the Lewis acid/Lewis base chemistry but rather acts an ancillary fragment impacting through inductive effects on the basicity or acidity of other centers. For example, it the β-carbon of Ru acetylide complexes are nucleophilic as a result of π interactions of the acetylide with the metal center. Thus, the steric demands of the metal substituents makes the β-carbon of the $[CpRu(PPh_3)_2(C{\equiv}CPh)]$ a bulky base that forms a FLP with $B(C_6F_5)_3$. This results in *para*-attack on the fluoroarene of the borane affording $[CpRu(PPh_3)_2({=}C{=}C(Ph)(C_6F_4)BF(C_6F_5)_2)]$ (**264**; Scheme 87).[156] This reactivity is directly analogous to the reactions of sterically encumbered phosphine donors with these Lewis acids.

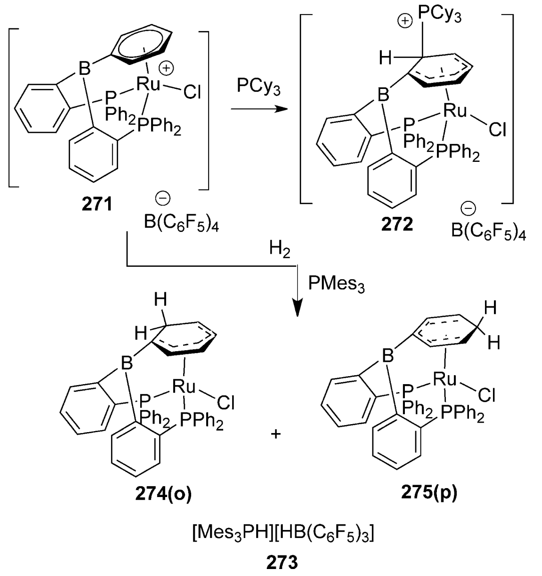
Such *para*-attack could be avoided by use of the Lewis acids $B(C_6F_4H)_3$[157] or $Al(C_6F_5)_3$. Thus reaction of $[(Indenyl)Ru(PPh_3)_2(C{\equiv}CPh)]$ with $B(C_6F_4H)_3$ or $Al(C_6F_5)_3$ and CO_2 gave the species $[(Indenyl)Ru(PPh_3)_2({=}C{=}C(Ph)(CO_2ER_3))$ ($ER_3 = B(C_6F_4H)_3$ (**265**), $Al(C_6F_5)_3$ (**266**)) and $[(Indenyl)Ru(PPh_3)_2({=}C{=}C(Ph)(C(OAl(C_6F_5)_3)_2))$ (**267**), respectively (Scheme 87).[158]

In a similar fashion, the FLPs composed of $[(Indenyl)Ru(PPh_3)_2(C{\equiv}CPh)]$ and $B(C_6F_4H)_3$ or $Al(C_6F_5)_3$ add across alkynes or aldehydes affording the species $[(Indenyl)Ru(PPh_3)_2({=}C{=}C(Ph)C(Ph){=}C(H)ER_3)$ ($ER_3 = B(C_6F_4H)_3$ (**268**), $Al(C_6F_5)_3$ (**269**)) and $[(Indenyl)Ru(PPh_3)_2({=}C{=}C(Ph)CH(Ph)OER_3)$ (**270**; $ER_3 = B(C_6F_4H)_3$ or $Al(C_6F_5)_3$), respectively (Scheme 88).[158] This behavior is directly analogous to the early reports of the corresponding reactions of P/B FLPs.[159]



Scheme 88. Products of reactions of Ru acetylides/Lewis acid FLPs with alkyne and aldehyde.

Another approach to an FLP system which incorporates an ancillary metal center was uncovered with the discovery of the complex $[((Ph_2PC_6H_4)_2B(\eta^6\text{-}Ph))RuCl][B(C_6F_5)_4]$ (**271**).[160] Reaction with sterically unencumbered phosphine yields the donor–acceptor adduct $[((Ph_2PC_6H_4)_2B(\eta^5\text{-}C_6H_5\text{-}o\text{-}PCy_3))RuCl][B(C_6F_5)_4]$ (**272**; Scheme 89). Perhaps surprisingly the most Lewis acidic site in the cation **271** is the carbon atoms of the Ru-bound π-arene moiety, despite the presence of the tricoordinate boron center. Sterically frustrating this donor–acceptor interaction with use of Mes_3P produced no reaction and confirmed generation of a FLP. Reaction of this combination of **271**/Mes_3P with H_2 results in the heterolytic cleavage of H_2 to give a 2:1 mixtures of the *ortho*- and *para*-substituted isomers of $[((Ph_2PC_6H_4)_2B(\eta^5\text{-}C_6H_6))PRuCl]$ (**274(o)** and **275(p)**; Scheme 89) and $[Mes_3PH][HB(C_6F_5)_3]$ (**273**). Thus, **271** acts as carbon-based Lewis acid and was also shown to be an effective catalyst for the hydrogenation of aldimines at room temperature. The mechanism of action is a typical FLP mechanism, in which the metal plays only an ancillary role.



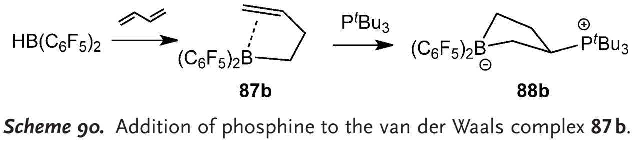
Scheme 89. Donor–acceptor and FLP reactions of **271**.

8. FLP Addition Reactions

Sterically demanding phosphine/borane combinations were reported earlier to add to alkenes[11] and alkynes[159] in stoichiometric additions to give zwitterionic phosphonium borates. This reactivity has been exploited in a variety of new stoichiometric reactions and more recently extended to catalytic reactions. Further addition reactions to cyclopropanes and ring-opening reactions have been generalized to give access to a variety of new compounds of potential synthetic utility.

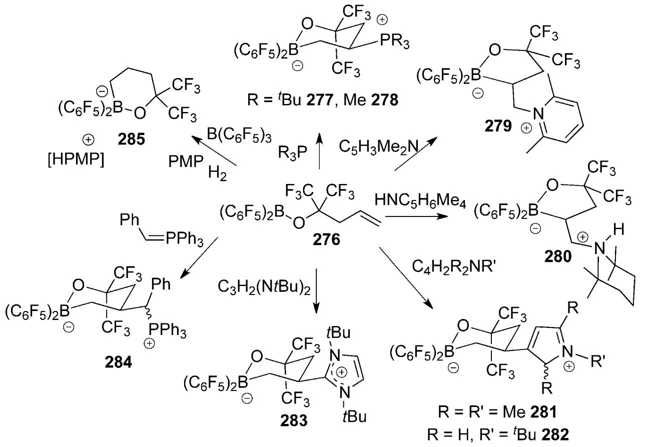
8.1. FLP Chemistry with Alkenes

As previously mentioned, Stephan has described the observation of the intramolecular van der Waals complex **87** between olefins and Lewis acidic B centers (Scheme 36 and Scheme 90). Such species provide access to a range of zwitterionic products by the simple addition of varyious Lewis bases.



Scheme 90. Addition of phosphine to the van der Waals complex **87b**.

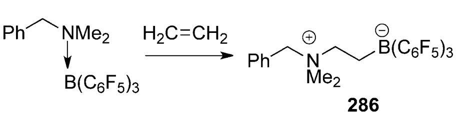
Altering the chain length between the B and olefin provided the straightforward access to the analogous van der Waals complex $B(C_6F_5)_2CH_2CH_2CH{=}CH_2$ (**87b**) which undergoes facile conversion into the five-membered zwitterionic compound **88b** (Scheme 90).[79]



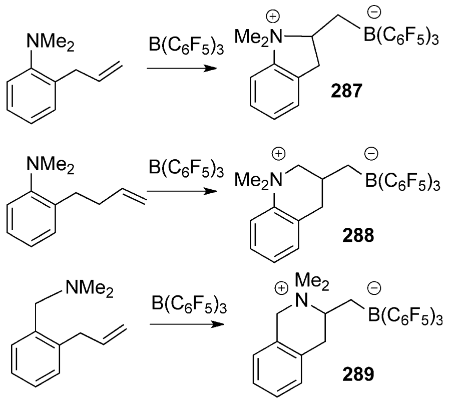
Scheme 91. Addition reactions of **276**. PMP = pentamethylpiperidine.

Moreover, this concept for reactivity could be generalized employing the van der Waals complex $B(C_6F_5)_2(OC(CF_3)_2CH_2CH{=}CH_2)$ (**276**).[161] This species reacts with $^t Bu_3P$ or Me_3P to give the addition products $B(C_6F_5)_2(OC(CF_3)_2CH_2CHCH_2)(PR_3)$ ($R = {}^tBu$ (**277**), Me (**278**); Scheme 91). In these species the phosphine adds to the internal carbon of the olefinic group. While the corresponding reaction of **276** with the bulky nitrogen-based nucleophiles 2,6-lutidine or 2,2,6,6-tetramethylpiperidine also leads to addition products. In contrast to **277** and **278**, the products $B(C_6F_5)_2(OC(CF_3)_2CH_2CHCH_2)(NR')$ ($NR' = C_5H_3Me_2N$ (**279**), $NHC_5H_6Me_4$ (**280**)) result from N-addition to the terminal carbon of the olefinic unit. Carbon-based nucleophiles including 1,2,5-trimethylpyrrole, N-*tert*-butylpyrrole, 1,3-di-*tert*-butylimidzadole-2-ylidene and benzylidene triphenylphosphorane afforded the zwitterions $B(C_6F_5)_2(OC(CF_3)_2CH_2CHCH_2)(R'')$ ($R'' = C_4H_2Me_2NMe$ (**281**), $C_4H_4N^tBu$ (**282**), 1,3-di-*tert*-butylimidzadole-2-ylidene (**283**), $P(CHPh)Ph_3$ (**284**)) which add to the olefin in an analogous fashion to that seen in **277** and **278** (Scheme 91). Reaction of the base 1,2,2,6,6-pentamethylpiperidine (PMP) with **276** in the presence of a catalytic amount of $B(C_6F_5)_3$ and H_2 effects the addition of hydride to the van der Waals complex **276** affording the salt $[HPMP][B(C_6F_5)_2(OC(CF_3)_2CH_2CH_2CH_2)]$ (**285**; Scheme 91).[161]

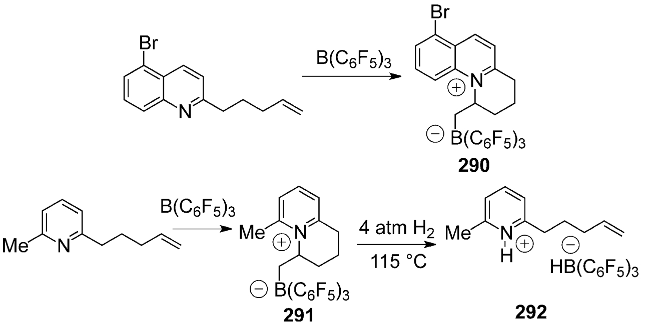
In an intermolecular addition reaction, the amine adduct $PhCH_2NMe_2B(C_6F_5)_3$ was shown to react with ethylene to give the zwitterion, $PhCH_2NMe_2CH_2CH_2B(C_6F_5)_3$ (**286**; Scheme 92).[94] In a similar fashion, this strategy can be extended to donors with pendant olefins to effect cyclizations. In this fashion, *o*-(2-propenyl)-*N*,*N*-dimethylaniline, *o*-(3-butenyl)-*N*,*N*-dimethylaniline, and *o*-(2-propenyl)-*N*,*N*-dimethylbenzylamine react to afford the *N*-heterocyclic zwitterions, $C_6H_4(NMe_2)CH_2CH(CH_2B(C_6F_5)_3)$ (**287**), $C_6H_4(NMe_2)CH_2CH_2CH(CH_2B(C_6F_5)_3)$ (**288**), and $C_6H_4(CH_2NMe_2)CH_2CH(CH_2B(C_6F_5)_3)$ (**289**; Scheme 93).[162]



Scheme 92. Formation of **286**.



Scheme 93. Preparation of N-heterocyclic zwitterions **287**–**289**.



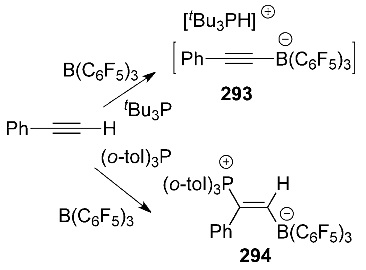
Scheme 94. Preparation of **290**–**292**.

More recently, this strategy has been further extended to prepare polycyclic organic derivatives.[163] For example, quinolines or pyridines with pendant alkyl-olefinic chains were treated with $B(C_6F_5)_3$ to effect the cyclization affording **290** and **291**, respectively (Scheme 94). Interestingly treatment of **291** with H_2 at 115 °C effects the ring-opening of the saturated heterocyclic ring and activation of H_2 affording **292**.[163]

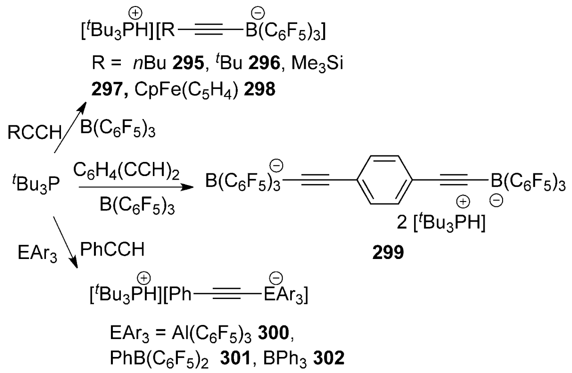
8.2. FLP Additions to alkynes

The reactions of FLPs with terminal alkynes have been shown to proceed by two pathways, deprotonation and addition, depending on the basicity of the base. Thus contrasting reactivity is seen for $^t\mathrm{Bu}_3\mathrm{P}$ and (o-tol)$_3$P where $^t\mathrm{Bu}_3\mathrm{P}$ gives $[^t\mathrm{Bu}_3\mathrm{PH}][\mathrm{PhCCB(C_6F_5)_3}]$ (**293**) and (o-tol)$_3$P gives E-(o-tol)$_3$P(Ph)C=C(H)$B(C_6F_5)_3$ (**294**; Scheme 95).[159]

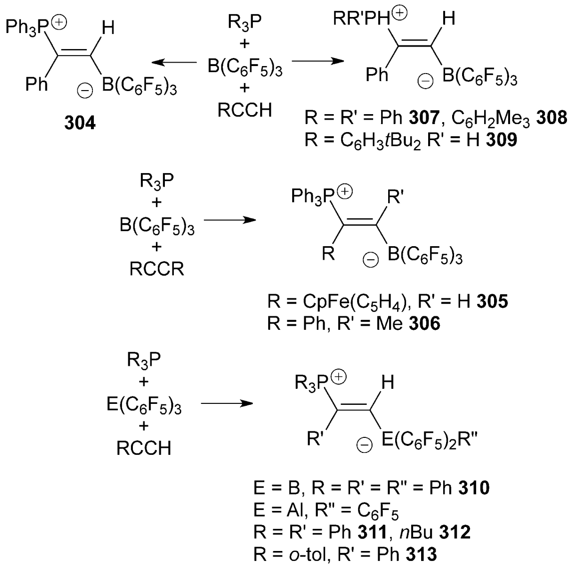
The deprotonation reaction course with $^t\mathrm{Bu}_3\mathrm{P}$ was replicated with a variety of terminal alkynes affording species of the form $[^t\mathrm{Bu}_3\mathrm{PH}][\mathrm{RCCB(C_6F_5)_3}]$ (R = C_4H_9 (**295**), ^{t}Bu (**296**), Me_3Si (**297**), and CpFe(C_5H_4) (**298**)). Similarly, 1,4-diethynylbenzene afforded the salt $[^t\mathrm{Bu}_3\mathrm{PH}]_2[(\mathrm{C_6F_5})_3\mathrm{BCC(C_6H_4)CCB(C_6F_5)_3}]$ (**299**; Scheme 96). Differing Lewis acids also afforded deprotonation products including $[^t\mathrm{Bu}_3\mathrm{PH}][\mathrm{PhCCEAr_3}]$ ($EAr_3 = Al(C_6F_5)_3$ (**300**), $PhB(C_6F_5)_2$ (**301**), BPh_3 (**302**); Scheme 96) while $Me_3SiCCSiMe_3$ afforded $[^t\mathrm{Bu}_3\mathrm{PSiMe}_3][\mathrm{Me_3SiCCB(C_6F_5)_3}]$ (**303**).[164]



Scheme 95. Possible reaction pathways of FLPs with alkynes.

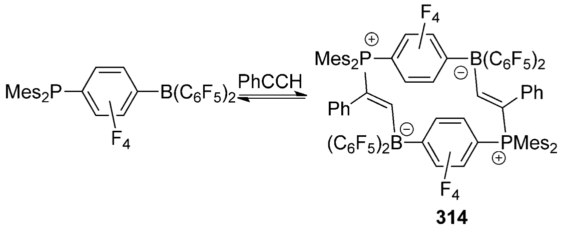


Scheme 96. Deprotonation reactions of FLPs with alkynes.



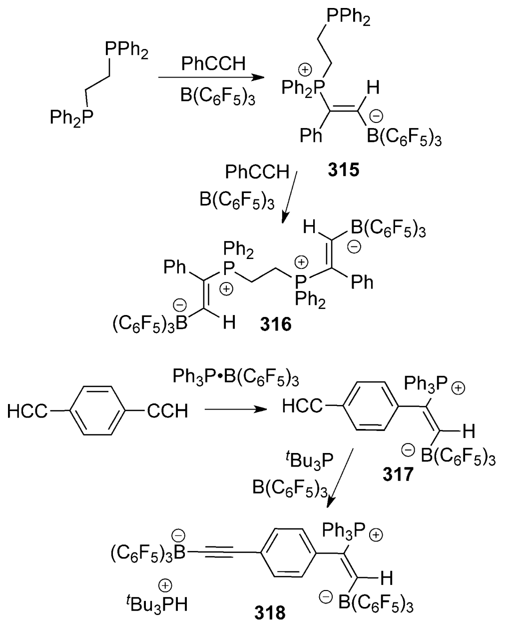
Scheme 97. Addition reactions of FLPs with alkynes.

Phosphine/borane addition reactions were observed with various alkynes as well. In this fashion, the species E-Ph_3P(Ph)C=C(H)$B(C_6F_5)_3$ (**304**; Scheme 97) and similarly E-Ph_3P(CpFe(C_5H_4))C=C(H)$B(C_6F_5)_3$ (**305**) and Ph_3P(Ph)C=C(Me)$B(C_6F_5)_3$ (**306**), E-R_2PH(Ph)C=C(H)$B(C_6F_5)_3$ (R = Ph (**307**), $C_6H_2Me_3$ (**308**)) and E-($C_6H_3{}^t\mathrm{Bu}_2$)PH_2(Ph)C=C(H)$B(C_6F_5)_3$ (**309**) were prepared. Again, variations of the Lewis acid afforded the analogues E-Ph_3P(Ph)C=C(H)EAr_3 ($EAr_3 = PhB(C_6F_5)_2$ (**310**), $Al(C_6F_5)_3$ (**311**)) and E-Ph_3P(C_4H_9)C=C(H)$Al(C_6F_5)_3$ (**312**) and E-(o-tol)$_3$P(Ph)C=C(H)$Al(C_6F_5)_3$ (**313**; Scheme 97).[164]



Scheme 98. FLP addition to PhCCH yielding macrocycle **314**.

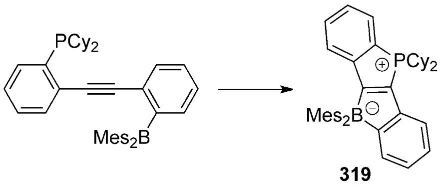
Such addition reactions have been exploited to give the macrocycle $[(H)C{=}C(Ph)Mes_2PC_6F_4B(C_6F_5)_2]_2$ (**314**; Scheme 98) from alkyne and $Mes_2PC_6F_4B(C_6F_5)_2$. Alternatively, the species E-$Ph_2PCH_2CH_2PPh_2(Ph)C{=}C(H)B(C_6F_5)_3$ (**315**) and E-$[CH_2PPh_2(Ph)C{=}C(H)B(C_6F_5)_3]_2$ (**316**) were derived from the reactions of $Ph_2PCH_2CH_2PPh_2$. Addition to 1,4-diethynylbenzene gave E-$HC{\equiv}CC_6H_4C(PPh_3){=}C(H)B(C_6F_5)_3$ (**317**) while subsequent treatment with ^{t}Bu$_3$P and $B(C_6F_5)_3$ yielded the salt/zwitterion [^{t}Bu$_3$PH][$(C_6F_5)_3BCCC_6H_4C(PPh_3){=}C(H)B(C_6F_5)_3$] (**318**; Scheme 99), which illustrates both reaction pathways in a single molecule.[164]



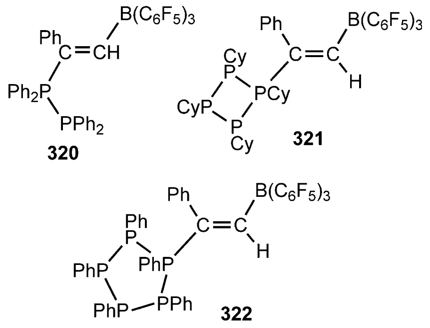
Scheme 99. FLP additions with diphosphines and diynes.

A related application of such P/B additions has been described by Yamaguchi and co-workers[165] who used the intramolecular addition of phosphines and boranes to make species including **319** that are of interest for electronic materials (Scheme 100).

These addition reactions have also been extended to polyphosphines. In this fashion the di-, tetra-, and pentaphosphines $(Ph_2P)_2$, $(CyP)_4$, and $(PhP)_5$ react with alkyne in the presence of borane to give the species **320**–**322** (Scheme 101).[166]

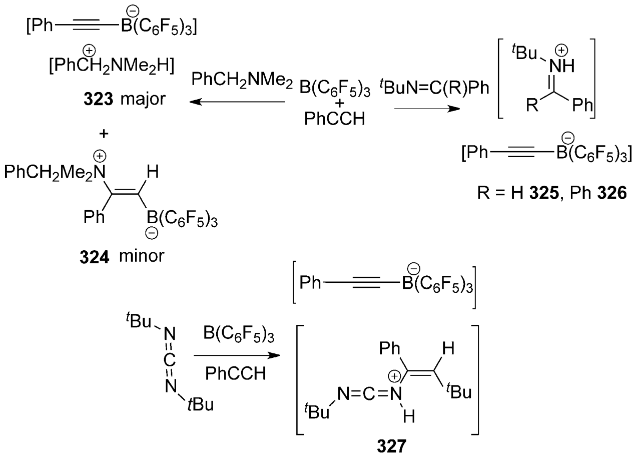


Scheme 100. P/B addition route to **319**.



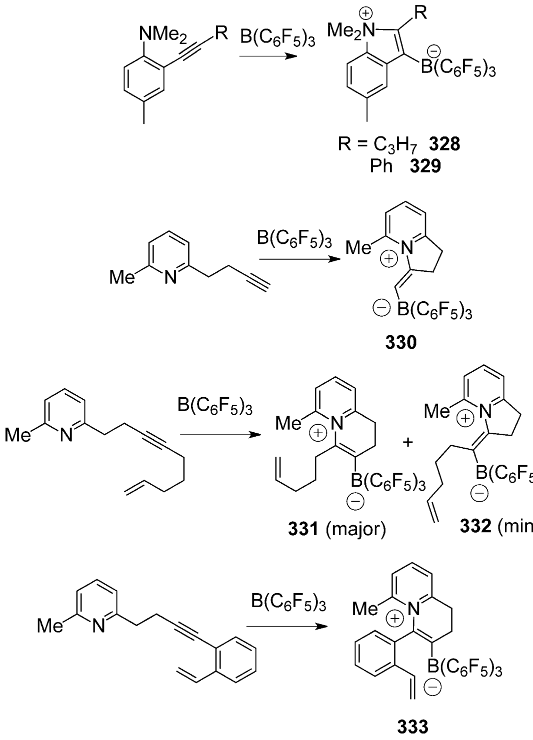
Scheme 101. Polyphosphine/borane addition reaction products.

Use of N-bases in FLP reactions with alkyne was also probed. $PhCH_2NMe_2$ with PhCCH and $B(C_6F_5)_3$ gave a 84:16 mixture of the deprotonation product $[PhCH_2NMe_2H][PhCCB(C_6F_5)_3]$ (**323**) and the addition species $PhCH_2NMe_2(Ph)C{=}C(H)B(C_6F_5)_3$ (**324**). Imines reacted to generate the iminium salts [(^{t}Bu)HN=CHPh][$PhCCB(C_6F_5)_3$] (**325**) and [(^{t}Bu)HN=CPh$_2$][$PhCCB(C_6F_5)_3$] (**326**) (Scheme 102).[164] The corresponding reaction of the carbodiimide ^{t}BuNCN^{t}Bu, $B(C_6F_5)_3$, and two equivalents of PhCCH led to the unusual product [^{t}BuNCN(H)C(Ph)=C(H)^{t}Bu][$PhCCB(C_6F_5)_3$] (**327**; Scheme 102). This species also results from both addition and deprotonation reactions.[164]



Scheme 102. N-bases in FLP additions.

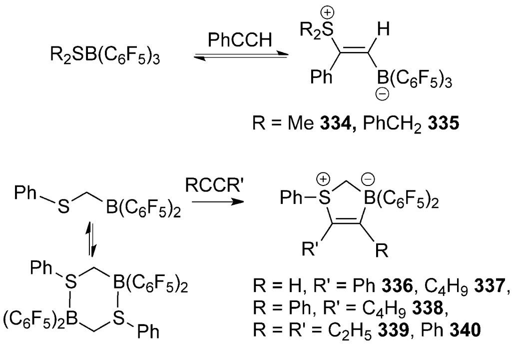
Similar to pendant olefins, alkyne fragments on an aniline ring have been exploited for intramolecular cyclizations.[162] Thus reaction of *o*-(pentynyl)-*N*,*N*-dimethyl toluidine or *o*-



Scheme 103. Intramolecular cyclizations with N/B FLPs and alkynes.

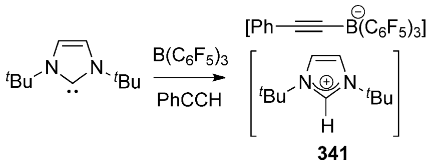
(phenylethynyl)-*N*,*N*-dimethyl toluidine with $B(C_6F_5)_3$ yielded the cyclized products **328** and **329** (Scheme 103). In a similar sense, intramolecular cyclizations using pendant alkyne substituents on pyridine or quinoline derivatives afforded synthetic routes to the zwitterionic products **330**–**333** (Scheme 103).[163]

Sulfur donors have also been employed in such FLP addition reactions. The sulfides R_2S gave *E*-$R_2S(Ph)C{=}C(H)B(C_6F_5)_3$ (R = Me (**334**), $PhCH_2$ (**335**; Scheme 104)[164] which exist in equilibria with the alkyne and thioether borane adduct. The related dimeric intramolecular FLP, $(PhSCH_2B(C_6F_5)_2)_2$ also reacts with the terminal and internal alkynes to give the species $(PhSCH_2B(C_6F_5)_2)(R'C{=}CR)$ (R = H, R′ = Ph (**336**), R = H, R′ = C_4H_9 (**337**), R = Ph, R′ = C_4H_9 (**338**), R = R′ = C_2H_5 (**339**), R = R′ = Ph (**340**)). Interestingly this intramolecular FLP effects a *cis* addition to these alkynes, in contrast to the intermolecular reactions (Scheme 104).[167]



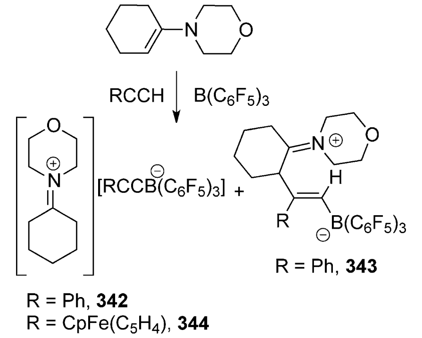
Scheme 104. FLP additions with S/B FLPs.

Use of carbon-based Lewis bases was also explored in reactions with alkynes and $B(C_6F_5)_3$. Use of the strongly basic N-heterocyclic carbene (NHC) I^tBu with $B(C_6F_5)_3$ and PhCCH resulted in the formation of the deprotonation product $[I^tBuH][PhCCB(C_6F_5)_3]$ (**341**; Scheme 105).[164]



Scheme 105. Deprotonation of alkyne by carbene/borane FLP.

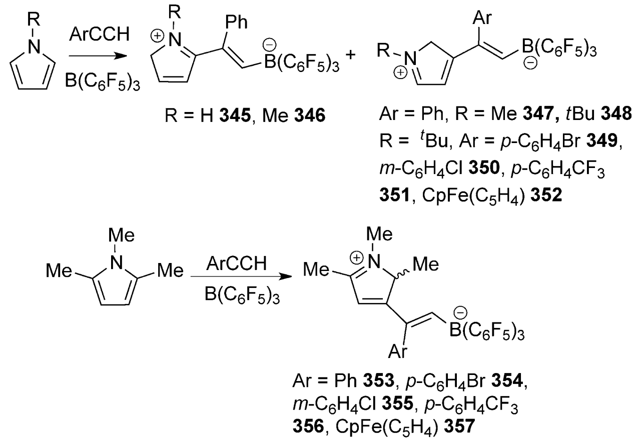
Attempts to use alternative C-bases in FLP addition reactions were targeted to yield C–C bond formation. In the case of the reaction of 1-morpholinocyclohexene with $B(C_6F_5)_3$ and phenylacetylene, a 50:50 mixture of two compounds $[C_6H_{10}N(CH_2CH_2)_2O][PhCCB(C_6F_5)_3]$ (**342**) and $C_6H_9(2\text{-}PhC{=}C(H)B(C_6F_5)_3)(N(CH_2CH_2)_2O$ (**343**) was observed. The analogous reaction with ethynylferrocene resulted in only the deprotonation product the alkynyl borate salt, $[C_6H_{10}N(CH_2CH_2)_2O][CpFe(C_5H_4)CCB(C_6F_5)_3]$ (**344**; Scheme 106).[168]



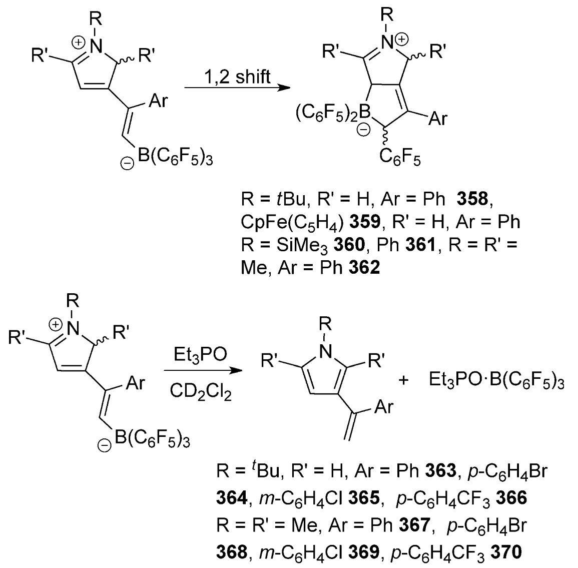
Scheme 106. FLP alkyne reactions with 1-morpholinocyclohexene.

The related reactions of pyrrole, phenylacetylene, and $B(C_6F_5)_3$ led to the vinyl borate addition product, $HNC_4H_4(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**345**). The corresponding reaction of *N*-methylpyrrole, phenylacetylene, and $B(C_6F_5)_3$ gave a 3:2 ratio of the products $MeNC_4H_4(2\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**346**) and $MeNC_4H_4(3\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**347**; Scheme 107). Finally *N-tert*-butylpyrrole provided the single product $^tBuNC_4H_4(3\text{-}PhC{=}C(H)B(C_6F_5)_3)$ (**348**). These reactions also tolerated variations in the aryl alkynes, affording the addition products $^tBuNC_4H_4(3\text{-}ArC{=}C(H)B(C_6F_5)_3)$ (Ar = *p*-C_6H_4Br (**349**), *m*-C_6H_4Cl (**350**), *p*-$C_6H_4CF_3$ (**351**), $CpFe(C_5H_4)$ (**352**)). Similarly using 1,2,5-trimethylpyrrole as the base afforded **353**–**357** (Scheme 107).[168]

Interestingly the species **348** and **349** rearrange on standingin solution to give $^tBuNC_4H_3(3\text{-}ArC{=}C(H)(C_6F_5)B(C_6F_5)_2)$ (Ar = Ph (**358**), $CpFe(C_5H_4)$ (**359**); Scheme 108). The species



Scheme 107. Reactions of pyrroles/boranes and alkynes.

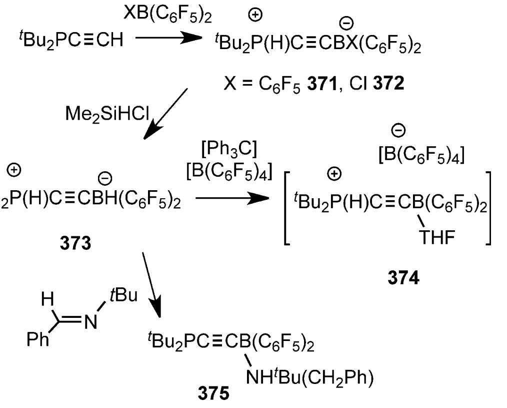


Scheme 108. Subsequent reactions of pyrrole/borane addition products.

$RNC_4H_3(3\text{-}PhC{=}C(H)(C_6F_5)B(C_6F_5)_2)$ (R = $SiMe_3$ (**360**), Ph (**361**)) and $MeNC_4H(2,5\text{-}Me_2)(3\text{-}PhC{=}C(H)(C_6F_5)B(C_6F_5)_2)$ (**362**) were derived directly from the reactions of the pyrrole, PhCCH, and $B(C_6F_5)_3$. Deprotonation of **348** gave the salt $[^tBu_3PH][^tBuNC_4H_3(PhC{=}C(H)B(C_6F_5)_3)]$ while Et_3PO mediated proton transfer in reactions with **348**–**351** or **353**–**356** to generate the corresponding vinyl pyrroles **363**–**370** (Scheme 108).[168]

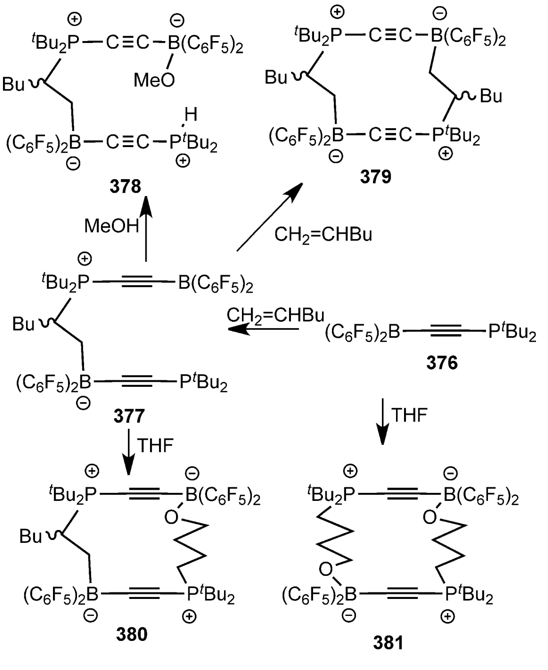
8.3. Alkynyl-Linked FLPs

Given the reactivity of **4**, the synthesis of alkynyl-linked phosphine boranes was targeted. In the first study,[169] the reaction of the phosphine $^tBu_2PC{\equiv}CH$ with $B(C_6F_5)_3$ afforded the zwitterionic species $^tBu_2P(H)C{\equiv}CB(C_6F_5)_3$ (**371**; Scheme 109). While reaction of $^tBu_2PC{\equiv}CH$ with $ClB(C_6F_5)_2$ proceeded to give $^tBu_2P(H)C{\equiv}CB(Cl)(C_6F_5)_2$ (**372**). Halide for hydride exchange using Me_2SiHCl provided $^tBu_2P(H)C{\equiv}CB(H)(C_6F_5)_2$ (**373**). Abstraction of the hydride with $[Ph_3C][B(C_6F_5)_4]$ yielded the salt $[^tBu_2P(H)C{\equiv}CB(C_6F_5)_2(THF)][B(C_6F_5)_4]$ (**374**). Compound **373** also reacts with the imine $^tBuN{=}CHPh$ to effect proton and hydride transfer and give the borane/amine adduct $^tBu_2PC{\equiv}CB(^tBuN(H)CH_2Ph)(C_6F_5)_2$ (**375**).[169]



Scheme 109. Synthesis and reactivity of **371**–**375**.

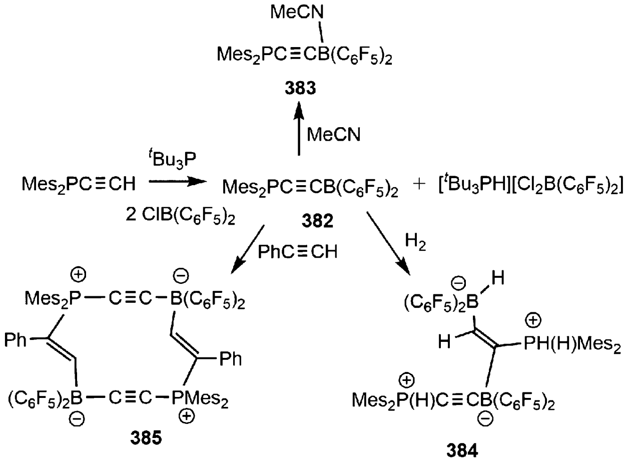
Reaction of **373** with $^tBu_3P$ and $B(C_6F_5)_3$ generated the phosphine/borane $^tBu_2PC{\equiv}CB(C_6F_5)_2$ (**376**). This species was not isolable but was found to react with 1-hexene to give FLP addition to the olefin affording the species $(^tBu_2PC{\equiv}CB(C_6F_5)_2)(BuCHCH_2)(^tBu_2PC{\equiv}CB(C_6F_5)_2)$ (**377**; Scheme 110).[170] Subsequent reaction with methanol or additional hexene gave $(^tBu_2P(H)C{\equiv}CB(C_6F_5)_2)(BuCHCH_2)(^tBu_2PC{\equiv}CB(C_6F_5)_2)(OMe)$ (**378**) or the macrocycle $[(^tBu_2PC{\equiv}CB(C_6F_5)_2)(BuCHCH_2)]_2$ (**379**), respectively. Alternatively, **377** reacts with THF to give the macrocycle $(^tBu_2PC{\equiv}CB(C_6F_5)_2)(BuCHCH_2)(^tBu_2PC{\equiv}CB$-



Scheme 110. Macrocyclic FLP derivatives.

$(C_6F_5)_2)(O(CH_2)_4)$ (**380**), while **376** reacts with THF to give the formation of $[(^tBu_2PC\equiv CB(C_6F_5)_2)(O(CH_2)_4)]_2$ (**381**; Scheme 110).[169]

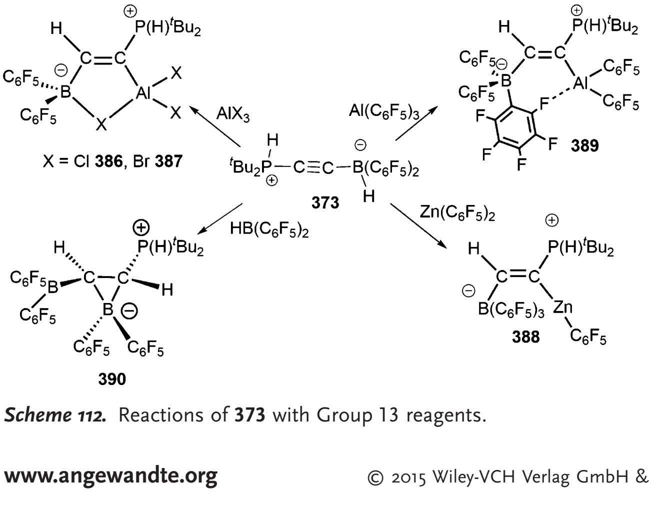
The related phosphine-borane $Mes_2PC\equiv CB(C_6F_5)_2$ (**382**) was generated in a similar reaction, although it was only isolable as an acetonitrile adduct $Mes_2PC\equiv CB(NCMe)(C_6F_5)_2$ (**383**). Nonetheless, **382** reacts with H_2 to give the dimeric zwitterionic product $(C_6F_5)_2(H)BHC{=}C(P(H)Mes_2)((C_6F_5)_2BC\equiv CP(H)Mes_2)$ (**384**; Scheme 111). Reaction with $PhC\equiv CH$ gave the macrocyclic product $[(Mes_2PC\equiv CB(C_6F_5)_2)(CH{=}CPh)]_2$ (**385**; Scheme 111).[169]



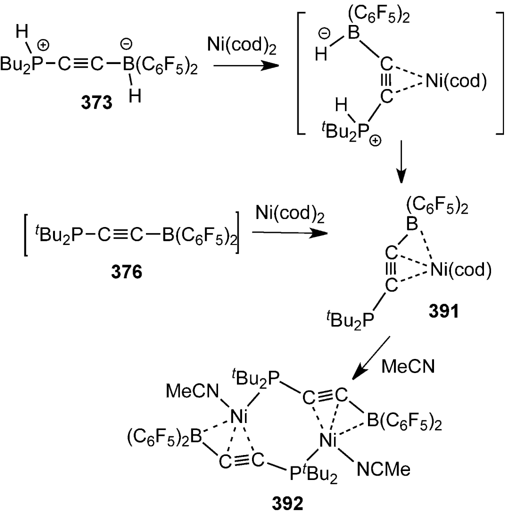
Scheme 111. Synthesis and reactions of **380**.

Compound **373** also reacted with AlX_3 (X = Cl, Br), $Zn(C_6F_5)_2{\cdot}C_7H_8$, $Al(C_6F_5)_3{\cdot}C_7H_8$, or $HB(C_6F_5)_2$ affording addition to the alkynyl unit to give $(C_6F_5)_2BHC{=}C(P(H)^tBu_2)(AlX_3)$ (X = Cl (**386**), Br (**387**)), $(C_6F_5)_3BHC{=}C(P(H)^tBu_2)(Zn(C_6F_5))$ (**388**), $(C_6F_5)_3BHC{=}C(P(H)^tBu_2)(Al(C_6F_5)_2)$ (**389**), or $((C_6F_5)_2B)_2HC{=}CH(P(H)^tBu_2)$ (**390**), respectively (Scheme 112).[169]

In a similar fashion, the Ni complexes, $[(^tBu_2PC\equiv CB(C_6F_5)_2)Ni(COD)]$ (**391**) and $[\{(^tBu_2PC\equiv CB(C_6F_5)_2)Ni(NCMe)\}_2]$ (**392**) were derived from the reaction of **373** and $[Ni(COD)_2]$ (Scheme 113).[171] Similar to that observed in the Zr complex **247**, these complexes exhibit metal–alkyne interactions in which the borane substituent bends towards the metal affording a Ni→B dative interaction.

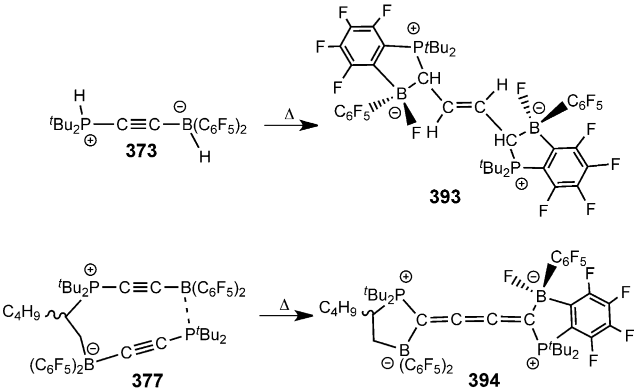


Scheme 112. Reactions of **373** with Group 13 reagents.



Scheme 113. Synthesis of the Ni complexes **391**–**392**. cod = cyclooctadienyl.

Interestingly, thermolysis of the alkynyl phosphonium borates, **373** and **377**, results in C–C coupling reactions leading to a C_4-alkene derivative $^tBu_2PCHBF(C_6F_4)(C_6F_5)CH)_2$ (**393**) and a cumulene derivative $(^tBu_2P)C_6F_4BF(C_6F_5)C_4B(C_6F_5)_2$ $(BuCHCH_2)(P^tBu_2)$ (**394**), respectively (Scheme 114).[170]

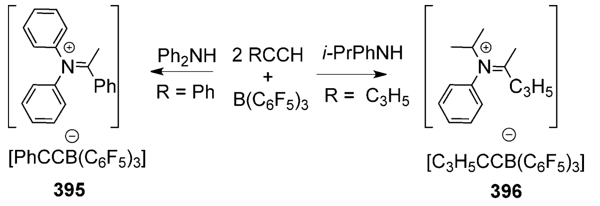


Scheme 114. Thermolysis products.

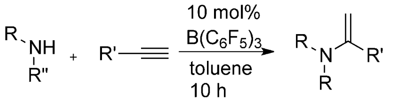
8.4. FLP-Catalyzed Hydroaminations of Alkynes

Stoichiometric reaction of Ph_2NH, $B(C_6F_5)_3$, and phenylacetylene afforded the salt $[Ph_2N{=}C(CH_3)Ph][PhC\equiv CB(C_6F_5)_3]$ (**395**; Scheme 115).[172] In the same vein, the species $[Ph(^iPr)N{=}CMe(^iPr)][(^iPr)C\equiv CB(C_6F_5)_3]$ (**396**) was prepared from the corresponding alkyne, aniline, and $B(C_6F_5)_3$.

These reactions can be adapted to a catalytic synthesis by using the amine in the presence of a catalytic amount of borane with slow addition of alkyne.[172] In this fashion, a series of arylamines was used to produce the corresponding



Scheme 115. Stoichiometric reactions of arylamine, borane, and alkyne.



R = R''= Ph, R' = C_6H_4OMe **397**, C_6H_4Me **398**, $C_{10}H_7$ **399**, Ph **400**, C_6H_4Br **401**, $C_{14}H_9$ **402**, 3,5-$F_2C_6H_3$ **403**, 3-$CF_3C_6H_4$ **404**

R'' = ^{i}Pr, R' = 2-SC_4H_4 **405**

R = *p*-FC_6H_4, R' = C_6H_4Br **406**,FC_6H_4 **407**, 2-SC_4H_4 **408**,$C_{14}H_9$ **409**, 3-FC_6H_4 **410**

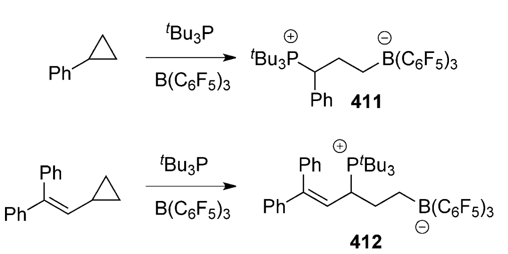
Scheme 116. Catalytic hydroaminations of alkynes.

aryl enamines **397–410** in yields between 62–84% (Scheme 116). Tandem hydroamination and subsequent hydrogenation were also possible affording the corresponding amines.

The mechanism of these hydroaminations is thought to proceed by amine-borane addition to the alkyne.[172] The acidity of the resulting ammonium proton prompts protonation of the β-carbon generating the enamine and releasing the borane for further catalysis. This accounts for the need to use arylamines, because more basic amines would neither add to the alkyne nor permit proton transfer to carbon. Slow addition of the alkyne is necessary to prevent excess alkyne from acting as the proton source generating the stoichiometric alkynyl borate salt.

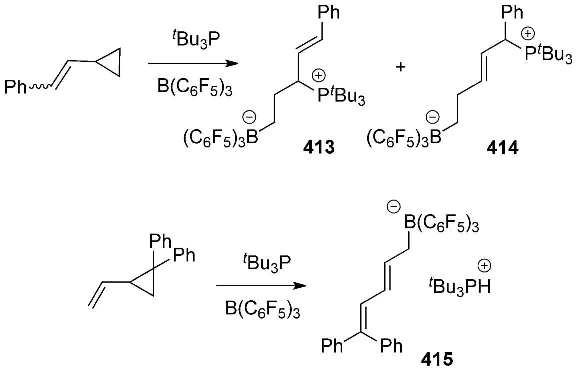
8.5. FLPs and Cyclopropanes

Reactions of FLPs with cyclopropanes result in ring opening, yielding phosphonium/borate products.[173] For example, reaction of the quintessential P/B FLP with the phenylcyclopropane gave the ring-opened product **411**. Similarly, the corresponding reaction with $Ph_2C{=}CH(C_3H_5)$ gives the substituted ring-opened product **412** (Scheme 117).



Scheme 117. Ring opening of cyclopropanes.

Further reactions of vinyl-substituted cyclopropanes were explored. In the case of $PhC(H){=}CH(C_3H_5)$ competitive pathways of 1,3- and 1,5-additions were observed (**413**, **414**). In contrast, reaction of $H_2C{=}CH(C_3H_5)$ gave rise to deprotonation affording the conjugated diene anion in **415** (Scheme 118).

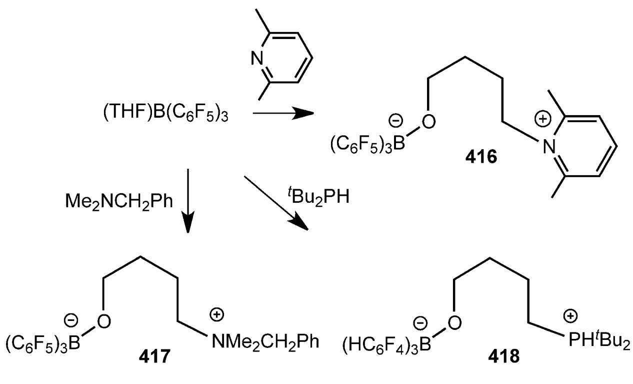


Scheme 118. Reactions of vinylcyclopropanes with FLPs.

8.6. FLP Ring-Opening Reactions with Heterocycles

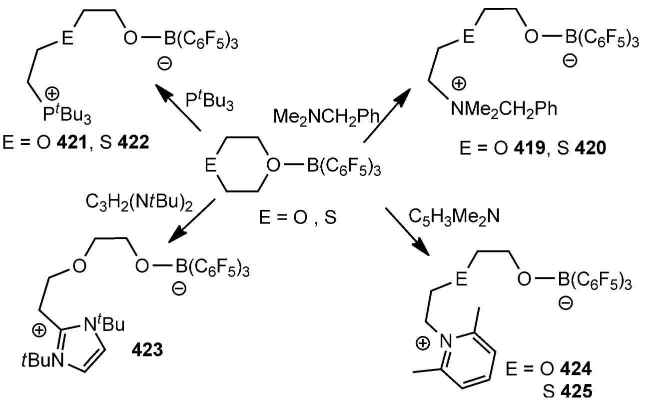
One of the early reactions recognized to result from the action of FLPs was the ring-opening of THF to give the linked phosphonium alkoxyborate.[174] Indeed, a number of previously reported examples of THF ring-opening can in retrospect be attributed to the action of an FLP.[15]

Such reactions have been extended to a variety of FLPs and other heterocyclic substrates.[175] For example, reaction of 2,6-lutidine with a THF solution of $B(C_6F_5)_3$ led to 2,6-$Me_2C_5H_3N(CH_2)_4OB(C_6F_5)_3$ (**416**; Scheme 119), while similar reactions with $C_6H_5CH_2NMe_2$ and $^tBu_2PH$ gave the analogues **417** and **418**. 1,4-dioxane and thioxane could also be ring opened to give **419–425** (Scheme 120).

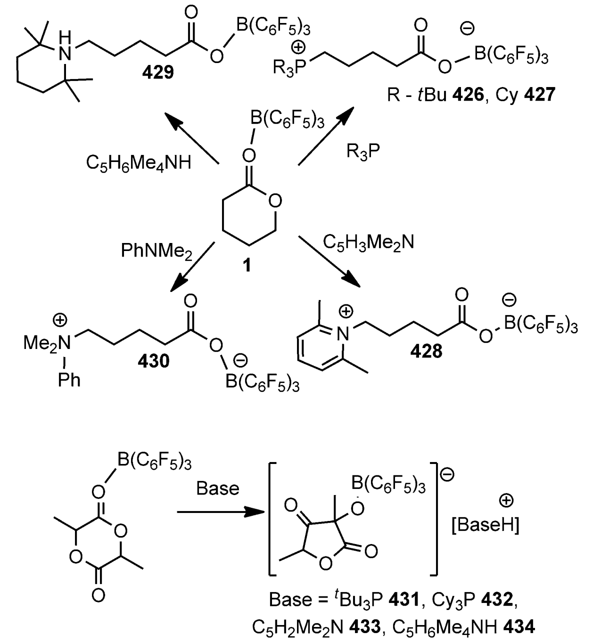


Scheme 119. Ring opening of THF by FLPs.

Similarly lactone and lactide react with FLPs derived from $B(C_6F_5)_3$ and phosphine or N-bases.[176] In the case of lactone, ring opening affording zwitterionic species of the form $L(CH_2)_4CO_2B(C_6F_5)_3$ **426–430** were obtained. In contrast, reaction with *rac*-lactide resulted in ring contraction to give



Scheme 120. Ring opening of dioxane and thioxane.

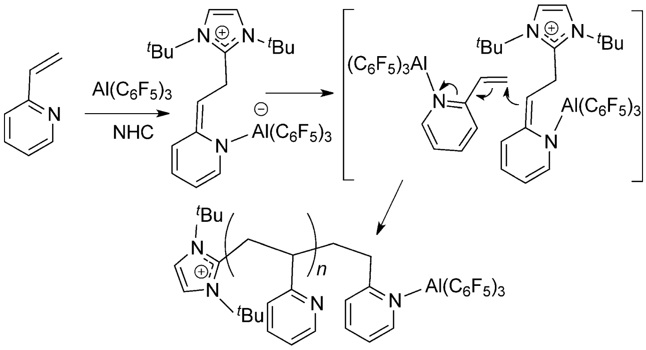


Scheme 121. Ring opening of a lactone and ring contraction of a lactide.

salts [baseH][OCCHMeOCO(CMe)OB(C_6F_5)$_3$] (base = ^{t}Bu$_3$P, Cy$_3$P, $C_5H_3Me_2N$, $C_5H_6Me_4NH$; **431–434**; Scheme 121).[176]

8.7. FLPs in Polymerizations

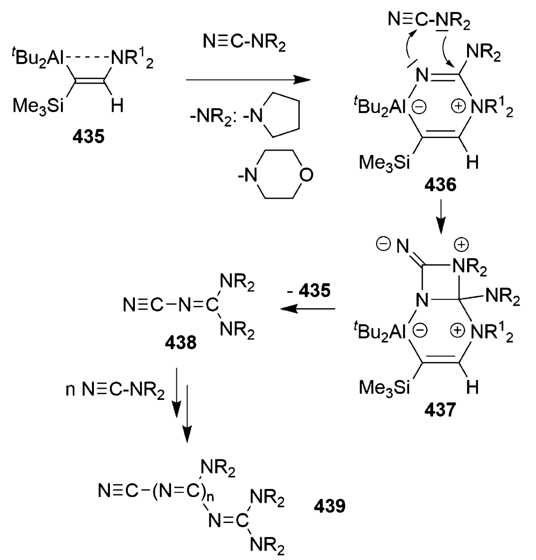
Chen and co-workers[177] have described the reaction of FLPs based on Al(C_6F_5)$_3$ in combination with phosphines and NHCs to effect the rapid polymerization of polar vinyl monomers, such as methyl methacrylate (MMA), methylene butyrolactones, α-methylene-γ-butyrolactone (MBL), and γ-methyl-α-methylene-γ-butyrolactone. This approach yields high-molecular-weight polymers often with narrow molecular-weight distributions and typically atactic or syndiotactic rich. Chiral phosphine bases did not alter the stereoselectivity, although highly syndiotactic polymethylmethacrylate was produced at −78 °C. These polymerizations are thought to proceed via zwitterionic phosphonium or imidazolium enolaluminate intermediates. Kinetic studies have revealed that the MMA polymerization is zero-order in monomer after an initial induction period. These data together with computation work support a bimolecular, activated-monomer propagation mechanism.[178] In a similar fashion, Chen and co-workers have also reported the polymerization of 2-vinyl pyridine and 2-isopropenyl-2-oxazoline using FLPs based on Al(C_6F_5)$_3$ and NHCs.[179] These are also proposed to form by a bimolecular, activated-monomer polymerization mechanism (Scheme 122).



Scheme 122. Proposed mechanism of FLP-induced polymerization of vinylpyridine.

While the corresponding borane-based FLPs, R_3P/B(C_6F_5)$_3$ are inactive for the polymerization of methyl methacrylate, Chen et al. have more recently reported the use of phosphine/borane Lewis pairs to effect the polymerization of γ-methyl-α-methylene-γ-butyrolactone.[180] In this regard it is also interesting to note that Chen et al. tested a series of linked phosphine-boranes and the most frustrated species were indeed the least active with the classical adduct Ph$_3$P(B(C_6F_5)$_3$) being the most active.

Würthwein et al. described the unprecedented selective linear oligomerization of cyanamides catalyzed by the intramolecular vicinal Al/N FLP **435**.[179] This reaction is quite unusual since nitriles are usually trimerized at suitable catalysts to give the thermodynamically preferred aromatic triazines rather than the linear oligomers or polymers. The linear cyanamide oligomerization is thought to be due to a kinetically favored FLP pathway involving the Al/N FLP addition product **436** which then undergoes a [2+2]cycloaddition reaction with the cyanamide to give **437** (Scheme 123). Ring opening then directly yields the (experimentally observed) cyanamide dimer **438**. Successive repetition of this sequence results in the formation of the linear cyanamide trimer **439** (with $n = 1$; Scheme 123), which was actually isolated and characterized by X-ray diffraction, and the linear cyanamide oligomers with n up to 24.

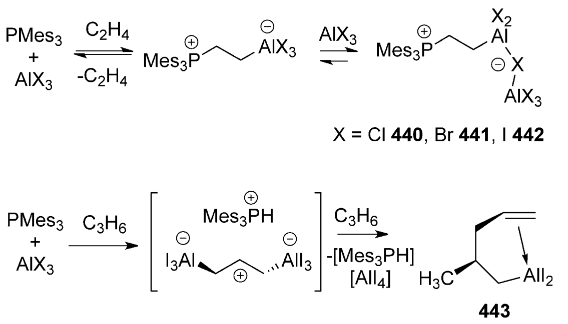


Scheme 123. FLP-catalyzed linear oligomerization of cyanamides.

9. New Lewis Acids in FLP Chemistry

9.1. Al-Based FLPs

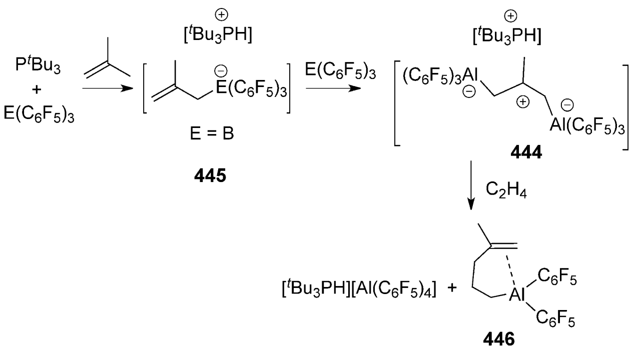
Although $Al(C_6F_5)_3$ has been used as a Lewis acid in FLP chemistry, use of simple Al halides in FLP chemistry has also emerged. FLPs derived from R_3P (R = *o*-tol, Mes) and AlX_3 (X = halide or C_6F_5) add to ethylene to give the addition products **440**–**442** while with propylene, dimerization by a C–H bond activation and C–C bond formation afford an Al-bound 2-methyl-pentene complex **443** (Scheme 124).[181]



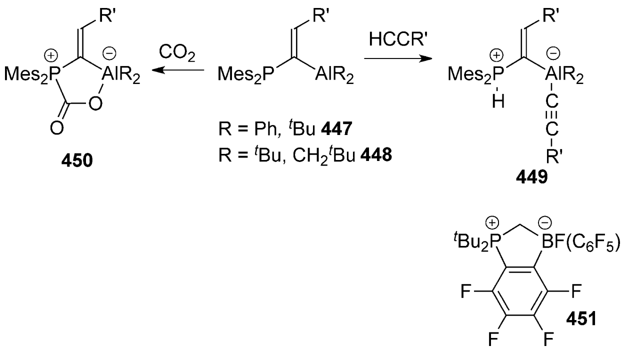
Scheme 124. Reactions of Al/P FLPs with ethylene and propylene.

The analogous chemistry of isobutylene and the FLPs derived from $^tBu_3P$ and $E(C_6F_5)_3$ (E = Al, B) were shown to give $[^tBu_3PH][((C_6F_5)_3Al)_2((CH_2)_2CMe)]$ (**444**) and $[^tBu_3PH][(C_6F_5)_3B((CH_2)_2CMe)]$ (**445**), respectively. The product **444** also inserts ethylene to give $CH_2{=}C(Me)(CH_2)_3Al(C_6F_5)_2$ (**446**) and $[^tBu_3PH][Al(C_6F_5)_4]$ (Scheme 125).[182]

Uhl and Lammertsma have developed a wider variety of Al-based species of interest. For example, exploiting hydroalumination of alkynes, they[101] reported the synthesis of $R'CH{=}C(AlR_2)PMes_2$ **447** and **448** (R′ = Ph, ^tBu, R = ^tBu, $CH_2{}^tBu$). These intramolecular Al/P FLPs react with alkyne to afford species of the form $R'CH{=}C(AlR_2(CCR')PHMes_2$ (**449**). In the case of the phenylacetylene products, thermolysis gave the heterocylic species $R'CH{=}CAlR_2(CH{=}CR'$-$(PMes_2))$. Similarly the FLP binds CO_2 to give the heterocycle $R'CH{=}CAlR_2(O_2C)PMes_2$ (**450**; Scheme 126). While this reactivity is related to that seen with electrophilic boranes, it is noteworthy that electron-withdrawing substituents are not required on Al for this FLP. This situation is consistent with the view that Al derivatives are generally more Lewis acidic than their boron counterparts.[183] Efforts to make analogous geminal P/B FLP $(C_6F_5)_2BCH_2P^tBu_2$ were unsuccessful as this species effects *ortho*-C–F activation affording the heterocycle $(C_6F_5)C_6F_4BFCH_2P^tBu_2$ (**451**; Scheme 126).[170]

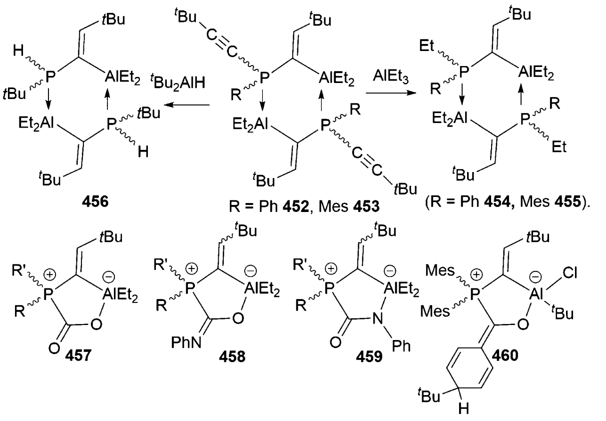


Scheme 125. Synthesis of compounds **444**–**446**.



Scheme 126. Reactions of geminal Al/P FLPs.

Analogous hydroaluminations[102] of $RP(CC^tBu)_2$ with Et_2AlH (R = Ph, Mes) afford dimeric, six-membered rings resulting from a Al–P donor–acceptor interaction $(^tBuCH{=}C(AlEt_2)PR(CC^tBu))_2$ (R = Ph (**452**), Mes (**453**)). Subsequent reaction with Et_3Al results in replacement of the P-alkynyl fragment by an ethyl group affording $(^tBuCH{=}C$-$(AlEt_2)PREt)_2$ (R = Ph (**454**), Mes (**455**)). The related reaction of $^tBu_2AlH$ with $^tBuP(CC^tBu)_2$ gave $(^tBuCH{=}C$-$(AlEt_2)PH^tBu)_2$ (**456**). Despite the dimeric nature, these species bind CO_2 or PhNCO affording products containing five-membered rings **457**–**459**. In the case of CO_2, *cis* and *trans* isomers of the products arise from the orientation of the substituent on the linking alkenyl fragment. In the case of PhNCO, isomers **458** and **459** resulting from Al-O/P-C and Al-N/P-C binding modes were observed and characterized. A subsequent publication revealed the reactions of PhCH=

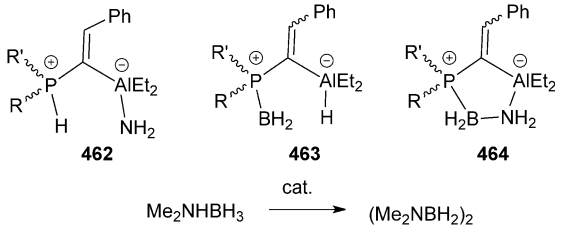


Scheme 127. Geminal Al/P FLPs.

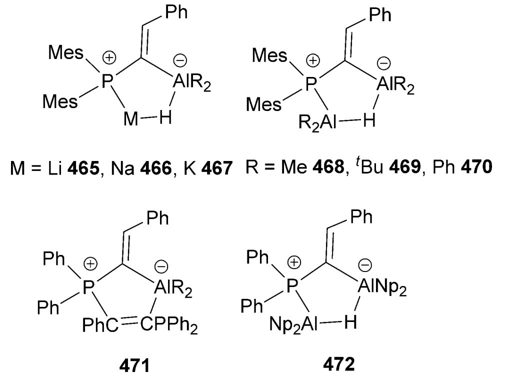
$C(Al^{t}Bu_2)PMes_2$ with benzaldehyde to give the corresponding C–O addition to the FLP, while the reaction with benzoylchloride gave the dearomatized species $PhCH{=}C(Al^{t}BuCl)PMes_2(OC{=}C_6H_5{}^{t}Bu)$ (**460**; Scheme 127).[184]

The Al/P FLP $PhCH{=}C(Al^{t}Bu_2)PMes_2$ (**461**) was also shown to react with NH_3, BH_3, and H_3NBH_3 to give the species $PhCH{=}C(Al^{t}Bu_2(NH_2))PHMes_2$ (**462**), $PhCH{=}C(AlH^{t}Bu_2)P$ $(BH_2)Mes_2$ (**463**), and $PhCH{=}C(Al^{t}Bu_2)PMes_2(H_2NBH_2)$ (**464**), respectively.[185] This reactivity also led to the catalysis of the dehydrogenative dimerization of Me_2NHBH_3, affording $(Me_2NBH_2)_2$ (Scheme 128)

The Al/P FLP **461** has also been shown to capture LiH, NaH, or KH generating **465–467** (Scheme 129). In this fashion the FLP acts as a solubilizing agent for phase-transfer catalysis effecting the conversion of Ph_3SiCl into Ph_3SiH.[186] Structural studies of the alkali-metal-hydride-FLP derivatives show interactions of P with Li and hydride with Al, however in the case of the Na and K analogues the alkali metal interacts with a mesityl substituent on P in a π-fashion. In a closely related study, Uhl and co-workers[187] have also shown that **461** will bind alanes of the form R_2AlH (R = Me, ^{t}Bu, Ph) to give **468–470**, respectively. These reactions afford five-membered AlCPAlH rings. Similarly, reaction of Ph_2PCCPh with $^{t}Bu_2AlH$ in a 2:1 ratio affords hydroalumination of the alkyne and subsequent capture of a second equivalent of the alkynylphosphine to give $PhCH{=}C(Al^{t}Bu_2)PPh_2(PhC{=}CPPh_2)$ (**471**). In contrast the corresponding reaction using Np_2AlH with Ph_2PCCPh results in the $PhCH{=}C(AlNp_2)PPh_2(Np_2AlH)$ (**472**; Scheme 129).[187]



Scheme 128. Reactions of Al/P with NH_3, BH_3, and NH_3BH_3.

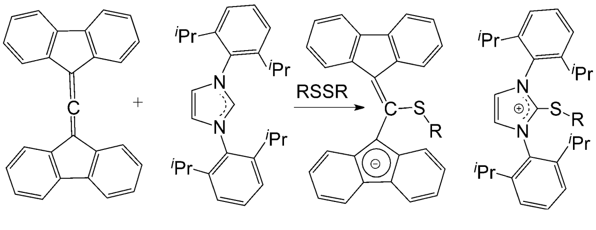


Scheme 129. Complexes 465-472. Np = neopentyl.

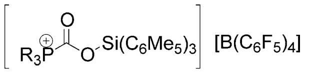
9.2. Carbon, Silicon-Based FLPs

Alcarazo and co-workers[188] have reported the use of all-carbon-based FLPs, employing a conjugated allene as the Lewis acid and a carbene as the Lewis base to effect the heterolytic cleavage of disulfides (Scheme 130).

Müller and co-workers have used the silylium cation $[(C_6Me_5)_3Si][B(C_6F_5)_4]$ as the Lewis acid to capture CO_2 in the species $[R_3P(CO_2)Si(C_6Me_5)_3]^+$ (R = ^{t}Bu (**473**), Cy (**474**); Scheme 131).[189]



Scheme 130. All carbon-based FLP.

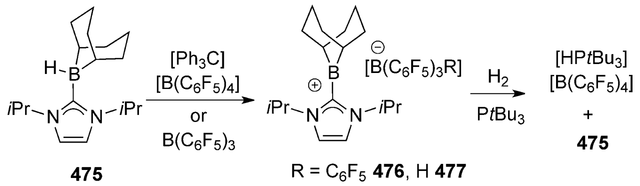

$$\left[R_3\overset{\oplus}{P}C(=O)O\text{-}Si(C_6Me_5)_3\right][B(C_6F_5)_4]$$

R = ^{t}Bu **473**, Cy **474**

Scheme 131. Complexes **473**–**474**.

9.3. Borenium Cations

The common use of fluoroaryl substituents generates Lewis acidity that permits the activation of H_2 among other substrates but at the same time this is limiting as such aryl–main-group-element bonds are susceptible to moisture and also limit the functional-group tolerance. One strategy to replace electrophilic boranes is to exploit a lesser studied class of boron-based Lewis acids, the borenium cations.[190] To this end, the NHC adduct of 9-BBN, $(I^{i}Pr_2)(HBC_8H_{14})$ (**475**), was prepared and the hydride abstracted by reaction with $[Ph_3C]$ $[B(C_6F_5)_4]$ affording the borenium salt $[(I^{i}Pr_2)(BC_8H_{14})][B(C_6F_5)_4]$ (**476**). This species does not react independently with



Scheme 132. Generation and reactivity of borenium cations.

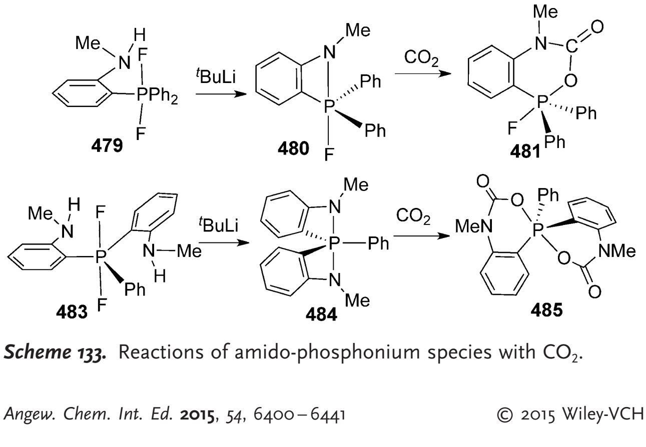
P^tBu_3, but the resulting FLP does react with H_2 to regenerate **475** and $[HP^tBu_3][B(C_6F_5)_4]$ (Scheme 132).

This ability to activate H_2 led to the application of the borenium cation as a catalyst for the hydrogenation of imines and enamines. This catalyst is generally operative at room temperature and 100 atm of H_2 with a 1–5 mol% catalyst loading. Under these conditions, hydrogenations were typically complete in 2–4 h. This catalyst was tolerant to the presence of bulky ketones, quinolones, pyridines, and esters but intolerant to sterically less-encumbered ketones. Nonetheless, this is a significant improvement from earlier generations of FLP hydrogenation catalysts.

Very shortly after the appearance of the above work, Crudden and co-workers described the generation of related borenium cations $[(DABCO)B(pin)]^+$.[191] This species acts as a catalyst for the hydroboration of imines although this process proceeds by a borenium-based mechanism rather than an FLP-type mechanism.

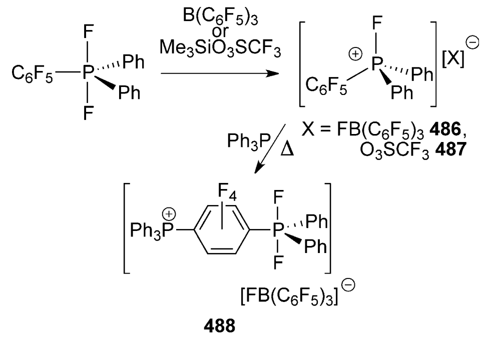
9.4. Electrophilic Phosphorus Cations (EPCs)

In seeking to broaden the chemistry of FLPs beyond traditional Lewis acids, we have recently described highly electrophilic Lewis acids based on P^V cationic centers. Our first efforts in the regard arose from the oxidation of the aminophosphine $C_6H_4(NMeH)PPh_2$ (**478**) with XeF_2 to give $C_6H_4(NMeH)PF_2Ph_2$ (**479**) and subsequent treatment with ^tBuLi affording $C_6H_4(NMe)PFPh_2$ (**480**). This species reacts with CO_2 to give the species $C_6H_4(NMe)(CO_2)PFPh_2$ (**481**; Scheme 132). In a similar manner, the diaminophosphine $(C_6H_4(NMe))_2PPh$ (**482**) is oxidized to $(C_6H_4(NMeH))_2PF_2Ph$ (**483**) and reacts with ^tBuLi affording two fused four-membered rings in $(C_6H_4(NMe))_2PPh$ (**484**). This species captures two equivalents of CO_2 to give $[C_6H_4NMe(CO_2)]_2PPh$ (**485**; Scheme 133).[192] These reactions are reminiscent of that of boron amidinates,[87] demonstrating that P^V acts as the Lewis acid.



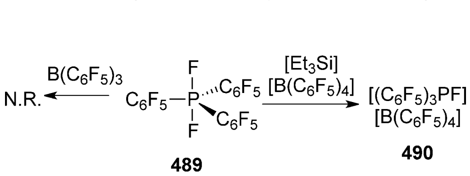
Scheme 133. Reactions of amido-phosphonium species with CO_2.

Building on this concept of electrophilic P^V cation (EPC) Lewis acids, the electron-deficient phosphine $Ph_2P(C_6F_5)$ was oxidized with XeF_2 and a fluoride ion abstracted from the resulting difluorophosphorane affording the EPC salts $[Ph_2P(F)(C_6F_5)][X]$ ($X = FB(C_6F_5)_3$ (**486**) or O_3SCF_3 (**487**)).[193] In the case of the salt **486**, variable temperature NMR data showed fluoride-ion exchange between $B(C_6F_5)_3$ and $[Ph_2P(F)(C_6F_5)]^+$, consistent with the P^V having a fluorophilicity comparable to $B(C_6F_5)_3$. Addition of Ph_3P to **486** and subsequent heating results in *para*-substitution at the C_6F_5 group of the phosphonium ion generating $[Ph_3P(C_6F_4)P(F)_2Ph_2][FB(C_6F_5)_3]$ (**488**; Scheme 134). This reactivity of the EPC with phosphine is directly analogous to that of $B(C_6F_5)_3$.



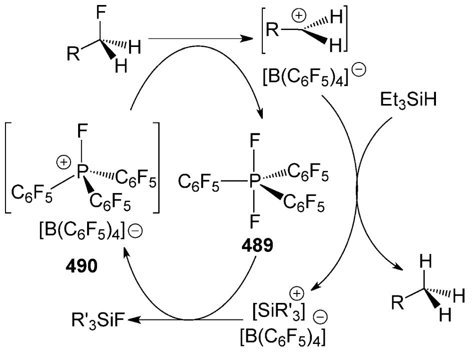
Scheme 134. Synthesis of **488**.

In an effort to generate an even more electrophilic cation, $P(C_6F_5)_3$ was oxidized to the corresponding difluorophosphorane **489**. Efforts to remove a fluoride ion with $B(C_6F_5)_3$ resulted in no reaction, inferring that the EPC $[FP(C_6F_5)_3]^+$ is indeed significantly more fluorophilic than $B(C_6F_5)_3$.[194] Nonetheless, reaction with $[Et_3Si][B(C_6F_5)_4]$ afforded isolation of the EPC salt $[FP(C_6F_5)_3]$ $[B(C_6F_5)_4]$ (**490**; Scheme 135). Computational studies are consistent with the major component of the LUMO of this EPC being in the space opposite the P–F bond, thus being sheltered by the arene rings.



Scheme 135. Synthesis of **490**.

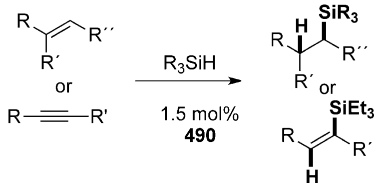
This highly fluorophilic species **490** was shown to catalyze the hydrodefluorination[194] of fluoroalkanes, including fluoropentane, fluorooctane, adamantylfluoride, and trifluorotoluene in the presence of silane in an hour with as little as 1 mol% catalyst. In the case of more highly fluorinated aryl species, the hydrodefluorination was selective for the alkyl–fluoride bonds, leaving the aromatic C–F fragment untouched. It is of note that stoichiometric reaction of the



Scheme 136. Catalytic cycle for dehydrofluorination.

EPC with fluoropentane afforded the isolation of the difluorophosphine. Thus in the catalytic cycle (Scheme 136) generation of this species with concurrent formation of the carbocation prompts hydride abstraction from silane affording the alkane product. However, the generated silylium cation then abstracts fluoride from the difluorophosphine to give the silylfluoride and regenerating the EPC catalyst.

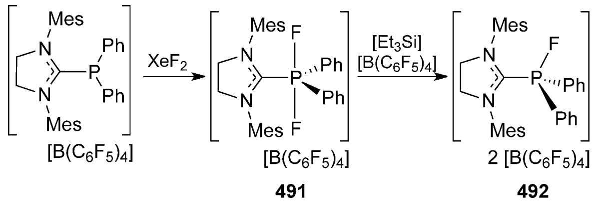
In a similar fashion the EPC **490** was shown to catalyze the isomerization of terminal olefins and the hydrosilylation of alkenes and alkynes (Scheme 137).[195] Generally these reactions proceed rapidly and in high yields. The EPC is thought to effect hydrosilylation by a mechanism similar to that documented for $B(C_6F_5)_3$.[111,196]



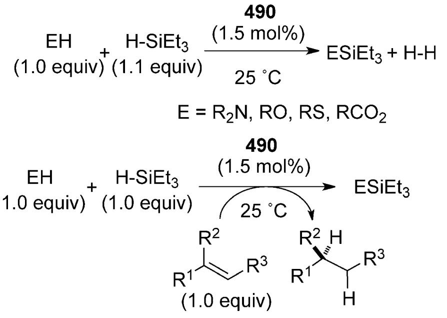
Scheme 137. Hydrosilylation with **490**.

Efforts to broaden the structural variety of EPCs has led to the synthesis of the formally dicationic $[(\text{SIMes})\text{PFPh}_2][B(C_6F_5)_4]_2$ (**492**).[197] This species is accessible by the XeF_2 oxidation of the phosphenium cation $[(\text{SIMes})\text{PPh}_2][B(C_6F_5)_4]$ to give $[(\text{SIMes})\text{PF}_2\text{Ph}_2][B(C_6F_5)_4]$ (**491**) and subsequent fluoride abstraction. The resulting species **492** (Scheme 138) is remarkably Lewis acidic in both stoichiometric reactions. Indeed this species abstracts fluoride from $(C_6F_5)_3PF_2$ (**489**) demonstrating an even higher fluorophilicity than the cation $[(C_6F_5)_3PF]^+$ of **490** (Scheme 137). The dication also acts as an effective catalyst for the hydrodefluorination of fluoroalkanes and the hydrosilylation of olefins. These finding opens the door to a large family of EPCs that is readily accessible from chlorophosphine and carbene donors.

Most recently, the electrophilicity of the cation $[FP(C_6F_5)_3]^+$ of **490** has been exploited to effect the catalytic dehydrocoupling of amines, thiols phenols, and carboxylic acids with silanes with the release of H_2 (Scheme 138).[198] This reactivity can be coupled to the hydrogenation of olefins. Thus performing the dehydrocoupling catalysis in the presence of olefins affords a metal-free route to transfer hydrogenation (Scheme 139). A mechanism for this has been proposed based on experimental and computational data.[198]



Scheme 138. Synthesis of **492**.



Scheme 139. Dehydrocoupling and transfer hydrogenation with **490**.

10. Conclusions

Frustrated Lewis pair chemistry is a young field, but it has grown rapidly during the last few years and has become quite internationally recognized. The cooperation of active non-quenched Lewis acids and Lewis bases has proven to be a surprisingly simple way of finding new reactions and has led to some remarkable discoveries in small-molecule activation. The unprecedented activation of dihydrogen by Lewis pairs derived from main-group elements has given this new field a high visibility from the beginning. The heterolytic cleavage of dihydrogen under very mild conditions, proceeding in many cases with remarkable ease and high reaction rates, had previously been thought to be the exclusive domain of d- and f-block metals. Moreover, in many cases the resulting proton/hydride pair has been transferred to a variety of unsaturated substrates leading to the development of metal-free catalytic hydrogenation. In the beginning this was limited to a few polar substrates. Meanwhile, metal-free FLP catalyzed hydrogenation has been achieved for a variety of different classes of compounds, including simple unfunctionalized alkenes and alkynes, arenes and heteroarenes, and even organic carbonyl compounds. For some classes of substrates, FLP catalyzed hydrogenation is close to becoming a practical solution, for others some additional development is needed. For us it is foreseeable that FLP hydrogenation catalysis will play a role in organic synthesis on a laboratory scale and beyond. It might at some time advance into other areas, such as material sciences, be it as catalysts for operating hydrogen-storage materials, as active components in metal-free fuel-cell applications or elsewhere. Asymmetric FLP catalyzed hydrogenation has seen its proof-of-principle and is expected to undergo further advancement in the not too distant future.

Contemporary FLP chemistry goes far beyond dihydrogen activation and hydrogenation catalysis. Small-molecule binding has seen initial success in finding new reaction pathways for transferring and utilizing small molecules in various ways. This has for example, become evident in the rapidly growing area of FLP/CO_2 reduction chemistry, although this is not yet a practical application. This is a field where the incorporation of new and more robust Lewis acid components may become of prime importance, including a return toward metal-containing systems at times.

FLPs exhibit coordination behavior toward small organic molecules that is reminiscent of metal-atom behavior. The Lewis acid and base functions of some FLPs bind cooperatively to CO or isonitriles in a fashion similar to typical d- or f-metal centers. Of course, the distinction is that the donor and acceptor sites reside on the different atoms. The formation of the unique persistent FLP/NO nitroxyl radicals are typical examples, formed by the cooperative addition of intramolecular P/B FLPs to nitric oxide (NO). The resulting FLP/NO radicals react as typical nitroxides, for example, in nitroxide-mediated radical polymerization (NMP).

Frustrated Lewis pair chemistry has reached out to many areas of chemistry, not the least to structural and computational chemistry, which in a fruitfully interplay between experiment and theoretical analysis has resulted in unveiling mechanistic aspects of a variety of the new FLP small-molecule reactions. At the same time FLP chemistry has been a welcome object for methodical developments in theoretical chemistry, spectroscopy, and physical chemistry. It has reached out to polymer chemistry, to materials and surface chemistry, where the first interesting implications of FLP chemistry have become visible.

Frustrated Lewis pair chemistry has taken a steep ascent in the recent years. It has taken some remarkable development from initial, metal-free dihydrogen activation to opening ways of finding new chemical reactions and interesting applications in an increasing array of chemical sub-disciplines. Nevertheless, FLP chemistry has not reached maturity. We still regard it as an emerging field, a still rather small chemical area, which seems to offer opportunities for discovering new reactions and making new chemical systems with interesting properties. Many young researchers have seen it as a field of opportunities, which might be one of the reasons that has made frustrated Lewis pair chemistry grow and expand so rapidly. To do without metals what we always thought only metals can do bears a great fascination and offers enormous potential and opportunities. It is for these reasons that frustrated Lewis pair chemistry is so fascinating at least for the two of us and many others as well.

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