

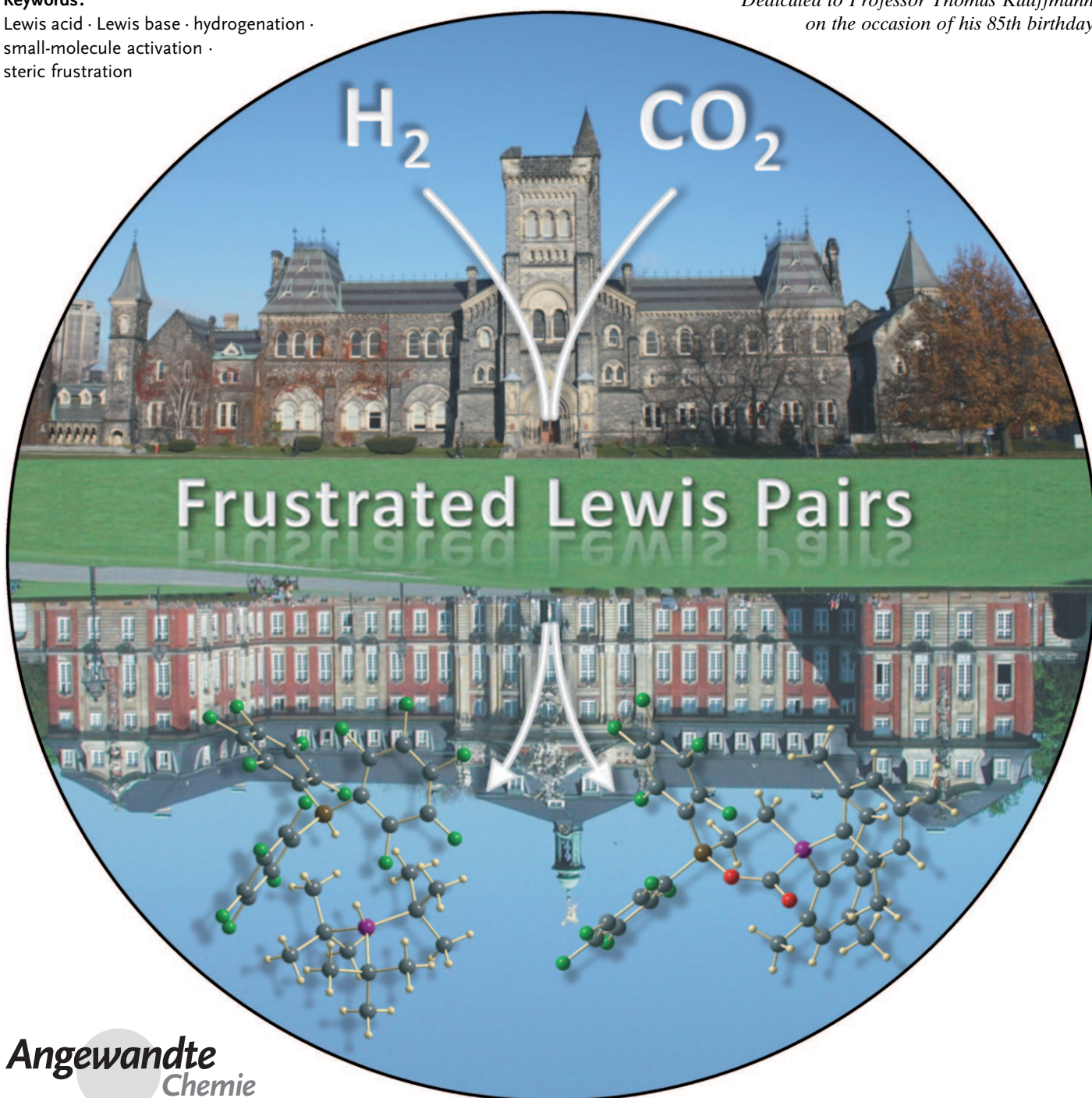
Frustrated Lewis Pairs: Metal-free Hydrogen Activation and More

Douglas W. Stephan and Gerhard Erker**

Keywords:

Lewis acid · Lewis base · hydrogenation ·
small-molecule activation ·
steric frustration

*Dedicated to Professor Thomas Kauffmann
on the occasion of his 85th birthday*

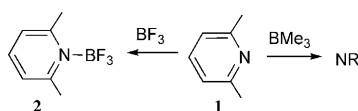


Sterically encumbered Lewis acid and Lewis base combinations do not undergo the ubiquitous neutralization reaction to form “classical” Lewis acid/Lewis base adducts. Rather, both the unquenched Lewis acidity and basicity of such sterically “frustrated Lewis pairs (FLPs)” is available to carry out unusual reactions. Typical examples of frustrated Lewis pairs are inter- or intramolecular combinations of bulky phosphines or amines with strongly electrophilic $RB(C_6F_5)_2$ components. Many examples of such frustrated Lewis pairs are able to cleave dihydrogen heterolytically. The resulting H^+/H^- pairs (stabilized for example, in the form of the respective phosphonium cation/hydridoborate anion salts) serve as active metal-free catalysts for the hydrogenation of, for example, bulky imines, enamines, or enol ethers. Frustrated Lewis pairs also react with alkenes, aldehydes, and a variety of other small molecules, including carbon dioxide, in cooperative three-component reactions, offering new strategies for synthetic chemistry.

1. Introduction

In 1923 Gilbert N. Lewis classified molecules that behave as electron-pair donors as bases and conversely electron-pair acceptor systems as acids.^[1] Lewis acids are characterized by low-lying lowest unoccupied molecular orbitals (LUMOs) which can interact with the lone electron-pair in the high-lying highest occupied molecular orbital (HOMO) of a Lewis base. These notions of Lewis acids and bases were used to rationalize numerous reactions. For example, the combination of a simple Lewis acid and Lewis base results in neutralization similar to the corresponding combination of Brønsted acids and bases.^[2] However, in the case of Lewis acids and bases, instead of forming water, the combination results in the formation of a Lewis acid/base adduct. This principle described by Lewis has come to be a primary axiom of chemistry.^[1–3] Lewis acid/base chemistry is central to our understanding of much of main-group and transition-metal chemistry and a guiding principle in understanding chemical reactivity in general.

While much chemistry can be considered in terms of the interaction of Lewis acids and bases, occasionally since 1923, researchers have encountered systems that appear to deviate from Lewis’ axiom. In 1942, Brown and co-workers^[4] while examining the interaction of pyridines with simple boranes, noted that although most of these combinations of Lewis acids and bases formed classical Lewis adducts, lutidine formed a stable adduct with BF_3 but did not react with BMe_3 (Scheme 1).^[4,5] Based on an examination of molecular models, they attributed this result to the steric conflict of



Scheme 1. Treatment of lutidine with BMe_3 and BF_3 . (NR: no reaction).

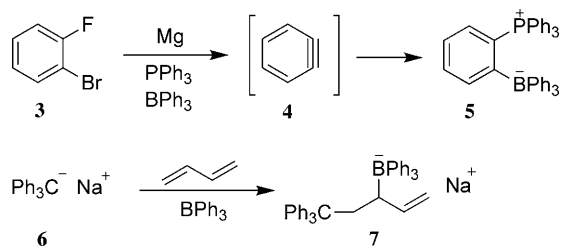
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the *ortho*-methyl groups of lutidine with the methyl groups of the borane. While Brown et al. noted this anomaly, they did not probe the impact on subsequent reactivity.

In 1959, Wittig and Benz described that 1,2-didehydrobenzene, generated in situ from *o*-fluorobromobenzene, reacts with a mixture of the Lewis base triphenylphosphine and the Lewis acid triphenylborane to give the *o*-phenylene-bridged phosphonium-borate **5** (Scheme 2).^[6] A few years later, Tochtermann, then a member of the Wittig school, observed the formation of the trapping product **7** (Scheme 2), instead of the usual formation of polybutadiene through anionic polymerization, upon addition of BPh_3 to the butadiene monomer/trityl anion initiator mixture. Both researchers realized the special nature of the bulky Lewis pairs that did not yield the classical Lewis acid/base adduct. This situation led Tochtermann to describe such a non-

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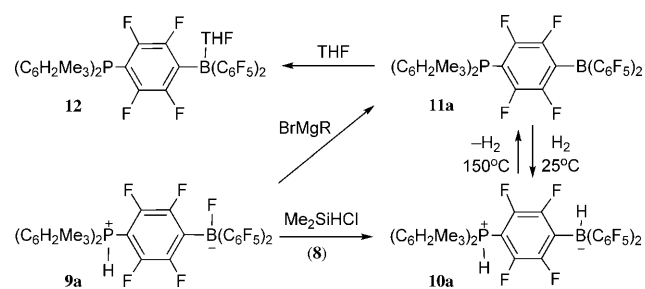
Scheme 2. Early FLP reagents.

quenched Lewis pair using the German term “antagonistisches Paar”.^[7]

2. Frustrated Lewis Pairs and H₂ Activation: The Beginning

2.1. (C₆H₂Me₃)₂PH(C₆F₄)BH(C₆F₅)₂: Reversible H₂ Activation

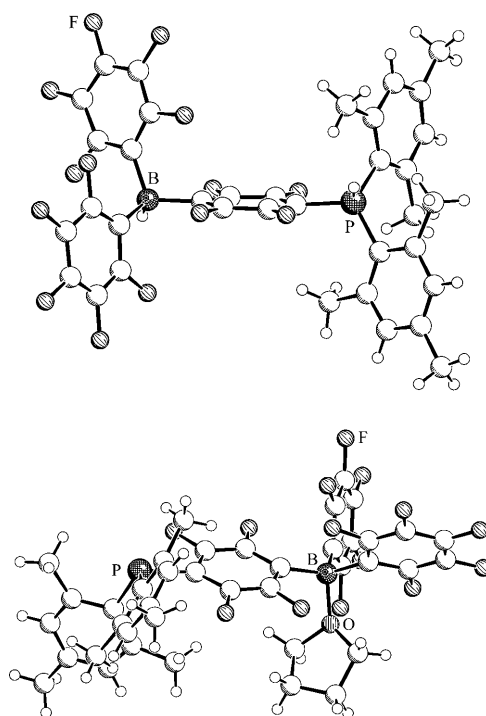
The Stephan group, in exploring the reactivity of main-group systems, queried the impact of systems in which Lewis acid and Lewis base functions were incorporated into the same molecule and sterically precluded from quenching each other. To this end, the zwitterionic salt **9a** (Scheme 3),



Scheme 3. Synthesis and reactions of complexes 9–12.

obtained from the nucleophilic aromatic substitution reaction of B(C₆F₅)₃ with dimesitylphosphine, was treated with Me₂SiHCl (**8**), yielding **10a** cleanly (Scheme 3). The zwitterionic species **10a** is a rare example of a molecule that contains both protic and hydridic fragments. Indeed, it was anticipated

that this species might spontaneously lose H₂, however, this was not the case. On the contrary, this species was air and moisture stable and as such quite robust. Nonetheless, heating this species to 150 °C prompted the elimination of H₂ generating the orange-red phosphino-borane **11a** (Scheme 3).^[8] This conversion was confirmed with X-ray crystallographic data for **10a**, **11a**, and the THF adduct of the generated phosphino-borane, **12** (Figure 1). Compound **11a**

Figure 1. View of the molecular structures of **10a** (top) and **12** (bottom).

was also accessible directly from **9a** by treatment with a Grignard reagent (Scheme 3). This species **11a** proved to be monomeric in solution, as both the B and P centers are sterically congested precluding dimerization or higher aggregation. As such, this molecule can be described as a sterically “frustrated Lewis pair”.

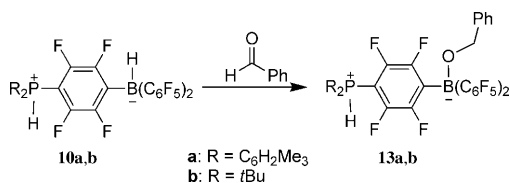


Doug Stephan attended McMaster University followed by the University of Western Ontario earning a PhD in 1980. He was a NATO postdoctoral Fellow at Harvard University (R. H. Holm) and in 1982 joined the faculty at Windsor, and was subsequently promoted through the ranks to University Professor in 2002. Most recently his group uncovered “frustrated Lewis pairs” and their chemistry. He has received a number of awards. In 2008, he took up a position as Professor of Chemistry and Canada Research Chair in Inorganic Materials and Catalysis at the University of Toronto. For 2009–11, he was awarded a Killam Research Fellowship.



Gerhard Erker studied chemistry at the University of Köln. He received his doctoral degree at the University Bochum in 1973 (W. R. Roth). After a post-doctoral stay at Princeton University (M. Jones, Jr.) he did his habilitation in Bochum and then joined the Max-Planck-Institut für Kohlenforschung in Mülheim as a Heisenberg fellow. He became a Chemistry Professor at the University of Würzburg (1985) and then (1990) at the University of Münster. For his scientific achievements he received many awards. He was the President of the German Chemical Society (GDCh) in 2000–2001 and a member of the Senate of the Deutsche Forschungsgemeinschaft (2002–2008).

Both compounds **10a** and **10b** were found to react with benzaldehyde to effect carbonyl insertion into the B–H bond affording the related zwitterionic compounds **13** ($R = C_6H_2Me_3$, **13a**; tBu , **13b**; Scheme 4).



Scheme 4. Reactions of **10a** and **10b** with benzaldehyde.

The elimination of H_2 from **10a** is perhaps not surprising however, a remarkable finding is that addition of H_2 to the phosphino-borane **11a** at $25^\circ C$ resulted in the rapid and facile regeneration of the zwitterionic salt **10a** (Scheme 3). The loss of H_2 from **10a** also results in a dramatic color change from colorless to orange-red (λ_{max} : 455 nm ; $\epsilon = 487\text{ L cm}^{-1}\text{ mol}^{-1}$; Figure 2). Weak π -donation from P, and electron acceptance

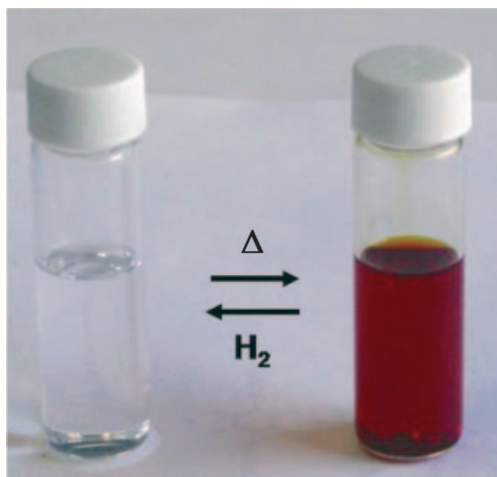


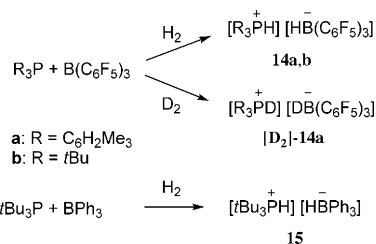
Figure 2. Solutions of the phosphonium-borate **10a** (left) and **11a** (right).

by B has been proposed to account for the intense color of the related acetylene-based phosphino-borane $Ph_2P\equiv C\equiv B(C_6H_2Me_3)_2$.^[9] In addition, it is noteworthy that phosphine-borane adducts $R_2PH(BH_3)$ thermally or catalytically eliminate H_2 to give cyclic and polymeric phosphino-boranes.^[10]

This remarkable finding represents the first non-transition-metal system known that both releases and takes up dihydrogen. Interestingly, the related species **10b** (Scheme 4) was stable to $150^\circ C$, inferring that the 2,4,6- $Me_3C_6H_2$ derivative **10a** provides the balance of acidity of the phosphonium with the hydricity of the BH fragment that permits H_2 elimination and uptake. This unique reactivity was attributed to the combination of a Lewis acid and Lewis base in which steric demands preclude classical adduct formation. Such systems have been termed “frustrated Lewis pairs” or “FLPs”.

2.2. Heterolytic Activation of H_2 by Phosphine/Borane

The observation described in Section 2.2 prompted questions regarding the generality of this heterolytic H_2 activation. In probing this question, solutions of the phosphines R_3P ($R = tBu$, $C_6H_2Me_3$) with $B(C_6F_5)_3$ were examined. These mixtures showed no evidence of a Lewis acid/base neutralization reaction. Indeed, the NMR spectroscopic data for these mixtures showed resonance signals identical to the individual constituents even on cooling to $-50^\circ C$.^[8b] In a facile and straightforward manner, exposure of these mixtures to an H_2 atmosphere resulted in the rapid generation of the salt **14** ($R = C_6H_2Me_3$, **14a**, tBu , **14b**; Scheme 5) resulting from the



Scheme 5. Heterolytic activation of H_2 or D_2 by phosphine/borane combinations.

heterolytic cleavage of dihydrogen.^[11] X-ray data for **14b** were unexceptional although it is noted that the cations and anions pack such that the BH and PH units are oriented towards each other with the BH...HP separation of 2.75 \AA (Figure 3). Despite this orientation in the solid state, heating

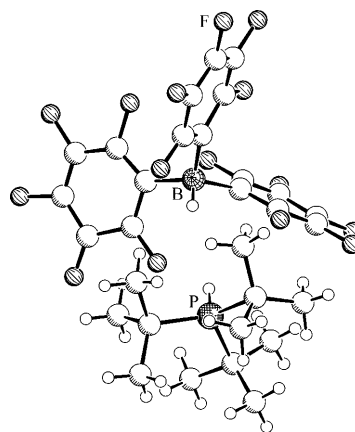


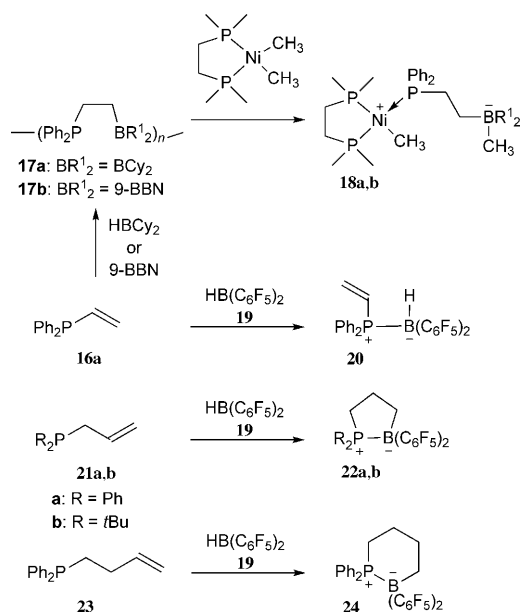
Figure 3. X-ray crystal structure of the salt $[tBu_3PH][HB(C_6F_5)_3]$ (**14b**).

of this species to $150^\circ C$ did not liberate H_2 , in contrast to **10a** (Section 2.1). The combination of $(C_6H_2Me_3)_3P$ and $B(C_6F_5)_3$ was also shown to activate D_2 affording $[D_2]\text{-14a}$ (Scheme 5). This result was evidenced by the triplet observed in the ^{31}P NMR spectrum at $\delta = -28.1\text{ ppm}$ with P,D coupling of 74 Hz and the corresponding resonance seen in the 2D NMR spectrum at $\delta = 7.5\text{ ppm}$ with the broad B–D singlet occurring at $\delta = 3.8\text{ ppm}$.

These unprecedented three-component reactions appear to result from the interaction of H_2 with the residual Lewis acidity and basicity derived from the frustrated Lewis pair. The range of Lewis acidity and basicity required for this facile heterolytic activation of H_2 was also probed. Reaction of tBu_3P and BPh_3 with H_2 slowly gave **15** (Scheme 5) although the salt was only isolated in 33% yield. The analogous combination of $(C_6H_2Me_3)_3P$ and BPh_3 , $(C_6F_5)_3P$ and $B(C_6F_5)_3$, or tBu_3P and $B(C_6H_2Me_3)_3$ resulted in no reactions with H_2 , despite the fact that no adducts were detected spectroscopically for these pairs of Lewis acids and bases. Based on these observations, it was concluded that a combined aggregate Lewis acidity and basicity is required to effect the activation of H_2 by a frustrated Lewis pair.

2.3. The Intramolecular FLP $(C_6H_2Me_3)_2PCH_2CH_2B(C_6F_5)_2$

The Erker group, in targeting new systems capable of H_2 activation, sought to develop linked phosphine-boranes. They noted that Tilley et al. had developed the synthesis of the phosphino-borane of the form $(Ph_2PCH_2CH_2BR^1)_n$ (**17a** $R^1 =$ cyclohexyl (Cy); **17b** $BR^1_2 = 9$ -borabicyclo[3.3.1]nonyl (9-BBN)) through the regioselective hydroboration of $Ph_2PCH=CH_2$ (**16a**) with either $(Cy_2BH)_2$ or the 9-BBN reagent.^[12] These systems have been exploited as “ambiphilic” ligands^[13] affording such complexes as the zwitterionic nickel species **18**. Targeting the incorporation of more electrophilic boron fragments, the Erker group treated **16a** with “Piers’ borane”,^[14] $HB(C_6F_5)_2$ (**19**). In this case, the classical Lewis acid/base adduct **20** (Scheme 6, Figure 4) was formed.^[15] In contrast, the corresponding allyl- and butenyl phosphines **21** (**21a**: $R = Ph$, **21b**: tBu) and **23** ($CH_2=CHCH_2CH_2PPh_2$) underwent clean hydroboration with $HB(C_6F_5)_2$ to yield the bifunctional phosphine-borane products, **22** ($R = Ph$ **22a**, tBu **22b**) and **24** (Figure 5), respectively



Scheme 6. Hydroboration of alkenyl phosphines.

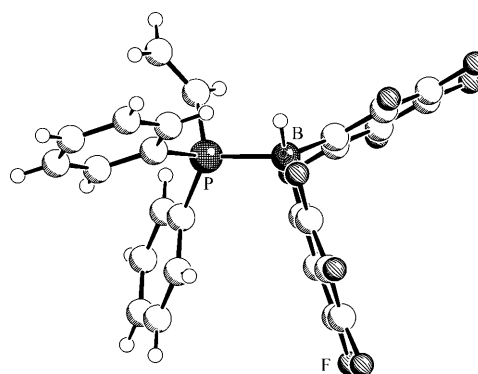


Figure 4. Molecular structure of the Lewis acid/Lewis base adduct **20**.

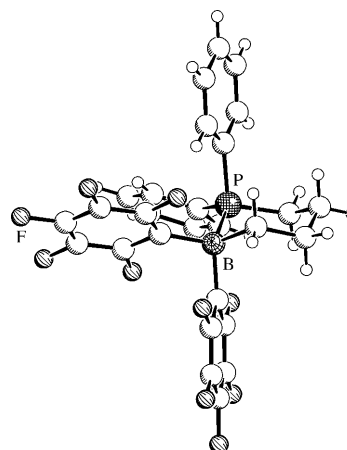
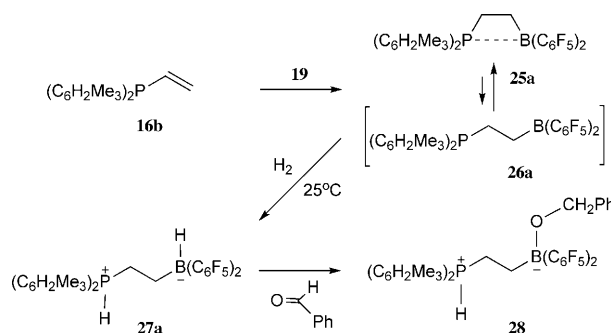


Figure 5. Chair-like conformation of the cyclic P-B adduct **24**.

(Scheme 6). These species formed strong intramolecular phosphorus/boron Lewis acid/base adducts.^[16,17,18] Studies of the conformational properties revealed heteroalkane-like behavior.

In contrast to the above systems, reaction of the bulkier (dimesityl)vinylphosphine **16b** with **19** produces the clean hydroboration product, **25a/26a** (Scheme 7).^[19] While this product was not characterized by X-ray diffraction, it was fully characterized spectroscopically. Theoretical analysis revealed that the global minimum for this monomeric bifunctional system features a four-membered heterocyclic struc-



Scheme 7. Synthesis and reactivity of **25a**.

ture with a weak P...B interaction^[20] [(P...B) calcd. 2.21 Å]. This geometry is supported in part by favorable π - π -stacking interactions^[21] between an electron-poor C₆F₅ arene ring on the boron and a parallel electron-rich mesityl substituent at phosphorus (Figure 6). Density functional theory (DFT)

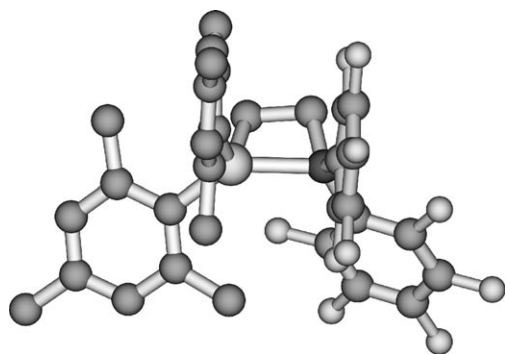


Figure 6. DFT calculated structure of the intramolecular P-B Lewis pair **25a**.

calculations also identified a gauche and an antiperiplanar conformation. These geometries are of similar energy, both calculated ca. 8 to 12 kcal mol⁻¹ higher in energy than the global minimum depending on the employed method.^[22]

Exposure of a solution of **25a** to an atmosphere of H₂ (1.5 bar) at ambient temperature immediately produced the zwitterionic product **27a** (Scheme 7) as a white precipitate (Figure 7). Heterolytic activation of H₂ to give a phosphonium-borate salt was confirmed by characteristic NMR spectral features. The corresponding reaction with D₂ gave the corresponding D₂-labeled zwitterionic product [D₂]-**27a**.

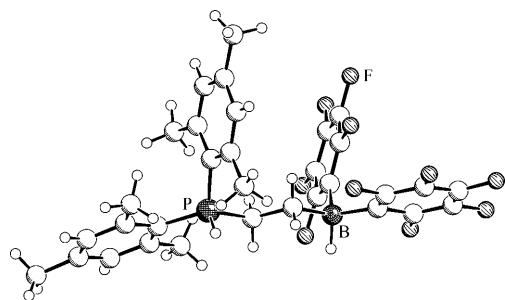


Figure 7. Molecular structure of the zwitterion **27a**.

The product **27a**, formed through the heterolytic splitting of H₂ by the intramolecular frustrated Lewis pair **25a**, shows a typical hydrido borate reactivity. It rapidly reduces benzaldehyde stoichiometrically to give the benzylalcohol derivative **28** that was characterized by X-ray diffraction (Scheme 7, Figure 8).^[19]

To obtain experimental information regarding the thermal ring-opening, several chiral derivatives were prepared by incorporation of substituents in the alkyl-chain linking boron and phosphorus.^[15] The substituted derivatives with substituents *alpha*- (R = CH₃ **26b**, Ph **26c**) or *beta*- (R = SiMe₃ **26d**) to phosphorus were prepared by analogous hydroboration

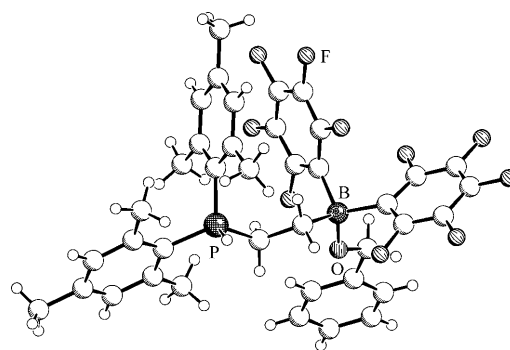
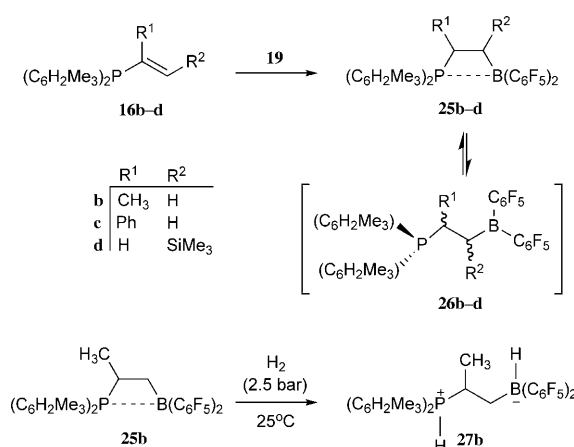


Figure 8. Molecular structure of **28**.

reactions of suitably substituted alkenyl(dimesityl)phosphines of the form (C₆H₂Me₃)₂PCR¹=CHR² (R¹ = CH₃, R² = H **16b**; R¹ = Ph, R² = H **16c**; R¹ = H, R² = SiMe₃ **16d**) (Scheme 8) with Piers' borane. Owing to the presence of a



Scheme 8. Synthesis and reactivity of substituted ethylene-linked phosphine-boranes.

chiral center in the bridge, the NMR spectra of each of these compounds feature signals arising from pairwise diastereotopic mesityl and C₆F₅ groups. The rapid equilibration of the open-chain and four-membered donor-acceptor forms of these phosphine-boranes does not affect the geometry at phosphorus, this remains pseudo-tetragonal and hence retains prochirality. In contrast, the rapid equilibration results in the coalescence of the respective NMR signals arising from the C₆F₅ rings on the boron center, as it interconverts from trigonal-planar geometry in the open isomer to tetrahedral geometry in the cyclic form. From the line-shape analysis of the temperature-dependent ¹⁹F NMR resonances (Figure 9) of the *p*-F atoms of the pair of C₆F₅ substituents for **26b**, a Gibbs activation energy^[23] for the reversible ring opening was determined to be $\Delta G^\ddagger_{\text{dis}}$ (280 K) \approx (11.7 \pm 0.4) kcal mol⁻¹. The substituted analogues **26c** and **26d** showed similar B-P dissociation energies.

Whereas compound **25b** reacts with H₂ to give the zwitterionic product **27b** (Scheme 8) at ambient temperature, the other analogues **26c** and **26d** did not react with H₂ under similar conditions.^[15]

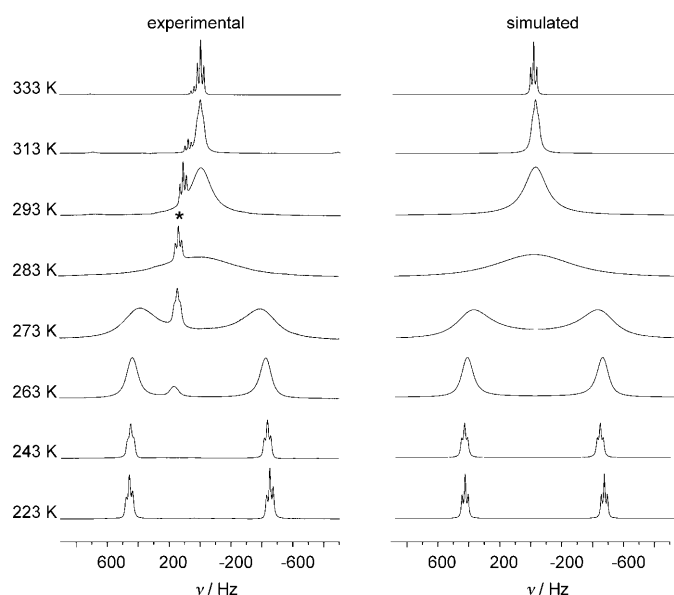
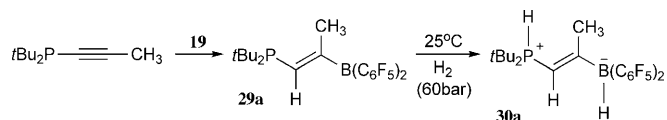


Figure 9. Dynamic ^{19}F NMR spectra of the *p*-F substituent of the $(\text{C}_6\text{F}_5)_2\text{B}$ subunit of **27b** (in $[\text{D}_8]\text{toluene}$, left: experimental, right: simulated, * impurity).

3. Other Phosphorus/Boron Systems in H_2 Activation

3.1. Alkenylene-Linked FLPs

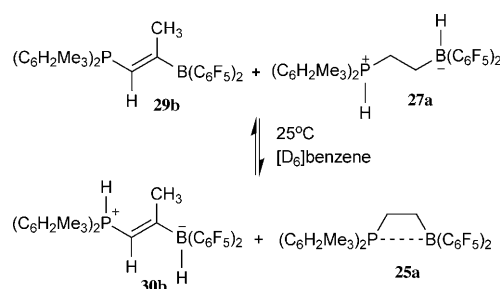
The developments outlined in Section 2.3 prompted an examination of related alkenylene-linked phosphine/borane systems. Such systems are readily derived from hydroboration of $t\text{Bu}_2\text{P}(\text{C}\equiv\text{CCH}_3)$ with **19**.^[24] The resulting orange product **29a** is inert to dihydrogen at ambient conditions but reacts cleanly at 60 bar H_2 to give the corresponding zwitterionic phosphonium hydridoborate **30a** (Scheme 9).^[25] This product exhibits the typical ^1H NMR doublet and quartet signals for



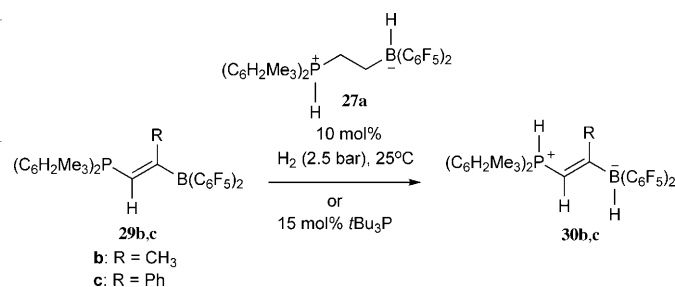
Scheme 9. Formation and reactivity of **29**.

the P–H and the B–H units, respectively. The dihydrogen splitting reaction was also confirmed by the corresponding D_2 experiment affording $[\text{D}_2]\text{-30a}$.

The corresponding hydroboration reactions of $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PC}\equiv\text{CCH}_3$ and $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{PC}\equiv\text{CPh}$ with Piers' borane gave the corresponding bright-red bifunctional products **29b** ($\text{R} = \text{CH}_3$) and **29c** (Ph), respectively. Both species are inactive toward H_2 even at elevated H_2 pressure (60 bar). However, upon mixing these compounds with the very reactive ethylene-linked hydrogen activation product **27a**, rapid proton and hydride transfer occurs to give equilibria affording **30b** ($\text{R} = \text{CH}_3$) and **30c** ($\text{R} = \text{Ph}$; Scheme 10 and Scheme 11). Employing this proton/hydride transfer equilibrium, it was possible to effect the complete conversion to **30a**–



Scheme 10. Proton/hydride exchange equilibrium yielding **30b**.



Scheme 11. Catalytic formation of **30**.

c using a catalytic amount of **27a** (10 mol %) in the presence of H_2 (2.5 bar). Alternatively, this conversion was also effected employing a catalytic amount of $t\text{Bu}_3\text{P}$ (15 mol %; Scheme 11). Similarly the corresponding dideuteride $[\text{D}_2]\text{-30}$ was obtained by the catalytic reaction using D_2 .^[25] In the case of **30b**, the structure of the zwitterion was confirmed crystallographically (Figure 10).

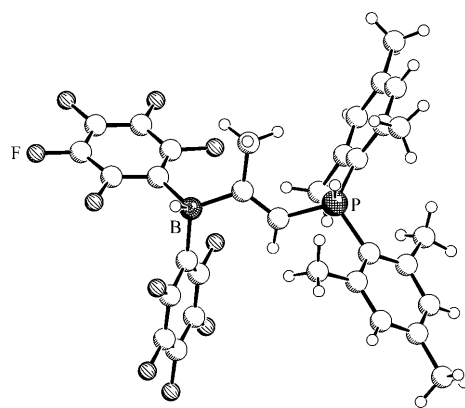
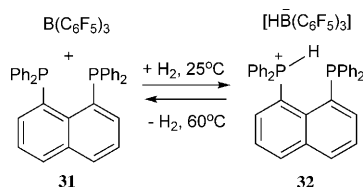


Figure 10. Molecular structure of **30b**.

3.2. Bisphosphino Naphthalene

The Erker group has also developed a new intermolecular frustrated Lewis pair based on 1,8-bis(diphenylphosphino)-naphthalene (**31**)^[26] which is capable of heterolytic H_2 cleavage. Combining this bidentate phosphine with $\text{B}(\text{C}_6\text{F}_5)_3$ ^[27] in a 1:1 molar ratio resulted in a non-quenched Lewis pair that activated H_2 (1.5 bar) to yield the phosphonium hydridoborate salt **32** (Scheme 12).^[28] A single proton rapidly exchanges between the two phosphine sites of the



Scheme 12. Reversible H₂ activation by **31**/B(C₆F₅)₃.

bisphosphine, although this exchange process is slowed at low temperature as evidenced by ³¹P NMR spectral data.^[29] This unsymmetrical structure was also confirmed crystallographically (Figure 11). The approach of the phosphonium cation

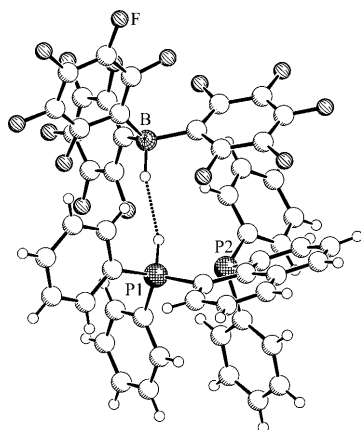


Figure 11. X-ray crystal structure of **32** featuring a short BH...HP separation (2.08 Å).

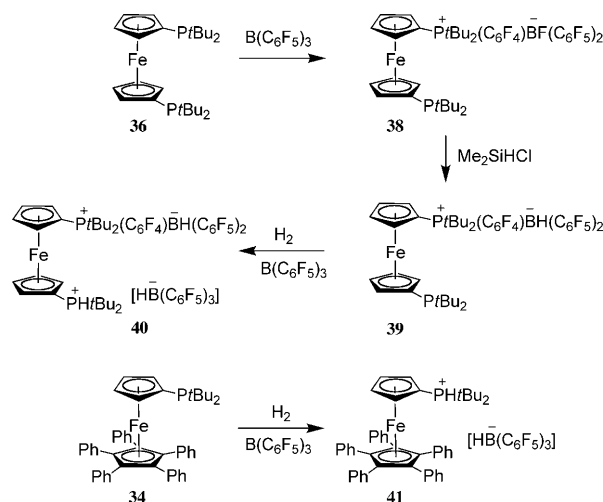
and [HB(C₆F₅)₃] anion featured a rather close PH–HB contact^[30] of 2.08 Å. This zwitterion **32** liberated H₂ at 60 °C regenerating the mixture of **31** and B(C₆F₅)₃,^[28] thus providing the second reported system capable of metal-free reversible activation of H₂.

3.3. Phosphinometalocene-Based FLPs

The use of ferrocene as a sterically demanding substituent on phosphorus has also been explored.^[31] To this end, the mono- and bis(phosphino)ferrocenes [(η⁵-C₅H₄PtBu₂)FeCp] (**33**; Cp = C₅H₅), [(η⁵-C₅H₄PtBu₂)Fe(C₅Ph₅)] (**34**), and [(η⁵-C₅H₄PR₂)₂Fe] (R = *i*Pr **35**, *t*Bu **36**) were combined with B(C₆F₅)₃. In the case of **33**, **35**, and **36**, reaction with B(C₆F₅)₃ results in the mono-*para*-substitution products of the form [(η⁵-C₅H₄-PtBu₂C₆F₄BF(C₆F₅)₂)FeCp] (**37**), [(η⁵-C₅H₄-PtBu₂C₆F₄BF(C₆F₅)₂)Fe(η⁵-C₅H₄PtBu₂)] (**38**; Scheme 13) and a di-*para*-substitution product [(η⁵-C₅H₄PiPr₂C₆F₄BF(C₆F₅)₂)₂Fe].

Species **38** was converted into **39** by reaction with silane. Subsequent addition of B(C₆F₅)₃ effected the heterolytic activation of H₂ yielding **40**. The more sterically encumbered ferrocene **34** forms a frustrated Lewis pair with B(C₆F₅)₃ which reacts with H₂ to give **41** (Scheme 13, Figure 12).

A related early-transition-metal metallocene derivative has been shown to exhibit similar frustrated Lewis pair



Scheme 13. Frustrated Lewis pairs derived from phosphinoferrocenes/B(C₆F₅)₃.

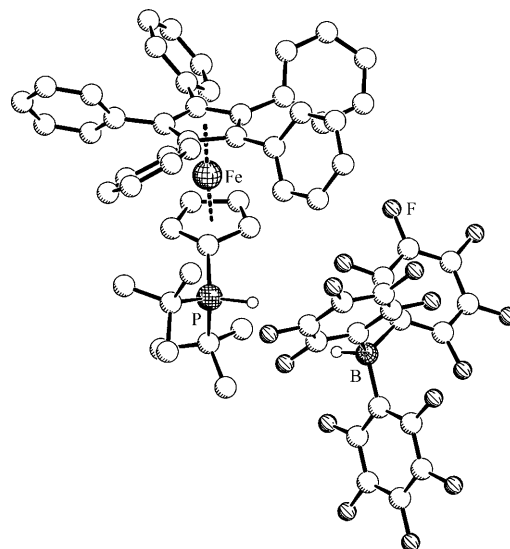
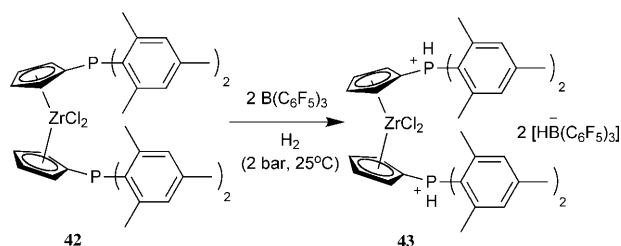


Figure 12. X-ray crystal structure of the salt **41** (hydrogen atoms omitted for clarity, except on P and B).

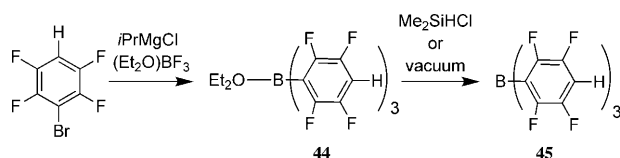
activation of H₂: The zirconocene complex **42** forms a frustrated Lewis pair with B(C₆F₅)₃ which heterolytically activates dihydrogen under very mild conditions to yield the salt **43** (Scheme 14).^[32]



Scheme 14. Activation of H₂ by the zirconium complex **42**.

3.4. FLPs with B(*p*-C₆F₄H)₃

Of the first frustrated Lewis pairs capable of heterolytic activation of H₂, only the initial arene-linked system and subsequently the system based on bis(phosphino)naphthalene/B(C₆F₅)₃ were capable of facile and reversible H₂ activation. Indeed, the simple salts, such as **14a**, **14b**, and **15b**, do not liberate H₂ even upon heating to above 100 °C.^[11] Thus, modification of the borane partners of the pairs were considered. While the early data implied that a strongly Lewis acidic system was required, the Stephan group targeted a Lewis acid designed to preclude attack by the phosphine in the *para* position and yet be Lewis acidic enough to effect H₂ activation. To address these issues the borane B(*p*-C₆F₄H)₃ (**45**) was prepared by treatment of BF₃(OEt)₂ with the appropriate Grignard reagent (Scheme 15).^[33] Initially, this species was isolated as the diethylether adduct **44**; sublimation resulted in the isolation of the base-free borane.



Scheme 15. Synthesis of B(C₆F₄H)₃.

This borane in combination with PR₃ (R = *t*Bu, Cy, *o*-C₆H₄Me) rapidly activates H₂ at 25 °C yielding the corresponding phosphonium hydridoborates (R = *t*Bu **46a**, Cy **46b** (Figure 13), *o*-C₆H₄Me **46c**). The case of **46c** stands in

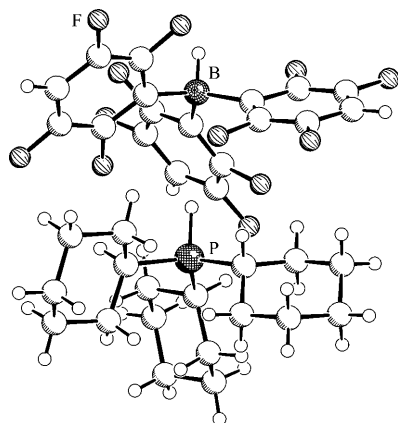
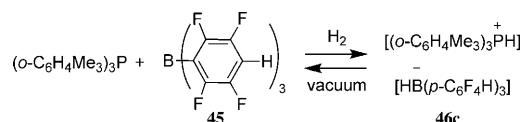


Figure 13. X-ray crystal structure of the salt **46b**.

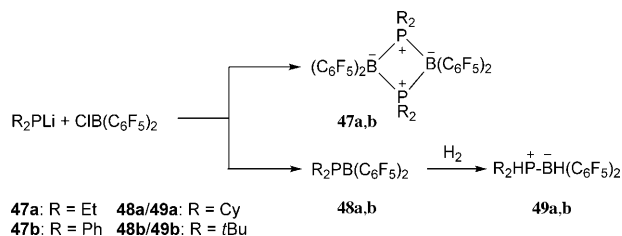
contrast to previous two-component systems, in that this salt loses H₂ under vacuum at 25 °C (Scheme 16).^[33] The reverse reaction to the starting frustrated Lewis pair is slow, it is only 85 % after 9 days at 25 °C. At 80 °C, this process is accelerated, and is completed in 12 h.



Scheme 16. Reversible H₂ activation at 25 °C by **46c**.

3.5. Phosphido-Boranes as FLPs

Given that frustrated Lewis pairs are derived from the combination of unquenched donor and acceptor sites, the Stephan group queried the possibility that such fragments could be directly bound to each other. With this in mind, the phosphido-boranes **47** (R = Et **47a**, Ph **47b**) and **48** (R = Cy **48c**, *t*Bu **48d**) were prepared^[34] from the reaction of secondary lithium phosphides (R₂PLi; R = Et, Ph, Cy, *t*Bu) with (C₆F₅)₂BCl.^[14a] While sterically undemanding substituents on phosphorus resulted in the formation of dimeric products **47a,b** (Scheme 17), more sterically demanding



Scheme 17. Synthesis and reactions of phosphido-boranes.

groups gave the monomeric species, **48a,b** (Figure 14) which retain the donor and acceptor properties at phosphorus and boron, respectively. In the case of **48b** the geometries about boron and phosphorus are pseudo-trigonal planar with a very short B–P distance of 1.786(4) Å.^[34]

Despite the geometries in the solid state, DFT calculations of the monomeric phosphido-boranes indicate that the HOMO B–P π bonding orbital is significantly polarized. Indeed, this polarization presumably accounts for the slow reaction of these species with H₂ (4 atm) at 60 °C affording the

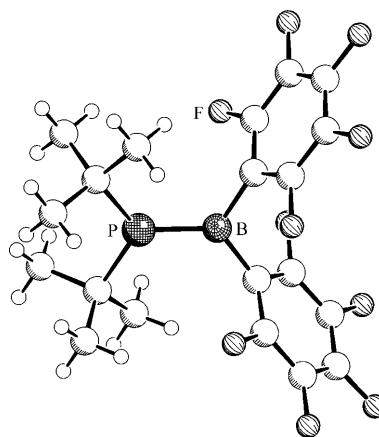


Figure 14. X-ray crystal structure of **48b**.

phosphine-borane adducts **49** ($R = \text{Cy}$ **49a**, $t\text{Bu}$ **49b**) in 48 h (Scheme 17). The B–P distance in the product of H_2 activation, **49b**, at 1.966(9) Å, is dramatically longer than in the precursor **48b** (Figure 15).^[34] In contrast, the dimeric phosphido-boranes show no reaction under similar conditions after 4 weeks.

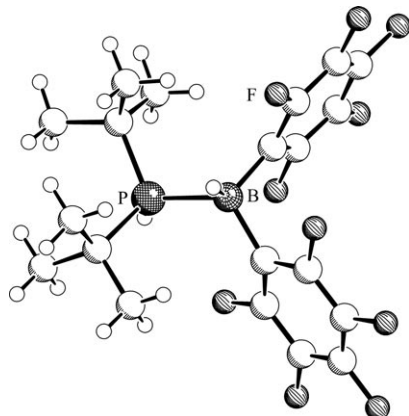


Figure 15. X-ray crystal structure of **49b**.

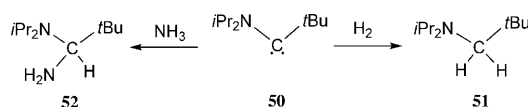
DFT studies of this activation of H_2 showed that H_2 initially attacks the Lewis acidic boron center, using the H–H bond as a Lewis base. Subsequent H_2 rotation such that the H–H bond lies parallel to the B–P bond occurs and the H–H bond is split with formation of the new P–H bond. Coordination of H_2 to boron provides an approximately 22 kcal mol^{−1} barrier for the process. Subsequent steps are essentially barrier-less. The overall reaction is exothermic (−43 kcal mol^{−1}) consistent with the irreversibility of the reaction.^[34]

4. Carbon/Boron and Nitrogen/Boron Systems in H_2 Activation

4.1. Carbenes in FLP Activation of H_2

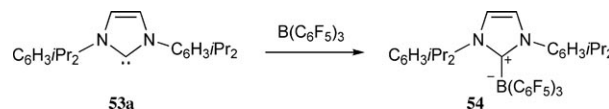
Following the initial report of the metal-free activation of H_2 by **11a**, Bertrand and co-workers^[35] demonstrated that N-heterocyclic carbenes (NHCs) did not react with H_2 , the alkylaminocarbene **50** reacts both with H_2 or NH_3 resulting in heterolytic cleavage of the H–H and N–H bond, respectively. These reactions afford the clean production of **51** and **52**, respectively. (Scheme 18). In contrast to NHCs, monoamino-carbenes apparently provide the required balance of Lewis basicity/acidity to activate H_2 or NH_3 .

Subsequently, the Stephan^[36] and Tamm^[37] research groups simultaneously reported the use of sterically hindered N-heterocyclic carbenes and $\text{B}(\text{C}_6\text{F}_5)_3$ in frustrated Lewis pair chemistry. Initially, it was established that the carbene **53a**,



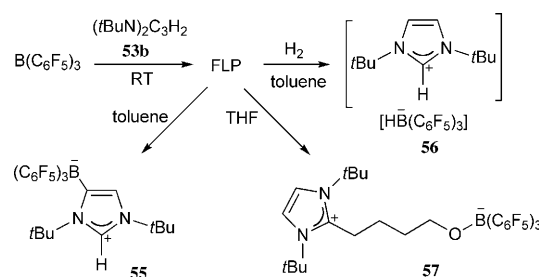
Scheme 18. Activation of H_2 and NH_3 by alkylamino-carbenes.

although considered bulky in transition-metal chemistry, forms a stable, classical Lewis acid/base adduct **54** with $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 19).



Scheme 19. Formation of **54**.

However, a frustrated Lewis pair is formed from the related carbene **53b** and the borane. Tamm et al. showed that these two components, on prolonged standing, react to give $\text{B}(\text{C}_6\text{F}_5)_3$ substitution on the backbone of the carbene, affording a zwitterionic product **55** (Scheme 20). Nonetheless,



Scheme 20. Frustrated Lewis pair chemistry of **53b**/ $\text{B}(\text{C}_6\text{F}_5)_3$.

exposure of the freshly generated frustrated Lewis pair mixture to H_2 results in the immediate formation of the imidazolium hydridoborate salt **56** (Scheme 20, Figure 16). Similarly the Tamm et al. have shown this frustrated Lewis pair also effects the ring opening of THF giving **57** (Scheme 20).

In addition, carbene **53b** was also shown to react with $\text{B}(\text{C}_6\text{F}_5)_3$ adducts of ammonia or amines **58a–f** (see Scheme 21). In the case of **58a–c**, the reaction results in the rapid N–H activation and formation of imidazolium amido-borates **59a–c** (Scheme 21). In the case of **59a**, X-ray methods revealed a B–N bond length of 1.532(8) Å (Figure 17). In

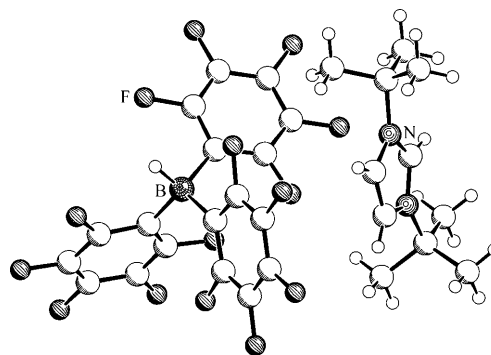
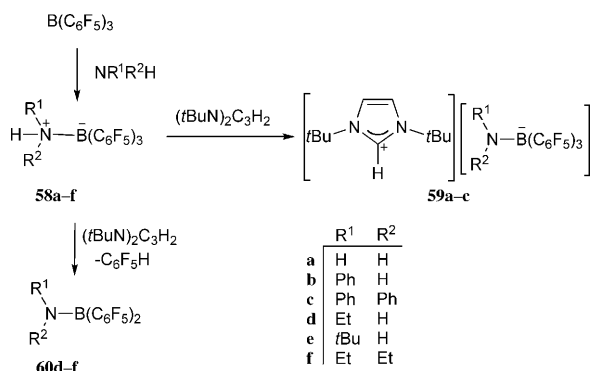


Figure 16. X-ray structure of the salt **56**.

contrast, while alkylamines are thought to react similarly, a subsequent reaction is detected: the imidazolium protonates an arene ring on boron to give C_6F_5H , and the amido-borane (**60d-f**; Scheme 21) with concurrent regeneration of the carbene. Consequently, the formation of the amido-borane can also be achieved catalytically in the presence of a 5 mol % of carbene.^[36]



Scheme 21. Activation of amine by N-heterocyclic carbenes/ $B(C_6F_5)_3$.

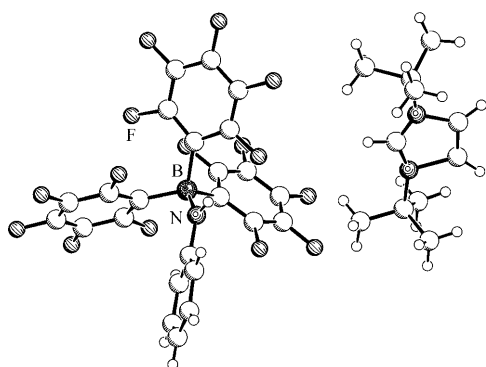
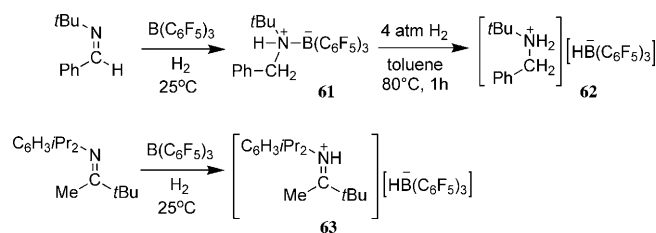


Figure 17. Molecular structure of the salt **59b**.

4.2. Imines and Amines in FLP Activation of H_2

The stoichiometric reaction between imine $tBuN=CPh(H)$ and $B(C_6F_5)_3$ with H_2 provides the amine-borane **61** (Scheme 22). This result infers the transient formation of an iminium hydridoborate which then undergoes hydride transfer to the iminium carbon atom affording the amine adduct. Further heating of this product at $80^\circ C$ for 1 h under H_2 (4–5 atm) resulted in additional H_2 activation to give salt **62** (Scheme 22).^[38] The X-ray crystal structure of **62** shows a $B-H \cdots H-N$ close contact of $1.87(3) \text{ \AA}$ (Figure 18), consistent with a nontraditional proton-hydride hydrogen bond^[30] similar to that seen in **14a**.^[11] The analogous reactions of the more sterically encumbered ketimine diisopropylphenyl- $N=CMe(tBu)$ with $B(C_6F_5)_3$ under H_2 yielded the iminium cation salt **63** (Scheme 22). This result suggests that the steric congestion precludes hydride transfer to the iminium carbon.^[38]



Scheme 22. Activation of H_2 by imines and amines with $B(C_6F_5)_3$.

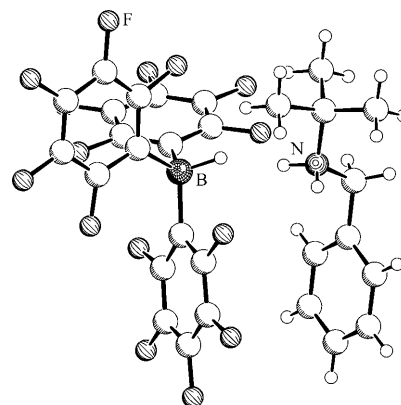
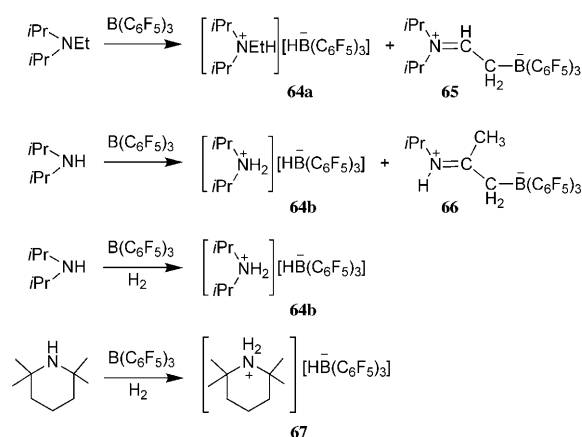


Figure 18. X-ray structure of the ammonium salt **62**.

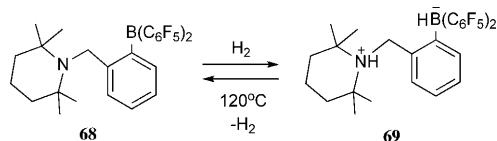
Reactions of iPr_2NEt and iPr_2NH with $B(C_6F_5)_3$ gave 50:50 mixtures of the corresponding ammonium salts **64** ($R = Et$ **64a**, H **64b**) with the zwitterionic products of amine dehydrogenation **65** and **66** (Scheme 23).^[39] Nonetheless, exposure of mixtures of iPr_2NH or $Me_4C_5H_6NH$ with $B(C_6F_5)_3$ to H_2 gave quantitative formation of the ammonium-borate **64b** and **67**, respectively (Scheme 23). Reactions employing BPh_3 in place of $B(C_6F_5)_3$ resulted in no reaction prompting the speculation that $CF-HN$ interactions (in addition to the difference in Lewis acidity) play a role in bringing amine and borane in close proximity permitting cooperative activation of H_2 .^[39]

In a similar fashion, the research groups of Repo and Rieger have very recently reported a linked amine-borane system **68/69** derived from tetramethylpiperidine



Scheme 23. Activation of H_2 by amines and $B(C_6F_5)_3$.

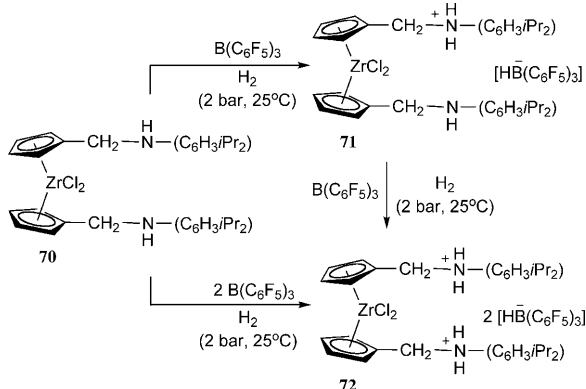
(Scheme 24).^[40] This system exhibits the ability to effect reversible H₂ activation and will be discussed in Section 6.3.



Scheme 24. Activation of H₂ by **68**.

4.3. Zirconocene Amines in FLP Chemistry

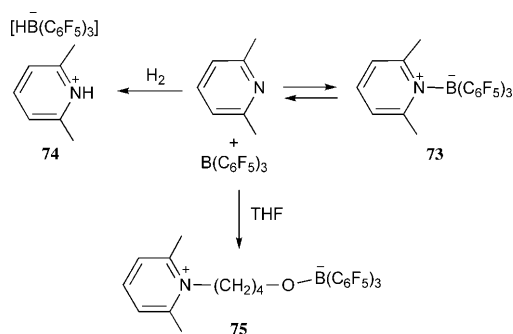
The Erker group has demonstrated that even a relatively unobstructed secondary amine functionality attached to the Cp ring of a Group 4 bent metallocene framework can be used as a suitable base in a frustrated amine/B(C₆F₅)₃ Lewis pair. Addition of one molar equivalent of B(C₆F₅)₃ to the doubly aminomethyl-substituted zirconocene substrate **70** generated a frustrated Lewis pair that rapidly reacted with H₂ under ambient conditions (2 bar, 25 °C) to form the organometallic monoammonium/hydridoborate salt **71**.^[41] Addition of a second equivalent of B(C₆F₅)₃ eventually afforded the zirconocene-bis(ammonium)/2[HB(C₆F₅)₃] product **72**. Both the synthesis of **70** by means of a metal-free hydrogenation procedure as well as the use of the **71/72** systems (Scheme 25) as effective metal-free hydrogenation catalysts are described in Section 6.3.



Scheme 25. Activation of H₂ by the zirconocene **70**.

4.4. Lutidine in FLP Chemistry

While pyridines are known to form adducts with B(C₆F₅)₃^[42] the Stephan group was prompted to study the case of lutidine after considering the early work of Brown et al.^[4] (see Section 1.) Reaction of 2,6-lutidine and B(C₆F₅)₃ gave rise to broad ¹H and ¹⁹F NMR spectra, suggesting the establishment of an equilibrium between free lutidine/B(C₆F₅)₃ and the Lewis acid/base product (2,6-Me₂C₅H₃N)B(C₆F₅)₃ **73**^[43] (Scheme 26). At low temperature, the ¹⁹F NMR



Scheme 26. Classical and frustrated Lewis pair reactivity of lutidine/B(C₆F₅)₃.

resonance signals sharpened and were consistent with the presence of primarily a dissymmetric product. Determination of the equilibrium constants as a function of temperature gave $\Delta H = -42(1) \text{ kJ mol}^{-1}$ and $\Delta S = -131(5) \text{ J mol}^{-1} \text{ K}$. Indeed upon cooling solutions of this mixture to -40°C , the classical adduct **73** was isolable as X-ray quality crystals (Figure 19).^[43] The structure reflects the steric congestion in that the B–N bond length of $1.661(2) \text{ \AA}$, was found to be significantly longer than that in (py)B(C₆F₅)₃ ($1.628(2) \text{ \AA}$; py = pyridine).^[42]

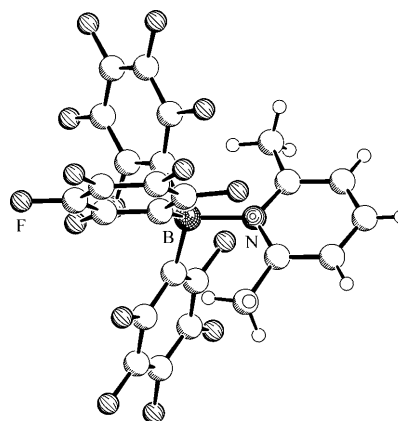


Figure 19. Molecular structure of **73**.

The observation of an equilibrium at room temperature suggested that frustrated Lewis pair chemistry may be accessible. Treatment of lutidine/B(C₆F₅)₃ with H₂ (1 atm, 2 h) gave the pyridinium salt **74** (Scheme 26, Figure 20 (top)). Similarly, treatment of lutidine/B(C₆F₅)₃ with THF yielded the zwitterionic species **75** (Scheme 26, Figure 20 (bottom)).

The formation of both classical products and frustrated Lewis pair products from lutidine/borane affirm that these reaction pathways are not mutually exclusive. Moreover, this finding points to the possibility that classical Lewis acid/base adducts may serve as precursors for new reaction pathways, despite the fact that such compounds have been regarded as unreactive.^[43]

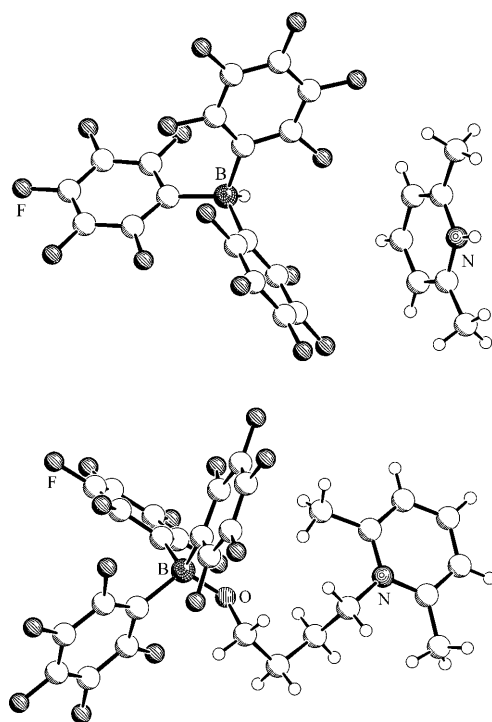


Figure 20. Molecular structure of the zwitterionic compound **75** (bottom) and the salt **74** (top).

5. Mechanistic Studies of H_2 Activation by FLPs

The details of the mechanism of action of frustrated Lewis pairs on H_2 have been the subject of study. In the first report of reversible H_2 activation by an frustrated Lewis pair system, Stephan and co-workers^[8] speculated on intramolecular processes based on initial indications of first-order kinetics for the loss of H_2 from **10a**. Efforts to confirm this experimentally have indicated that, at the elevated temperatures required to observe H_2 loss, the back-reaction is facile and rapid. The consequence is misleading kinetic data.^[44] Efforts to study the uptake of H_2 by phosphine/borane systems is also challenging as the reaction is rapid at low H_2 pressures even at -60°C . Moreover the control of H_2 concentrations in solution is experimentally difficult, leading to reactions that are diffusion controlled. Based on early computational studies^[45] of the interaction of BH_3 and H_2 , it was speculated that the activation of H_2 is initiated by Lewis acid activation of H_2 leading to protonation of the Lewis base. While this intuitively seems reasonable, it is noteworthy that previous low-temperature matrix-isolation work has demonstrated phosphines do interact with H_2 presumably via nucleophilic attack of the H_2 in an end-on fashion.^[46] Computational studies by Pápai and co-workers^[47] suggest generation of a phosphine-borane “encounter complex”, stabilized by $H\cdots F$ interactions. In this “species” the boron and phosphorus centers approach but fail to form a dative bond as a result of steric congestion. Interaction of H_2 in the reactive pocket between the donor and acceptor sites (Figure 21) results in heterolytic cleavage of H_2 . A related mechanism has been described for **11**.^[48]

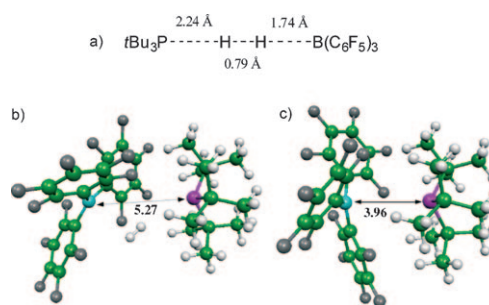
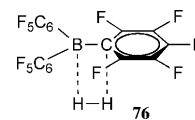


Figure 21. Computational models of phosphine-borane activation of H_2 . a) Pápai et al.,^[47] b) and c) Grimme et al.^[49]

Calculations reported by the Tamm group^[37] showed the transition state for the activation of H_2 by carbene and borane gave rise to a carbene-borane “encounter complex” similar to that proposed by Pápai et al.

Very recent computational studies by Grimme et al.^[49] of the (quasi)linear $P \cdots H-H \cdots B$ activation mechanism of **11** (see Figure 21) cast some doubt on the “reality” of the corresponding transition state. According to these new results, a transition state in a linear arrangement only appears for rather large $P \cdots B$ distances over 4.5 Å. Such values seem to be artificially induced by the quantum chemical method (B3LYP) which is well-known to overestimate steric congestion. With properly dispersion-corrected density functionals,^[49b] no linear transition state exists and only one minimum with a rather large $H-H$ distance of about 1.67 Å could be found. This points to an alternative bimolecular mechanism in which the “entrance” of H_2 into the “frustrated” $P \cdots B$ bond is rate-determining. Further theoretical studies to address this important question are currently underway.

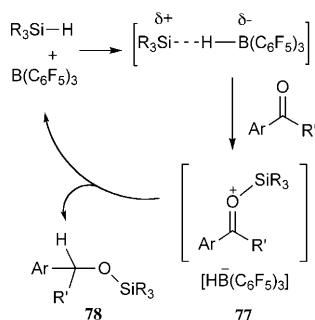
According to DFT calculations^[49a] $B(C_6F_5)_3$ forms the van der Waals complex **76** with H_2 (Scheme 27), although this is unlikely to contribute to the H_2 activation pathway. However, it is noteworthy that Piers et al. have exploited a related reaction to prepare $HB(C_6F_5)_2$ through direct treatment of $B(C_6F_5)_3$ with triethylsilane.^[14]



Scheme 27. van der Waals complex **76** of H_2 and $B(C_6F_5)_3$.

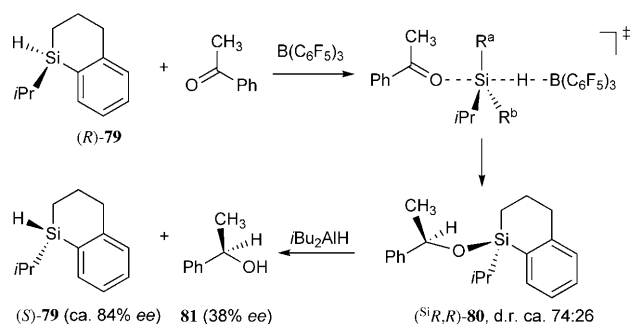
Unfortunately, the H_2 splitting reaction does not provide stereochemical information. However, such information is available in the related $B(C_6F_5)_3$ -catalyzed hydrosilylation reaction of ketones^[50] and related substrates.^[51] Piers et al. have shown that this reaction proceeds by Lewis acid^[14] activation of the silane rather than by the carbonyl compound.^[16,52] Hydride transfer from Si to B followed by (or concomitant with) carbonyl addition to the silylium ion then generates an intermediate **77** activated for hydride addition en route to the hydrosilylation product **78** (Scheme 28).^[53]

In a very elegant study, Oestreich et al. determined that the $B(C_6F_5)_3$ -induced hydrosilylation of acetophenone with the highly optically enriched chiral silane **79** (“Oestreich silane”)^[54] proceeds with inversion of the configuration at



Scheme 28. Catalytic hydrosilylation of ketones using $B(C_6F_5)_3$.

silicon.^[55] This result rules out the involvement of a free silylium ion and indicates an S_N2 -type process with a Walden inversion at the silicon atom (subsequent cleavage of the Si–O bond of (*Si*,*R*)-**80** by treatment with *i*Bu₂AlH proceeds with retention of configuration at Si). Interestingly, the alcohol **81** which is set free in the final step of the reaction sequence was found to be enantiomerically enriched (38 % ee) (Scheme 29). This process is a remarkable asymmetric induction given that the system involves only a single-point of attachment.



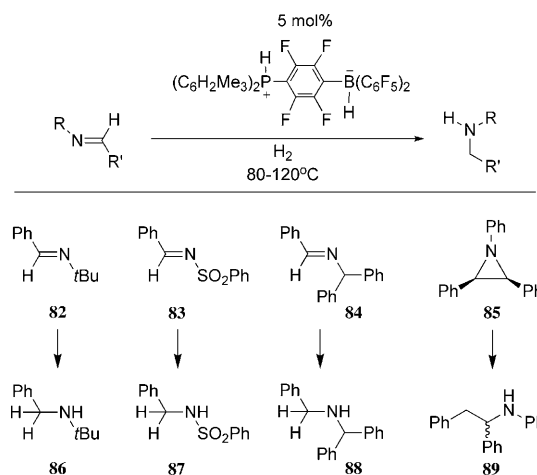
Scheme 29. Stereochemical analysis using the "Oestreich silane".

6. Metal-Free Catalytic Hydrogenation

6.1. Catalytic Hydrogenations by Phosphine/Borane FLPs

Soon after the discovery of metal-free activation of H_2 by the frustrated Lewis pair **10a/11a**, the application of this finding for hydrogenation catalysis was envisioned. This notion was reinforced by the analogy to the Noyori-hydrogenation catalysts.^[56] In those systems, a metal complex effects heterolytic cleavage of H_2 yielding a metal hydride and a protonated ligand. Frustrated Lewis pairs effect similar heterolytic H_2 activation without the need for a transition metal. However, for hydrogenation to be catalytic, proton and hydride transfer from a phosphonium hydridoborate to a substrate must occur with regeneration of the frustrated Lewis pair. This frustrated Lewis pair would reactivate H_2 and be available for subsequent substrate reduction. In the first exploration of this concept, the salts **10a** and **10b** were treated with aldimines. Stoichiometric addition resulted in the formation of the amine adducts $(R''_2P)(C_6F_4)B(C_6F_5)_2-(NHRCH_2R')$ demonstrating that both proton and hydride

were transferred to the substrate. Subsequently the salts were employed in a catalytic amount. Simple heating of the solutions to between 80 and 120 °C under 1–5 atm of H_2 effected catalytic reduction of imine substrates **82–84** to **86–88** in high yields (Scheme 30).^[57] In addition to imines, catalytic reductive ring opening of the *N*-aryl aziridine

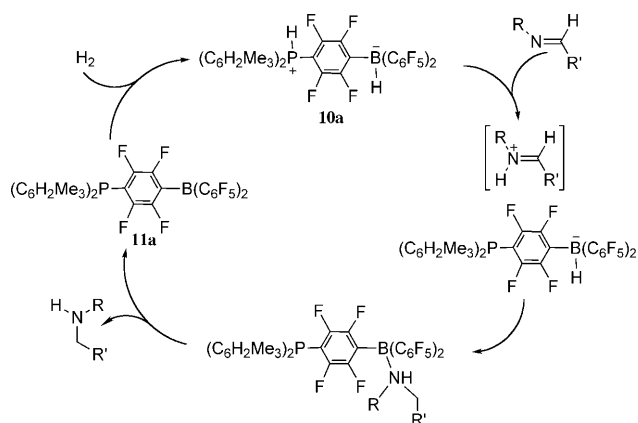


Scheme 30. Metal-free catalytic hydrogenation of imines and an aziridines.

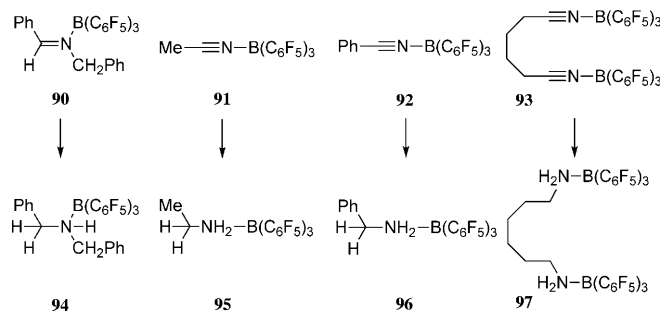
(PhCH)₂NPh (**85**) to the corresponding amine (**89**) also proceeded readily under similarly mild conditions. Reductions of imines that incorporated bulky substituents on the nitrogen atom proceeded in high yields. Compounds with electron-withdrawing substituents on the nitrogen require longer times and/or higher temperatures suggesting that protonation of the nitrogen atom may be rate determining.

Imines with less sterically demanding substituents on the nitrogen atom, such as benzyl, are only stoichiometrically reduced, presumably because the corresponding amines bind more strongly to the boron center. Nonetheless, where catalytic reduction was observed, the catalyst showed "living" character, that is, after complete conversion of the starting material to hydrogenated product, addition of more substrate starts the catalytic reduction again. Studies designed to probe the mechanistic details of these reductions revealed that the process is initiated by protonation of the imine followed by borohydride attack of the iminium salt intermediate (Scheme 31).^[57]

Sterically less encumbered imines were reduced by the phosphonium-borate catalyst by using $B(C_6F_5)_3$ as a protecting group. As $B(C_6F_5)_3$ is a stronger Lewis acid than the boron center in the catalyst (**11**), reduction proceeds because the amine formed does not inhibit activation of H_2 by the phosphine-borane catalyst. A similar strategy was applied to nitriles. Thus, **90–93** were reduced to give the corresponding amine- $B(C_6F_5)_3$ products **94–97** in near quantitative yields using a phosphonium-borate catalyst (Scheme 32). While this strategy demonstrates the principle of metal-free hydrogenation of imines and nitriles, it is recognized that $B(C_6F_5)_3$ is not



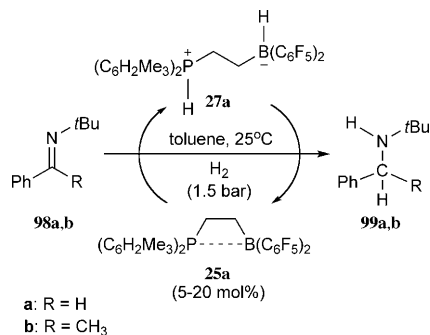
Scheme 31. Proposed mechanism for metal-free catalytic hydrogenations using **10a/11a**.



Scheme 32. Metal-free catalytic hydrogenation of borane-protected imines and nitriles.

an inexpensive protecting reagent and must be used stoichiometrically.^[57]

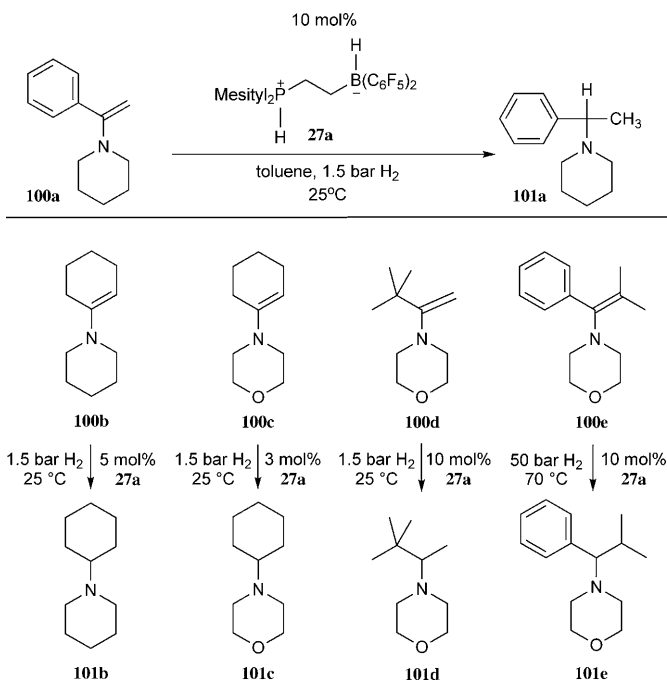
The **25a/27a** pair is an even more active catalyst for the metal-free hydrogenation of imines as it operates effectively at ambient conditions. For some substrate types, it is the most active metal-free hydrogenation catalysts to date. For example, the **25a/27a** system catalyzes the hydrogenation of the aldimine **98a** at ambient conditions (25 °C, 1.5 bar H₂) although in this case at least 20 mol % of the catalyst system are required. In contrast, catalytic hydrogenation of the related ketimine **98b** is much more effective (Scheme 33), complete hydrogenation is achieved with 5 % of the metal-



Scheme 33. Catalytic hydrogenation of imines using **25a/27a**.

free P/B catalyst system under very mild reaction conditions.^[25]

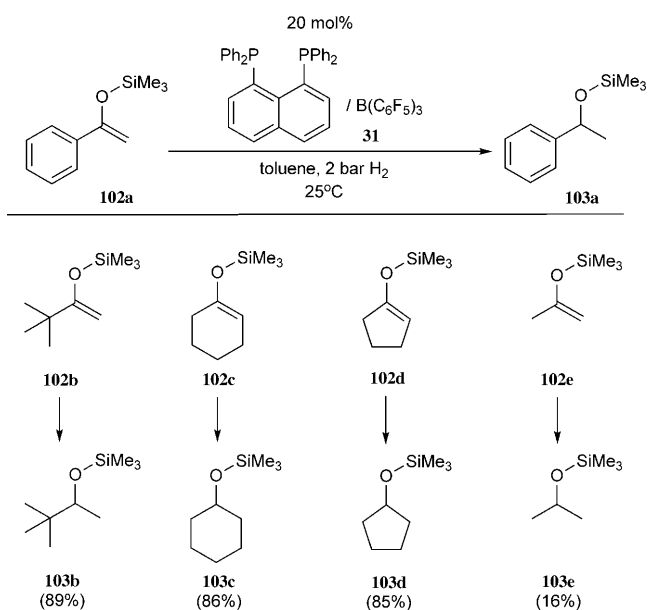
Since it is conceivable that these reactions proceed by means of the corresponding iminium-ion intermediates, other substrates amenable to iminium-ion formation were considered as they might also be suitable substrates for metal-free catalytic hydrogenation by PH⁺/BH[−] systems. Indeed, this turns out to be the case. The Erker group observed that the ethylene-linked system **27a** reacts rapidly with the enamine **100a** to form the amine **101a** with re-formation of the frustrated Lewis pair precursor **25a**.^[25] This reaction can be carried out catalytically (Scheme 34). With 10 mol % of the



Scheme 34. Metal-free catalytic hydrogenation of enamines.

catalyst **27a** a practically quantitative conversion of the enamine **100a** into the amine **101a** was achieved at 25 °C and under 1.5 bar H₂ in toluene solution. A variety of examples (**100b–e**) gave similar results. In some cases, 3 mol % of catalyst was sufficient to achieve near-complete enamine hydrogenation under these mild reaction conditions.^[41] In the case of the very bulky enamine **100e**, slightly more forcing conditions were required. Using 50 bar H₂, 70 °C, and 10 mol % catalyst, the amine **101e** was isolated in over 80 % yield.^[58]

The salt **32**, derived from heterolytic cleavage of H₂ by the frustrated Lewis pair **31**/B(C₆F₅)₃, rapidly transfers proton and hydride stoichiometrically to the silyl enolether **102a** at room temperature. The reaction can also be carried out catalytically at 25 °C and 2 bar H₂ using 20 mol % of the **31**/B(C₆F₅)₃ catalyst system. Similarly, this catalyst hydrogenates a variety of silyl enolethers (**102a–d**; Scheme 35) giving good yields of the corresponding silyl ether products (**103a–d**).^[28,59] In the case of the silyl enolether **102e** only a stoichiometric hydrogenation was observed under the typically mild conditions, however, the apparent product inhibition could be



Scheme 35. Metal-free catalytic hydrogenation of silylenolethers.

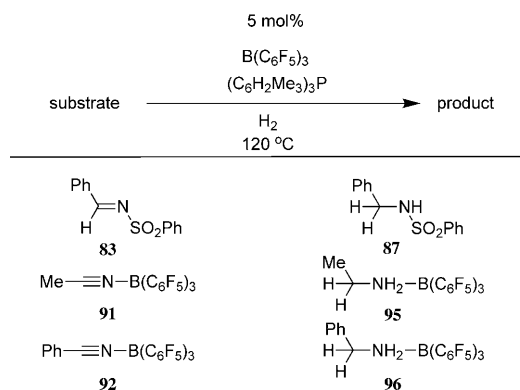
overcome using more forcing reaction conditions (60 bar H_2 , 70 °C).

6.2. Substrates as Bases in FLP Catalysts

Having demonstrated the metal-free catalytic hydrogenation of imines, the Stephan group then probed the notion that the substrate could serve as the base-partner of a frustrated Lewis pair. Thus employing a catalytic amount of $B(C_6F_5)_3$ in the presence of an imine substrate (and H_2), it was indeed possible to effect the catalytic reduction of the imine to the corresponding amine. In this fashion, the simple combination of an imine substrate and H_2 results in reduction of imines (**82–84**) to amines (**86–88**) under conditions similar to those described in Section 6.1 for the phosphino-borane catalysts. Mechanistically these reductions proceed by H_2 cleavage and protonation of the imine to give iminium cations which are then attacked by hydridoborate affording the amine (Scheme 36).^[38]

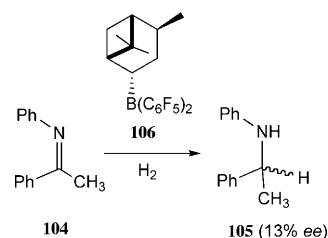
It is noteworthy that in cases where the imine is a poor base, as in **83**, addition of a catalytic amount of $P(C_6H_2Me_3)_3$ gave an accelerated and essentially quantitative hydrogenation

in 8 h, compared to 41 h in the absence of phosphine. The acceleration was attributed to the enhanced ability of phosphine/borane to cleave H_2 heterolytically. In a similar fashion, the nitrile-borane adducts, **91** and **92** were reduced to **95** and **96** under H_2 in the presence of a catalytic amount of $P(C_6H_2Me_3)_3$ and $B(C_6F_5)_3$, whereas in the absence of phosphine no reduction was observed (Scheme 37).^[38]



Scheme 37. Catalytic hydrogenation of selected imines by $B(C_6F_5)_3$ in presence of $(C_6H_2Me_3)_3P$.

Analogous reductions employing $B(C_6F_5)_3$ in combination with imine substrates were subsequently reported by Chen and Klankermayer.^[60] In one example, they showed that employing the chiral borane **106** in the asymmetric reduction of imine **104** to amine **105** (Scheme 38) gave an enantiomeric excess of 13 % ee.^[60]

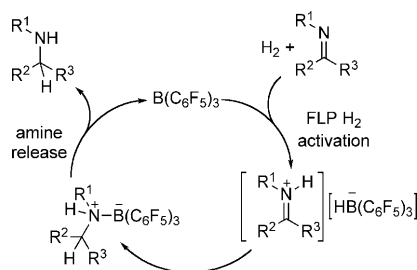


Scheme 38. Catalytic asymmetric hydrogenation of imine **104** by **106**.

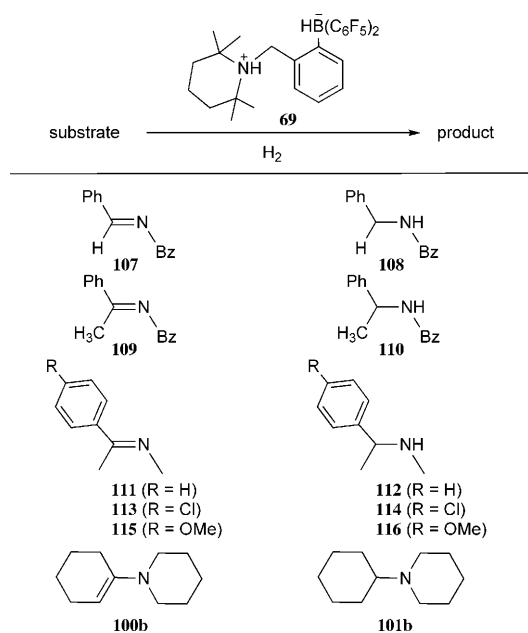
6.3. Catalytic Hydrogenations Employing Amine-Borane FLPs

The research groups of Repo and Rieger^[40] have employed the linked amine-borane **68/69** in the catalytic hydrogenation of imines and enamines. (Scheme 39).^[40] While generally this catalyst was effective, affording near quantitative reduction of the substrates, sterically less-encumbered substrates, such as **109**, **111**, **113**, **115** were only hydrogenated in 4 % yield.

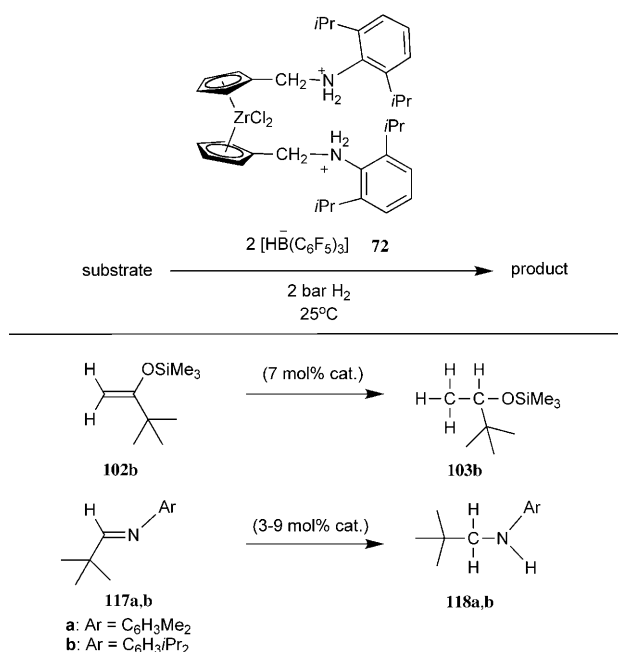
Following the demonstration that ammonium/[HB(C_6F_5)₃] salts can be used for catalytic hydrogenation reactions, the organometallic zirconocene-based ammonium/[B]H[−] salt **72** was also studied. It was shown to efficiently catalyze the hydrogenation of the bulky imines **117a,b** as well as of the silyl enol ether **102b** to the respective saturated products (Scheme 40).^[41] In these cases, the use of 3–9 mol %



Scheme 36. Proposed mechanism of catalytic hydrogenation of imines by $B(C_6F_5)_3$.



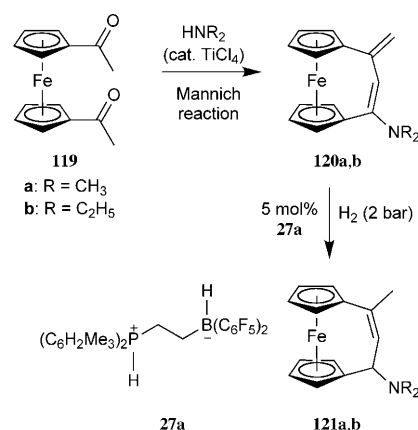
Scheme 39. Catalytic hydrogenation of selected imines and enamines by **69**. Bz = benzoyl.



Scheme 40. Catalytic hydrogenations employing the zirconocene **72**.

of the catalyst system was sufficient for high product conversion under mild reaction conditions.

The conformationally rigid dienamine **120** can readily be obtained by Mannich coupling of acetyl groups at the ferrocene framework (Scheme 41).^[61] Stoichiometric reaction of **120a,b** with the zwitterion **27a** gave an approximately 1:1 mixture of the mono(dihydrogen) and bis(dihydrogen) addition products **121a,b** and **122a,b** (see Schemes 41 and 42).^[62] Experimental evidence indicates that **122** may originate from a slow subsequent hydrogenation reaction of **121** under the



Scheme 41. Catalytic 1,4-hydrogenation of **120**.

specific reaction conditions employed. The product **121a** was characterized by X-diffraction (Figure 22). In contrast, the substrates **120a,b** are catalytically hydrogenated with 5 mol % of **27a** under H_2 to selectively yield the formal 1,4-hydrogenation products **121a,b** with only marginal amounts of the saturated products.^[58,63]

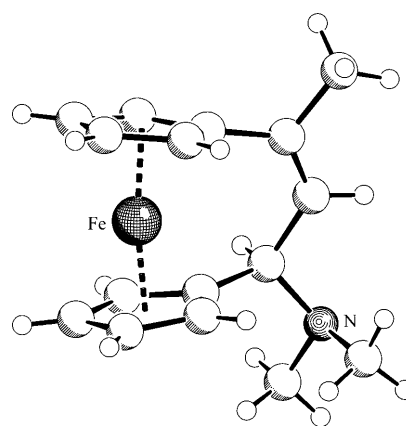
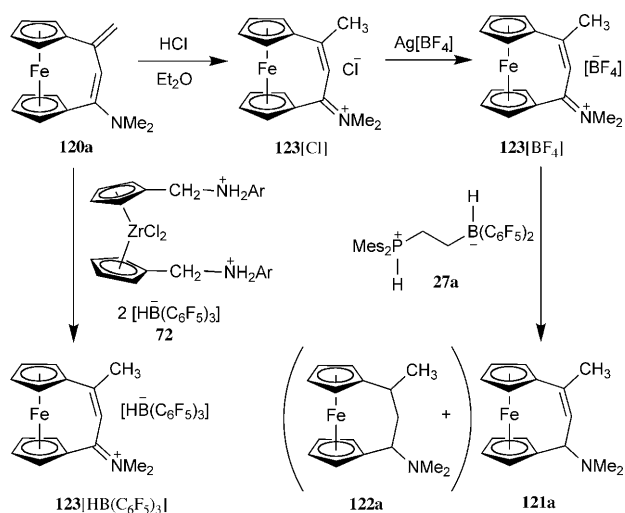


Figure 22. Molecular structure of the 1,4-hydrogenation product **121a**.

The iminium-ion intermediate of this catalytic metal-free hydrogenation was independently prepared by selective protonation of the dienamine **120a** with HCl in diethyl ether.^[64] Subsequent anion exchange gave **123[BF₄]**. Remarkably, protonation of **120a** with the zirconocene-ammonium/[HB(C₆F₅)₃] system **72** gave **123[HB(C₆F₅)₃]**, which was isolated and characterized by an X-ray crystal structure analysis (Scheme 42 and Figure 23).^[64] These systems apparently represent borderline cases in which the ferrocenyl-stabilized iminium ions are slow to react with hydride.^[65] Thus, the system **123[HB(C₆F₅)₃]** is stable and isolable, whereas treatment of **123[BF₄]** with the slightly more nucleophilic reagent **27a** results in the formation of the respective stoichiometric hydrogenation products **121a** and **122a**.



Scheme 42. Formation and reactions of the iminium cations **123**.

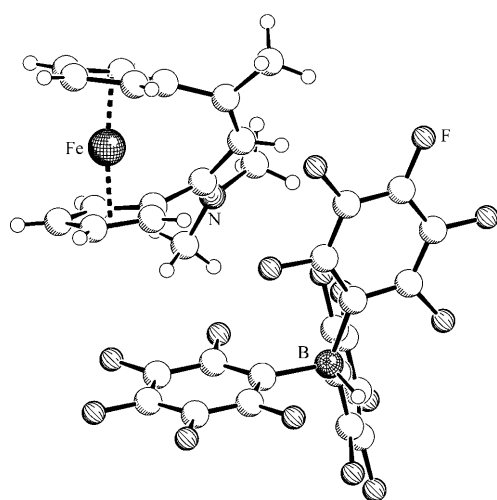


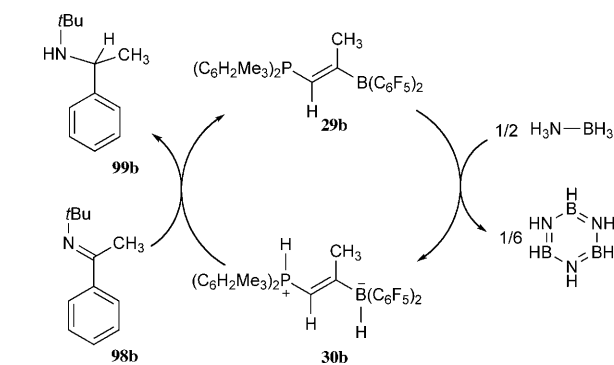
Figure 23. Molecular structure of the salt **123**[HB(C₆F₅)₃].

6.4. Hydrogenations using Ammonia-Borane

The systems **29** do not activate H₂ by themselves under typical conditions, but they do react rapidly with ammonia-borane.^[66] Treatment of (H₃N)BH₃ with a stoichiometric amount of **29b** in [D₈]THF gave **30b**. This reaction can be adapted for the catalytic metal-free hydrogenation of the bulky imine **98b**. Thus, treatment of an imine/(H₃N)BH₃ mixture with a catalytic amount of **29b** (ca. 10 mol%) in THF resulted in the rapid formation of the corresponding amine **99b** and borazine (Scheme 43).^[67]

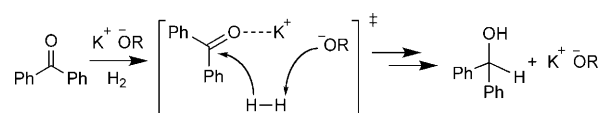
6.5. Other Metal-Free Catalytic Hydrogenation Reactions

There are a variety of other metal-free hydrogenation reactions reported in the literature, some of which are catalytic. An early example was reported by Walling and Bollyky.^[68] They had observed that benzophenone is reduced



Scheme 43. Catalytic reduction of an imine using H₃NBH₃.

to diphenylmethanol with dihydrogen in the presence of the strong base, potassium *tert*-butoxide. The reaction conditions were quite forcing, typically using over 100 bar H₂ pressure and a high reaction temperature (ca. 200 °C).^[69] Berkessel et al. studied this reaction in some detail^[70] and proposed a reaction pathway (Scheme 44) related to the asymmetric ruthenium-complex-catalyzed Noyori hydrogenation^[71] of prochiral ketones.

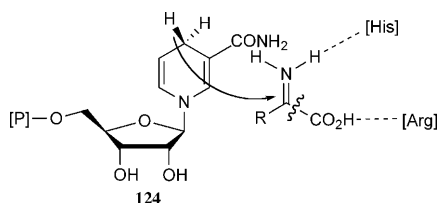


Scheme 44. Reduction of benzophenone by KOR/H₂. R = *t*Bu.

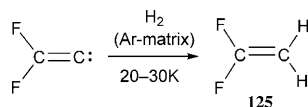
Metal-free hydrogenation can be induced by strong acids under forcing conditions. Aromatic hydrocarbons as well as cyclic alkenes and dienes were hydrogenated using H₂ at elevated pressure, in the presence of strong acids, such as HF/TaF₅, HF/SbF₅ or HBr/AlBr₃. This approach gave saturated hydrocarbon products, some with rearranged carbon frameworks.^[72] Köster et al. reported borane-catalyzed hydrogenation of condensed arenes to fully or partly hydrogenated derivatives at high temperature (ca. 200 °C) and under high H₂ pressures.^[73] Haenel et al. described a related procedure for the liquefaction of coal using homogeneous borane catalysts.^[74]

Dihydropyridines are increasingly used as alternative hydrogen sources for the organocatalytic hydrogenation of carbonyl and imine substrates by means of proton and hydride transfer. Asymmetric hydrogenation using chiral Brønsted acids has become an increasingly important variant.^[75] In this regard, it should not be forgotten that NADH (**124**), provides a metal-free hydrogenation in natural systems (Scheme 45) which bears some relation mechanistically to the metal-free reduction with the PH⁺/BH[−] systems.^[76]

In an early example, Sander et al. showed that the strongly electrophilic carbene difluorovinylidene reacts directly with H₂ in an argon matrix at 20–30 K with practically no activation barrier to yield 1,1-difluoroethene (**125**; Scheme 46).^[77] Formal insertion of examples of monoamino carbenes into the H–H bond in solution were recently reported by Bertrand et al.^[35] (Scheme 18). Remotely related



Scheme 45. NADH reduction.

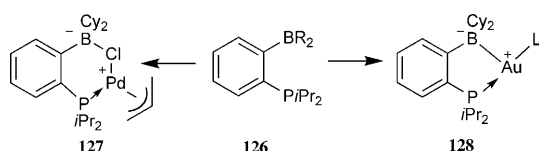


Scheme 46. Reduction of a carbene.

reactions of a diaryldigermylene and by the carbene-like diarylstannylenes had been described by Power et al.^[78]

7. Applications in Organometallic Chemistry

There are a variety of systems reported that contain trivalent phosphorus and trivalent boron centers connected by unsaturated organic linkers.^[13,20c,24c-e] The photophysical properties of such “conjugated phosphine-borane” systems have been examined.^[79] Some of these π -conjugated P/B systems form internal adducts,^[80] while some show reactivities reminiscent of frustrated Lewis pairs, undergoing bifunctional addition reactions to organometallic substrates. For example, the products **127** and **128** were formed by such addition reactions employing the P/B system **126** (Scheme 47).^[81,82]

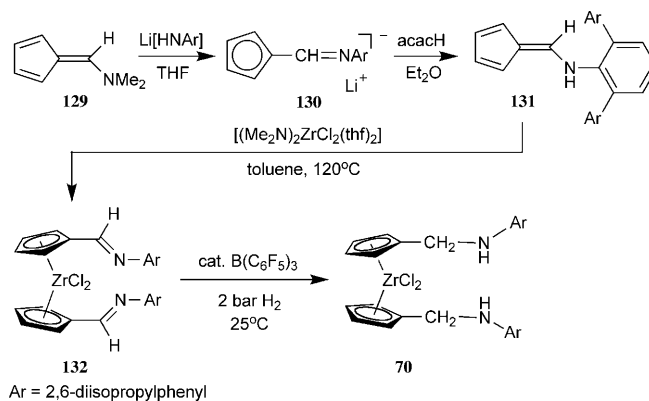
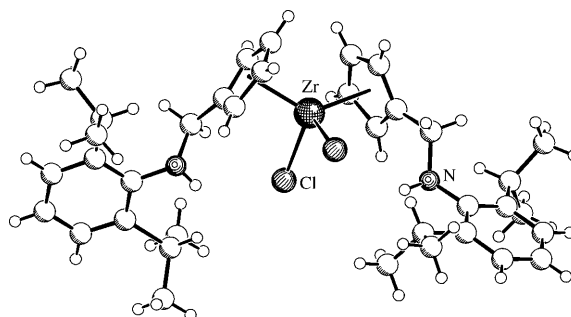


Scheme 47. Formation of metal complexes with P–B ligands. Cy = cyclohexyl.

Carrying out organic functional-group transformations on many organometallic frameworks is tedious owing to the often high sensitivity of these metal-containing compounds. This is especially true for many early-transition-metal systems for which only recently a variety of suitable methods for organic functional-group interconversion are beginning to emerge.^[61b-e,83] Metal-free catalytic hydrogenation using frustrated Lewis pair catalysts provides a suitably mild method for such sensitive systems. Below some examples are described.

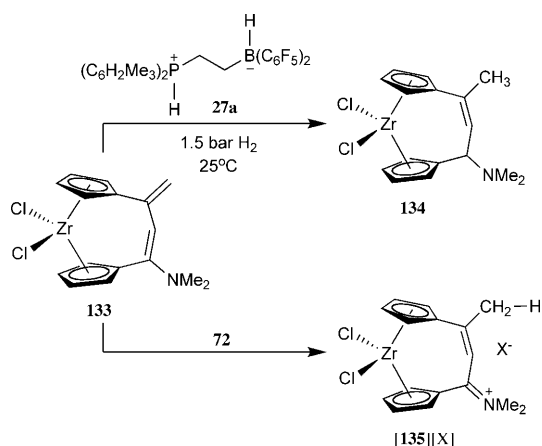
Treatment of 6-dimethylaminofulvene (**129**)^[84] with lithium anilides results in exchange of the amino component with formation of the formally imino-substituted cyclopentadienide **130**.^[85] Protonation under carefully controlled conditions with the Brønsted acid acetylacetone, gave the bulky *sec*-aminofulvene **131**. This species was subsequently metallated

by treatment with the $[(\text{Me}_2\text{N})_2\text{ZrCl}_2(\text{thf})_2]$ to give **132** (Scheme 48). The functionalized bent metallocene forms a frustrated Lewis pair with $\text{B}(\text{C}_6\text{F}_5)_3$, which under H_2 (2 bar H_2 , 25 °C) effects a “quasi-autocatalytic” metal-free hydrogenation reaction of the imino groups giving the aminomethyl-substituted zirconocene complex **70** (Figure 24).

Scheme 48. Preparation of **70**. acac = acetylacetone.Figure 24. Molecular structure of the hydrogenation product **70** of an organometallic imine.

The ansa-metallocene **133** was easily available by acid-catalyzed intramolecular Mannich coupling of the respective bis(enamino)-substituted zirconocene.^[61b-e] In the analogous [3]ferrocenophane derivatives **120**, catalytic hydrogenation opened a pathway for the synthesis of a variety of useful ligands for asymmetric catalysis.^[62,86] Carrying out similar hydrogenation reactions of the unsaturated bridge of the ansa-zirconocene systems **133** was difficult because of the high sensitivity of these systems. However, metal-free catalytic hydrogenation offered a solution to this problem. The ansa-zirconocene **133** was selectively 1,4-hydrogenated to **134** using the catalyst system **27a**.^[63] (Scheme 49). The proton/hydride transfer reaction is thought to follow a similar course as in the ferrocene system **120** discussed above. Protonation of **133** with a variety of Brønsted acids followed by treatment with NH^+/BH^- system **72** gave the corresponding ansa-zirconocene-derived conjugated iminium salts **[135][X]** ($[\text{X}] = [\text{HB}(\text{C}_6\text{F}_5)_3]$ or $[\text{ZrCl}_5]$; Scheme 49, Figure 25).^[64]

Sometimes organometallic Lewis base components complicate the reactions. For example, treatment of “Ugi’s amine” (*N,N*-dimethyl-1-ferrocenylethylamine) with methyl



Scheme 49. Selective 1,4-hydrogenation of ansa-zirconocenes **133**. $X = \text{HB}(\text{C}_6\text{F}_5)_3^-$.

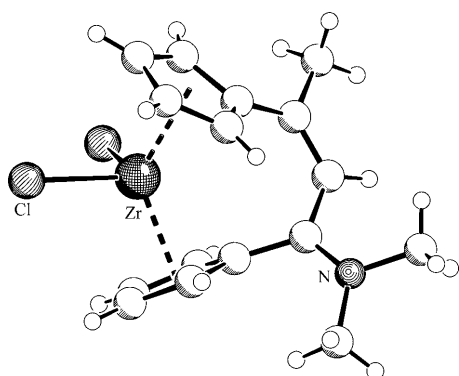
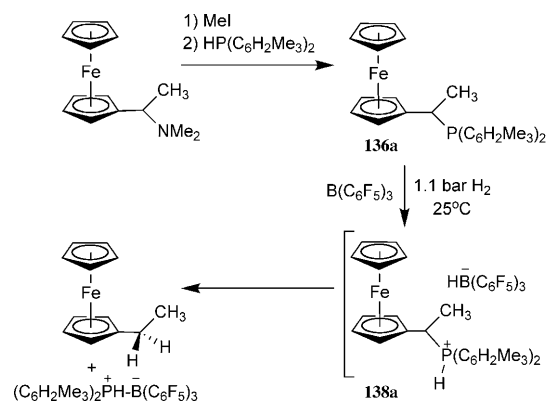


Figure 25. A view of the cationic part of the ansa-zirconocene iminium salt **[135][ZrCl₅]**.

iodide and then by dimesitylphosphine gave rise to complex **136a**. Reaction with $\text{B}(\text{C}_6\text{F}_5)_3$ and H_2 results in loss of the phosphine fragment. Complex **136a** probably forms a frustrated Lewis pair with $\text{B}(\text{C}_6\text{F}_5)_3$, which under very mild conditions reacts with H_2 to yield ethylferrocene and the $(\text{C}_6\text{H}_2\text{Me}_3)_2\text{P}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3$ adduct. It is assumed that this reaction proceeds via the salt **138a**. However, under the reaction conditions this intermediate salt is unstable towards $\text{S}_{\text{N}}1$ -substitution, leading to hydride from $[\text{HB}(\text{C}_6\text{F}_5)_3]$ effecting displacement of $\text{HP}(\text{C}_6\text{H}_2\text{Me}_3)_2$ with anchimeric assistance by the iron center (Scheme 50).^[65,87]

The analogous reaction was also observed in the related [3]ferrocenophane series. The product **137** was independently synthesized and characterized (Figure 26). The assumed reaction course was supported by the observed stereoselective formation of the *trans*-product, *trans*-**[D₁]-137**, upon treatment of the **136b**/ $\text{B}(\text{C}_6\text{F}_5)_3$ frustrated Lewis pair with D_2 ^[87] (Scheme 51).

Surprisingly, the analogous reaction of the closely related *ortho*-bromo- or *ortho*-iodo[3]ferrocenophane derivative **136c,d** features a different outcome. The frustrated Lewis pairs **136c,d**/ $\text{B}(\text{C}_6\text{F}_5)_3$ split H_2 heterolytically to yield the stable organometallic phosphonium/hydridoborate salts



Scheme 50. Reaction of the frustrated Lewis pair of **136a** with hydrogen.

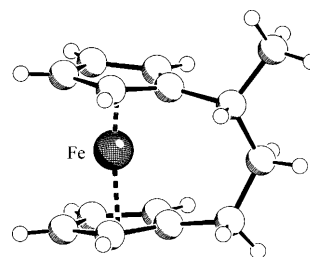
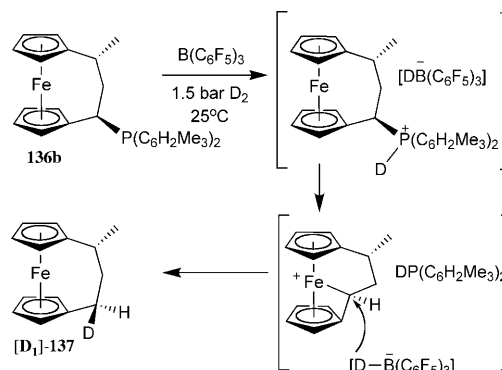
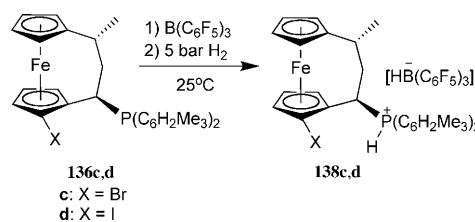


Figure 26. Molecular geometry of the [3]ferrocenophane derivative **137**.



Scheme 51. Proposed reaction path for the formation of **137**.

138c,d (Scheme 52). The X-ray crystal structure analysis of **138d** (Figure 27) features a close $\text{PH}\cdots\text{halide}$ contact that might make the $\text{HP}(\text{C}_6\text{H}_2\text{Me}_3)_2$ moiety a slightly less-favorable leaving group in this special case.^[88]



Scheme 52. Formation of the salt **138**.

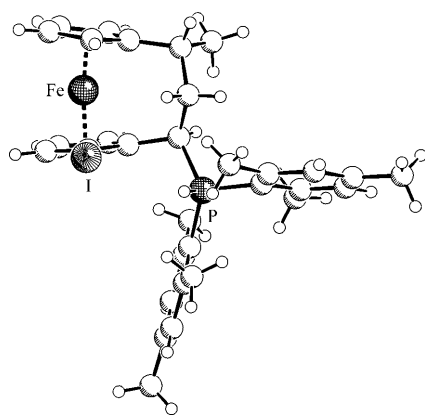


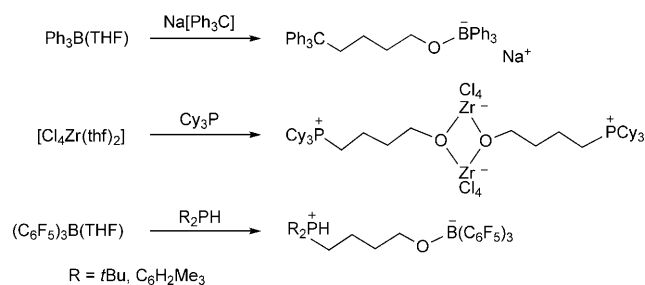
Figure 27. Molecular structure of **138d** (only the cation is depicted).

8. Activation of Other Small Molecules by FLPs

As frustrated Lewis pairs retain most of the typical reactivities of their Lewis base and Lewis acid components, they undergo reactions that are characteristic for each separate component. However, in addition they add cooperatively to a variety of substrates. This extends the scope of their potential use far beyond their application for metal-free heterolytic H_2 activation and metal-free hydrogenation catalysis. In this section, this emerging development is illustrated with selected examples.

8.1. Ring Opening of THF

Wittig and Rückert, in 1950, described the reaction of Ph_3CNa with $THF(BPh_3)$.^[89] Conventional thought would have predicted that treatment of the Lewis acid/base adduct with a strong nucleophile would simply result in the displacement of the weaker donor by the stronger, resulting in formation of the stronger acid/base adduct. However, Wittig and Rückert reported that the trityl anion effected THF ring opening affording the anion $[Ph_3C(CH_2)_4OBPh_3]^-$ (Scheme 53). Since this early study, the ability of Lewis acidic centers to promote THF ring-opening reactions has been observed for a number of systems. For example, in 1992 Breen and Stephan showed that treatment of $[ZrCl_4(thf)_2]$ with PCy_3 gave the zwitterionic dimer $[(Cl_4Zr(\mu-O-(CH_2)_4PCy_3))_2]$ (Scheme 53).^[90] Related combinations of

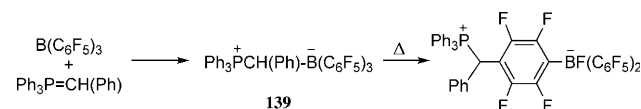


Scheme 53. Examples of Lewis acid induced THF ring-opening reactions.

Lewis acids and Lewis bases exhibit similar THF ring-opening chemistry. These include systems involving Lewis acidic transition metals, such as U,^[91] Sm,^[92] Ti,^[93] and Zr^[90,94] and main-group Lewis acids including carborane,^[95] alane,^[96] tellurium species,^[97] and boranes^[98] in combination with either nitrogen- or phosphorus-based Lewis bases (Scheme 53). The most pertinent of these to the present discussion is the zwitterionic species $R_2PH(CH_2)_4OB(C_6F_5)_3$ ($R = tBu, C_6H_2Me_3$) derived from the treatment of $(THF)B(C_6F_5)_3$ with sterically encumbered phosphines.

8.2. para-Substitution Reactions

In reactions of sterically encumbered amines with trityl cation, conventional Lewis behavior was not observed, rather, the trityl cation abstracts a proton from the carbon *alpha* to the nitrogen atom yielding an iminium cation.^[99] In related chemistry, reactions of pyridine with trityl cation also failed to prompt quaternization of the nitrogen center. Instead, it was suggested that pyridine attacks the carbon *para* to the carbocation,^[100] although this report was subsequently disputed.^[101] In 1998, Doering et al.^[102] described the reaction of the Lewis acid $B(C_6F_5)_3$, which is isoelectronic to the trityl cation, with the ylide Ph_3PCHPh . It was shown that the classical Lewis adduct, $(Ph_3PCHPh)B(C_6F_5)_3$, formed reversibly at room temperature and rearranged at higher temperature to effect attack at the *para*-position of one of the C_6F_5 rings. Concurrent fluoride transfer to B affords the zwitterionic phosphonium-borate $[Ph_3PCHPh(C_6F_4)BF(C_6F_5)_2]$ (Scheme 54).^[102]

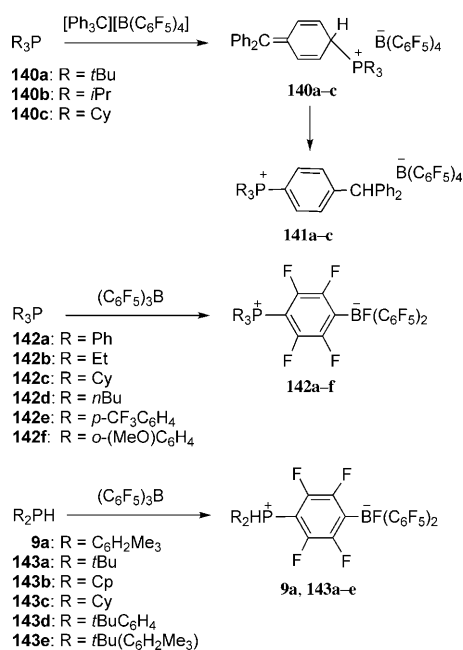


Scheme 54. Synthesis and thermal rearrangement of **139**.

In a related study of the reactions of trityl borates with Lewis donors,^[103] bulky phosphines ($R = tBu, iPr, Cy$) were unable to attack the central carbocation and instead effected nucleophilic substitution at the carbon *para* to the carbocation, giving the salts **140** or **141** (Scheme 55).^[103] More recently, this reactivity has been shown to be general and the *para*-substitution was demonstrated to occur for classical phosphine adducts of $B(C_6F_5)_3$ under warming, yielding the air- and moisture-stable zwitterions **142**, **9a**, **143** (Scheme 55).^[104] Analogous species are obtained with smaller phosphines after the combined toluene solutions of the reagents are heated under reflux.^[105]

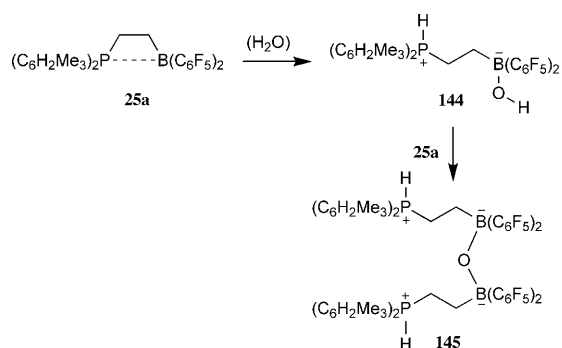
8.3. Addition to Boron

The boron center in **25a** is quite Lewis acidic. Therefore, it adds a variety of typical, small, donor ligands. Among them a sometimes unwanted reaction partner is the H_2O molecule. Reaction of **25a** with H_2O occurs in a well-defined way if



Scheme 55. *para*-substitution reactions of Lewis acids with phosphines.

insufficient precautions are taken to exclude moisture from reaction mixtures. Addition of H₂O to the B(C₆F₅)₂ unit substantially increases the Brønsted acidity of the water molecule.^[106] Rapid intramolecular deprotonation by the adjacent mesityl₂P base then rapidly leads to the formation of **144** (Scheme 56, Figure 28). The [B]-OH unit in **144** is still quite acidic. Therefore, it may react further with **25a** if



Scheme 56. Reaction of **25a** with water.

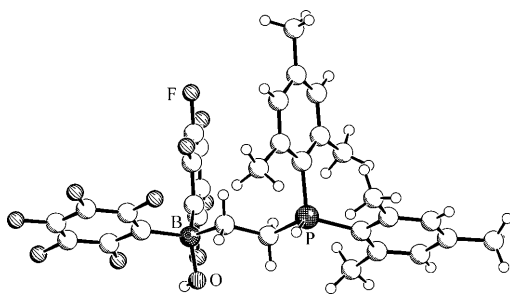


Figure 28. A view of the molecular structure of the product **144** of H₂O addition to the frustrated Lewis pair **25a**.

present in an excess, ultimately providing compound **145** (Figure 29, B1-O: 1.578(3) Å, angle B1-O-B2: 131.3(2)°).^[107]

The frustrated Lewis pair **25a** adds terminal alkynes in a similar fashion. Thus **146** is produced from the reaction of **25a**

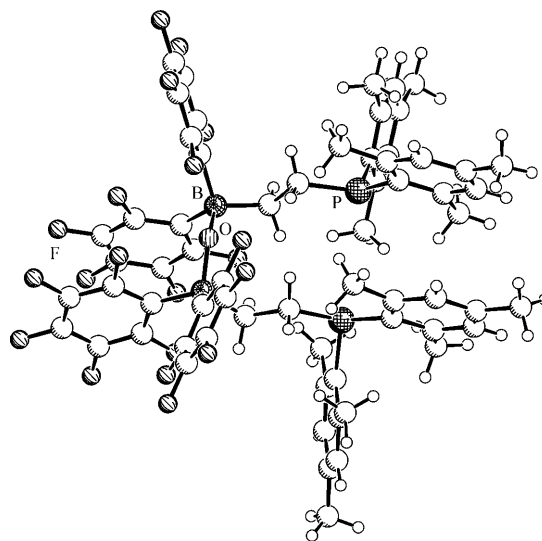
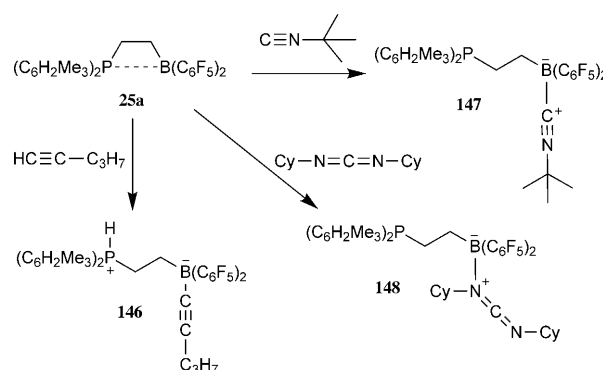


Figure 29. Molecular structure of **145**.

with 1-pentyne in good yield (Scheme 57, Figure 30; **146**: B-C3 1.589(4) Å, C3-C4 1.198(4) Å; **147**: B-C3 1.622(4) Å, C3-N1: 1.138(3) Å). *tert*-Butylisocyanide adds cleanly to the



Scheme 57. Addition products with **25a**.

boron center of **25a** to give the adduct **147**. Even some imines react in a similar way. For example, dicyclohexylcarbodiimide forms the Lewis acid/Lewis base adduct **148** with **25a** (Scheme 57, Figure 31).^[107]

8.4. Reactions with Carbonyl Groups

Frustrated Lewis pairs undergo 1,2-addition reactions to carbonyl compounds. Addition to the reactive C=O double bond of isocyanates is common. Typical examples are the formation of **149a** from **25a** and phenylisocyanate^[107] and the related reversible formation of **149b** from the “ambiphilic”

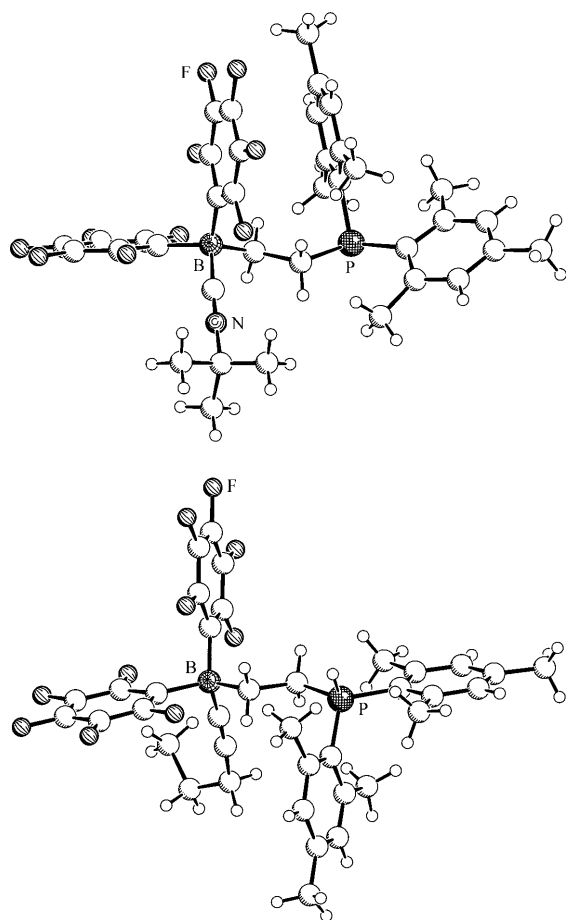


Figure 30. Molecular structures of 147 (top) and 146 (bottom).

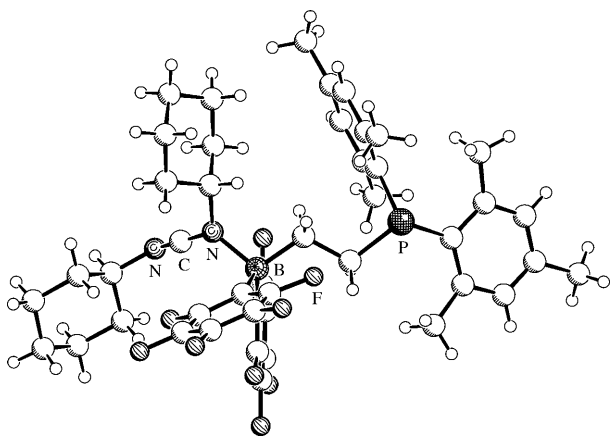
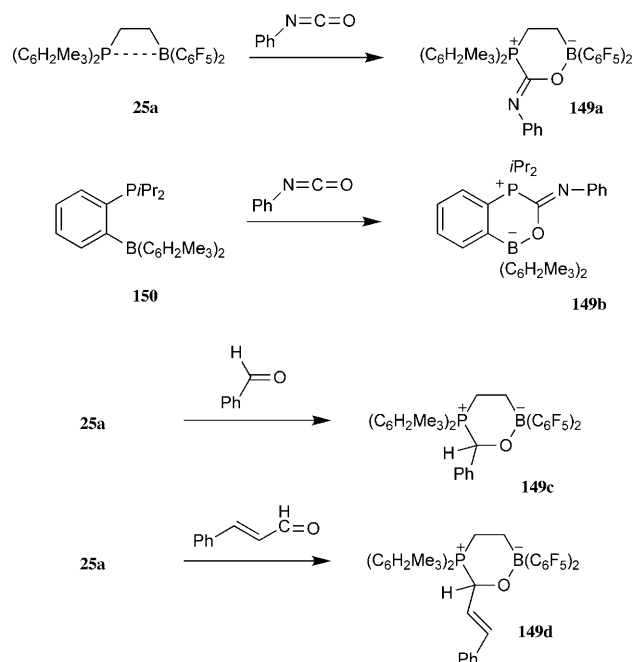


Figure 31. Molecular structure of 148.

intramolecular pair **150**.^[108] Benzaldehyde adds rapidly to **25a** to form the six-membered heterocycle **149c** which adopts a distorted chair conformation in the solid state (Scheme 58, Figure 32). In the case of the reaction of cinnamic aldehyde, it was not clear whether the frustrated Lewis pair **25a** would add to the electron-deficient C=C double bond or the carbonyl function. Experiment shows that 1,2-addition to the carbonyl group is preferred (**149d**; Scheme 58).^[107]



Scheme 58. Reactions of frustrated Lewis pairs with carbonyl compounds.

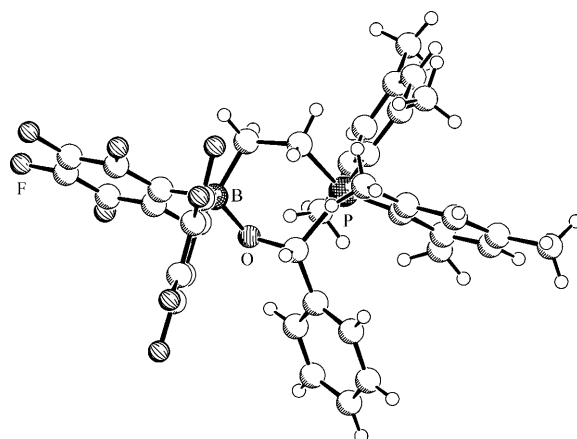
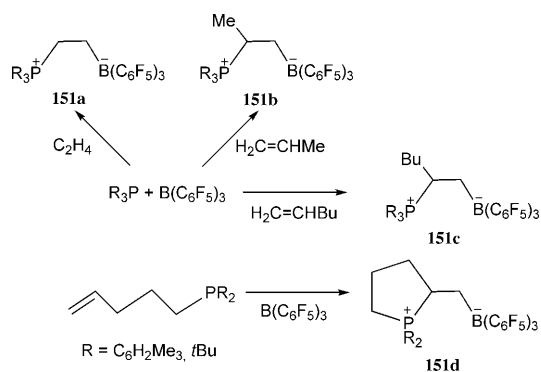


Figure 32. Molecular structure of 149c.

8.5. Activation of Alkenes, Dienes, and Alkynes

The Stephan group has also demonstrated that frustrated Lewis pairs add to alkenes. For example, exposure of a solution of $t\text{Bu}_3\text{P}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ to ethylene resulted in the formation of the zwitterionic species $[\text{tBu}_3\text{P}(\text{C}_2\text{H}_4)\text{B}(\text{C}_6\text{F}_5)_3]$ (Scheme 59).^[109] Similarly, the products $[\text{tBu}_3\text{P}(\text{CH}(\text{R})\text{CH}_2)\text{B}(\text{C}_6\text{F}_5)_3]$ ($\text{R} = \text{CH}_3, \text{C}_4\text{H}_9$), were derived from propylene and 1-hexene, respectively. In addition, reaction of $\text{CH}_2=\text{CH}-(\text{CH}_2)_3\text{PR}_2$ ($\text{R} = t\text{Bu}, \text{C}_6\text{H}_2\text{Me}_3$) with $\text{B}(\text{C}_6\text{F}_5)_3$ generates the cyclic phosphonium-borate **151d** ($\text{R} = t\text{Bu}, \text{C}_6\text{H}_2\text{Me}_3$) (Scheme 59).^[109] In all of these products, the boron center adds to the less-hindered carbon atom. The structures of these compounds were confirmed by X-ray data (Figure 33, Figure 34). Mechanistically, activation of the alkene by the Lewis acid is thought to initiate these reactions, prompting



Scheme 59. Addition of P/B Lewis pairs to alkenes.

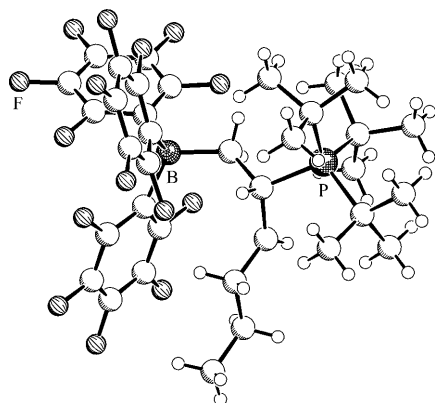


Figure 33. Molecular structure of **151c**.

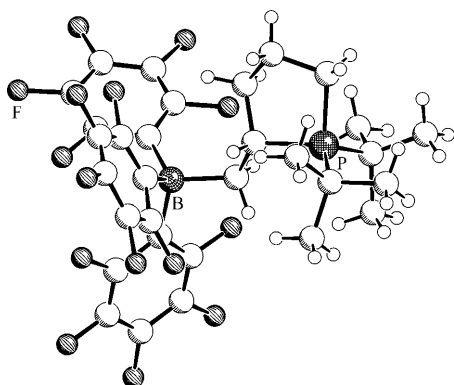
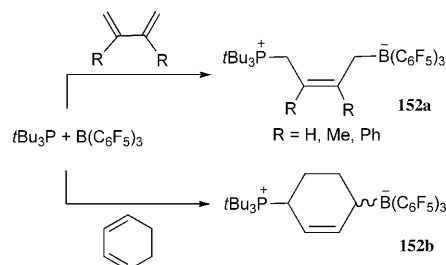


Figure 34. Molecular structure of **151d**.

attack by the phosphine at the more-substituted carbon of the alkyne. Older IR studies have demonstrated the formation of BF_3 -ethylene and BF_3 -propylene complexes in an argon matrix at 93–125 K,^[110] supporting this notion of Lewis acid-activation of alkenes. In addition computational studies have suggested weak π -donation complexes for ethylene–alane and ethylene–borane adducts.^[111]

Similarly the Stephan group has probed the related reactions of frustrated Lewis pairs with conjugated dienes. Again, in these cases, addition reactions are observed, although the regiochemistry is predominantly that of 1,4-addition. Thus in the reaction of $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ with buta-

diene, 2,3-diphenylbutadiene, 2,3-dimethylbutadiene, and 1,3-cyclohexadiene, 1,4-addition products **152** were isolated in 50–60% yield (Scheme 60, Figure 35).^[112] These reaction mixtures contain other species that may arise from other stereoisomers or 1,2-addition products although these latter byproducts could not be isolated or fully characterized.



Scheme 60. Frustrated Lewis pair reactions with conjugated dienes.

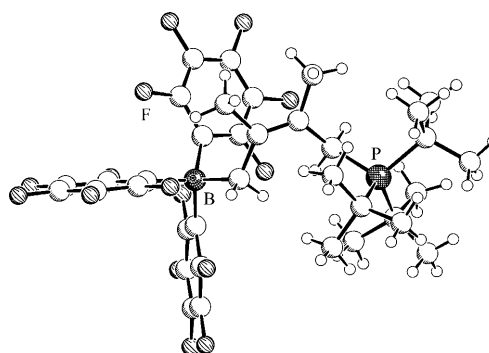
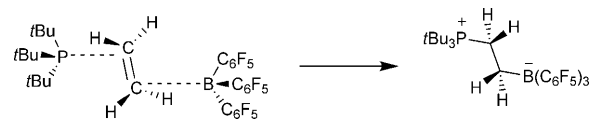


Figure 35. Molecular structure of **152a** ($\text{R} = \text{CH}_3$).

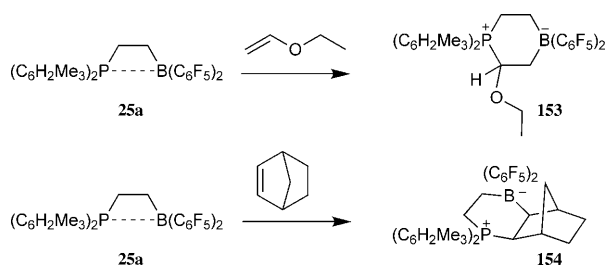
In a theoretical study, Pápai et al. described the reaction of the $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ pair with ethylene as an antarafacial asynchronous concerted 1,2-addition reaction (Scheme 61).^[113]



Scheme 61. Concerted antarafacial addition of a frustrated Lewis pair and ethene.

The intramolecular frustrated Lewis pair **25a** undergoes a rapid and regioselective 1,2-addition reaction to the electron-rich ethylvinylether to yield compound **153** (Scheme 62 and Figure 36).^[107]

In related chemistry, Erker and co-workers showed that the reaction of **25a** with norbornene gives the *exo*-2,3-addition product **154** selectively (Figure 37). Comparison with DFT data indicated that the product **154** was formed under kinetic control. This means that product formation occurs either in a stepwise reaction with very rapid trapping of



Scheme 62. Addition reactions of the intramolecular frustrated Lewis pair **25a** with alkenes

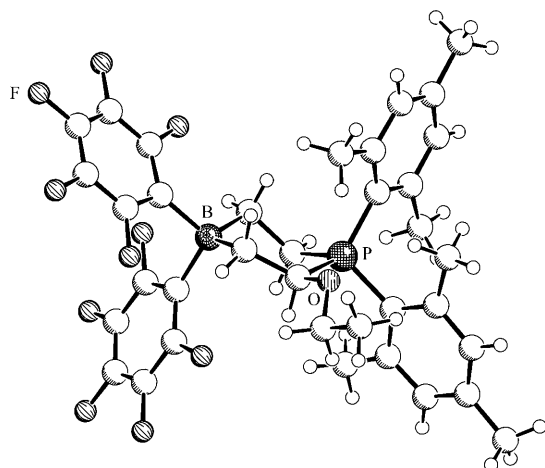


Figure 36. A view of the chair conformation of the heterocyclic compound **153**.

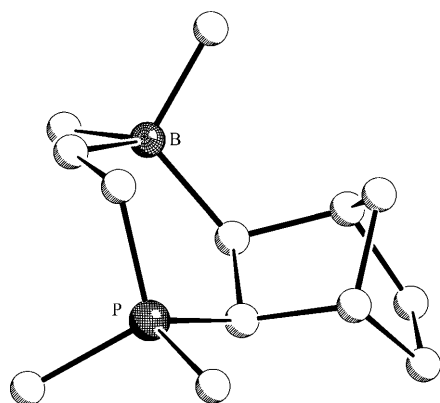


Figure 37. Molecular structure of the *exo*-2,3-addition product **154** of the frustrated Lewis pair **25a** to norbornene (only the core atoms of the reagent **25a** are depicted).

the intermediate or concertedly. Results of a detailed theoretical analysis favor the concerted mechanism. The DFT analysis located a transition-state structure characterized by a markedly stronger B–C than P–C interaction (Figure 38), suggesting an asynchronous concerted *cis* addition. The reaction might be considered as a “two-site cheletropic” reaction type.^[107,114] Norbornadiene undergoes

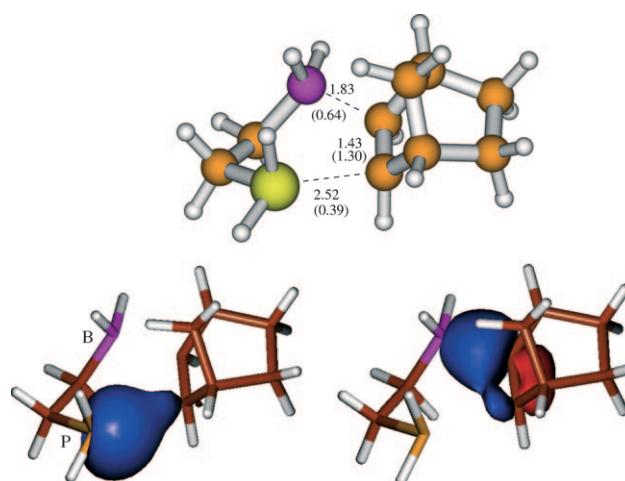
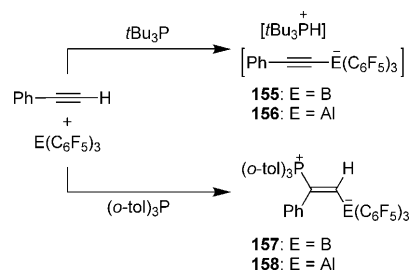


Figure 38. DFT-calculated transition-state geometry of the concerted addition of **25a** (without substituents) to norbornene (top: orange C, white H, yellow P, violet B). Separations in [Å], covalent bond orders in parenthesis and corresponding localized molecular orbitals (LMO) at P (bottom left) and B (bottom right).

an analogous two-fold *exo* addition reaction with the frustrated Lewis pair **25a**.^[107]

Frustrated Lewis pairs may also add to alkynes.^[115] Combinations of $\text{B}(\text{C}_6\text{F}_5)_3$ or $(\text{PhMe})\text{Al}(\text{C}_6\text{F}_5)_3$ with $(o\text{-C}_6\text{H}_4\text{Me})_3\text{P}$ generated frustrated Lewis pairs, these react with $\text{PhC}\equiv\text{CH}$ to give the zwitterionic species **157** and **158** (Scheme 63, Figure 39). In marked contrast the reaction of



Scheme 63. Alternative reactions of frustrated Lewis pairs with 1-alkynes.

$\text{B}(\text{C}_6\text{F}_5)_3$ or $(\text{PhMe})\text{Al}(\text{C}_6\text{F}_5)_3$ ^[116] and $t\text{Bu}_3\text{P}$ with $\text{PhC}\equiv\text{CH}$ gave the salts **155** and **156**, respectively, in near quantitative yields (Figure 40).

The isolated and classical Lewis acid/base adduct $\text{Ph}_3\text{PB}(\text{C}_6\text{F}_5)_3$ was also shown to react with $\text{PhC}\equiv\text{CH}$ to give the addition product, $\text{Ph}_3\text{PC}(\text{Ph})=\text{C}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3$.^[115] This result is surprising in that for the adduct $\text{Ph}_3\text{PB}(\text{C}_6\text{F}_5)_3$ no evidence of dissociation is found by NMR spectroscopy. This accessibility of frustrated Lewis pair chemistry from classical Lewis acid/base adducts suggests the possibility that many more examples of compounds, otherwise thought to be unreactive, may indeed offer access to new reactivity.

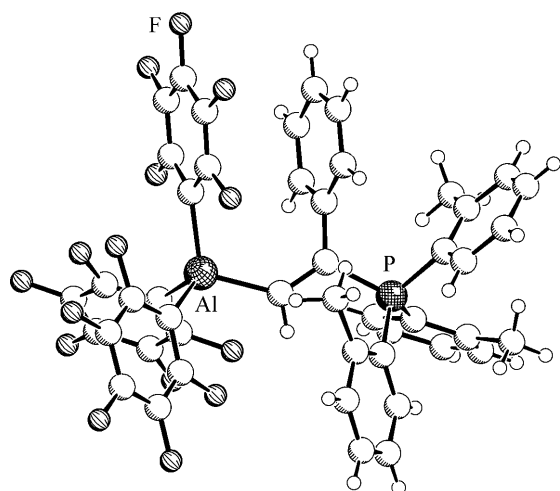


Figure 39. Molecular structure of 158.

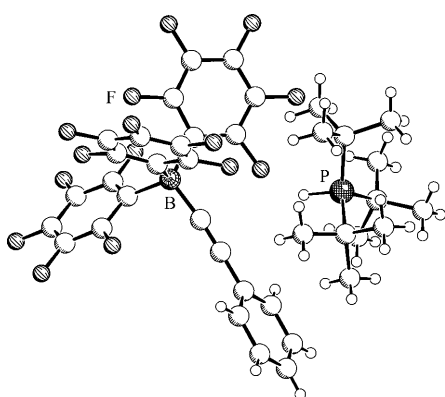
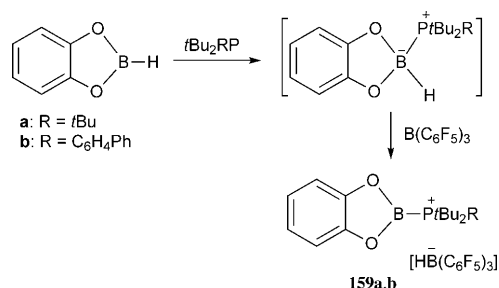


Figure 40. Molecular structure of the salt 155.

8.6. Activation of B–H Bonds

Frustrated Lewis pairs have also been shown to prompt the activation of the B–H bond of catecholborane. Thus treatment of $t\text{Bu}_2\text{RP}$ ($\text{R} = t\text{Bu}$, $\text{C}_6\text{H}_4\text{Ph}$) and $\text{B}(\text{C}_6\text{F}_5)_3$ with catecholborane affords the products **159** (Scheme 64, Figure 41).^[117] These reactions are presumed to proceed by initial coordination of phosphine to catecholborane, thus activating the B–H bond for hydride abstraction by $\text{B}(\text{C}_6\text{F}_5)_3$. DFT calculations were used to address the nature of the



Scheme 64. Frustrated Lewis pair reaction of catecholborane.

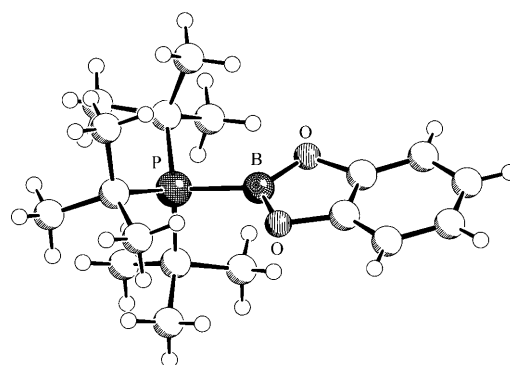


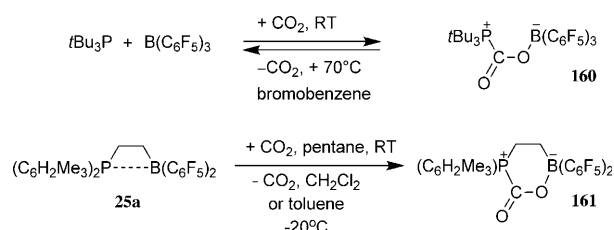
Figure 41. Molecular structure of the salt 159a (only the cation is depicted).

resulting cations. This approach led to the localization of the positive charge on the phosphorus atom, which prompts the description of these species as borylphosphonium cations rather than as a phosphine-stabilized borenium cations. Nonetheless, this cation is the first three-coordinate boron cation, ligated by oxygen donors.^[118]

8.7. Activation of CO_2

Owing to its role as a greenhouse gas, the development of new methods for both the sequestering of CO_2 and its use as an alternative C_1 chemical feedstock is rapidly gaining increasing attention.^[119] Chemical conversion of CO_2 often utilizes the special properties of metal complexes.^[120] The ruthenium-based hydrogenation of CO_2 to formic acid derivatives is a prominent example.^[121] There are a number of reactions of main-group-element reagents with CO_2 , such as the trapping reaction with amines^[122] or main-group-metal amides,^[123] or the conversion of CO_2 into bicarbonate induced by organic bases in the presence of hydroxide.^[124] Some chelate complexes of zinc catalyze the addition of CO_2 to epoxides.^[125] Recently, N-heterocyclic carbenes (NHCs) were shown to add to CO_2 and to induce its organocatalytic addition reactions to organic substrates^[126] or its reduction to methanol.^[127]

In a collaborative report, Stephan et al. and Erker et al. found that CO_2 reacts with frustrated Lewis pairs in a straightforward fashion.^[22] For example, the components of the $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ pair add to CO_2 at room temperature in bromobenzene with P–C and O–B bond formation, yielding the product **160** (Scheme 65, Figure 42).^[128] Cleavage and

Scheme 65. Reactions of frustrated P/B Lewis pairs with CO_2 .

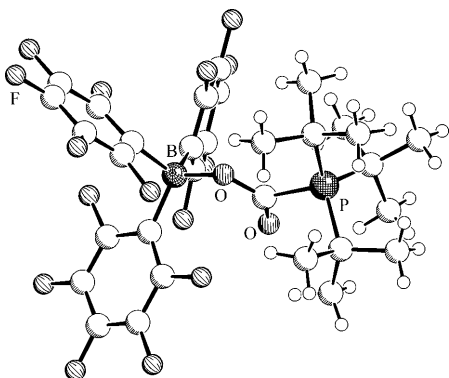


Figure 42. Molecular structure of the CO₂ adduct **160**.

liberation of CO₂ occurs upon heating to +70°C, indicating that the CO₂ addition reaction is reversible.

Similarly, the intramolecular frustrated Lewis pair **25a** also reacts with CO₂ under analogous reaction conditions.^[22] Pressuring a solution of **25a** in pentane with CO₂ (2 bar) leads to the precipitation of the adduct **161**. In this case, the carboxylation of the frustrated Lewis pair is reversible as the product **161** rapidly loses CO₂ in solution at temperatures above –20°C to reform the starting material **25a**. At temperatures below this limit, compound **161** can be handled without decomposition. Single crystals of compound **161** were obtained at –36°C. (Figure 43) The examples **160** and **161** may be regarded as phosphonium analogues of carbamic acid derivatives.^[129–131]

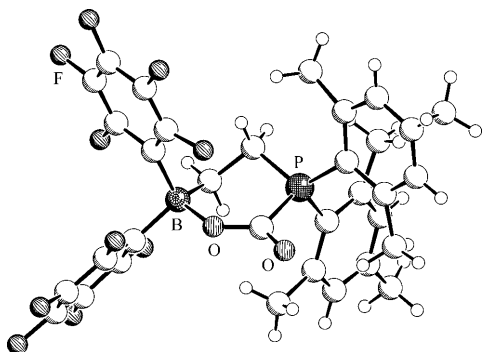


Figure 43. Molecular geometry of the CO₂ adduct **161**.

Grimme et al. examined these reactions of CO₂ by DFT calculations.^[22] The detailed theoretical analysis revealed that the CO₂ addition reaction to **25a** to yield **161** is close to thermoneutral, whereas the analogous addition of the open *t*Bu₃P/B(C₆F₅)₃ pair is remarkably exothermic. Analysis of the **25a**/CO₂ system showed the formation of a weakly bound van der Waals complex of CO₂ and the open isomer (**26a**), followed by a concerted addition reaction to **161** (calculated activation energy: 7.7 kcal mol^{–1} from the van der Waals complex). In contrast to the very unsymmetrical transition state found in the corresponding addition reaction of **25a** to norbornene (see Section 8.3), both the formation of the P–C

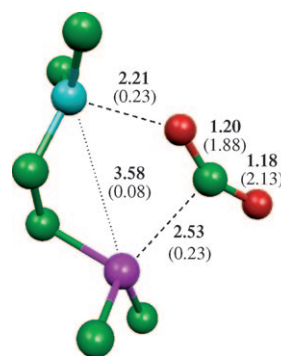


Figure 44. DFT-calculated structure of the transition state of the addition reaction of the frustrated Lewis pair to carbon dioxide (with calculated distances in [Å] and covalent bond orders in parentheses).

and the O–B bonds are almost equally advanced in the cyclic transition state (Figure 44) of the **25a**/CO₂ addition reaction.

9. Conclusions

The concept of “frustrated Lewis Pairs” (FLPs) advanced herein is rooted in the early observations of Brown, Wittig, and Tochtermann. However in the flurry of research that has taken place in recent years, frustrated Lewis pairs have developed from chemical curiosities into a new strategy for the activation of a variety of small molecules.

The remarkable ability of these systems to reversibly activate hydrogen presents a new line of thought for those developing and applying hydrogenation catalysis and perhaps even for the field of hydrogen storage. While any commercial impact of catalytic systems derived from frustrated Lewis pairs developed to date remains to be seen, the potential for metal-free hydrogenation catalysis is an attractive notion given the reductions in both cost of production and of environmental impact of these main-group catalysts.

While H₂ activation is of broad interest to the chemical community, the demonstration that frustrated Lewis pairs are capable of reactions with alkenes, dienes, alkynes, boranes, and CO₂ suggests a parallel between the chemistries of frustrated Lewis pairs and that of transition metals. In organometallic chemistry, the activation of small molecules is known to be the first step towards a mediated transformation. This analogy suggests that new patterns of reactivity and catalysis will emerge from these early findings of small-molecule activation by frustrated Lewis pairs.

Finally and perhaps more generally, the notion of frustrated Lewis pairs draws attention to the importance of molecular interactions that are not in themselves chemically productive and are generally not discernible spectroscopically. The attractive forces that bring the Lewis acid and Lewis base together in an frustrated Lewis pair are such interactions. While these forces do not prompt a chemical transformation, they offer a new “species” capable of unique reactivity. Fundamental understanding of such systems will be critical to the further development of their unique reactivity. Moreover, the application of these concepts in other, as yet unstudied systems, may provide the roots for further discovery.

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