A review of quantum chemical studies of Frustrated Lewis Pairs

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Abstract

This review endeavours to explore the power of quantum chemistry, especially density functional theory (DFT) to unravel mechanisms underlying the fascinating field of FLP chemistry. Apart from the fundamental mechanism of hydrogen activation by FLPs, borylation, silylation, polymerization, formation of heterocycles, reaction with small gaseous molecules, alkenes, terminal alkynes have also been reviewed. The role of DFT in understanding regio-selectivity, steric effects, London dispersion and covalent Interactions in FLPs are also discussed.

Keywords: Frustrated Lewis Pairs (FLPs), DFT, Hydrogenation

1 Introduction

Frustrated Lewis Pairs (FLPs) are a category of encumbered inter- or intra-molecular Lewis pairs that are not able to form classical adducts due to their size and/or electronic factors. The inability of sterically overcrowded Lewis pairs to form classical adducts was first reported in 1942 when Brown[1] et al reported that lutidine formed an adduct with BF_3 but not with the less Lewis acidic and bulkier $B(CH_3)_3$.
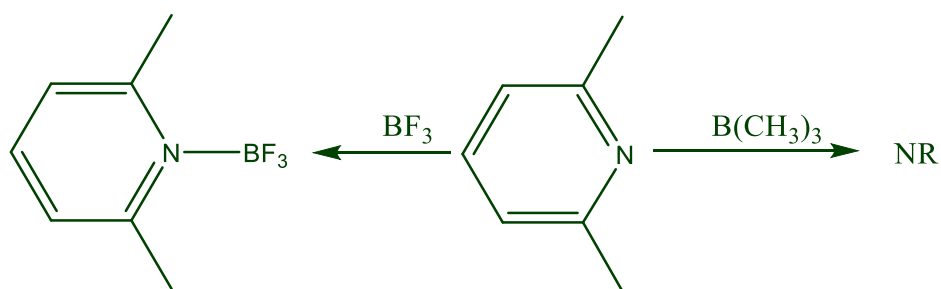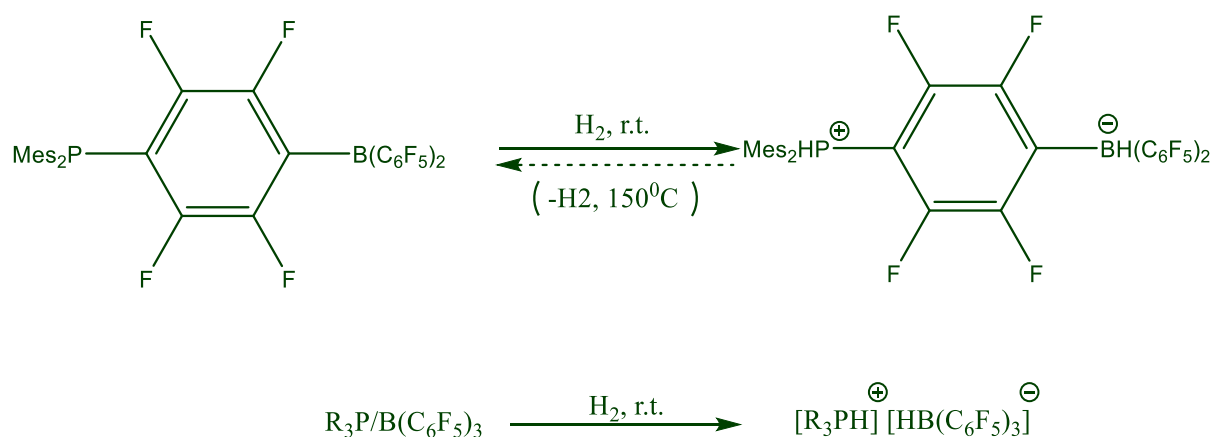
Scheme 1 Reaction of lutidine with Lewis acids.

In 1959 Wittig and Benz[2] reported unusual activity of FLPs, showing that PPh_3 and BPh_3 did not form a classical adduct on mixing but instead underwent 1,2-addition reactions by *in situ* generated benzyne. In 1966 Tochtermann[3] observed that on addition of BPh_3 to a butadiene monomer/triphenylmethane anion mixture, instead of a classical Lewis adduct, a trapped product was obtained. He described these systems as *'Antagonistisches Paar'* or antagonistic pair.

In 1996 Piers[4] reported the $B(C_6F_5)_3$ catalysed hydrosilylation of ketones, considered as the first example of FLP chemistry. Although discovered ten years previous, it was not until 2006 that the unprecedented reactivity of FLPs was fully uncovered by Stephan and co-workers. They reported intra[5]- as well as inter[6]-molecular FLPs that were able to split dihydrogen. The term FLP was subsequently coined by Stephan[7] in 2007.

Since then, it led to application of FLPs to various polar substrates such as imines, enamines, olefins, polyaromatics, alkynes, ketones, and aldehydes. Ability of the FLPS to activate small molecules like olefins, alkynes, CO_2, SO_2, NO, CO, N_2O has led to novel metal free strategies like CO and CO_2 reduction and SO generation. FLP

chemistry has also extended to newer vistas of organic chemistry that has led to newer approaches for hydroamination, hydroboration, cyclization, and boration reactions. A great deal of work has been reported on FLPs and their varied chemistry, which has been covered in numerous excellent reviews[8-10]. The focus of this review is recent efforts to use theoretical methods, usually but not exclusively based on density functional theory (DFT), to model FLP chemistry with a focus mainly on transformations that are catalysed by different classes of FLP.

$$Mes_2P\text{—}C_6F_4\text{—}B(C_6F_5)_2 \underset{(-H_2, 150^0C)}{\overset{H_2, r.t.}{\rightleftharpoons}} Mes_2HP^{\oplus}\text{—}C_6F_4\text{—}BH(C_6F_5)_2^{\ominus}$$

$$R_3P/B(C_6F_5)_3 \xrightarrow{H_2, r.t.} [R_3PH]^{\oplus} [HB(C_6F_5)_3]^{\ominus}$$

Scheme 2 Splitting of dihydrogen by intra- and intermolecular FLPs.

2. Theoretical Studies of FLP Chemistry

2.1 Hydrogenation by FLPs

Mane[11] et al used computational methods to study FLP catalysts for hydrogenation of unsaturated compounds. Their investigations suggested making them more efficient by reducing the frustration through lowering the steric demand and acid/base strength, i.e. Less Frustrated Lewis Pairs (LFLPs). They used M06-2X/TZVP//PBE-D3/TZVP approach for studying this new generation of FLPs. Solvent effects were accounted for by using COSMO (Conductor like Screening Model) model with different solvents (benzene, diethyl ether, dichloromethane and

toluene). Data indicate that turn over frequencies (TOFs) are significantly increased if LFLPs are used instead of FLPs, although sometimes unwanted side reactions may be present if steric demand is reduced without reducing the frustration.

Dong[12] et al have reported dialkylsilylenes that show FLP behaviour when combined with either a Lewis acid or Lewis base due to the amphoteric nature of silylene. The feasibility of the proposed mechanism was checked by comparing the relative energies of the intermediates and products at M06-2X/6-311+G(d,p) level. Their studies reveal that the new FLP can split dihydrogen successfully. Although the dihydrogen activation step is slightly endothermic, the final step involving the formation of the product is exothermic.

Dorko[13] et al synthesized and studied a series of triaryl-boranes with a general BX_2Y structure for FLP hydrogenation. They have characterized these molecules exhaustively with emphasis on the effect of substituting meta- and para-hydrogen atoms with fluorine or chlorine. Hydrogen anion affinities of these molecules were calculated using B3LYP-D3/6-311G(d,p) level and compared with experimental results. Solvent effects were studied using solvents like toluene, chloroform and dichloromethane by IEFPCM model. Single point energy calculation for each localized structure was re-calculated at B3LYP-D3/6-311++G(3df,3pd) level and indicate that, although Lewis acidity increased on replacing hydrogen by fluorine in meta-positions, there was negligible change upon replacing hydrogen with chlorine.
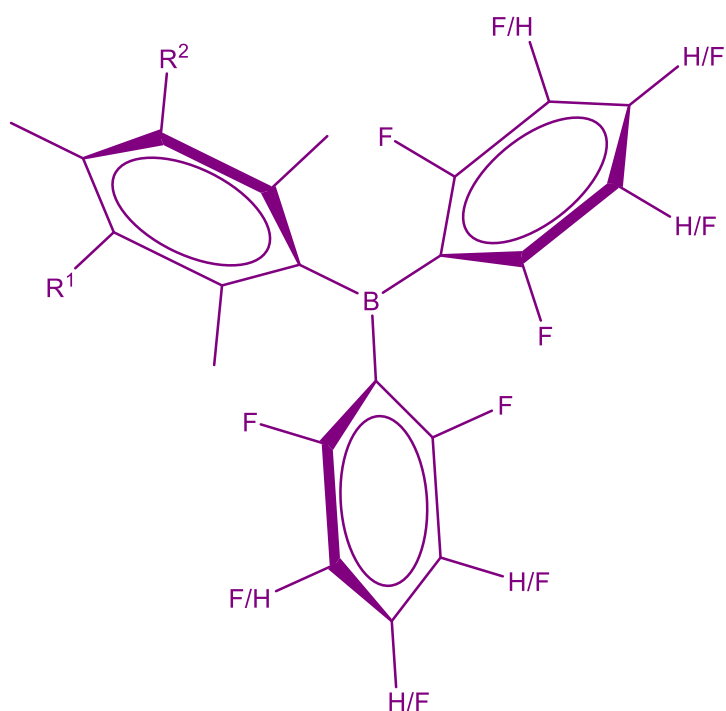
Figure 1 General structure of the triarylboranes studied.

Chernichenko[14] et al have reported novel 2-(dialkylamino)phenylboranes containing BXZ group, where X, Z = C_6F_5, Cl, H, which are able to cleave H_2 under mild conditions. Their computational studies using DFT at ωB97X-D/6-311G(d,p) level in simulated toluene reveal that FLPs having boron attached with C_6F_5 or Cl group have activation barriers much lower than those with a hydrogen attached, which may be attributed to the stabilization acquired due to dimerization in the first two cases.

Dative   Open   Dimer

$X,Z = C_6F_5, Cl, H$

Figure 2 2-(Dialkylamino)phenylboranes containing BXZ group that may exist in dative, open or dimer form.
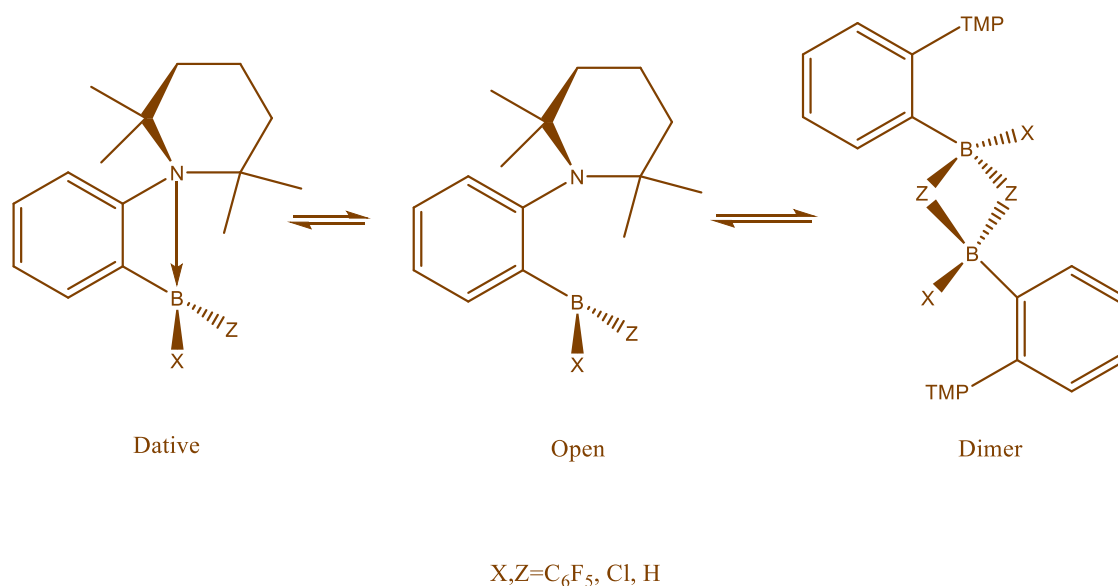
Liu et al used PBE-D3 with a plane wave basis set to carry out metadynamics (DFT-MD) study[15] to map free energy surface (FES) at 298 K, mapping out the lowest energy pathway for hydrogen activation by FLPs, particularly $^tBu_3P/B(C_6F_5)_3$. The results obtained by dynamics study are different from static calculations. While the results of earlier static DFT calculations predicted the role of FLP to cleave the H−H bond in a cooperative way, dynamics suggest that after initial polarization, hydride transfer to boron (which is the rate determining step of the reaction) and proton transfer to phosphorus occurs by proton and electron transfer.

Rochette[16] et al have reported reduction of hydroborane in a dimer formed by crystallization of ansa-aminohydroborane $1-NMe_2-2-(BH_2)C_6H_4$ without usage of any catalyst. $\omega B97XD/6-31++G^{**}$ level of theory with SMD model of toluene solvent has been utilized to delineate the mechanism of this transformation. This indicates that it

is the FLP moiety in the dimer which activates the B-H bond and thus leads to synchronous formation of B-B bond of diborane and expulsion of H_2 on heating.

Courtemanche[17] et al have reported an unusual multidentate FLP [bis(2-(TMP) phenyl]chloroborane (TMP = 2,2,6,6-tetramethylpiperidine) which reacts with H_2 to reversibly form a zwitterionic intermediate. This further releases HCl to form another novel FLP Bis(2-(TMP)phenyl) borane. ωB97XD/6-31G(d,p) level of theory and SMD model of benzene solvent was used to study the computational details. It has been found that the new FLP is quite efficient in activating dihydrogen. It has also been shown that the isomer in which proton directly faces hydride is more endergonic as compared to the crystallized one.

Wang et al[18] used theoretical methods to design novel metal free hydrogen storage compounds employing C/P and B/N FLPs. BP86-GD3BJ/6-311++G(3d,2p) method was used to optimize the structures while MP2/cc-pVTZ method was used to calculate single point energies. These revealed that B/N pairs are not as frustrated as corresponding C/P compounds, and that hydrogenation is directly proportional to the difference between the two relevant atomic charges. It was also shown that hydrogenation is easier with atoms that undergo a small change in atomic charge after the addition.

Yepes et al[19] have computationally investigated heterolytic splitting of H_2 using a new class of α,α-disubstituted geminal aminoborane-based FLPs. M06-2X/ def2-TZVPP was employed to explore the reaction mechanism. Activation strain model of reactivity combined with the energy decomposition analysis method has been utilized to quantitatively study the physical factors controlling the activation pathway.

Studies revealed that this is a concerted reaction in which good electron withdrawing groups or soft/poor π donors at boron significantly reduce the activation barrier.
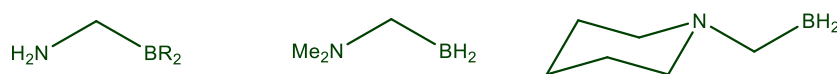

Figure 3 α, α-Disubstituted geminal aminoborane-based FLPs

Zhivonitko et al[20] have reported novel FLPs derived from ansa-aminoboranes (AAB), known as "molecular tweezers" because they stretch, but do not completely split, H_2 molecules. ωB97X-D/6-311G(d,p) level of theory was used for geometry optimizations and for calculating coupling constants between the NH and BH protons of BorylCAT–H_2, the AAB with the smallest boryl site (-BH_2).This reveals that all these new metal free catalysts have the ability to provide parahydrogen-induced polarization (PHIP) which in turn is able to substantially increase the intensity of NMR signals and eventually may be used for *in vivo* MRI applications.
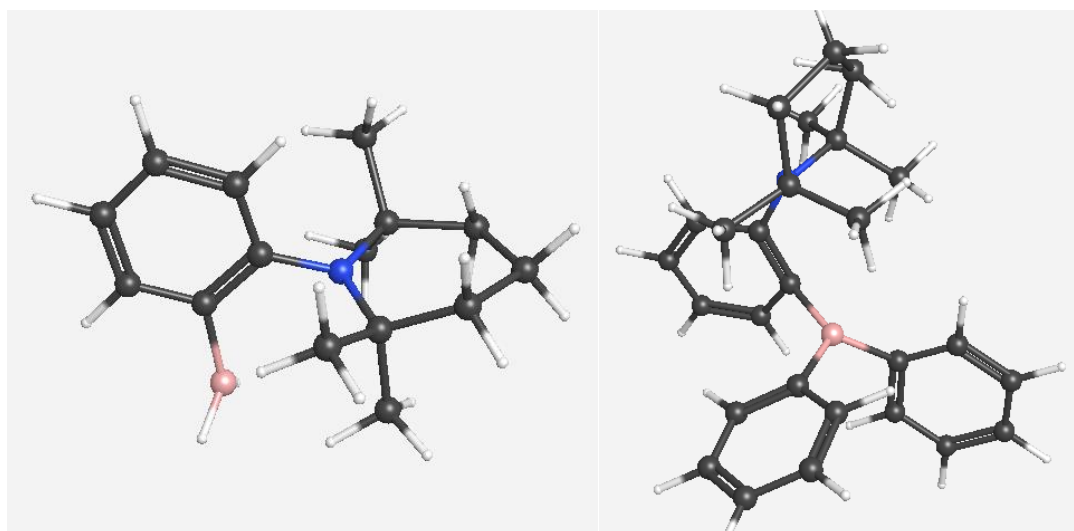
BorylCAT   Phenyl CAT
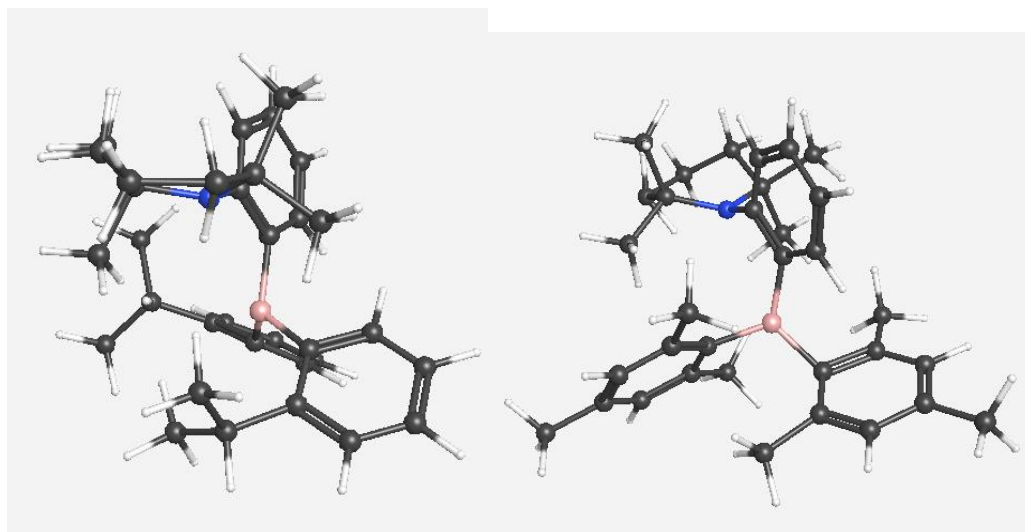
iPrPhenylCAT   MesitylCAT

Figure 4 Molecular Tweezers used in reference 17.

Perez et al[21] used ωB97X-D/6-311G(d,p) to study of the mechanism of hydrogen activation using some novel FLPs, and to analyse reactivity indices namely electronic chemical potential, hardness, electrophilicity and nucleophilicity followed by activation energies and finally catalytic activity of the hydrogenated FLPs. This showed that the activation of hydrogen via these FLP catalysts occurs with low activation energies via a polarized TS in one step.

Clark et al[22] have reported N-methylacridinium salts (Lewis acids) which form FLPs with weak bases like 2,6-lutidine and activate H_2, even in the presence of H_2O. Hydrogen ion affinities of these compounds have been computed at M06-2X/ 6-311G(d,p) level, using PCM model of DCM solvent. Computationally as well as experimentally these salts have proven to have an appropriate HIA to be useful as carbocationic Lewis acids in FLPs for H_2 activation and hydride transfer. Some of

these salts are also able to catalyse hydrosilylation of unhindered imines due to their low acidity towards hard Lewis bases and some can be used as cheap, air- and moisture-stable catalysts for dehydrosilylation of alcohols.

Rokob et al[23] have attempted to interpret the facile heterolytic cleavage of H_2 by FLPs with the help of two alternative reactivity models. Both models propose that the reaction takes place via reactive intermediates with preorganized acid/base partners, but the difference lies in the mode of action. An electron transfer (ET) model envisages hydrogen activation by synergistic electron donation processes involving simultaneous active centres and a bridging hydrogen. Electric field (EF) model on the other hand suggests the heterolytic bond cleavage by polarization due to strong EF present in the cavity of the reactive intermediates. The study was done using ωB97X-D functional. For geometry optimization, vibrational frequency determination, electronic structure analysis, and calculation of EFs, 6-311G(d,p) basis set was used, and for single-point energies 6-311++G(3df,3pd) basis set was employed. The results of the studies indicate that the electric-field-based reactivity model supersedes the previously published framework suggesting synergistic donor$\rightarrow\sigma$*(H_2) and σ(H_2)$\rightarrow$acceptor components as key elements.

Hounjet et al[24] have reported activation of H_2 by dialkyl ether/$B(C_6F_5)_3$ catalysts which have been utilized for hydrogenations of 1,1-diphenylethylene. To understand the mechanism, optimizations were carried out at TPSS-D3/def2-TZVP levels while single point calculations used B2PLYP-D3/def2-QZVP levels. Thermal corrections for free energy and ZPVE were added and solvation free energy corrections were performed using COSMO-RS model. It was found that the barrier to complex formation as result of H_2 activation is quite accessible which on dissociation leads to ions [$Et_2O\cdots H\cdots OEt_2$]$^+$ and [$HB(C_6F_5)_3$]$^-$ which leads to hydrogenation.

Greb et al[25] have studied metal free hydrogenation of various olefins utilizing FLPs which are able to activate H_2 at the lowest possible temperatures andutilized this reaction for metal free hydrogenation of various olefins. They employed B2PLYP-D3(BJ)/def2-TZVP//TPSS-D3(BJ)/def2-TZVP level of theory for calculation of energies. Solvent effects were studied COSMO-RS model of CH_2Cl_2. It was observed that, in the case of phosphines, both the Lewis pair adduct formation and the zwitterionic hydrogen activation is endergonic but reduction of the olefinic double bond is highly exergonic.

Guo et al[26] carried out DFT calculations to study the possibility of using FLPs as bifunctional metal-free dehydrogenation catalysts of ammonia-borane NH_3BH_3 (AB). N/B pair was chosen to explore the possibility that FLPs extract H_2 from AB. According to these authors, the mechanism involve two steps: firstly, AB is dehydrogenated by the N/B pair to form the NH/BH compound and NH_2BH_2 at low temperature; and in the next step H_2 is released from the NH/BH compound at 110 °C and the N/B pair regenerates. All calculations used B3LYP/6-31G(d,p) basis set. They utilized CPCM model of CH_2Cl_2 to include solvent effects. Calculations show that the dehydrogenation of AB by the N/B pair has the lowest free-energy barrier as compared to the uncatalyzed reaction which leads to a possibility that FLPs can act as bifunctional catalysts to release H_2 from AB under appropriate conditions.
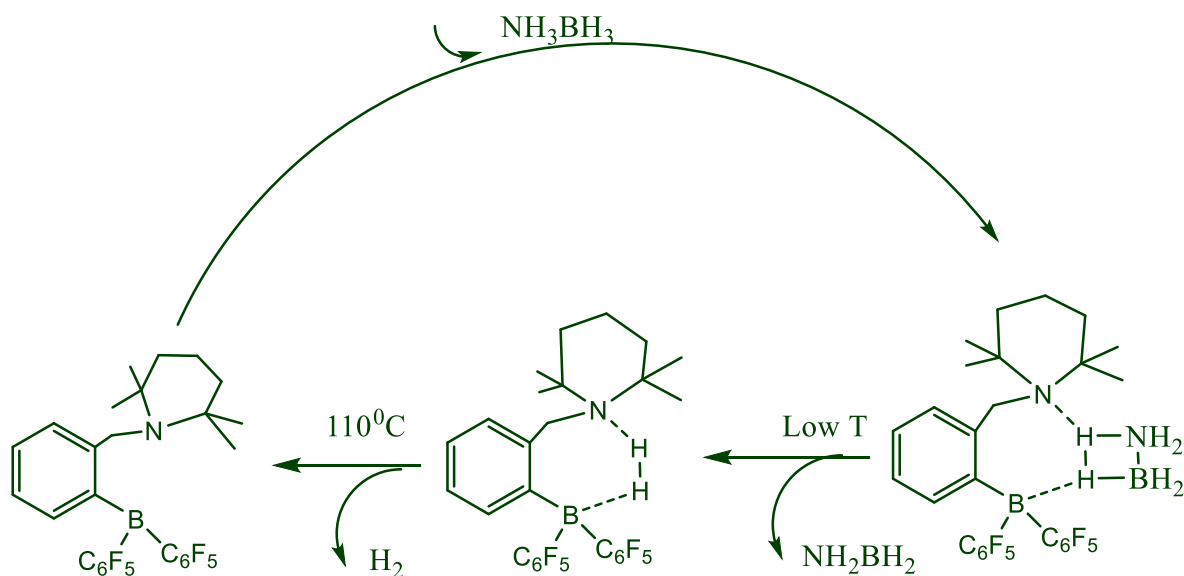
Scheme 3 Catalysis by metal free bifunctional dehydrogenation catalysts.

Rokob et al[27] have calculated the acid-base strength of non-linked and linked FLPs in order to analyse their ability to undergo heterolytic hydrogen splitting reactions with the help of quantum chemical calculations. The geometries of all species have been optimized using density functional theory at the M05-2X/6-31G(d) level, with IEF-PCM model of toluene. In the non-linked FLPs the calculated reaction free energies correlated well with the cumulative acid−base strengths as the products are very similar to them in structure, but the intramolecular FLPs systems lose less entropy when reacting with H_2 than the non-linked systems. As a consequence, lower acid−base strength and stabilization may be sufficient to produce reactive compounds.

Chase et al[28] investigated the capability of N-heterocyclic carbene (1,3-di-tert-butyl-1,3-imidazol-2-ylidene) in combination with $B(C_6F_5)_3$ to activate H_2 and N-H bonds in various amino boranes. The $[ItBuH][HB(C_6F_5)_3]$ salt was formed post-H_2 activation and various amido boranes by N-H bond activation. Molecules were optimized at HF

levelusing3-21G basis set or 6-31+G(d) basis set in which peripheral H atoms are treated by 3-21G basis set. Re-optimization of the structures was done by using two-layer ONIOM technique and the MPW1K functional. Single point energies were calculated using M06/6-311++G(d,p) level of theory. It has been observed that N-H bond activation depends on the type of amine substituents and if they are electron-donating then amino boranes are formed by the loss of C_6F_5H.

Ghara et al[29] have reported hydrogenation of CO_2 by a bridged B/N FLP. They have elucidated the two possible pathways for the reaction at M06-2X-D3/ 6-31G(d) level of theory. Energy decomposition analysis (EDA) along with the natural orbital for chemical valence (NOCV) method at BP86-D3/TZ2P// M06-2X-D3/6-31G(d) level of theory reveal that the HOMO of the FLP donates electron density to the LUMO of H_2, the HOMO of which in turn donates electron density to the LUMO of CO_2, and several occupied MOs of CO_2 donate electron density to the LUMO of FLP at the TS.
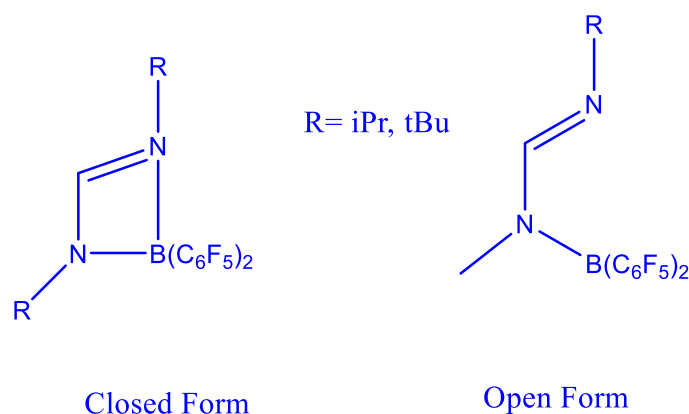
R= iPr, tBu

Closed Form   Open Form

Figure 5 Bridged B/N FLP used for hydrogenation of CO_2.

Zhuang et al[30] have investigated anti-aromaticity promoted H_2-activation in FLPs by ωB97x-D/cc-pVTZ calculation. Their studies have revealed that anti-diaromaticity

can reduce the barrier for heterolytic cleavage of H-H bond while the aromaticity of a compound makes it kinetically unfavourable.
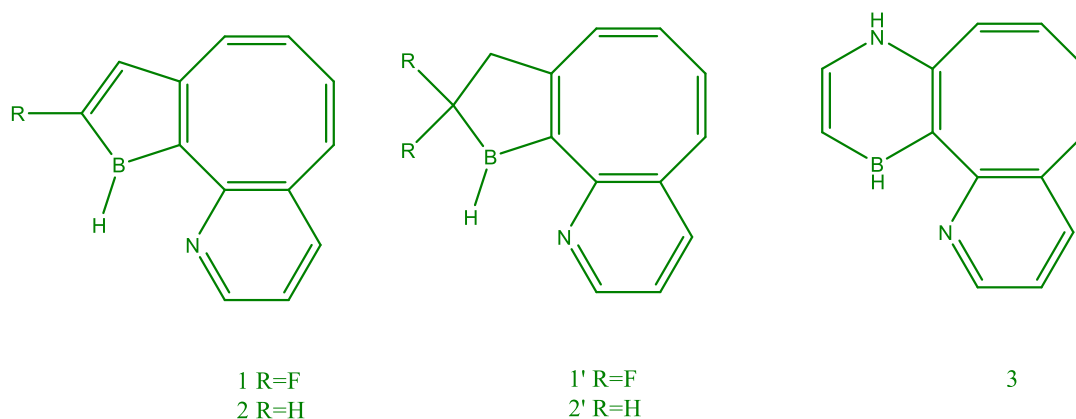

Figure 6 Molecules used for investigating anti-aromaticity promoted H2 activation in FLPs.

2.2 Silylation and Borylation by FLPs

Fasano et al[31] have reported a new family of Lewis acids i.e. N-Me-benzothiazolium salts which can undergo FLP type catalysis and are reported to activate Si-H σ bonds. M06-2X/6-311G(d,p) method and H/D scrambling experiments have been used to screen various Lewis acids by changing C2 aryl substituents in these cations. Studies revealed that the Lewis acidity of these cations towards hydride is comparable to triarylboranes but is lower towards hard Lewis bases. They have been found to be effective for Si-H bond activation and as catalysts for the (de)hydrosilylation of imines.

Cabrera-Trujillo et al[32] have reported geminal FLPs having a borole fragment that are able to activate small molecules like H_2, CO_2, CS_2, HCRCH, SiH_4 and CH_4toform

corresponding adducts .They utilized GIAO-B3LYP/def2-SVP//M06-2X/def2-SVP level of theory to understand the whole mechanism of activation. DFT indicates that a gain in aromaticity along the reaction co-ordinate is the key factor that enhances the activity of these FLPs.
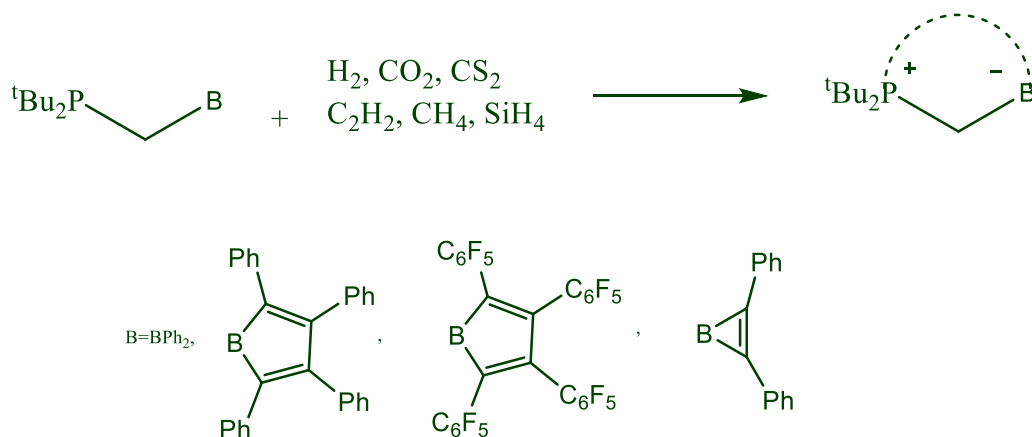
Scheme 4 Geminal FLPs having a borole fragment that activates small molecules

Rochette et al[33] have reported metal free borylation of thiols with the help of ambiphilic FLP $(NMe_2-C_6H_4-BH_2)_2$ which can be applied for one pot Michael additions from these reactants. $\omega B97XD/6-31++G(d,p)$ has been utilized to investigate the mechanism of the reaction, revealing that release of H_2 is the driving force in this reaction.

Lavergne et al[34] have reported two new ambiphilic aminoboranes, $(1-Pip-2-BH_2-C_6H_4)_2$ (Pip = piperidyl) and $(1-NEt_2-2-BH_2-C_6H_4)_2$ (NEt2 = diethylamino), FLPs that were used for borylation of heteroarenes. These new FLPs had less steric hindrance as compared to their previously synthesized analogues. $\omega B97XD/6-31+G(d,p)$ with SMD model of chloroform was utilized to study the energies of the species involved. The results of the computational studies reveal that these new catalysts were much

more effective than their older bulkier versions. Calculations also indicate that the rate determining step maybe the dissociation of the dimer and removal of hydrogen.
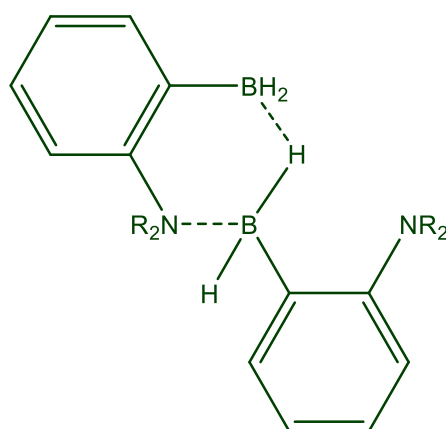

NR_2=piperidyl, NEt_2

Figure 7 AmbiphilicaminoboraneFLPs.

Tang et al[35] have reported 1,1-hydroboration of Ph_2CN_2 with $HB(C_6F_5)_2$ and have also isolated diazomethane–borane adduct involved. Semi-empirical (PBEh-3c) and DFT (DSD-BLYP/def2-TZVPP) methods were utilized, along with COSMO-RS solvent model, to study the reaction system. This method was employed to study not only the diazomethane-borane adduct but also an exergonic carbene adduct of $B(C_6F_5)_3$ formed by the loss of N_2 from the former. Calculations reveal that the 1,1-hydroboration proceeds via a concerted mechanism which involves H-atom migration from boron to the proximal nitrogen.

Ye et al[36] have utilized $Mes_2PCH_2CH_2B(C_6F_5)_2$ P/B FLPs and $HB(C_6F_5)_2$ to reduce carbon monoxide to give a FLP stabilized borane product which readily inserts sulfur dioxide. DFT analysis at the PW6B95-D3(BJ)/def2-QZVP and PBEh-3c level of theory, with COSMO-RS model of CH_2Cl_2, were utilized to study the mechanism of

insertion and the results indicate that insertion is initiated by opening of a B^2-O linkage rather than B^1-O linkage as former requires lower energy.

McQuilken et al[37] have synthesized new FLP isomers by hydroboration of bulky isocyanates with Piers borane ($HB(C_6F_5)_2$). These isomers are a new class, termed "confused FLPs" which are substrate free aminoboranes having short covalent N-B bond without any direct O-B interaction. This confused FLP isomer was studied using PW6B95-D3/def2-QZVP//PBEh-3c level of theory with COSMO-RS, model of fluorobenzene. The studies revealed that the confused FLP isomer has lower free energy as compared to its normal counterpart although this intramolecular arrangement places the sterically demanding $^{Ph2tBu}ArN$ moiety adjacent to the $B(C_6F_5)_2$ group. These compounds isomerize to the normal FLP isomer which then shows typical N/B FLP-type reactivity with isocyanates and isocyanides but the confused isomer itself does not lead to facile reactions with substrates like H_2 or CO_2. The plausible reason for this observation can be the kinetic and thermodynamic barriers between these isomers which may be required for substrate capture.
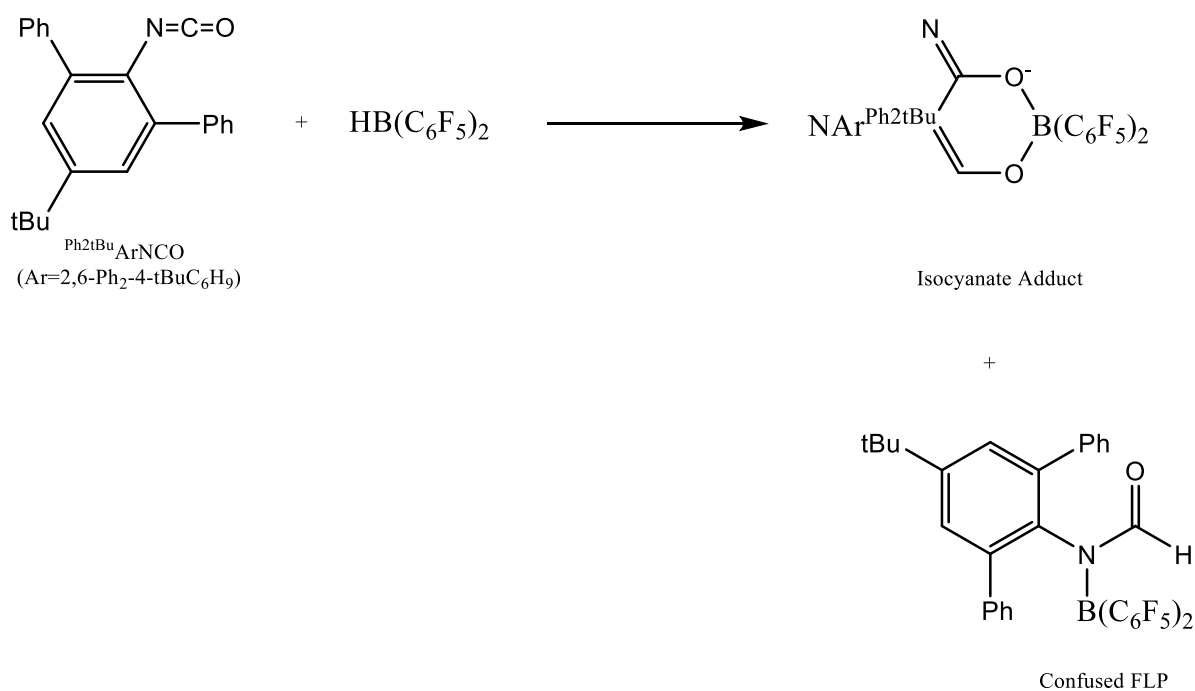
Scheme 5 Confused FLP from bulky isocyanates.

Ito and et al[38] have reported photo-promoted skeletal rearrangement reaction of phosphine–borane FLPs using M06-2X/6-31G(d,p) in simulated THF. They indicate that the reaction proceeds via zwitterionic boranorcaradiene intermediate leading to the formation of cyclic phosphonium borate compounds having a 1,4-phosphaborin framework.
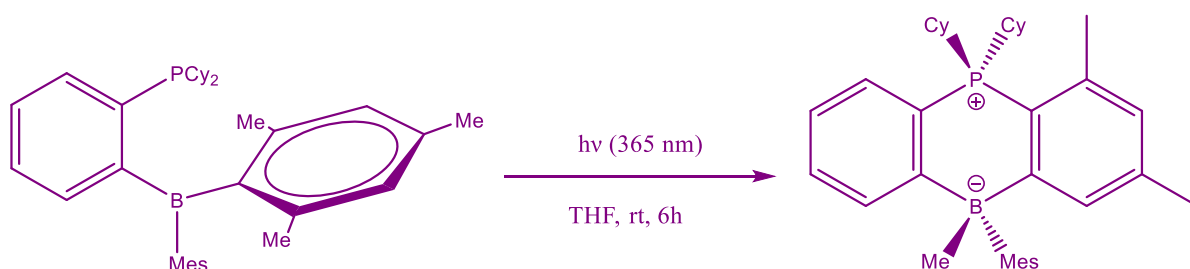
Scheme 6 Photo-promoted skeletal rearrangement reaction of phosphine-borane FLPs.

Bhattacharjee et. al.[39] have reported dimethylxanthene-derived B,P-FLP-catalyzed dehydrogenation of dimethylamine-borane (DMAB) using M06-2X/6-1++G(d,p)// M05-2X/BS1 with CPCM solvent. The studies reveal that the dehydrogenation proceed via B-H activation.
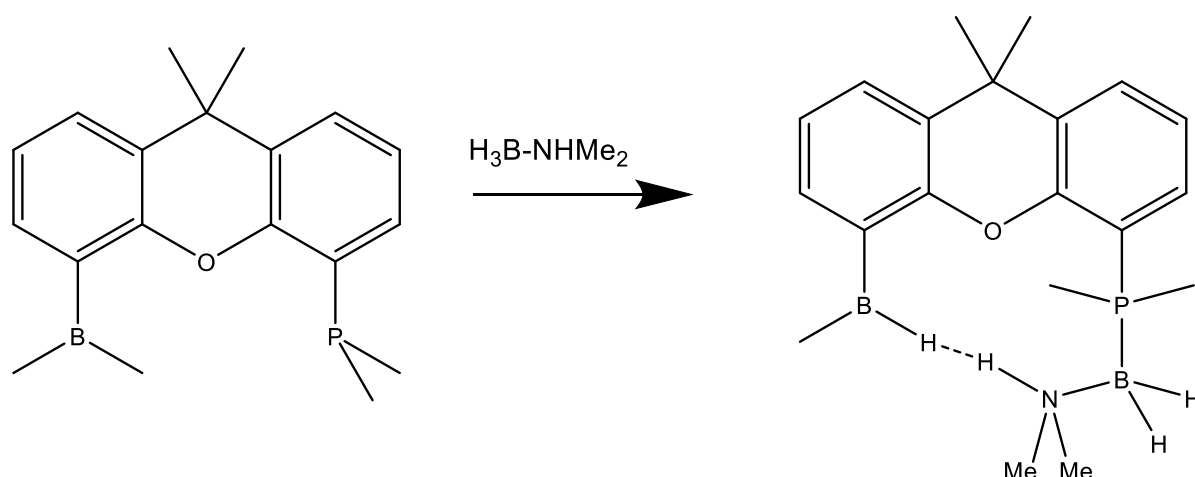
Scheme 7 Dehydrogenation of dimethylamine-borane (DMAB) by dimethylxanthine derived B,P-FLP

2.3 Polymerization and heterocycle formation by FLPs

Ottou et al[40] have shown that organic Lewis pairs involving tris(2,4,6-trimethoxyphenyl) phosphine (TTMPP) as a Lewis base, and N-(trimethylsilyl) bis(trifluoromethane sulfonyl) imide (Me$_3$SiNTf$_2$) as a Lewis acid can directly initiate the polymerization of methyl methacrylate (MMA) at room temperature in toluene. M06-2X/6-311++G(d,p)//M06-2X/6-31G(d,p) calculations with SMD model of toluene enabled them to choose the silane (Me$_3$SiNTf2 rather than Me$_3$SiOTf) capable of activating MMA, locating two FLP structures and a transition state connecting them. Theoretical calculations indicated the reaction to proceed via a FLP mediated

preorganized complex in which the phosphine interacted with activated MMA by multiple hydrogen bonds.

Boom *et. al.*[41] have reported four, five and six membered heterocycles by the reaction of phenyl-, mesityl-, tert-butyl and trimethylsilyl azide with the geminal FLP $tBu_2PCH_2BPh_2$. The mechanism was studied using wB97X-D/6-31G(d,p) calculations which reveal that all products proceed via a six-membered ring structure that is thermally stable with an N-phenyl group but rearranges when bulky substrates are used instead.

Zhu et al[42] have reported the formation of several heterocycles by addition reactions of POB based intramolecular FLPs ($R_2POBcat$) with small molecules like PhOH, CO_2, CS_2, PhNCO, MesCNO, O_2, 9,10-phenanthrenedione, and diazomethanes. These reactions were computationally monitored using TPSS-D3/def2-TZVP + COSMO(DCM) level of theory. It was found that these FLPs react readily despite perceived poor activity of the boron centre. This study also provided a facile route for diazomethane capture.

Rochette et al[43] have reported cleavage of a Csp^3-H bond in the α position of a nitrogen atom by ambiphilic FLP $(2-NMe_2-C_6H_4)_2BH$ to form a new N-B heterocycle. Computational studies were done using ωB97XD/6-31++G(d,p) with SMD model of benzene to understand the ability of FLP to activate the intramolecular Csp^3-H bond. Studies indicate that simultaneous release of H_2 along with product formation makes the thermodynamics favourable although the products are a little higher in energy.
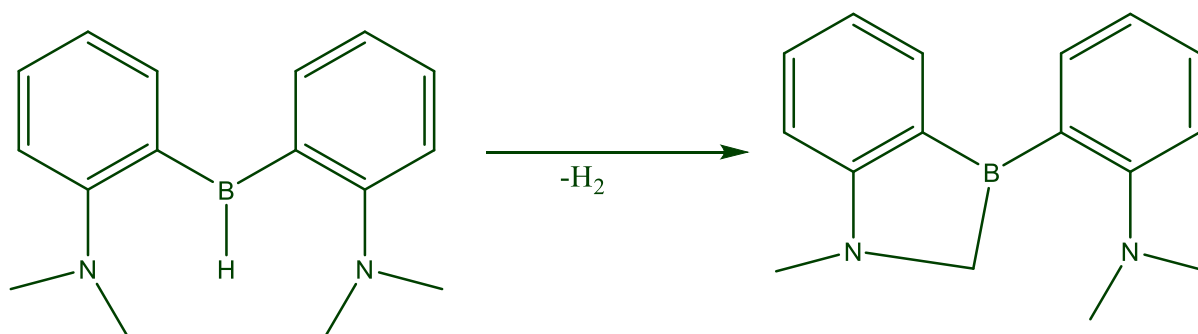
Scheme 8 Cleavage of a Csp^3-H bond by ambiphilic FLP.

2.4 Reaction of FLPs with small gaseous molecules

Sajid et al[44] have reported addition of SO_2 to the intermolecular FLP $^tBu_3P/B(C_6F_5)_3$, which leads to the formation of a zwitterionic adduct ($^tBu3P^+$–S(O)–OB$^-$(C_6F_5)$_3$) and six membered addition products in the case of intramolecular vicinal P/B FLPs. The reaction was investigated by B2PLYP-D3/def2-TZVP//TPSS-D3/def2-QZVPP with COSMO-RS solvation. The investigations revealed that [B]–O–(O)S–[P] conformational isomers (equatorial and axial) were slightly more stable than the hypothetical [B]–S(O)–O–[P] regioisomers (equatorial and axial) and that the kinetic barrier forFLP-SO$_2$ adduct formation was remarkably low.
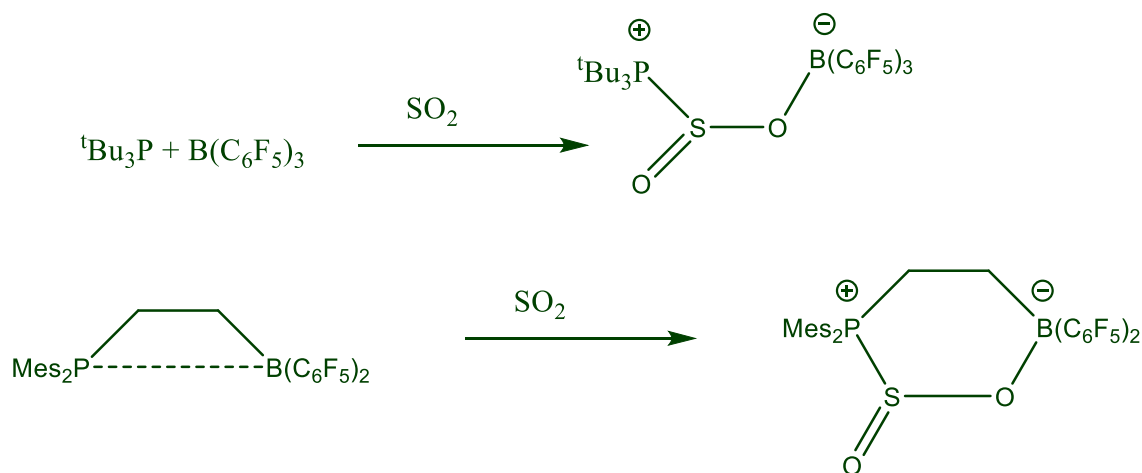
Scheme 9 Zwitterionic adducts formed by inter- and intramolecular FLPs.

Adenot et al[45] have reported FLPs having a guanidine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) skeleton and the substituted derivatives [TBD–SiR$_2$]$^+$ and TBD–BR$_2$. They have compared the ability of these FLPs to activate SO$_2$andCO$_2$. They employed M06/6-311+G(d) PCM solvent (Et$_2$O, pentane, benzene, acetonitrile, CH$_2$Cl$_2$ and pyridine) to study the activation by these FLPs. Experimental as well as theoretical studies have revealed that, although the adducts formed with SO$_2$ are similar to those with CO$_2$, they are thermodynamically more stable.

Wang et al[46] have reported some new macrocyclic dimers and trimers formed by carbonylated trifunctional P/B/B FLPs having some bulky aryl groups like Dmesp (2,6-dimesitylphenyl), Tipp (2,4,6-triisopropylphenyl) and Mes* (2,4,6-tri-tertbutylphenyl) at phosphorus. Structures involved in the study were optimized using PBEh-3c method, while PW6B95-D3/def2-TZVP was employed for single point calculations. Solvation free energies were computed with COSMO-RS method. DFT studies indicate that the key CO insertion step is exergonic, and that this eventually leads to macrocyclic ring closure.

Peuser et al[47] have synthesized formate complexes from the reaction of CO$_2$ and P/B FLPs. They utilized meta-GGA TPSS/def2-TZVP basis set along with D2 dispersion correction to study the activation of CO$_2$ by these FLPs. This revealed that the FLPs can successfully capture CO$_2$ and formate fragments, but also that the adducts cannot be derivatized because of their thermal instability.
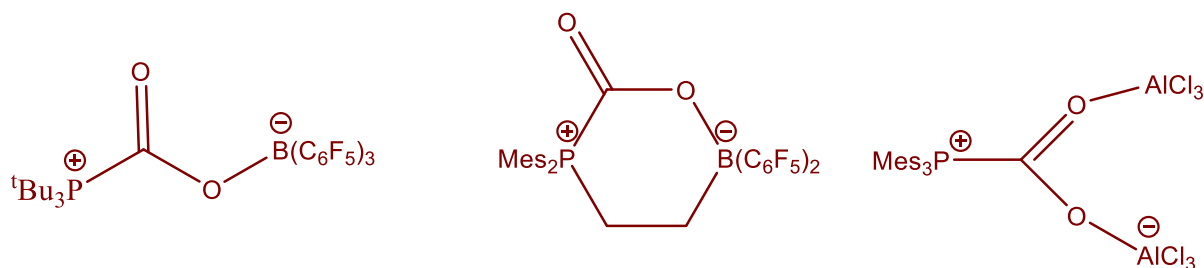
Figure 8 Complexes of FLP with CO_2.

Momming et al[48] have studied reversible and metal free binding of CO_2 with inter- and intra-molecular B/P FLPs to form carbonic acid derivatives. Both reactions were studied using B97-D/TZVPP', B2PLYP-D/TZVPP', and B2PLYP-D/QZVP(-g,-f) levels of theory and indicate that formation of P-C and B-O bonds is concerted and synchronous. The reaction is found to be exothermic overall.

Pereira et al[49] have done a kinetic and computational study of the reaction of NO with the intramolecular bridged P/B FLP *endo*-2-(dimesitylphosphino)-*exo*-3-bis(pentafluorophenyl)boryl-norbornane to give a persistent FLP-NO aminoxyl radical. Free energies were calculated at the TPSS-D3/def2-TZVP level along with thermal and solvent corrections in toluene, and also with PW6B95-D3 functional. Calculations show this FLP to have an unfavourable orientation for concerted reaction. The observed barrier is rationalized in terms of the reversible formation of a [B]-NO complex intermediate followed by a slower isomerization–ring closure step to the cyclic aminoxyl radical.

Sajid et al[50] have reported a novel intramolecular cyclohexylene-bridged P/B FLP [$Mes_2P-C_6H_{10}-B(C_6F_5)_2$] that reacts rapidly with NO to give the persistent FLP-NO aminoxyl radical which further undergoes a H-atom abstraction (HAA) reaction with 1,4-cyclohexadiene to give the diamagnetic FLP-NOH. According to the authors this

FLP-NO radical exhibits greater oxygen centred HAA/O-atom functionalization chemistry owing to significant polarization of the unpaired electron density toward the O. Optimizations were performed at the TPSS level using the basis set def2-TZVP and single-point calculations at the B2PLYP level. Both methods were enhanced with D3 dispersion correction. DFT calculations point towards the stability of the FLP-NO linkage.

Otten et al[51] have reported complexes containing PNNOB linkages from the reaction of N_2O with an equimolar mixture of ${}^tBu_3P$ and $B(C_6F_5)_3$. B3LYP/ 6-31G(d) level of theory was utilized to investigate the type of bonding in these complexes to show that the tBu_3P and $B(C_6F_5)_3$ fragments are arranged in a transoid geometry with respect to N=N bond.

Sun et al[52] have reported reductive cleavage of the CO by vicinal frustrated PH/BH Lewis pair. They have employed PW6B95-D3//TPSS-D3/def2-TZVP level of theory to understand the mechanism. They found that FLP reacted with CO in the presence of $B(C=F_5)_3$ to form a five-membered cyclic product by reductive coupling that further reacts with CO_2 to form another bicyclic compound.
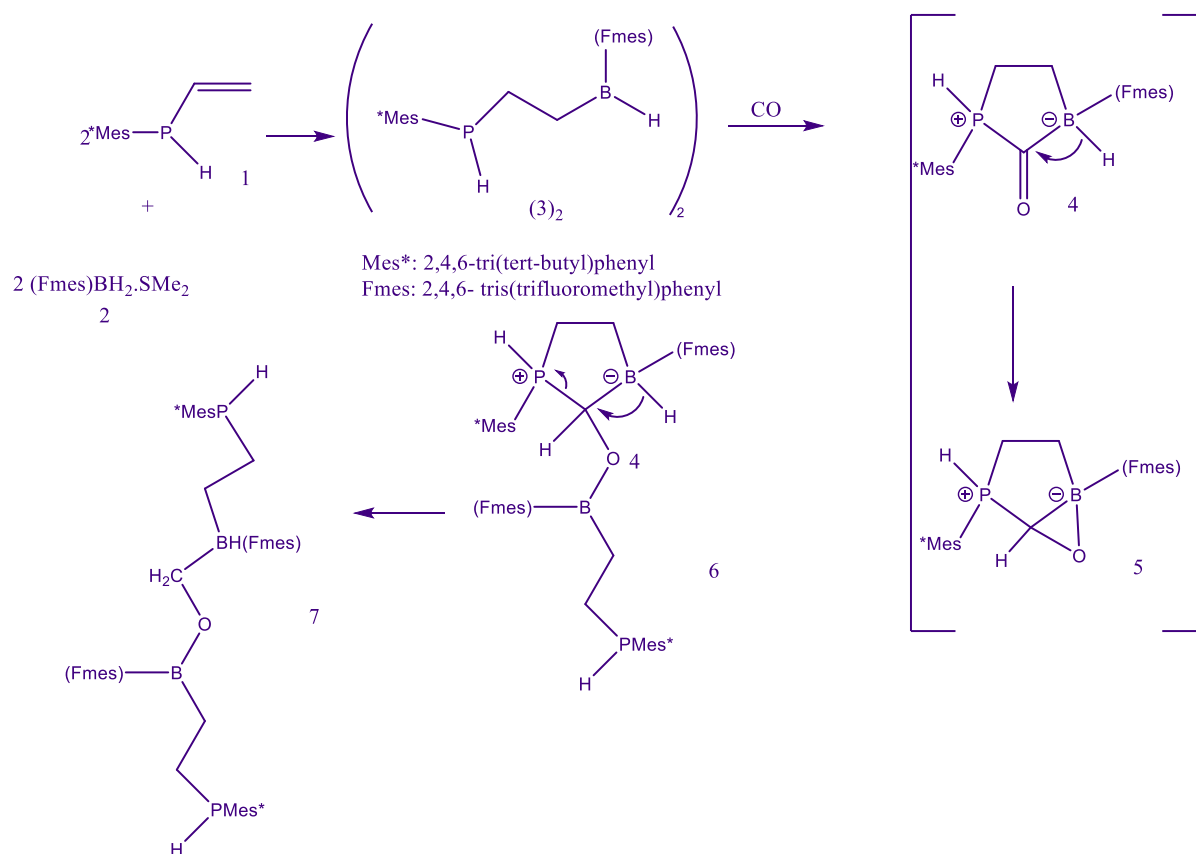
Scheme 10 Reductive cleavage of CO by vicinal frustrated PH/BH Lewis pair.

Briceno-Strocchia et al[53] have used FLP derived from $PhC(O)CF_3$ and a super-basic proazaphosphatrane (Verkade's base) to understand C-F activation using PBE1PBE/def2TZVPP//PBE1PBE/def2SVPP. They concluded that the FLPs have potential to intervene in the reactions of interest to form synthons that will further lead to a myriad of reactions.

Li et al[54] have studied secondary PH/BH functional groups of an active geminal frustrated Lewis Pair for carbon monoxide reduction and reactions with nitriles and isonitriles using PW6B95-D3//TPSS-D3/def2-TZVP+ COSMO-RS (pentane) level of theory. It was found that the mechanism in this case utilizes protolytic feature at

phosphorous and hydridic one at boron in sequential steps leading to reductive conversion of small added molecules.

Ghara et al[55] used M06-2X-D3 method with 6-31+G(d,p) and 6-311+G(d,p) basis sets in SMD model of benzene solvent to explore hydrogen activation and subsequent reaction with CO_2 by a novel set of intramolecular FLP based on pyridine substituted with boron ligands featuring B-X (X = O, N, S) interactions. They found low barriers to H_2 activation, and assigned the importance of specific orbital interactions and aromaticity by use of energy decomposition (EDA-NOCV) and nucleus independent chemical shift (NICS) analysis.

Rouf et al[56] used ωB97X-D with cc-pVDZ and cc-pVTZ in gas phase to screen intramolecular FLPs based around N-heterocyclic carbenes and tricoordinated boranes for activation of N2. They find that a suitably designed combination of borane and NHC results in low barrier (17 kcal/mol) for activation and stabilisation (-46 kcal/mol) of resulting FLP-N2 adduct.

Zhu[57,58] has utilized ωB97X-D/cc-pVTZ level of theory in gaseous phase to explore metal free dinitrogen activation by using carbon-boron FLP that is thermodynamically as well as kinetically more favourable. His studies revealed that aromaticity played an important part in stabilizing transition state as well as the product.

Mück-Lichtenfeld and Grimme[59] used TPSS-D3 with def2-TZVP in gas phase to study activation of H_2, Br_2 and CO_2 by model FLPs based on intermolecular combination of $BF_3/P(CH_3)_3$ and analogues thereof. They mapped out reaction coordinates for activation and examined pairwise and many-body effects, as well as deformation of electron density due to these interactions to obtain deeper insight into polarization effects on reactions.

Liu et al[60] used B3LYP and M06-2X with 6-31G(d) and 6-311++G(2d,p) in PCM model of benzene to examine the structure and energetics of a novel FLP based on boron-boron interaction. Interaction with and activation of small molecules was examined, indicating that activation is reversible at high temperatures.

Qu et al[61] used PW6B95-D3 and TPSS-D3 methods with TZVP basis set and COSMO model of THF to model FLP-catalysed reduction of CO_2 to high-value chemicals using hydroboranes. They show that strong O or N Lewis bases promote hydride transfer, but that these also bind tightly to reduced species, a process that can be hindered by modification of the Lewis acid centre.

Zhu and An[62] used M062X/6-31+G(d) with PCM model of THF to map out the reaction pathway of CO_2 capture by amidophosphoranes. They identify the importance of ring strain and *trans* influence in accessing this reaction under realistic conditions.

An and Zhu[63] used M06-2X with 6-31+G(d,p) in gas phase to compare reaction of P/N FLPs with CO_2 and CS_2. They show that the barrier to reaction is higher for CS_2 despite its weaker bond, an effect that is traced to the different bond polarization in this compared to C=O bonds.

Zhuang[64] et al used M06-2X with 6-31+G(d,p) in gas phase to explore the role of aromaticity in FLP-based CO_2 capture. They show that in suitably designed FLP systems, the stabilisation brought about by increased aromaticity in transition states can lead to significantly reduced barriers for reaction with CO_2. NICS measures of aromaticity were shown to have excellent correlations with such barriers.

## 2.5 Reaction of FLPs with alkenes and alkynes

Guo et al[65] have studied addition reactions of FLPs with olefins based on two different reaction systems: A three-component system involving a sterically demanding phosphane [P(tBu)$_3$], borane [B(C$_6$F$_5$)$_3$], and ethylene and a two-component system involving an olefin derivative of the phosphane [CH$_2$=CH–(CH$_2$)$_3$P(tBu)$_2$] and B(C$_6$F$_5$)$_3$. The details of these mechanisms were calculated using B3LYP/6-311++G(d,p) for C=C and H atoms bound to C=C, B, and P, and those carbon atoms bonded to B or P, and 6-31G basis set for the rest of atoms. Results of the calculations reveal that in a two-component system the reaction proceeds in a concerted manner while in a three-component system reaction is initiated by the weak association of B(C$_6$F$_5$)$_3$ with ethylene leading to the formation of a transient species which is then followed by a transition state similar to the concerted mechanism of two-component system. Studies also indicate that in a two-component reaction the CH$_2$=CH group and in a three-component reaction C$_2$H$_4$ may act as bridges for electron transfer from the Lewis base centre P to the Lewis acid centre B.

Iashin et al[66] have reported a new FLP formed by reaction between 1,2,2,6,6-pentamethylpiperidine (PMP) and boron trifluoride unit. This pair reacts with terminal acetylenes to give the products of C(sp)-H borylation as tetra- or trialkynylboron compounds and pentamethylpiperidinium tetrafluoroborate. Details of the mechanism were investigated using wB97X-D/6-311G(d,p) basis set. Since PMP shows efficient C-H borylation and can also be readily recovered, it represents an atom-efficient approach for the synthesis of new organofluoroborate compounds.

Chernichenko et al[67] have utilized computational techniques to elucidate the mechanism for chemoselective and stereoselective hydrogenation of internal alkynes into the respective cis-alkenes under mild conditions using ansa-aminohydroborane

as a catalyst. ωB97X-D 6-311G(d,p) was used for geometry optimizations while 6-311++G(3df,3pd) basis set was utilized for single point energy calculations. Calculations along with the experimental results have revealed the mechanism to consist of three discrete steps: hydroboration of alkyne (substrate binding), followed by heterolytic H_2 cleavage to formvinylborane, and finally intramolecular protodeborylation of the vinyl substituent which recovers catalyst and releases the cis-alkene.

Metal free cis selective hydrogenation of alkynes catalyzed by a boroxypyridine has been studied by Wech et al[68] employing revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c within SMD model of n-Hexane. Their studies revealed that boroxypryirdine activates the hydrogen just like intramolecular FLPs but there is difference in the coordination with hydrogen which leads to the dissociation of pryridone hydroborane complex subsequently leading to the hydroboration of alkyne.
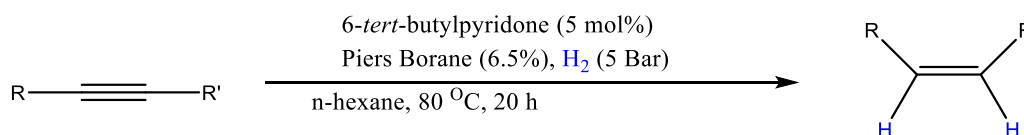
Scheme 11 *cis* selective hydrogenation of alkynes by boroxypyridine.

Ghara et al[69] have investigated cycloaddition of ethylene, cyanoethylene, and propylene to a five-membered P/B frustrated Lewis pair (FLP) using M06-2X-D3/def2-SVP. They have found that all these reactions are concerted and highly energetically favourable.
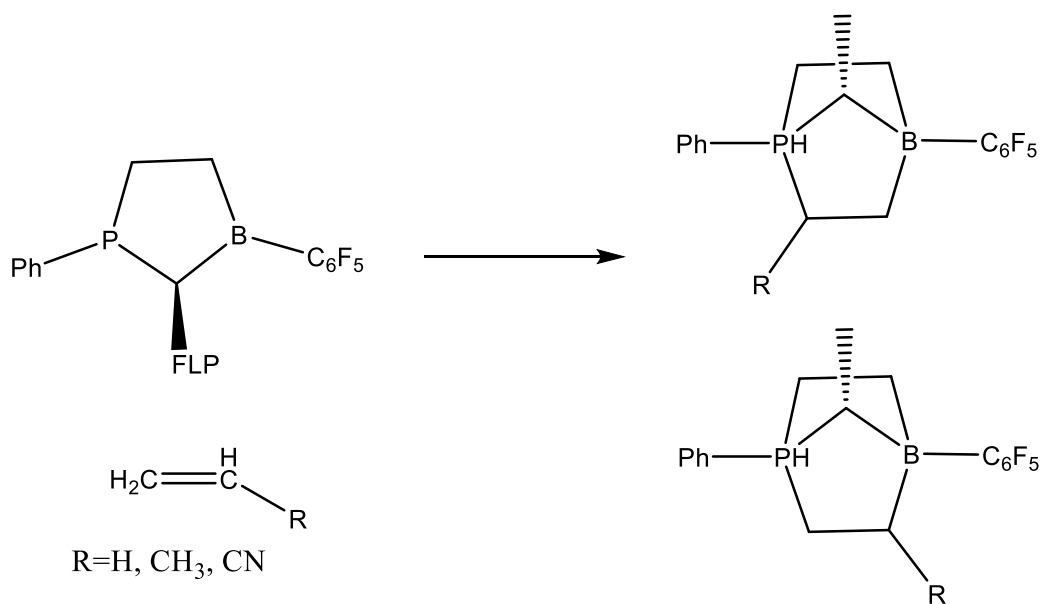
Scheme 12 Cycloaddition of ethylene, cyanoethylene and propylene to P/B FLP

2.6 Regio-selectivity, steric effects, London dispersion and Covalent Interactions in FLPs

Using M062X/6-311+G(d), Liu et al[70] have utilized electrostatic force to predict regioselectivity and steric force to stereochemical inclination of numerous chemical processes, including FLPs. It has been seen that in the case of electrophilic attack the electrostatic force is very less at the reaction centre thus making electron donation easier while it is just the converse in case of nucleophilic attack. Steric forces are smaller on the preferred side (side of the reaction centre with less bulky groups) of the substrates.

Bistoni et al[71] have done detailed theoretical investigations on a series of classical adducts as well as FLPs formed by tris(pentafluorophenyl)borane and various substituents like phosphines, carbenes and amines to understand the role of London dispersion in these compounds. For this study they have utilized domain based local pair natural orbital coupled-cluster (DLPNO-CCSD(T)) method along with Local Energy Decomposition (LED) analysis. Studies have confirmed that London dispersion governs the stability in classical adducts as well as FLPs. It has been found that by increasing the bulk near the basic centre this effect is augmented, but steric hindrance increases the energy required to bring the fragments close to one another for interaction. Hence tuning is required by choosing the substituents carefully.

Wiegand et al[72] have studied covalent interactions between the Lewis acid and Lewis base functionalities in a series of FLPs composed of substituted vinylene linked intramolecular phosphane–borane adducts using solid-state nuclear magnetic resonance techniques and DFT calculations. Geometry optimizations, starting with the crystal structure if available, were performed using TPSS-D3/def2-TZVP basis set. Calculation of electric field gradients were performed using B97-D, indicating complete suppression of covalent interactions between the Lewis acid and base centres may not be present. In fact, they suggest that the residual electron density between the reaction centres may be a necessary requirement for the typical FLP behaviour.

2.7 Reactions by some novel boron compounds

Clarke et al[73] have reported the formation of some novel di- and tri-azaborines formed by insertion of a NHC-carbene into the B-H bond of 9-borabicyclo-[3.3.1]nonane, followed by ring expansion. M06-2X/6-311-G(d,p) with PCM model for THF have been used to probe the regioselectivity observed in this mechanism. It has been found that the initial migration of hydride from B to carbene constitutes the rate determining step. It is suggested that the regioselectivity seen in this mechanism may be attributed to the energy difference between alkyl migration and ring expansion step which favours migration in ylide formed from attack of N1.

Devillard et al[74] have utilized the intramolecular pyridine-stabilized silylium hydroborate ion-pair, formed by reaction between tertiary silane 2-[(diphenylsilyl)methyl]-6-methylpyridine and tris(pentafluorophenyl)borane (BCF), to cleave the CO bond in carbon monoxide. Cleavage leads to the formation of a complex (B-(diarylmethyl)-B-aryl-boryloxysilane) with double $C-C_{sp2}$ bond formation which further reacts with pinacol to form bis(pentafluorophenyl)-methane. BP86-D3/def2-TZVP studies reveal that deoxygenation of CO leading to the formation of new C-C bonds is possible without using transition metals.

Thakur et al[75] have reported an unusual N-heterocyclic carbene (aNHC), 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenylimidazol-5-ylidene which along with $B(C_6F_5)_3$ is capable of activating CO_2 and N_2O more effectively than sterically demanding nNHC/$B(C_6F_5)_3$ system containing 1,3-di-tert-butylimidazolin-2-ylidene. aNHC/$B(C_6F_5)_3$ reagent system is also capable of effective ring opening in tetrahydrofuran and tetrahydrothiophene. M05-2X/6-311G(d,p) calculations revealed

that the adduct is energetically much less stable than the products it forms afterwards. It is envisaged that this may indeed be the driving for the reaction.

Zeng et al[76] have explored pincer-type phosphorus compounds for the hydrogenation of carbon dioxide with ammonia−borane. Geometry optimization was done utilizing B3PW91 functional while electronic energies were computed by ONIOM(CCSD-(T):MP2) or CCSD(T). Studies reveal that these compounds are quite efficient for hydrogenation which proceeds via phosphorus-ligand cooperative catalysis. Further, the activity of the catalyst is more if the phosphorus has NNN ligand rather than ONO ligand.

Von Grotthuss et al[77] have reported a new class of molecules prepared by injecting two electrons to 9,10-dihydro-9,10-diboraanthracene (DBA) which show ambiphilic behaviour like metals towards hydrogen. B2GP-PLYP-D/CBS(T,Q)// PBE0-D/6-31+G(d,p) level of theory with SMD solvation have been utilized to investigate the intricacies of the mechanism. Studies have revealed that this new class of MGA's (main group ambiphiles) undergo homolytic cleavage under mild conditions, like transition metals. Li_2[DBA]/H_2 system has been shown to successfully convert Me_3SiCl into Me_3SiH.

Ghara et al[78] used M06-2X-D3 method with TZVP and related basis sets to examine the binding of noble gases to gold-FLP complexes, reporting substantial binding energies of Ar to Rn in the range 6 to 13 kcal/mol. Energy decomposition, electron density and bond order analysis indicated significant charge transfer and orbital contributions to binding.

3. Summary

Frustrated Lewis pair chemistry has come a long way from initial metal free dihydrogenation to interesting new reactions in various dimensions of chemistry. Applications in catalysis are particularly prevalent in the field of hydrogenation of imines, nitriles and aziridines, asymmetric hydrosilylation, hydrogenation of alkynes and borylations.

Quantum chemical methods play an important role in understanding and predicting structures, properties and reaction mechanisms of these fascinating molecules. DFT is the method of choice in most studies, with many using dispersion correction, range-separation and/or meta-GGA approaches, with M06-2X, wB97x-D and TPSS functionals particularly evident. *Ab initio* methods such as CCSD(T) and MP2 are rarer, while modern semi-empirical methods like PBEh-3c are gaining in popularity. A minimum basis set size of split-valence with a single set of polarization functions is recommended, as is a model of solvation using SMD, PCM or COSMO-RS methods.

DFT has been widely used to explore the frustrated nature of the Lewis pair, and the Lewis acidity, in terms of hydride ion affinity, in FLPs, allowing rational design of catalysts for specific applications. A great deal of focus has been placed on establishing reaction pathways for activation and subsequent reaction in hydrogenation, hydroboration and hydrosilylation. While specific details vary, a broad pattern emerges of slightly endothermic activation followed by exothermic reaction with a suitable substrate. Other applications to a wide range of FLP chemistry demonstrate the utility of quantum chemistry in complementing experimental studies, and promise rich future for this area of research.

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