

Review

Activation of Small Molecules and Hydrogenation of CO₂ Catalyzed by Frustrated Lewis Pairs

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Abstract: The chemistry of frustrated Lewis pair (FLP) is widely explored in the activation of small molecules, the hydrogenation of CO₂, and unsaturated organic species. A survey of several experimental works on the activation of small molecules by FLPs and the related mechanistic insights into their reactivity from electronic structure theory calculation are provided in the present review, along with the catalytic hydrogenation of CO₂. The mechanistic insight into H₂ activation is thoroughly discussed, which may provide a guideline to design more efficient FLP for H₂ activation. FLPs can activate other small molecules like, CO, NO, CO₂, SO₂, N₂O, alkenes, alkynes, etc. by cooperative action of the Lewis centers of FLPs, as revealed by several computational analyses. The activation barrier of H₂ and other small molecules by the FLP can be decreased by utilizing the aromaticity criterion in the FLP as demonstrated by the nucleus independent chemical shift (NICS) analysis. The term boron-ligand cooperation (BLC), which is analogous to the metal-ligand cooperation (MLC), is invoked to describe a distinct class of reactivity of some specific FLPs towards H₂ activation.

Keywords: frustrated Lewis pair; catalysis; hydrogen activation; hydrogenation of CO₂; boron-ligand cooperation



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1. Introduction

The application of catalysts in expediting the rate of chemical reactions has very high industrial importance. Most chemical reactions, especially hydrogenation reactions [1–3], rely on transition metal (TM) compounds for the catalytic activity. TM coordination complexes acting as homogenous catalysts can be very easily monitored in the solution phase. They can produce higher chemo- and stereoselectivity, making them industrially important especially in the domains of medicine and food. The discrete efficiency of a specific TM complex to direct such transformations is a direct consequence of the presence of partially filled *d*-orbitals in their valence shell (i.e., a set of electrophilic and nucleophilic frontier orbitals with low energy difference). This allows them to simultaneously interact with an incoming substrate with both the orbitals, hence activating it in the process. Since TMs are associated with high levels of toxicity, low availability, and high cost, efforts are being made towards the use of TM-free catalysts in an attempt to remove these hurdles [4,5]. It was seen that the chemistry of the main group elements often resembles that of the TMs in terms of their structure and bond characteristics and hence, can react with small molecules such as, CO, H₂, C₂H₄, NH₃, etc. under normal conditions [6]. Some examples include the use of singlet carbene (R₂C:) [7,8] in the activation of hydrogen and ammonia. The mechanism of the activation process is observed to be similar to that in the oxidative addition of H₂ to the TM. In other words, two electron transfer (ET) processes are functioning between the lone pair of electrons and the empty *p* orbital of carbene with

the antibonding (σ^*) and the bonding (σ) orbitals of H_2 respectively. Heavier congeners of carbene such as silylene [9], germylene [10], stanylene [11], and higher analogs of acetylene, such as $ArGeGeAr$ [12] and $ArSnSnAr$ [13], are also found to activate H_2 .

Another class of promising catalysts, known as the frustrated Lewis pair (FLP), is introduced based on the idea that a pair of bulky Lewis acid (LA) and Lewis base (LB) cannot form adduct due to steric repulsion. An alternative reaction channel is opened as a result of this steric inhibition produced by the aforementioned FLP [14]. Since the discovery of FLPs by Stephan et al., a variety of combinations of LAs and LBs has been reported both as non-linked (also known as intermolecular FLP) and linked (intramolecular FLP) systems. The LA component includes, from neutral boranes and alanes, to cationic silyliums, phosphoniums, borenium, carbocations, titanocenes, zirconocenes, and others [15–23]. Conversely, the LB component includes various amines, imines, pyridines, phosphines, carbenes, ethers, carbanions, silylenes, and the like [24–29]. Structures of some inter- and intramolecular FLPs, along with their important roles, are listed in Tables 1 and 2. A comparison of energetics for H_2 activation by TM and FLPs is provided in Table 3 to better understand the effectiveness of FLPs in metal-free H_2 activation. FLPs act as good catalyzing agents in reactions involving activation of small molecules such as, CO , CO_2 , N_2O , NO , SO_2 , alkenes, alkynes, catalytic hydrogenation, and so on [30–34], all of which are discussed later in this article. H_2 activation by bridged P/B FLPs, and the role of boron-ligand cooperation (BLC) in activating the same, is explored. Simultaneous activation of H_2 and CO_2 molecules is also demonstrated in this review. The B–X (X = O, N, S) bond of the FLPs plays a crucial role in activating the molecular hydrogen, where it changes from B^+-X^- electron-sharing type of interaction to $B\leftarrow X$ dative bond upon H_2 activation.

Table 1. Structures of the Lewis acid and Lewis base units of some intermolecular FLPs and their roles.

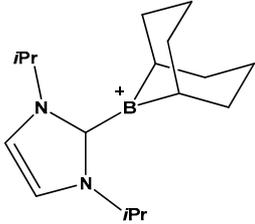
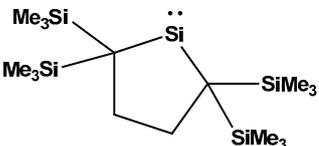
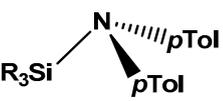
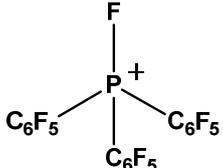
Serial No.	Intermolecular FLP		Small Molecules Activated	Reference Number
	Donor	Acceptor		
1	$PtBu_3$		H_2	[15]
2		$(Me_5C_6)_3Si^+$	H_2	[16]
3	$PtBu_3$	$Al(C_6F_5)_3$	H_2 , Alkyne	[17,35]
4			H_2	[18]

Table 1. Cont.

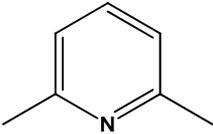
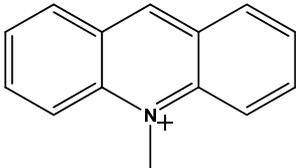
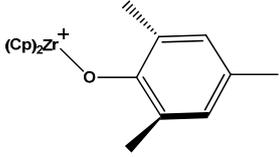
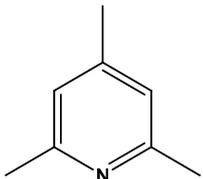
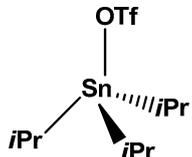
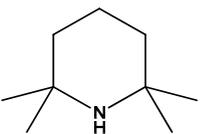
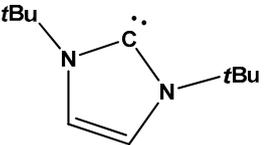
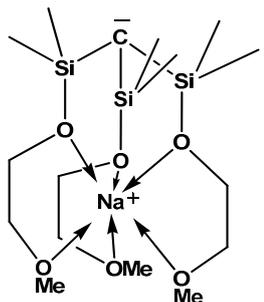
Serial No.	Intermolecular FLP	Small Molecules Activated	Reference Number
5			H ₂ [19]
6	PtBu ₃		H ₂ , CO ₂ , THF, Phenylacetylene [20]
7			H ₂ [21]
8		B(C ₆ F ₅) ₃	H ₂ [24]
9		B(C ₆ F ₅) ₃	H ₂ [25]
10		BPh ₃	H ₂ [28]
11	PtBu ₃	B(C ₆ F ₅) ₃	H ₂ , N ₂ O, Ethylene, Alkyne, 1,3-Diene, B-H bond [35–40]

Table 2. Structures of some intramolecular FLPs and their role.

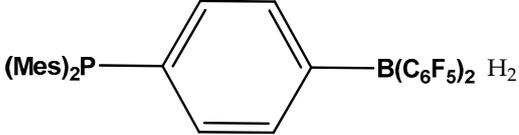
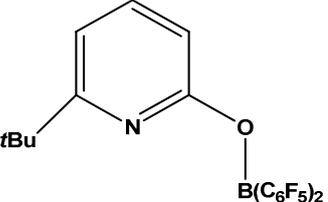
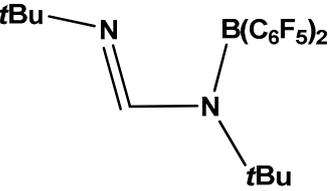
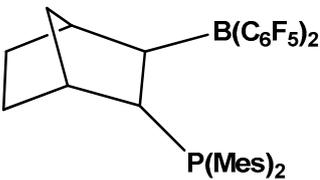
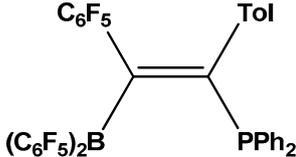
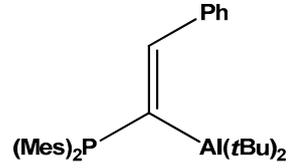
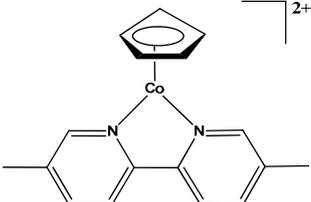
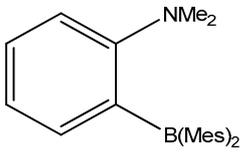
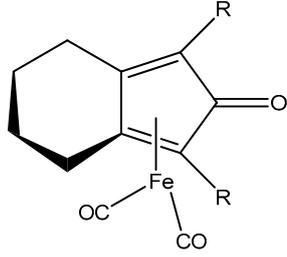
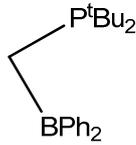
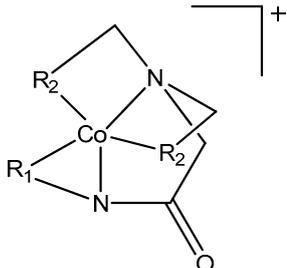
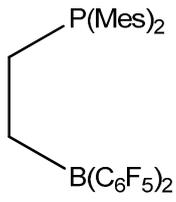
Serial No.	Intramolecular FLP	Small Molecules Activated	Reference Number
1		H ₂	[14]
2		H ₂	[41]
3		CO, CO ₂ , RNC, PhCCH, MeCN	[42]
4		SO ₂ , NO, Olefin, N-Sulfinylamine	[43–46]
5		CO	[47]
6		RNC	[48]
7		Acetylene, CO ₂	[49]

Table 3. A comparison of energetics for H₂ activation by TM and FLPs.

H ₂ Cleavage by Transition Metal		H ₂ Cleavage by FLP	
Complex	Free Energy Barrier of H ₂ Activation	FLP	Free Energy Barrier of H ₂ Activation
	16.8 Kcal/mol at SMD(Water)-M06/6-311++G(2df,p)//M06/6-31+G(d,p) level		21.7 Kcal/mol at SMD(Benzene)-ωB97XD/6-31++G(d,p) level
	32.3 Kcal/mol at SMD(Methanol)-M06/6-31++G(d,p) level		28.9 Kcal/mol at PCM(toluene)-M06-2X/def2-TZVP//M06-2X/def2-SVP level
	5.9 Kcal/mol at SMD(Water)-M06/6-31++G(d,p) level		20.7 Kcal/mol at PCM(CH2Cl2)-B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) level

2. H₂ Activation by FLPs

In 2006, Stephan synthesized an ambiphilic molecule and zwitterionic phosphonium hydridoborate [Mes₂HPC₆F₄BH(C₆F₅)₂], where P center acts as the LB and the B center as the LA. On heating at 150 °C, it releases H₂ gas producing the ambiphilic phosphinoborane [Mes₂PC₆F₄B(C₆F₅)₂], which in turn forms the original phosphonium hydridoborate compound upon heating with H₂ at room temperature [50]. This entire process is essentially the heterolytic cleavage of H₂ facilitated by phosphinoborane. A similar process was tried in 2007 with the help of tris-(tertiarybutyl) phosphine (*t*Bu₃P) and tris-(pentafluorophenyl) borane (BCF) [36].

There are a few mechanistic paths of H₂ activation by FLPs reported in the literature, proposed by various scientists over the years. A mechanistic path, proposed by Welch and Stephan in 2007, describes an initial polarization of H₂ occurring as a result of a side-on interaction between H₂ and the LA (B(C₆F₅)₃) forming the adduct, H₂ ... B(C₆F₅)₃ [36,51], from which a phosphine LB (*P*tBu₃) abstracts a proton (mechanism shown in Figure 1a). Unfortunately, no such adduct is detected experimentally even at higher H₂ pressure (4 atm). Although some computational reports showed the existence of BH₅, where H₂ is weakly bound to BH₃ via an η² binding mode [52]. Alternatively, H₂ may initially interact with the LB followed by the hydride abstraction by the LA. Again, no such H₂ ... LB adduct is detected experimentally. In 2008, another significant mechanistic proposal put forward by Rokob and co-workers [53], on the activation of molecular hydrogen by a phosphine/borane FLP, reinvestigated the interactions of H₂ with B(C₆F₅)₃ and *P*tBu₃ separately. Both are found to be repulsive when the components are within a certain distance. From these results, they concluded that another reaction channel should exist for

the reactivity of the phosphine/borane pair towards H_2 . They proposed that the LA and LB components of an FLP are preorganized together to form an “encounter complex” (EC) [54] (Figure 1b), which is stabilized by weak non-covalent interactions (C–H ... F hydrogen bond and dispersion interactions). The role of weak dispersion interaction to stabilize the EC was also suggested from NMR spectroscopy [55]. The molecular dynamics simulation study further confirmed the existence of the EC [56]. Afterward, the H_2 molecule enters into the reactive pocket of the EC and interacts with both the active centers of the FLP. Now, the Lewis basic phosphorus center of tBu_3P donates the lone pair of electron density into the anti-bonding orbital of H_2 . Conversely, the Lewis acidic B center of $B(C_6F_5)_3$ accepts electron density into its empty p-orbital from the bonding orbital of H_2 . As the reaction progresses, this synergistic ET mechanism leads to the continuous weakening of the H–H bond, which ultimately breaks to form P–H and B–H bonds. This mechanism of H_2 activation by FLP is termed as the ET model [57] (Figure 2).

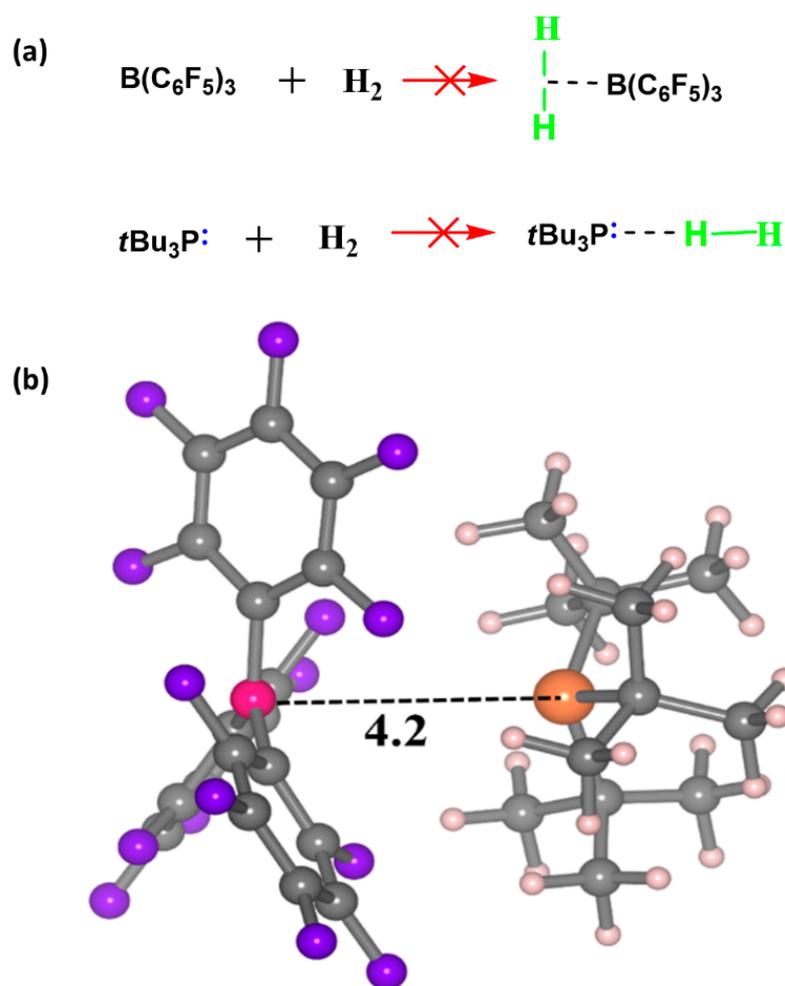


Figure 1. (a) Two proposed intermediates for the reactivity of $B(C_6F_5)_3$ and tBu_3P towards H_2 . (b) Structure of an “encounter complex” formed by a combination of $B(C_6F_5)_3$ and $PtBu_3$ pair, where the distance between boron (pink) and phosphorous (yellow) centers are given in angstrom.

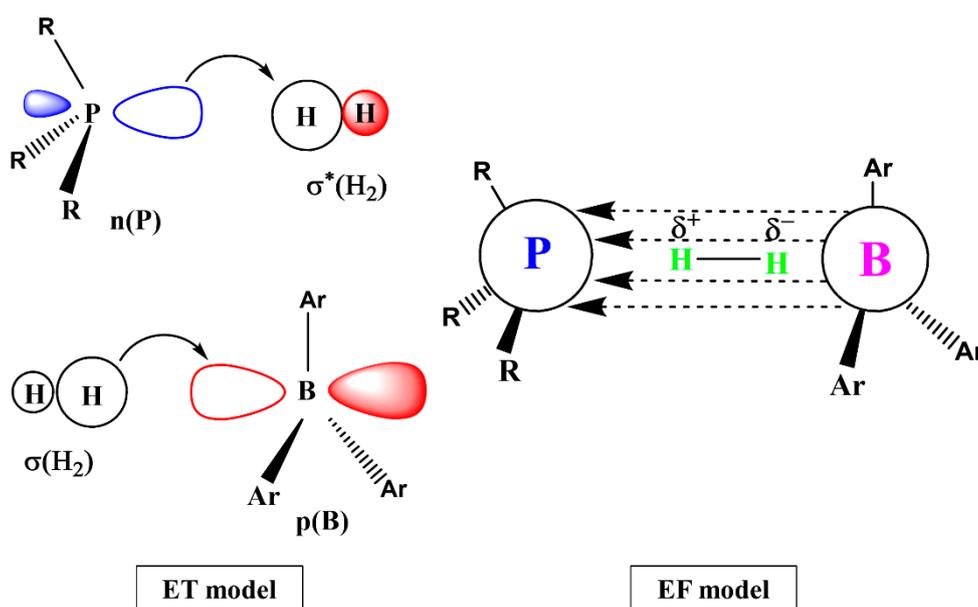


Figure 2. Schematic figure of the electron transfer (ET) and electric field (EF) model-based interpretations of FLP-mediated H_2 activation.

In 2010, Grimme et al. [58] proposed a completely different explanation of the H_2 activation mechanism by FLP. They suggested that the EC constructed from bulky LA and LB creates an electric field (EF) inside its cavity. On entering this cavity, the H_2 molecule becomes polarized by the EF and undergoes a heterolytic cleavage. Therefore, while the entrance of H_2 into the FLP cavity is an energy-demanding process, its splitting happens in a barrierless way. This mechanism of H_2 activation by FLP is termed the EF model (Figure 2). By re-investigating the mechanism, Rokob et al. predicted a higher acceptance of the ET model compared to the EF model [59]. Recently, Skara et al. [60] reexamined both the ET and EF models of H_2 activation and clarified their applicability in two distinct cases. The former is better suited for high energy transition state (TS), having a longer H-H and smaller LB $\cdots H_2$ distance (also known as geometrically “late”). In this case, the electron donation from the Lewis basic center to the $\sigma^*(H_2)$ orbital is predominant. The EF model, conversely, is applicable for low energy TS (geometrically “early”) with smaller H-H separation and longer LB $\cdots H_2$ and LA $\cdots H_2$ distances. End-on LA $\cdots H_2$ interaction is predominant in this case.

Moreover, the kinetics and thermodynamic aspects of H_2 activation are also investigated and reported in the literature. In particular, a theoretical study performed by Rokob et al. [61] demonstrates the H_2 activation by FLP as the overall result of five hypothetical steps as depicted in Figure 3, which includes separating the LA-LB pair, heterolytically cleaving the molecular H_2 , proton abstraction by LB, hydride abstraction by LA, and stabilization by pairing $[LBH]^+$ and $[LAH]^-$ ions. The type of FLP is so chosen so that the LA-LB separation energy (ΔG_{sep}) is low in the first step. The second step, i.e., the heterolytic cleavage of H_2 into proton and hydride ions, is endergonic and associated with a free energy of $\Delta G_{HH} \approx +128.8$ kcal/mol (in toluene; not dependent on the type of FLP used). In most cases, no dative bonds exist between the Lewis centers in equilibrium, and thus the ΔG_{HH} is the only endergonic contribution. In the cases where the dative bonds are present, however, an additional endergonic term (ΔG_{prep}) is required to break such bonds in order to generate free donor and acceptor centers available to receive the H^+ and H^- ions. The proton attachment by the LB center and the hydride attachment by the LA center are ΔG_{pa} and ΔG_{ha} , respectively. The final step involves the ion pair formation with a binding free energy (ΔG_{stab}), which stabilizes the ion pair formed from the separate $[LBH]^+$ and $[LAH]^-$ ions. The energy corresponding to this last step remains mostly the same for any

LA-LB pair. Thus, the thermodynamics of the overall reaction predominantly depends on the H^+ and H^- attachments to the LB and LA, respectively. While the former case is backed by experimental data in the form of pK_a values (solvent-dependent) [62], no such data are available for the latter [63]. The H^- affinity of LA is qualitatively linked to other experimental measurements of Lewis acidity by Heiden and Latham [64].

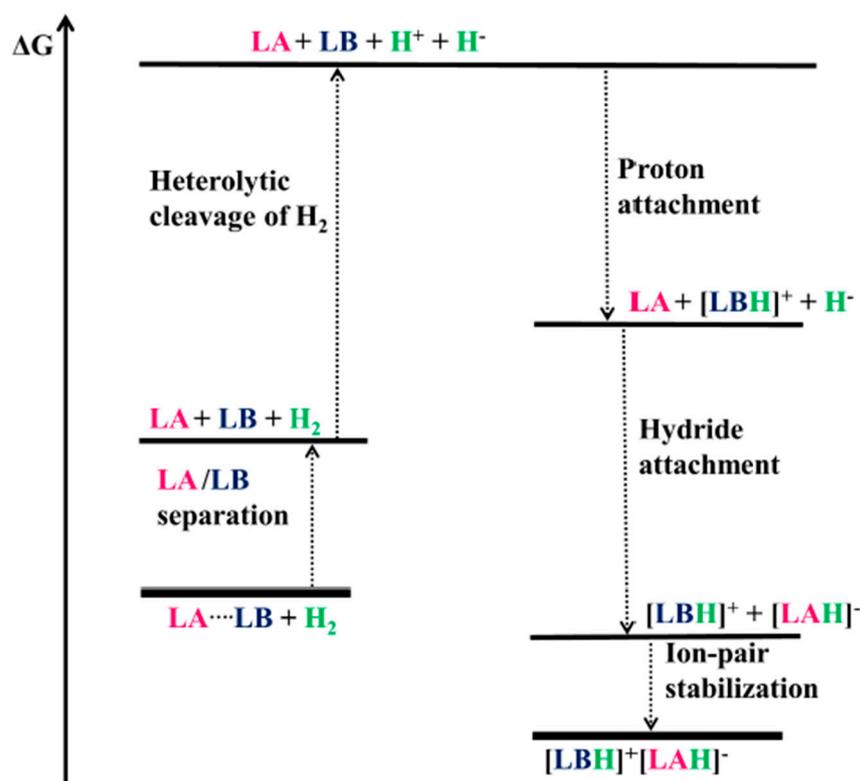


Figure 3. Partitioning scheme of the reaction of free energy to interpret the thermodynamic requirement of H_2 activation by FLP.

In a study performed by our group [41], we have explored the influence of boron-ligand cooperation (BLC) in H_2 activation and the associated effects on the corresponding activation barrier. The bridged FLP systems considered for the study along with the reaction are provided in Figure 4. System 1 is boroxypyridine, where the oxygen unit at the *ortho* position of the pyridine ring is replaced by NH and S units to produce Systems 2 and 3, respectively. Systems 4, 5, and 6 are the results of adding $-NMe_2$ moiety at the *para* position of 1, 2, and 3, respectively.

All the H_2 activation processes are exergonic, with Gibbs free energy barrier ranging within 17–25 kcal/mol, where FLP 6 has the lowest barrier. Wiberg bond indices (WBIs) calculated at the bond critical points (BCPs) of the bonds, B–X and C–X ($X = O, N$ and S), along with the changes in the respective bond distances, suggest that on H_2 activation, the B–X bond weakens and C–X strengthens. The reason behind this is the change in the nature of the B–X bond from B^+X^- in the parent FLPs to $B\leftarrow X$ dative type in the products. In the cases of the C–X bonds, they develop double bond character. EDA-NOCV performed on the transition state structures support the electron transfer model describing a synchronous transfer of electron density occurring as $LB_{(FLP)} \rightarrow \sigma^*_{(H_2)}$, and $\sigma_{(H_2)} \rightarrow LA_{(FLP)}$, resulting in the weakening of the H–H bond. A nucleus independent chemical shift (NICS) analysis reveals a reduction in the aromaticity of the pyridine rings upon H_2 activation. Hence, the influence of the BLC is demonstrated through the change in the nature of the B–X ($X = O, N$ and S) bonds in all the FLP systems considered for the study. Possible hydrogenation of CO_2 is explored with these hydrogenated FLPs, which is discussed later in the article.

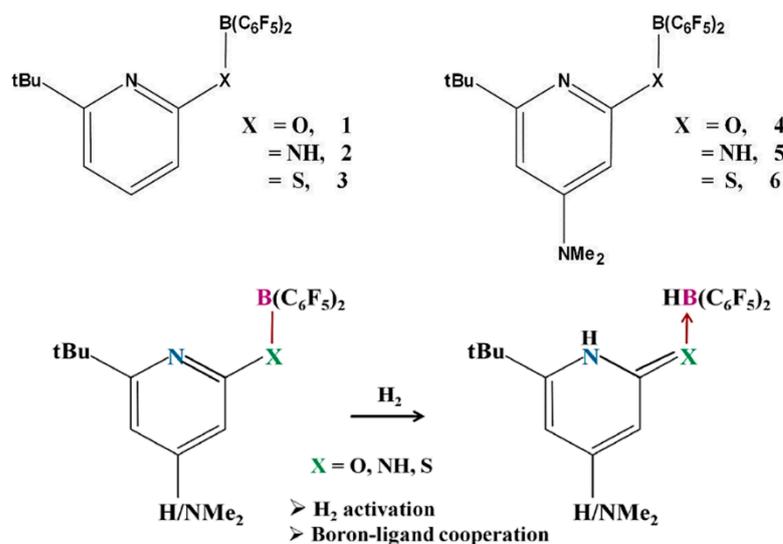


Figure 4. Chemical structure of the bridged FLP systems and the studied reaction.

3. Catalytic Hydrogenation by FLPs

FLPs can effectively activate molecular hydrogen and hence can be used as a viable alternative catalyst to undergo a metal-free hydrogenation. The general process involves H_2 activation followed by sequential H^+ and H^- transfer from the hydrogenated FLP to the substrate and regeneration of the parent FLP. Catalytic hydrogenation of nitrile, imine, and aziridine using $Mes_2PC_6F_4B(C_6F_5)_2$ [65,66] is demonstrated by Stephan et al. The same occurs for sterically hindered imines is shown using just an LA, $B(C_6F_5)_3$, since the imine itself acts as the LB [67]. In the case of less basic imines, the rate of reaction can be increased by adding a small amount of LB $P(C_6H_2Me_3)_3$. In 2014, the groups of Stephan [68] and Ashley [69] separately worked on the hydrogenation of carbonyl compounds to alcohol where $B(C_6F_5)_3$ and the ether solvent (1,4-dioxane) act as the FLP catalyst. It first splits the H_2 molecule and subsequently reduces the carbonyl group. The hydrogenation of aldehydes and ketones to alcohol by $B(C_6F_5)_3$ /cyclodextrine FLP in a non-polar solvent, and the transformation of aryl ketone to a deoxygenated aryl compound, are also demonstrated by Stephan's group [68,70]. Other polar compounds such as enons, enamines, silyl enol ethers, oximes, etc. can also be hydrogenated by FLPs [71–73].

The hydrogenation of non-polar compounds like olefins, however, involves a slightly different process. Here the LB part of the FLP needs to be a weak base so that its conjugate acid (produced on H_2 activation) is strong enough to protonate the less reactive olefin [74]. The H^- abstraction then occurs from the $[HB(C_6F_5)_3]^-$ in the following step. The use of FLPs in a plethora of hydrogenation reactions followed in subsequent years. Alkene hydrogenation by ether/ $B(C_6F_5)_3$ FLP occurs via the generation of $[Et_2O \dots H \dots OEt_2]^+$ and $[HB(C_6F_5)_3]^-$ ions, as reported by Hounjet et al. [27]. It is noted that the catalytic hydrogenation of electron-rich olefins by FLP are much easier than that of simple olefins [74]. Conversion of alkyne to cis-alkene using ansa-aminohydroborane [75], aniline to N-cyclohexyl ammonium salt using a $H_2/B(C_6F_5)_3$ pair [76], and anthracene, tetracene, and tetraphene, using $Ph_2PC_6F_5/B(C_6F_5)_3$ [77], etc., are a few examples of FLP-mediated hydrogenations reported throughout the years. Some N-heterocyclic compounds like acridine, quinoline, and phenanthroline can also be hydrogenated by $B(C_6F_5)_3$ catalyst [78].

The aforementioned hydrogenation reactions occur by an initial H_2 activation followed by H transfer to the substrate. This H^+ and H^- transfer to the substrate can occur in two different mechanisms. For strong LA components (e.g., $B(C_6F_5)_3$), substrate activation by protonation or H-bonding interaction is required since the conjugate base is not strong enough to deliver H^- on its own. Thus, protonation should occur before the H^- transfer [79–81]. In such cases, oftentimes, the substrate itself acts as the LB [81]. The other

$\text{HOMO}_{(\text{FLP})} \rightarrow \text{LUMO}_{(\text{H}_2)}$, $\text{HOMO}_{(\text{H}_2)} \rightarrow \text{LUMO}_{(\text{CO}_2)}$, and from several occupied MOs of CO_2 to $\text{LUMO}_{(\text{FLP})}$. The steps of the reaction include the formation of a formate ion attached to the Lewis acidic B center of the FLP followed by a proton transfer from the Lewis basic N center of the FLP to the O center of the formate unit. The first step has a higher barrier which may inhibit the process at ambient conditions, but it can be overcome at higher temperature and pressure. In the case of the other mechanism (i.e., LB activating CO_2 and LA activating H_2), the catalytic cycle takes two more steps where the COOH unit (attached to the Lewis basic N center of the FLP) reorients itself so as to come closer to the BH moiety to facilitate the proton transfer from the BH to the COOH moiety. Both the catalytic cycles are shown in Figure 6a,b. Heterogeneous CO_2 reduction to HCOOH is also reported [89] by silica nanopowder supported FLP where the said system forms an FLP-CO_2 adduct on the silica surface. The activation of H_2 is followed by the conversion of the captured CO_2 to HCOOH . Again, substitution of C_6H_5 groups on B and P centers increases the effectiveness of the whole process compared to C_6F_5 (too electron-deficient) and C_6H_{11} (too electron-rich) substituents.

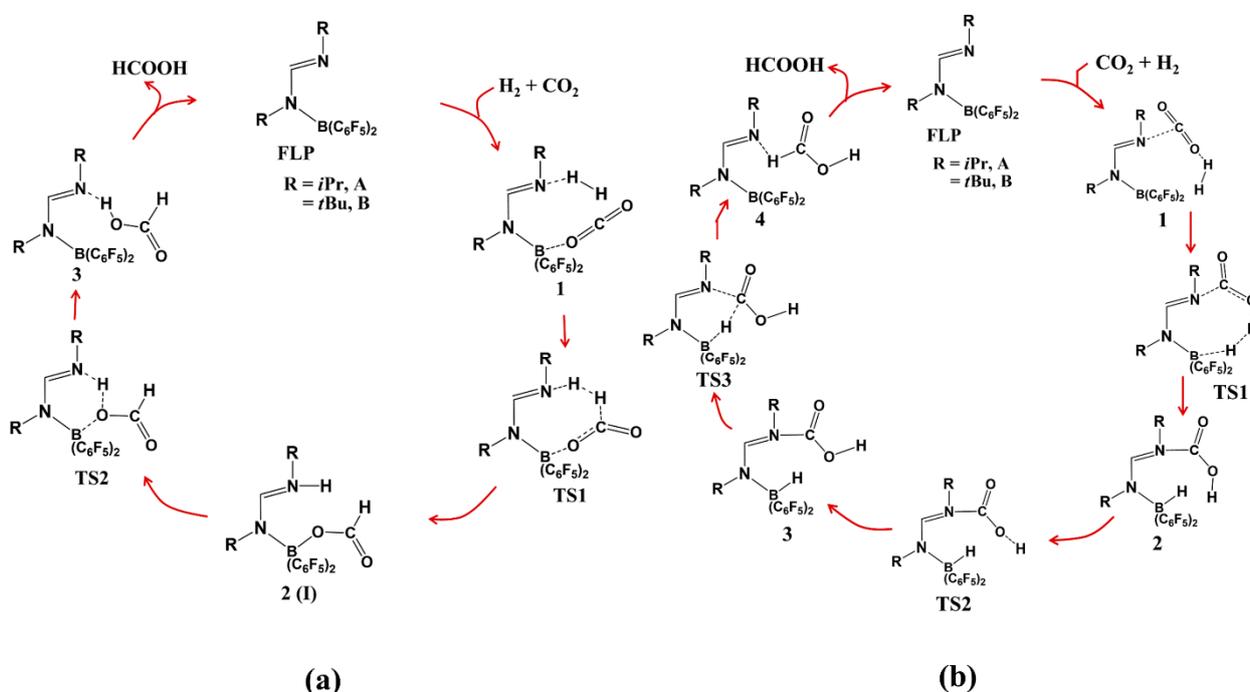


Figure 6. Proposed mechanistic cycles for hydrogenation of CO_2 catalyzed by FLPs A and B, where Lewis base of FLP activates (a) H_2 and (b) CO_2 . (Reprinted from ref. [87] with permission from Springer Nature. Copyright © 2022, Springer Science Business Media, LLC).

In a recent article [90], the CO_2 capture by $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ FLP was reported. They studied the whole reaction path to discover that the LA unit plays a more important role in the catalytic action of the FLP, both thermodynamically and kinetically. Whereas the LB unit has a higher impact in the FLP formation. It was thus recommended by this group to select a pair of strong LA and weak LB in designing an FLP for CO_2 activation to make the reaction thermodynamically and kinetically feasible.

5. Activation of Other Small Molecules

Apart from H_2 activation, FLPs have proven to be useful in the activation of several other small molecules, such as CO , CO_2 , N_2O , NO , SO_2 , alkenes, alkynes, and so on, which remain unaffected in the presence of either component of the Lewis pair (Figure 7). A schematic representation of the activation mechanism in π -systems by FLPs and optimized geometries of some transition state structures are provided in Figure 8. Despite

its significant thermochemical stability, CO₂ reacts with FLP to produce novel carbonic acid derivatives [91]. Reaction with SO₂ also occurs similarly [43]. A slightly different reaction occurs with nitrous oxide, which produces an additional compound containing the LB–N=N–O–LA unit [37]. Cooperative addition of FLPs is seen in the cases of CO with an intramolecular P/B FLP (Mes₂PCH₂CH₂B(C₆F₅)₂) [47], *t*-butylisocyanide with an unsaturated vicinal P/B FLP [48], and in P-ligand C–H bond activation [92]. With NO, FLP forms an adduct producing N-oxyl radical [44], and with olefins [38] and alkynes [87] they form zwitterionic addition products. Alternatively, phosphine-borane FLPs can also deprotonate terminal alkynes to form phosphonium alkynylborates [35,45].

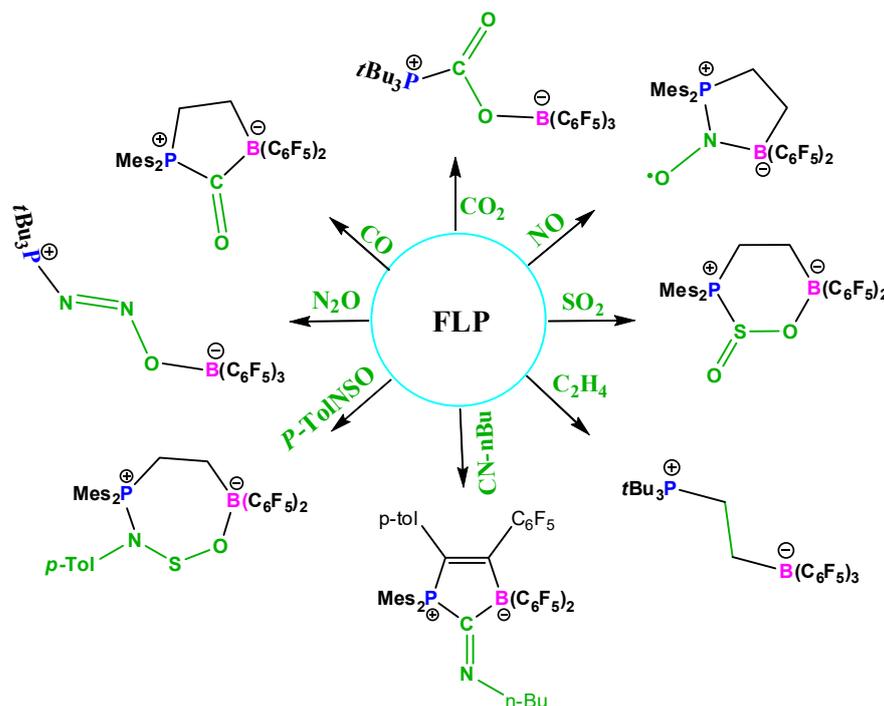


Figure 7. Some examples of small molecule activation by FLPs.

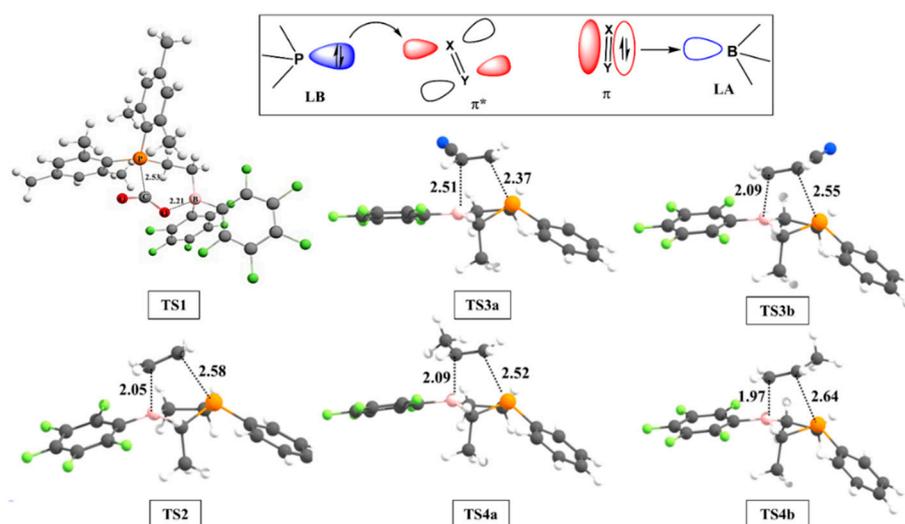


Figure 8. Schematic representation of activation of π -systems by FLPs, and optimized geometries of the transition states (TS) for the activations of CO₂ (TS1), ethylene (TS2), cyanoethylene (TS3a and TS3b), and propylene (TS4a and TS4b) with the P/B FLP. The bond distances are provided in Å unit. (Adapted from ref. [93] with permission from American Chemical Society. Copyright © 2022, American Chemical Society).

A DFT-based study performed by Trujillo et al. [94] shows the effect of aromaticity in the activation power of FLPs. Replacing a BPh₂ group with a borole unit to act as the LA moiety in a geminal P/B FLP, an enhancement in its ability to activate small molecules is theoretically predicted. Our group has investigated the dihydrogen activation of a five-membered P/B FLP (1) reported by Dong et al. [95], along with two other FLPs (2 and 3) modeled with some modification on the former (Figure 9) [96]. The H₂ activation brought on by the designed FLPs (2 and 3) turns out to be more favorable, both thermochemically and kinetically, than that by FLP 1. An investigation into the aromaticity of the FLPs, by evaluating NICS (0) and NICS (1) (zz) values at the C₄B ring, shows a decrease in the anti-aromatic nature of FLPs 2 and 3 from the reactants to the corresponding TSs where they reach their minimum values. This decrease is steeper in the latter, as an influence of the strong withdrawing –C₆F₅ groups around the B center. Thus, the anti-aromaticity in FLPs 2 and 3 boost their reactivity by reducing the activation barrier, compared to FLP 1. A similar relation between aromaticity and activation power of FLPs was observed by Zhuang et al. [97] in a DFT study on CO₂ activation. Rouf et al. [98] demonstrated an increase in the reaction feasibility of dinitrogen activation by FLPs due to an increase in aromaticity.

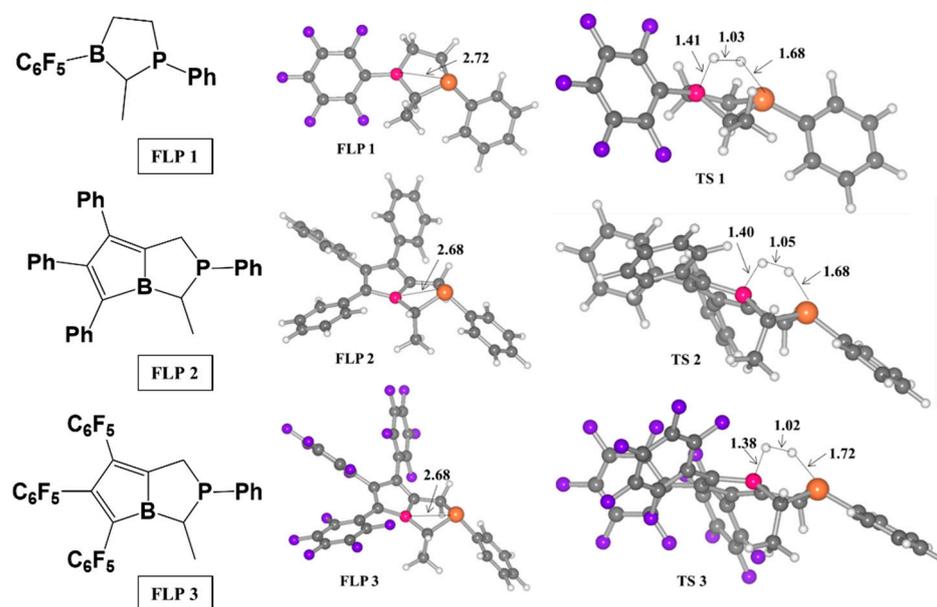


Figure 9. Schematic diagrams and optimized geometries of the FLPs and the related TSs for H₂ activation. Bond distances are provided in Å unit. (Adapted from ref. [96] with permission from Springer Nature. Copyright © 2022, Springer-Verlag GmbH Germany).

Some reactions with FLPs were discovered a few years ago, such as *N*-sulfinyltolylamine (*p*-TolNSO) yielding a seven-membered cyclic product where binding occurs via N and O centers of *p*-TolNSO [46]. The reaction of a phosphine-borane FLP with 1,3-dienes is reported by Ulrich et al. to produce the 1,4-addition product [39]. An 1,2-addition with the C=O group of an α , β -unsaturated aldehyde is reported by Momming et al. [88]. FLP mediated cleavage of B–H bond to produce oxygen-ligated borenium cation is also studied [40]. In the case of intramolecular cyclization involving sterically hindered amine with olefin or acetylene groups, the FLP reactivity increases, as reported by Stephan and Erker [99].

For hydrogenation of terminal alkynes, Liu et al. [100] recently developed an extremely stable polymeric LA (P-BPh₃) to tackle the problem of FLP deactivation due to the tight bond formation between the LA and terminal alkynes. The high stability also allows the recycling of the FLP up to 12 times in the catalytic process. Another case of catalyst deactivation occurs in the dehydrogenation of amine-boranes. The solution is reported by Bhattacharjee et al. [101] where they have used a P/B FLP to dehydrogenase dimethylamine

borane (DMAB). Its reaction mechanism follows an indirect activation of the B-H bond facilitated by an additional DMAB molecule, followed by deprotonation of the PPh_2 unit. FLP mediated amide hydrogenation [102], which uses $\text{B}(2,6\text{-F}_2\text{-C}_6\text{H}_3)_3$ with chloride LB, reveals a very important role of the halide. The reaction exhibits high generality, especially extendable to tertiary benzoic acid amides and α -branched carboxamides.

Recently FLPs are utilized in the activation of a single C-F bond in trifluoromethyl group as reported by Young's group [103]. A combination of phosphine or pyridine base with $\text{B}(\text{C}_6\text{F}_5)_3$ activates the C-F bond in the trifluoromethyl group to generate difluoromethyl product. In a separate study, the same group [104] further demonstrates the single C-F bond activation in gem-difluoroalkanes by using $\text{Al}(\text{C}_6\text{F}_5)_3$ instead of $\text{B}(\text{C}_6\text{F}_5)_3$. We have also performed a theoretical study on the activation of the C-F bond in fluoroalkanes by using a combination of lutidine base with either $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Al}(\text{C}_6\text{F}_5)_3$ acids [105]. It reveals that the C-F bond activation mediated by $\text{Al}(\text{C}_6\text{F}_5)_3$ /lutidine pair is more favorable than that mediated by $\text{B}(\text{C}_6\text{F}_5)_3$ /lutidine pair. Hence, the $\text{Al}(\text{C}_6\text{F}_5)_3$ acid is superior to the $\text{B}(\text{C}_6\text{F}_5)_3$ acid for such unusual bond activation. Last year, Ison and Tubb [106], made a simple yet important calculation for $\text{M}(\text{C}_6\text{F}_5)_3$ ($\text{M} = \text{B}, \text{Ga}, \text{Al}$) Lewis acids. They evaluated the ratio between orbital interaction energy (E_{Orb}) to the electrostatic and exchange repulsion energy (E_{Steric}) in an energy decomposition analysis (EDA). A correlation between this ratio and the reactivity drawn reveals that only the $\text{B}(\text{C}_6\text{F}_5)_3$ carries out a catalytic hydrosilylation in ketones. This ratio can be used as a guiding parameter in designing of FLPs in the future. In recent years, FLPs are being increasingly used in polymerization catalysis [107–109], polymer chemistry [110,111], and organic synthesis [112,113] as well.

6. Summary

The high thermochemical and kinetic stability of the greenhouse gas, CO_2 , makes its transformation to useful chemical compounds a challenging task. It requires efficient catalysts, most of which have high levels of toxicity, is costly, and has low availability. To that end, we present a thorough discussion on metal-free catalytic hydrogenation of CO_2 by a class of compounds known as frustrated Lewis pair (FLP). They are produced when a pair of Lewis acid and Lewis base are unable to form an adduct due to steric hindrance. We also provide a detailed discussion on the hydrogen activation ability of FLPs, which has been utilized for the catalytic hydrogenation of imines, nitriles, enamines, alkenes, alkynes, ketones, CO_2 , etc. Apart from the H_2 activation, FLPs may activate and react with other small molecules as well; examples include CO_2 , N_2O , CO , NO , SO_2 , C_2H_4 , C_2H_2 , etc. The mechanisms involved in the activation of molecular hydrogen, activation, and the catalytic hydrogenation of carbon dioxide are thoroughly discussed. The term boron-ligand cooperation (BLC) in analogy to metal ligand cooperation (MLC) is introduced to describe a distinct approach of reactivity for some specific FLPs to activate a chemical bond. The B-X bond ($\text{X} = \text{O}, \text{N}$ and S) present in the concerned FLPs plays an important role in the activation of molecular hydrogen. The B-X bond changes from B^+-X^- in the parent FLPs to $\text{B}\leftarrow\text{X}$ dative type in the products.

The aromaticity/anti-aromaticity of an FLP has been reported to have a relation to its reactivity in activating small molecules on several occasions, and hence, can be used as a guide in designing new and effective FLP systems. The boron-ligand cooperation, applicable at the LA site of an FLP, is established in the case of dihydrogen activation. This boron atom can be replaced by another group with 13 elements to verify if similar cooperation is exhibited, and if so, whether it enhances the reactivity of the new FLP. The ability of FLPs to activate small molecules opens up new avenues in metal-free catalysis, which was previously believed to be the exclusive domain of transition metals. The H_2 reactivity of FLP, in particular, continues to be useful in both homo- and heterogenous catalysis. Other than CO_2 reduction and small molecules activation, FLPs are being actively researched in surface chemistry owing to the cooperative action of LA and LB centers. They are increasingly utilized in polymerization catalysis, polymer chemistry, and organic synthesis, etc. Application of FLP as a catalyst in the reduction of CO_2 can occur either

by the concerted or stepwise transfer of both the activated hydrogens, or by simultaneous activation of CO₂ and H₂ as highlighted through several computational studies. These mechanistic insights may provide experimental researchers with tools to design better catalytic FLPs.

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