

On The Concept of Frustrated Lewis Pairs

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Summary

In this concept article, we consider the notion of “frustrated Lewis pairs” (FLPs). While the original use of the term referred to steric inhibition of dative bond formation in a Lewis pair, work in the intervening decade demonstrate the limitation of this simplistic view. Analogies to known transition metal chemistry and the applications in other areas of chemistry are considered. In light of these findings, we present reflections on the criteria for a definition of the term FLP. Segregation of the Lewis acid and base and the kinetic nature of FLP reactivity are discussed. We are led to the conclusion that while an all-inclusive definition of “FLP” is challenging, the notion of “FLP chemistry” is more readily recognized.

Introduction

As early as 1942, H.C. Brown had noted that the combination of donor and acceptor lutidine and BMe_3 failed to form classical Lewis acid-base adduct (Fig. 1).[1] Brown contrasted this combination with that of lutidine and BF_3 which forms a dative bond and rationalized the former anomaly on the basis of steric congestion. Two decades later, reactions in which donor and acceptors reacted with a substrate emerged. Wittig described the reactions of BPh_3 and PPh_3 with benzyne, to give the zwitterionic addition product $(\text{C}_6\text{H}_4)(\text{BPh}_3)(\text{PPh}_3)$. [2] Tochtermann described a similar addition reaction of trityl anion and BPh_3 to butadiene to give $[\text{Ph}_3\text{CCH}_2\text{CH}_2\text{CH}(\text{BPh}_3)\text{CH}=\text{CH}_2]^-$ and $[\text{Ph}_3\text{CCH}_2\text{CH}_2\text{CH}=\text{CHCH}_2(\text{BPh}_3)]^+$ (Fig. 1).[3] These systems were described as “antagonistische Paar”, although further reactivity was not reported.

In the late 1990s, it was Piers’ insightful description of the $\text{B}(\text{C}_6\text{F}_5)_3$ catalyzed hydrosilylation of ketones[4] that is now recognized as the first example of what has come to be known as FLP chemistry (Fig. 1). In this case, contrary to expectations, Piers showed that it was the activation of the Si-H bond by $\text{B}(\text{C}_6\text{F}_5)_3$ and subsequent attack by ketone that effected this catalysis. Thus, the basic ketone and the Lewis acidic borane act in concerted fashion on the Si-H bond. This mechanism was subsequently substantiated by the elegant work of Oestreich and coworkers[5] in which they used a chiral silane to confirm the inversion of stereochemistry at Si. This cooperative action of the donor and acceptor on the Si-H bond foreshadowed the finding of the FLP activation of H_2 , that occurs 10 years later.

Now part of some freshman chemistry curricula, the common understanding is that a “frustrated Lewis pair” (FLP) is a compound or mixture containing a Lewis acid and a Lewis base that, because of steric hindrance or geometry constraints, cannot combine to form a classical Lewis adduct. This definition emerged as a result of the initial examples of FLP systems capable of the activation of H_2 , including $\text{Mes}_2\text{P}(\text{C}_6\text{F}_4)\text{B}(\text{C}_6\text{F}_5)_2$, [6] $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$ [7] and combinations of bulky phosphines (eg. *t* Bu_3P , Mes_3P) with $\text{B}(\text{C}_6\text{F}_5)_3$ [8] (Fig. 1). However, over the past decade the range of examples of FLP systems has broadened dramatically. A number of these systems point to the limitations of this simple definition.

This concept article was prompted a few years ago when Fred Fontaine read the following question on a popular science blog: “How do you synthesize a frustrated Lewis pair (FLP)?” Initially this question brought a smile, as intermolecular FLPs are generated simply from the combination of commercially available Lewis acids and bases. But lurking behind the seeming naiveté of this question and its answer, is a deeper, more profound fundamental question for which the full answer is far from trivial: What constitutes an FLP? In this article, we consider the evidence and attempt to provide broader considerations of the features that give rise to FLP chemistry. At the same time, we highlight

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the relationship of FLP chemistry to “classical” main group and organometallic chemistry. As a pedagogical tool, we hope these considerations will clarify the nature of FLPs. After a decade of FLP chemistry, it is our hope that this account will provide a clearer perspective to new comers to the field and prompt discussions among specialists.

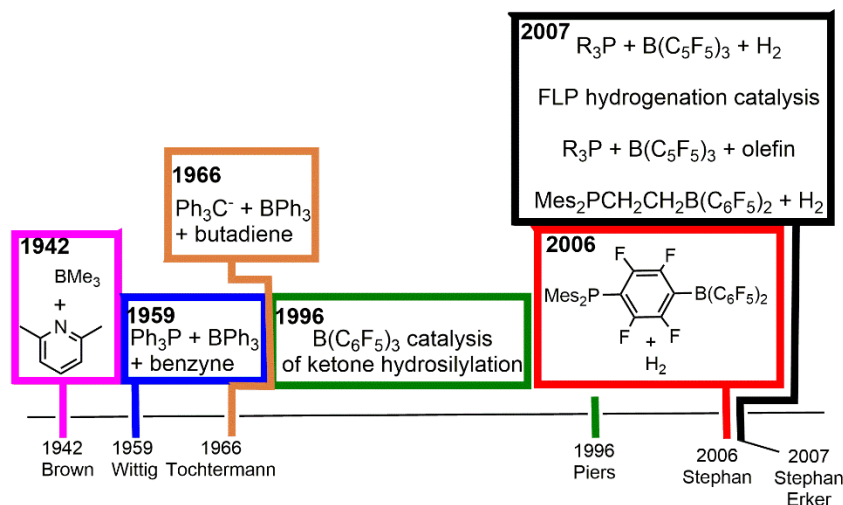


Fig. 1. Historical timeline leading to the early development of FLP chemistry.

Discussion

The term “frustrated Lewis pair” (FLP), was coined in 2007,[9] a year after the finding that Mes₂P(C₆F₄)B(C₆F₅)₂ reacted reversibly with molecular hydrogen under very mild conditions.[6] This reaction was remarkable as prior to that time, the reversible reactions with H₂ had been limited to transition metal chemistry. In the ensuing year, it was shown that simple combinations of sterically encumbered phosphines and boranes effected similar activations of H₂. [8] Moreover, this reactivity was also extended to intramolecular FLPs as well as to metal-free hydrogenation catalysis.[10] However, it was the further expansion of the reactivity of FLPs to the reactions with olefins that prompted the first use of the term FLP.[9] Collectively, these observations had made it clear that sterically precluding or “frustrating” dative bond formation offered a unique route to new reactivity and thus the field of FLP chemistry was born.

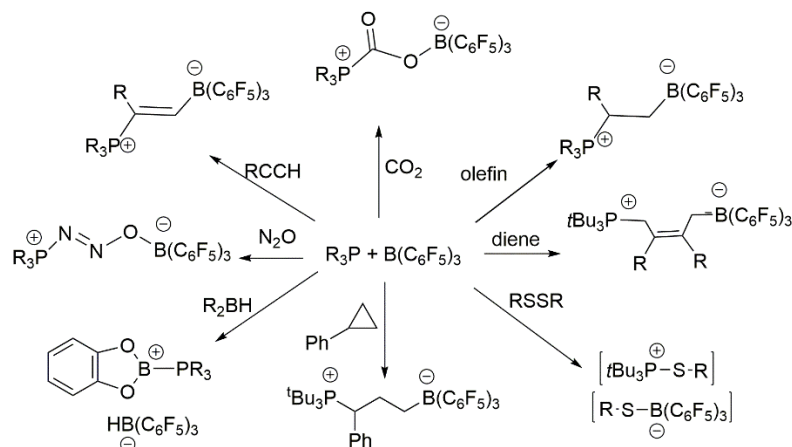


Fig. 2. Examples of FLP chemistry with phosphine/borane combinations.

In the past decade, many examples of both intramolecular and intermolecular FLPs have emerged and been shown to activate hydrogen and react with an ever-widening variety of other substrates (Fig. 2).[11-13] While many of these advances have exploited the typical bulky phosphines and B(C₆F₅)₃ (Fig.2), this chemistry has also been broadly expanding to include a range of Lewis bases derived from B, C, N, O, S, Se and Te donors, with Lewis acids based on B, Al, Ga, In, C, Si, Sn, N and P(V).[14] Such developments have uncovered new reactivity of main group systems and led to advances in metal-free catalysis.[15]

The concept is also finding analogies and applications in a number of other areas of chemical science beyond main group chemistry.[16] Early applications of the concept have found applications in organic, polymer and radical

synthesis while applications of the notion of FLPs to transition metal based systems have also emerged.[16] More recently further applications of the concept have been used to rationalize the mechanisms of reactions in the diverse areas of materials chemistry, heterogeneous catalysis and enzymatic chemistry.

Analogy to Metal and Enzyme Systems

The mechanism of FLP activation of H_2 bears a close resemblance to the mechanism of action of the Noyori-type catalysts.[17] The latter system reacts with H_2 affording concerted transfer of a proton to N and a hydride to the metal center (Fig. 3A). In that sense, the Noyori-bifunctional activation of H_2 involves the basic N and the Lewis acidic metal center. In the same vein, the reactivity of FLPs, particularly with H_2 , is reminiscent of concerted oxidative addition of H_2 to a transition metal. In that case, the LUMO of the metal accepts the electrons from the H_2 σ -bond while the HOMO of the metal donates electron density to the σ^* -orbital of H-H bond. Of course, in the case of oxidative addition to a metal center, the HOMO and LUMO reside on the same atom; whereas in FLP chemistry the donor and acceptor orbitals reside on disparate atoms. Thus, one can draw a parallel between the required orthogonality of the filled and empty orbitals on a transition metal needed for oxidative addition and the “frustration” required for an FLP to ensure the accessibility of donor and acceptor orbitals.

One can also draw parallels between FLP reactivity and enzymatic processes. At some level, a role of protein structure is to provide binding sites for electron-rich and electron deficient centers and at the same time maintain separation so that redox chemistry can occur in an orchestrated fashion. In that sense, enzymes are nature’s FLPs. A more direct similarity is the derived from Ni-Fe, Fe-Fe or Fe-only hydrogenases.[18-20] The Fe-Fe enzyme effect the reversible oxidation of H_2 to protons, via the cooperative action of an electron deficient metal centers and a pendant non-coordinating N-donor (Fig. 3B). Similarly, the [Fe] hydrogenase heterolytically splits H_2 to deliver a hydride to mononuclear Fe-guanylylpyridinol cofactor affording methylenetetrahydromethanopterin and a proton (Fig. 3C). These examples point to the role of non-metal species in the cleavage of H_2 but moreover emphasize the importance of the restricted approach of the electron acceptor and donor provided by the protein structure.

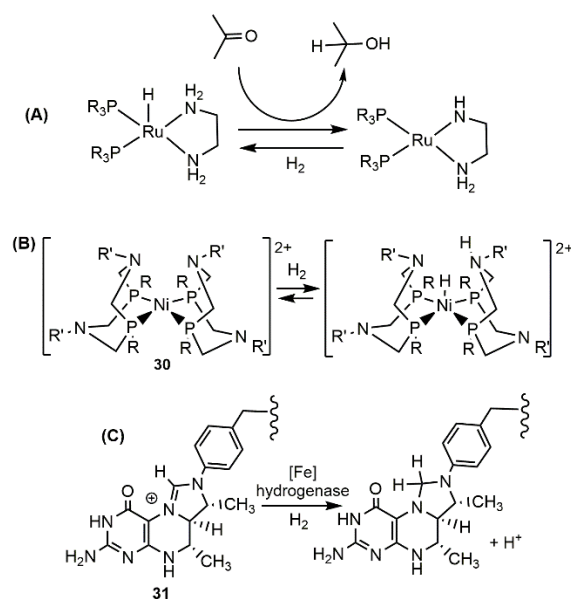


Fig. 3. Metal and enzyme systems analogous to FLP reactivity. (A) Noyori-catalyst; (B) Bullock models of Ni-Hydrogenase; (C) conversion of guanylylpyridinol cofactor to methylenetetrahydromethanopterin and a proton by Fe-hydrogenase.

Segregation of Donor and Acceptor

The presence of a Lewis acid and base in close proximity to a substrate allows for two-electron transfer cascade reactions to occur. Whether it is the activation of H_2 , alkenes, carbon dioxide, or C-H bonds, the common feature of all these transformations is the transfer of two electrons from the HOMO of the Lewis base to a substrate, which in turn transfers two electrons to the LUMO of the Lewis acid. Interestingly the relative energies of the HOMO and LUMO are tuned by selection of the respective Lewis acid and base. Moreover, in the case of H_2 activation, the bond strengths in the resulting protonated Lewis donor and the hydride on the Lewis acceptor will determine the efficiency of proton and hydride delivery in a catalytic process. Lewis acidic species, such as $B(C_6F_5)_3$, will be quite effective at H_2 cleavage, but hydride delivery to a substrate for hydrogenation will be slowed by the relatively strong B-H bond strength. Conversely, use of weak Lewis bases will generate strongly acidic protons facilitating protonation of a substrate prompting subsequent hydride delivery.

Many ambiphilic systems activate bonds through a concerted mechanism in which a low barrier is associated with the availability of resonance forms and electron delocalization between the nucleophilic and electrophilic centers. Indeed, all reactions involve the migration of electron density from an electron-rich center to an electron-poor one and yet clearly not all reactions would be considered FLP reactions. Thus, the question is what is distinct about FLP reactivity? One could consider the idea that an FLP reaction begins with the segregated donor and acceptor sites. While such segregation is clearly the case for many FLP systems, there are certainly some systems that exhibit FLP chemistry and yet this separation of donor and acceptor is transiently masked by dative interactions. For example, in the case of lutidine and $B(C_6F_5)_3$ (Fig.4), a classical Lewis acid base adduct is present in the mixture.[21] Nonetheless, this adduct exists in an equilibrium with the free base and acid. This allows access to the segregated donor and acceptor sites and initiate FLP reactivity.

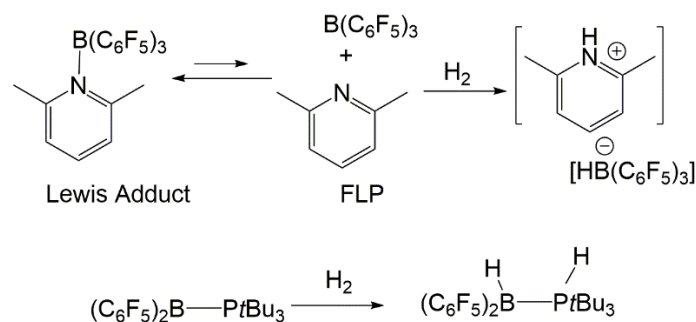


Fig. 4. Examples of FLP systems that are not “sterically frustrated”.

That being said, is segregation of the donor and acceptor sites the key feature that defines FLP reactivity? While this certainly encircles many of the obvious cases, the species $R_2PB(C_6F_5)_2$ were shown to react with H_2 (Fig 4).[22] This reactivity was attributed to the energetic mismatch between the lone pair of electrons on P and the acceptor orbital on B. This mismatch “segregates” the nucleophile and the electrophile allowing the reaction with H_2 to proceed. Perhaps an extreme case is to consider the reaction of cyclic amino alkyl carbenes (CAAC) with H_2 . [23] Here in that case, the donor and acceptor are located on the same carbon atom. Is this an FLP reaction? Certainly, there is an analogy, although one could also describe this as a formal concerted oxidative addition where the HOMO and LUMO are orthogonal on a single atom, highlighting a gray zone between FLPs and this chemistry. Thus, we must conclude that systems comprised of segregated Lewis acid and base centers may be obvious FLPs. However, other systems point to the deficiencies of this feature as the sole criteria for the definition of an FLP. Nevertheless, all these reactions have Lewis acid and basic centers that are not mutually neutralized when reaction occurs, suggesting that FLPs are defined by their reactivity rather than by their structural features.

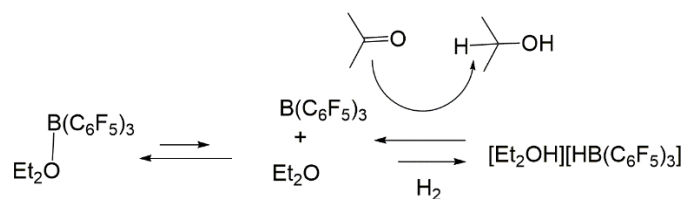


Fig.5 Example of sterically unhindered FLPs.

A Kinetic Phenomenon

In 2014, Stephan[24] and Ashley[25] simultaneously reported the hydrogenation of ketones using $B(C_6F_5)_3$ in ethereal solvents. In these cases, the solvent, an ether, acts as the Lewis base in concert with the Lewis acid to effect H_2 activation (Fig. 5). This stands in apparent conflict with the known ability of $B(C_6F_5)_3$ to form stable ether adducts. Similarly, Repo[26, 27] and Fontaine[28-30] reported catalytic processes with amine-boranes of the type $R_2NC_6H_4BH_2$ where the Lewis acid is neutralized by formation of either intermolecular Lewis adduct or 2-electron-3-centre bonds. Even the least sterically encumbered analogue, $Me_2NC_6H_4BH_2$, which exists as a dimeric species, exhibits reactivity typical of FLP chemistry.[31] These findings further illustrate that prior segregation of the Lewis acid and base is but one sufficient avenue to FLP reactivity. However, it is certainly not required. What emerges from these findings is the notion that FLP reactivity may be accessed by an equilibrium, which provides access to the transiently free Lewis acid and base. Even if the equilibrium constant is small, reaction of the free species with H_2 or other substrates provides an avenue to FLP reactivity via Le Chatelier principle. This perspective on FLP chemistry thus de-emphasizes the role of steric “frustration”. The importance of transient FLP species was also demonstrated in 2013 by Fontaine and coworkers *Phil. Trans. R. Soc. A*.

when they reported the hydroboration of carbon dioxide by ambiphilic phosphine-borane FLP catalysts.[32, 33] This catalyst did not react independently with hydridoboranes or carbon dioxide, yet catalysis did occur. This illustrates that favorable kinetics for the concerted action of the Lewis partners on a substrate can overcome the apparent neutralization of Lewis acid and base. In this sense, FLP chemistry should be viewed as a kinetic phenomenon.

Returning to the question “what is a FLP?”, it is clear that a formal definition that provides for the variety of systems described to date remains challenging. Thus one is left with the seemingly trivial conclusion that a FLP is a combination of a Lewis acid and base that exhibits FLP chemistry. Nonetheless, the notion of FLP chemistry is more straightforwardly defined. Indeed, all known examples conform to the notion that FLP chemistry involves the concerted action of a Lewis acid and base segregated at the transition state on a substrate molecule.

Conclusions

Above we considered the initial notion that an FLP is a combination of a Lewis acid and base that do not form an adduct. It is clear that this “definition” does not encompass all the systems that exhibit FLP chemistry. A considerable breadth of known FLPs systems are comprised of Lewis acid-base combination where dative bonding is thermodynamically favoured. Nonetheless, such seemingly classical Lewis pairs access the free components via dissociative equilibria and thus realize FLP reactivity. This chemistry is more readily defined as a kinetic phenomenon in which a Lewis acid and base act on a substrate molecule. Thus, while an all-encompassing definition of the term “FLP” remains elusive, “FLP chemistry” is more readily recognized. The focus on the chemistry seems fitting. The original findings extended reactivity with H₂ to areas of the periodic table where this was previously unknown and indeed the potential for future impact of this area of chemistry lies in its ability to stimulate discovery of new reactivity.

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Data Accessibility

There is no supplementary data for this article.

Competing Interests

We have no competing interests.

Authors' Contributions

Fred Fontaine and Doug Stephan wrote this in a joint effort.

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