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Zero valent iron complexes as base partners in Frustrated Lewis Pair chemistry

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ABSTRACT: The prototypical iron(0) complex [Fe(CO)₃(PMe₃)₂] (1) forms a frustrated Lewis pair (FLP) with $B(C_6F_5)_3$ (BCF). In this FLP, the iron complex acts as the Lewis base partner, and the borane as the Lewis acid partner. This FLP is able to cleave H-H, H-Cl, H-O and H-S bonds in H₂, HCl, H₂O and HSPh. The FLP 1/BCF is shown to catalyze the hydrogenation of alkenes under mild conditions, where terminal alkenes are preferentially reduced. Mechanistic studies using D₂ gas suggest that a branched intermediate in an alkene insertion cycle or an ionic cycle is favored for this catalytic reaction.

Small molecule activation for functionalization purposes has become highly developed for noble metal catalysts. However, the relative cost and toxicity of noble metals has driven chemists to derive new means to activate and functionalize small molecules.¹ This is perhaps most true for the hydrogen molecule, and its subsequent use in hydrogenation reactions.²

To circumvent the need for noble metals in hydrogenation reactions, chemists have looked to employ earth-abundant elements in catalysis. Two strategies to accomplish this that have been employed are (i) to enhance first row transition metal reactivity through combination with weak field, strong field or redox active ligands or metal-metal and metal-ligand cooperativity,³ and (ii) to use main-group elements in Frustrated Lewis Pair (FLP) chemistry.⁴ While both approaches have obvious benefits in moving away from noble metal catalysis, neither has accomplished comparable activities to noble metal catalysts.

Many reported main-group FLP systems are known to cleave dihydrogen in a facile manner. However, such systems generally perform poorly as hydrogenation catalysts for imines, ketones, alkenes and alkynes, requiring high loadings to achieve complete conversions.⁵ Furthermore, the reactivity of such systems is generally restricted to ionic hydrogenations, with classical hydride insertion chemistry rare.⁶

Conversely, many base metal systems are able to exploit their ability to partake in organometallic type reactivity (e.g. carbonyl migratory insertion, olefin insertion) but require elevated temperatures and/or high pressures to cleave dihydrogen.⁷

To counter the limitations of base metal and FLP H₂ activation/hydrogenation, efforts have been made to combine transition metal and FLP reactivity in a synergistic fashion. To date, most metal based FLP systems have focused on utilizing transition metals as the Lewis acid partner.⁸ For example, both Wass and Erker have reported inter- and intra-molecular zirconium-phosphine FLP systems.⁹ These systems are capable of hydrogen activation and reaction with carbon dioxide, ketones, alkenes, alkynes and ethers (*inter alia*). Generally, such systems generate very basic hydrides which are prone to hydrolysis and the formation of inactive hydroxide or oxide byproducts.

Systems that utilize metals as the Lewis base partner are restricted to a report by Wass of H₂ activation by platinum(0) and $[B(C_6F_5)_3]$ (BCF),¹⁰ a platinum(0)/gold(I) all-metal reversible FLP system reported by Campos,¹¹ and a rhenium oxide complex reported by Ison that was able to hydrogenate alkenes in cooperation with BCF (Figure 1A).¹² It must be noted that Pt(0)



Figure 1. A Previous transition metals used as Lewis bases in FLP chemistry. B The well-studied iron(0) complex $[Fe(CO)_3(PMe_3)_2]$ (1) has been used as a Lewis base in forming iron-Lewis acid adduct, but the activation chemistry of these adducts has not been explored, nor has 1 been used in FLP chemistry. BCF = B(C_6F_5)_3.

is capable of H₂ activation in the absence of BCF or gold(I), and hydrogen activation in these systems may have been due to separate H₂ activation and hydride abstraction steps, although computational analysis of various reaction pathways does suggest Campos' Au(I)/Pt(0) system activates H₂ in its FLP form.^{11b} Furthermore, in Ison's system, the Re metal center isn't directly involved in H₂ activation, with the Re oxo-ligand acting as the base partner.

Systems that utilize base metals as Lewis base partners in Lewis adducts are well known.¹³ Indeed, Braunschweig and Bigorgne have utilized the prototypical zero valent iron complex [Fe(CO)₃(PMe₃)₂] (1) to report a number of Fe(0) adducts with gallium, silver and mercury (Figure 1B).¹⁴ Surprisingly, none of these systems have been exploited for small molecule activation.

We reasoned that unique umpolung reactivity might be observed employing base metals as Lewis base partners in FLP activations. Furthermore, the activity of base metal catalysis

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Figure 2. Activation of H_2 with the FLP 1/BCF yields the salt [1-H][BH(C₆F₅)₃]. The reverse reaction to release hydrogen was not found to proceed.



Figure 3. The FLP 1/BCF was found to activate HCl, H₂O and HSPh.

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may be improved and/or better understood through cooperative use in FLP chemistry. Herein, we report on the activation of hydrogen and other small molecules utilizing an iron(0) system as a Lewis base partner in cooperation with BCF.

To examine the ability of iron metal bases to activate H₂ in combination with main group Lewis acids, we chose to utilize the prototypical Fe(0) complex, $[Fe(CO)_3(PMe_3)_2]^{15}$ (1) in our investigations (Figure 2). Mixing complex 1 with BCF in a 1:1 ratio resulted in no apparent change in the ³¹P NMR signals of 1 nor the ¹¹B NMR signal of BCF. FTIR analysis of the reaction mixtures also resulted in no change from pure samples of 1, indicating the pairing of complex 1 with BCF is an FLP.

Addition of H₂ at 77 K to a sample of 1 and BCF in chlorobenzene (PhCl) resulted in an immediate colour change from light pink to light yellow upon thawing. ³¹P NMR analysis showed the formation of a new signal at 16.1 ppm corresponding to the iron hydride complex, $[FeH(CO)_2(PMe_3)_2]^+ \{[1-H]^+\}$ with an NMR yield of 63% after 24 hours at room temperature. The formation of the iron hydride was confirmed through the observation of a high field signal in the ¹H NMR spectrum appearing as a triplet at $\delta_{\rm H}$ -10.3 (²J_{PH} = 35.8 Hz). Concurrently, a signal in the ¹¹B NMR spectrum at δ_B -25.0 (d, ¹J_{BH} = 96.1 Hz) signified the formation of $[BH(C_6F_5)_3]^-$. The formation of the ion pair $[1-H][BH(C_6F_5)_3]$ was found to be highly favored, with degassing the solution resulting in little to no regeneration of 1 or BCF. Indeed, independently prepared samples of [1-H][BAr^F₄] {BAr^F₄ = B(3,5-(CF₃)₂-C₆H₃)₄} and [$^{n}Bu_{4}N$][BH(C₆F₅)₃] failed to generate any 1 or BCF when mixed, even after freezepump-thaw degassing and heating at 100 °C for 24 hours.

The synergistic role of complex 1 and BCF in the activation of hydrogen was confirmed from a number of control experiments. Firstly, it was observed that exposing 1 to H₂ in the absence of BCF did not result in $[1-H]^+$ or any other iron hydride



Figure 4. Molecular structure of $[1-H][BCl(C_6F_5)_3]$. Hydrogen atoms (except H1) omitted, thermal ellipsoids shown at 50%. H1 was located in the Fourier Difference map. Selected bond distances (Å) and angles (°): Fe1-P1, 2.256(1); B1-Cl1, 1.910(2); H1-Cl1 (closest contact), 7.62(3); P1-Fe1-P2, 166.6(1).



Figure 5. Molecular structure of $[1-H][(\mu-OH){B(C_6F_5)_3}_2]$. Hydrogen atoms (except H1 and H2) omitted, thermal ellipsoids shown at 50%. H1 was located in the Fourier Difference map. Selected bond distances (Å) and angles (°): Fe1-P1, 2.252(1); B1-O1, 1.557(2); H1-O1 (closest contact), 8.06(3); P1-Fe1-P2, 170.8(1).



Figure 6. Molecular structure of $[1-H][B(SPh)(C_6F_5)_3]$. Hydrogen atoms (except H1) omitted, thermal ellipsoids shown at 50%. H1 was located in the Fourier Difference map. Selected bond distances (Å) and angles (°): Fe1-P1, 2.245(1); B1-S1, 1.963(2); H1-S1 (closest contact), 3.31(3); P1-Fe1-P2, 170.7(1).

species. Secondly, the addition of $[Ph_3C][BAr^F_4]$ to **1** and hydrogen did not result in any observation of $[\mathbf{1}-H]^+$ or triphenylmethane, ruling out the possibility that **1** activates hydrogen reversibly, and that BCF simply perturbs this equilibrium by reacting with small concentrations of an iron dihydride species.

Confirmation that heterolytic cleavage of dihydrogen was the H-atom source for the formation of $[1-H][BH(C_6F_5)_3]$ was obtained via reaction of 1 and BCF with D₂. In a similar reaction to that described above, addition of D₂ to a sample of 1 and BCF at 77 K in PhCl once again resulted in a new signal at 16.1



2d 48% 2e 2% 2f 6% 2g 0% 2h 0% Figure 7. Hydrogenation of terminal alkenes and attempted hydrogenation of internal alkenes with 1/BCF. Yields determined by 1 H NMR analysis.

ppm in the reaction's ^{31}P NMR spectrum, with a NMR yield of 65% after 3 hours at 60 °C. The ^{11}B NMR spectrum of the reaction showed the appearance of a broad signal (FWHM = 75 Hz) at δ_{B} -25.0. However, explicit evidence for the formation of the isotopologues came from the ^2H NMR spectrum of the reaction mixture that showed a sharp triplet signal at δ_{D} -10.4 ($^{2}J_{\text{PD}}$ = 5.6 Hz) and a broad signal at δ_{D} 3.9, assigned to the iron deuteride and borodeuteride signals respectively.

Activation of other small molecules using **1** and BCF was also achieved (Figure 3). While, addition of HCl to **1** resulted in no reaction, in the presence of one equivalent of BCF, the product $[1-H][BCl(C_6F_5)_3]$ was formed within minutes quantitatively. The spectroscopic data for $[1-H]^+$ are identical to those

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The FLP 1/BCF was found to readily activate O-H and S-H bonds. Stoichiometric quantities of complex 1 with two equivalents of BCF activated water to generate [1-H][(u-OH) $\{B(C_6F_5)_3\}_2$] quantitatively. Similarly, equal quantities of 1 and BCF generated $[1-H][B(SPh)(C_6F_5)_3]$ in 62% yield when mixed with benzenethiol. This could be improved to 91% yield based on iron when two equivalents of BCF were employed. In contrast to the molecular structure of $[1-H][(\mu-OH)\{B(C_6F_5)_3\}_2]$ (Figure 5), which exhibits two BCF motifs coordinated to the [OH]⁻ fragment, a molecular structure of the product from the reaction with PhSH (Figure 6) revealed only a single BCF present in the anion {i.e. [PhS-BCF]-}, suggesting the higher conversion with two equivalents of BCF may arise from perturbation of an equilibrium. Additionally, the salts $[1-H][BCl(C_6F_5)_3]$ and $[1-H][(\mu-OH){B(C_6F_5)_3}_2]$ display large minimum distances between the iron hydride position and any of the anion B-Cl or positions (Figures 4 and 5), while complex [1-B-O H][B(SPh)(C_6F_5)₃] displays a Fe–H···S–B distance of 3.31(3) Å, indicating a weak electrostatic interaction between the anion and iron hydride (Figure 6).

It was found that reaction of $[1-H][BH(C_6F_5)_3]$ with a stoichiometric amount of 1,1-diphenylethylene generated the hydrogen transfer product 1,1-diphenylethane in 35% yield after 48 hours at 80 °C with concurrent formation of 1 (as adjudged by ³¹P NMR analysis). As such, the FLP 1/BCF was utilized in the catalytic hydrogenation of unactivated alkenes under mild



Figure 8. Proposed hydride insertion and ionic hydrogenation mechanisms leading to observed deuteration ratios in 3a when 2a is reacted with 1/BCF and D₂.

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Page 4 of 5

conditions. In isolation, complex 1 and BCF were found to be catalytically inactive for the hydrogenation of 1,1-diphenylethene (Figure 7). Additionally, the iron hydride [1-H][BAr^F₄] was tested under hydrogenation conditions and found to be inactive.

In contrast, the combination of 1 and BCF at 5 mol % loading under 4 atm of hydrogen was capable of reducing 1,1-diphenylethene (2a) to 1,1-diphenylethane (3a). Heating this reaction for 24 h at 60 °C resulted in a 29% yield of 3a after 24 hours, however, increasing the reaction temperature to 130 °C resulted in a yield of 76% after 24 hours. Although this result is not noteworthy when compared to the activity of noble metal catalysts, it is comparable in yield and conditions to other FLP catalyzed alkene hydrogenation reactions.¹⁶ For example, the rhenium oxide system reported by Ison operates at 100 °C with 10 mol % loading of BCF to hydrogenate 1,1-diphenylethlene in 84% yield.¹² Further, main group FLP systems capable of ionic hydrogenation of alkenes using BCF combined with either electron poor phosphines^{16a,b} or ethers^{16c} operate between 20-40 mol % catalyst loading, and electron poor alkenes can be reduced with BCF combined with 1,4-diazabicyclo[2.2.2]octane (DABCO)^{16d,e} or 2,2,6,6-tetramethylpiperidine (TMP)^{16f} in 5-20 mol % loadings.

The above reaction conditions were applied to a range of alkenes (Figure 7). It was found that terminal olefins 2a-d provided average yields of the corresponding reduced products after 24 hours. However, very little to no product was observed for internal alkenes 2e-h.

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Insight into the mechanism of hydrogenation was sought using deuterium (D₂) in place of hydrogen (Figure 8). A sample of 2a was loaded with 5 mol % 1/BCF and 1 atm of D2 was introduced at -196 °C. The sample was then thawed and heated at 60 °C for three days, after which time it was analyzed by ¹H, ²H and ³¹P NMR spectroscopies.

Analysis of the ²H NMR spectrum of the reaction revealed deuteration of 2a at both the 1- and 2-positions in a ratio of 10:4 respectively representing formation of a range of isotopologues of 3a. Furthermore, deuterium scrambling had resulted in a substantial concentration of the isotopologue 2a-2-D, where a deuterium had substituted a 2-position hydrogen atom in alkene 2a.

Given that this system is a hybrid transition metal FLP, both hydride insertion and ionic hydrogenation mechanisms are plausible (Figure 8). In the case of a hydride insertion mechanism, a high barrier for deuteride transfer from [BH(C₆F₅)₃]⁻ to a linear iron alkyl intermediate as compared to a branched intermediate may give rise to the observed deuterium ratioin 3a. Coupled with alkene insertion/ β -hydride elimination processes that allow H/D scrambling between [1-D]⁺ and 2a to give rise to significant concentrations of 2a-2-D, a higher incorporation of deuterium into the 1-position of 3a would be expected (as compared to the 2-position).

Given the high concentration of deuterium observed in the 1-position, it can be stated that catalytic turn-over would be favoured from the branched intermediate in this mechanism.

Alternatively, an ionic hydrogenation mechanism would form the intermediate carbocation $[C(CH_2D)Ph_2]^+$ (Figure 8). This could reversibly eliminate H or D to generate 2a or 2a-2-D, thus also allowing H/D scrambling between [1-D]⁺ and 2a. Complex [1-H]⁺ and 2a can then form [CMePh₂]⁺, that would react with $[BH(C_6F_5)_3]^-$ to give **3a-1-D**, thus also providing a plausible mechanism for the enrichment of deuterium in the 1-position of product 3a.

The ionic hydrogenation mechanism provides a simple explanation for the deuterium enrichment in the 1-position of 3a, and it would also not require the dissociation of any ligands to generate a vacant site for the alkene to coordinate. However, it is observed that terminal alkenes (2a-d) gave much better results than internal alkenes (2e-h). This selectivity is normally observed for transition metal hydride insertion reactions. DFT and kinetic mechanistic studies to understand this discrepancy are ongoing.

In summary, we have developed the first FLP system that employs a base metal as the Lewis base partner. In contrast to previously reported systems that may activate H₂ without direct intervention by then metal center (i.e. [Re=O]/BCF) or in a non-FLP mechanism (i.e. [Pt] systems), this iron based system is shown to activate hydrogen and other small molecules in an FLP manner where iron acts as the Lewis base partner.

We have also shown basic proof-of-principle that the combination of FLP chemistry with base metal chemistry can improve the catalytic efficiency of catalytic hydrogenation. Importnatly, the use of an FLP strategy allows the catalytically inactive complex 1 to be utilized in olefin hydrogenation. Given that we have shown activation of other small molecules, the opportunity exists to explore a number of other catalytic reactions employing this FLP system and small molecules that can be activated by it.

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Conflict of Interests

The authors declare no competing financial interest.

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Table of Contents artwork

