Synthetic Methods

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Metal-Free Hydrogenation of Unsaturated Hydrocarbons Employing Molecular Hydrogen

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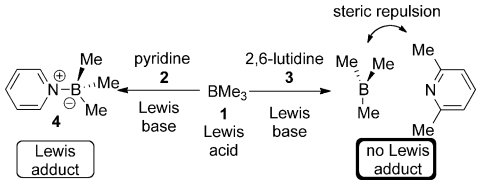
boranes · frustrated Lewis pairs · hydrogenation · metathesis · olefins

The metal-free activation of hydrogen by frustrated Lewis pairs (FLPs) is a valuable method for the hydrogenation of polarized unsaturated molecules ranging from imines, enamines, and silyl enol ethers to heterocycles. However, one of the most important applications of hydrogenation technology is the conversion of unsaturated hydrocarbons into alkanes or alkenes. Despite the fast development of the FLP chemistry, such reactions proved as highly challenging. This Minireview provides an overview of the basic concepts of FLP chemistry, the challenge in the hydrogenation of unsaturated hydrocarbons, and first solutions to this central transformation.

1. Introduction

The hydrogenation of unsaturated hydrocarbons is one of the most valuable and key technologies in biology and chemistry, and especially in industrial processes.[1] For such purposes transition-metal complexes or heterogeneous catalysts have been intensively investigated and very successfully applied. Transition-metal-free systems which react directly with hydrogen (H_2) are scarce. Biological systems[2] and main-group compounds have been shown to activate H_2.[3] However, a metal-free process that is capable of cleaving and liberating H_2 reversibly was introduced by Douglas W. Stephan in 2006.[4] This system takes advantage of Lewis-basic (phosphine or amine) and Lewis-acidic (borane) molecules, which, when combined do not extinguish their reactivity. Such counterintuitive reactivity was already observed by Herbert C. Brown, who studied "Steric Strains as a Factor in the Relative Stability of Some Coordination Compounds of Boron" in 1942 (Scheme 1).[5]

He found that steric congestion is primarily responsible for the formation of Lewis adducts. This behavior was exemplified by the reaction of trimethylborane (**1**) with either pyridine (**2**) or 2,6-lutidine (**3**). While pyridine readily forms the Lewis adduct **4**, the methyl groups in **3** prevent the formation of the corresponding Lewis adduct, thus leaving the reactive centers unquenched. Later on, this phenomenon led to the revolutionary finding that such reactivity enables the activation of small molecules, for example, H_2, and was introduced as frustrated Lewis pairs (FLPs).[6]



Scheme 1. Reactivity of trimethylborane (**1**) with different Lewis bases.[5]

2. Concept of Frustrated Lewis Pairs (FLPs)

The consequence of the conserved reactivity of the Lewis components was first reported in the seminal work by the group of Stephan[4,7] in which they reported the reversible, metal-free H_2 activation (Scheme 2a).

This reactivity was very quickly extended to intermolecular frustrated Lewis pairs (Scheme 2b),[8] which naturally opened up a vast number of combinations of Lewis bases with the commonly used tris(pentafluorphenyl)borane [$B(C_6F_5)_3$ (**5**)].[9] The strength of this concept can be found in its

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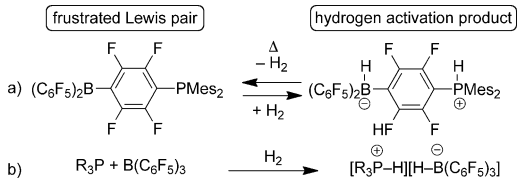

Scheme 2. Concept of frustrated Lewis pairs and metal-free H_2 activation.

simplicity and clearness. The conserved reactivity of the Lewis pair can now be exploited for the activation or fixation of a number of small molecules, for example, CO_2,[10] CO, SO_2,[11] NO,[12] N_2O,[13] and H_2.[14] In fact, the activation of the latter has attracted the most attention because of the multifaceted application for hydrogenation reactions.[6b,9a,14,15]

The investigation of the H_2 activation mechanism is of current interest, and theoretical chemists provide invaluable information.[16] On a basic level the heterolytic H_2 activation can be described by the donor→$\sigma^*(H_2)$ interaction, thus reducing the bond order in molecular H_2. At the same time the acceptor←$\sigma(H_2)$ interaction also weakens the H–H bond and finally results in the heterolytic splitting of H_2 (Figure 1). Since the potential surfaces are quite low, weak dispersion

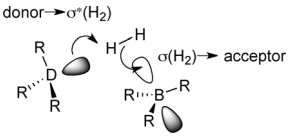

Figure 1. Orbital interactions for the synergistic, heterolytic hydrogen cleavage.

forces and electrostatic fields have significant impact on the energies of transition states.[17]

Accordingly, H_2 activation was also achieved by other Lewis bases or Lewis acids, for example, amines,[15b,18] carbenes,[19] borenium cations,[20] and alanes.[21] However, most FLP-catalyzed hydrogenations employ amines or phosphines as Lewis bases in combination with boranes as Lewis acids. These catalyst systems are most commonly used in reductions of polarized double bonds.

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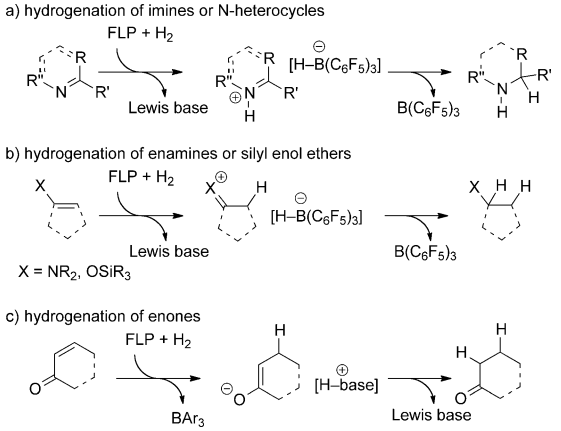
3. Application in Homogeneous Hydrogenation

3.1. Hydrogenation of Polarized Double Bonds

The most fascinating aspect of FLP-catalyzed hydrogenations is the formation of onium hydridoborates directly from heterolytic splitting of H_2 (compare to Scheme 2). Such borohydrides are well known for their versatility in carbonyl reductions, thus resulting in the first catalytic metal-free hydrogenation of imines with H_2.[7,22] Quickly this methodology was extended to other electron-deficient compounds such as ketimines,[7,18c,23] nitriles,[15b,18c] and heterocycles (Scheme 3a).[18d,24] Additionally, electron-rich compounds



Scheme 3. FLP-catalyzed hydrogenation of a) electron-deficient and b) electron-rich substrates, as well as c) α,β-unsaturated carbonyls.

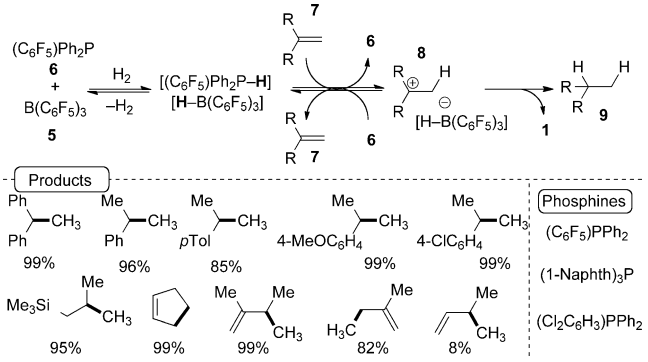
such as silyl enol ethers[25] and enamines[25b,26] were viable substrates for FLP-catalyzed hydrogenations (Scheme 3b). Generally the products are obtained in high yield under mild reaction conditions (25–120 °C, 4–80 bar H_2 pressure).

A common key mechanistic feature in the reduction of electron-deficient and electron-rich substrates is the formation of a strongly electrophilic carbonyl moiety by protonation or coordination of a Lewis acid (Scheme 3a,b). Imines, ketimines, and nitrogen-containing heterocycles need to be activated by a Lewis acid or Brønsted acid to enhance the electrophilicity of the carbonyl carbon atom. Here the protonation can occur by proton transfer from the onium cation after H_2 activation. Alternatively, the substrate can be directly utilized as a Lewis base for the H_2 cleavage in combination with $B(C_6F_5)_3$, thus furnishing the activated carbonyl which undergoes hydride addition (Scheme 3a). The protonation of electron-rich enamines or silyl enol ethers yield an activated carbonyl moiety which is subsequently attacked by the borohydride (Scheme 3b).[25–27] In marked contrast, the reduction of strongly electron-deficient α,β-unsaturated compounds requires more nucleophilic hydridoborates. Modifications of the borane to less electrophilic Lewis acids allowed the reduction of enones,[22] malonates,[28a] acrylates[28b] and nitroolefins[28b,c] (Scheme 3c).

3.2. Hydrogenation of Olefins

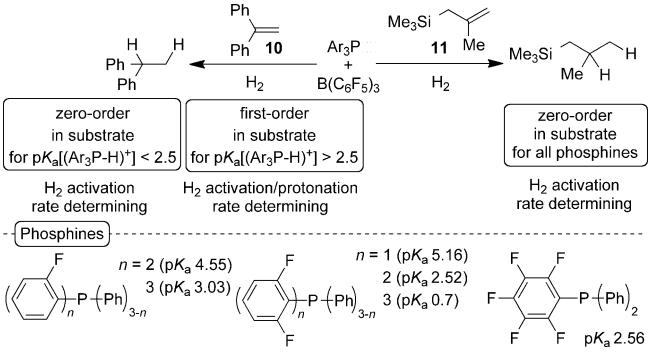
The hydrogenation of unpolarized olefins is more challenging because of the absence of heteroatomic sites which are susceptible to any of the activation mechanisms discussed in Section 3.1 (Scheme 3). However, double bonds can be activated for a nucleophilic attack either by transition-metal coordination or by reaction with strong electrophiles, for example, hydrohalic acids. The extension of such a protonation/addition sequence to FLP chemistry would require the formation of a strong Brønsted-acidic onium ion together with the hydridoborate upon H_2 activation. Most of the reported FLP systems derived from Lewis base/borane (phosphine, amine, pyridine, carbene or phosphinimide) combinations have demonstrated their capability to activate H_2, but none of the resulting Brønsted acids were strong enough to protonate an olefinic double bond.

In contrast to general belief, it was found that less electron-donating phosphines are capable of activating H_2 in combination with $B(C_6F_5)_3$ (**5**).[29] In fact, the H_2 cleavage becomes highly reversible with fluorinated phosphines so that the primary activation product, $[Ar_3P\text{-}H][H\text{-}B(C_6F_5)_3]$, can only be identified by NMR spectroscopy at low temperatures (up to −80 °C). The temperature for the observable H_2 activation is directly linked to the corresponding pK_a of the conjugate acid of the phosphine. For example, a comparably high pK_a of 5.16 leads to activation temperatures of 20 °C while a relatively low pK_a value of 0.7 leads to activation temperatures of −60 °C.[29b] Such fluorinated phosphines were used in the FLP-catalyzed hydrogenation of olefins.[29a] The reaction proceeds by transient hydrogen activation by the FLP **6**/**5** which transfers a proton to the olefin **7**, thus forming the carbocation **8**. Subsequent irreversible reaction with the hydridoborate liberates the hydrocarbon **9** and **5**, thus regenerating the FLP (Scheme 4).



Scheme 4. Hydrogenation of olefins.[29a]

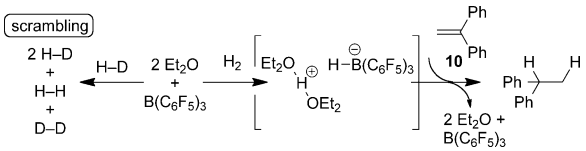
The transient nature of the carbocation **8** was proved by trapping experiments with nucleophiles, for example, *N*-phenyl-*N*-methyl aniline[29a] or di(2-fluorophenyl)phenylphosphine.[29b] The hydrogenation proceeded smoothly with electron-rich olefins in excellent yield. The nature of the Lewis base not only influences the reaction rate but is moreover responsible for the formation of undesired by-products arising from Friedel–Crafts dimerization (see below). For a more detailed picture of the reaction, six fluorinated triphenylphosphine derivatives, which only differed in their degree of fluorine content, were subjected to kinetic investigations of the FLP-catalyzed hydrogenation of 1,1-diphenylethene (**10**) and trimethyl(2-methallyl)silane (**11**).[29b] This first kinetic study of the Lewis base's influence on the FLP-mediated hydrogen activation and on FLP-catalyzed hydrogenation revealed that both H_2 activation and substrate activation play a crucial role for the overall rate (Scheme 5).



Scheme 5. Kinetic investigation of the FLP-catalyzed hydrogenation of olefins.[29b]

For weakly basic phosphines in combination with $B(C_6F_5)_3$ the H_2 activation becomes rate-limiting resulting in zero-order rates in olefin **10**. For stronger Lewis bases (p$K_a > 2.5$) the rate is dependent upon both the H_2 activation and the protonation of **10**. Keeping this in mind more nucleophilic olefins, such as **11**, should be more easily protonated. Hence the overall reaction rate is mostly affected by the H_2 cleavage. Indeed the rates for the hydrogenation of **11** correlate with the capability of the FLP to cleave H_2, with the most electron-releasing phosphine (high pK_a) having the highest rate and the least electron-releasing phosphine (lowest pK_a) having the lowest rate.

Recently it was disclosed that even diethyl ether can act as a Lewis base in combination with $B(C_6F_5)_3$ as a hydrogenation catalyst for olefins.[30] The presence of two equivalents of Et_2O relative to $B(C_6F_5)_3$ was found to facilitate H_2 cleavage. Quantum chemical calculations revealed that the addition of one molecule of ether is necessary to stabilize the diethyloxonium cation through a hydrogen bond (Scheme 6). Experimentally H_2 activation was verified by a H–D scrambling experiment which resulted in the catalytic isotope equilibration of H/D to a 2:1:1 statistical mixture of HD, H_2



Scheme 6. Diethylether as Lewis base in FLP-catalyzed hydrogenation.[30]

and D_2, respectively. The FLP system was catalytically active for the hydrogenation of **10** and anthracene[31] as was earlier demonstrated for the initial $(C_6F_5)PPh_2/B(C_6F_5)_3$ system with polycyclic aromatic hydrocarbons.

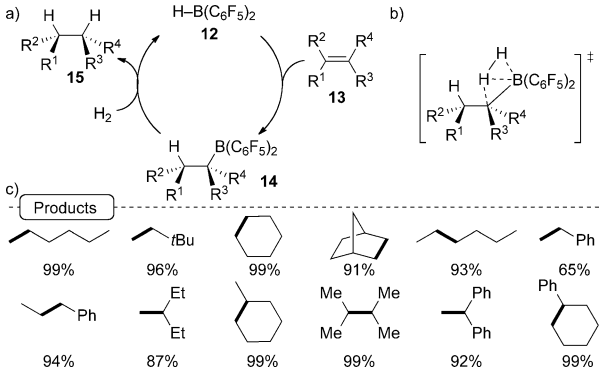
However, the hydrogenation experiments with other olefins resulted in the formation of Friedel–Crafts dimers because of the high acidity of the diethyloxonium cation. If related ethers, for example,$(Me_3Si)_2O$ or Ph_2O, were used instead of Et_2O only the dimerization products were observed. This clearly underlines the fact that the nature of the Lewis base plays a crucial role not only for the reaction rate but also for the selectivity.

So far electron-rich olefins were successfully hydrogenated using the FLP chemistry. As clearly seen from a mechanistic point of view the protonation of simple olefins will be more challenging. An alternative approach was reported by Wang et al., and it takes advantage of the well-known reactivity of olefins towards hydroboranes such as BH_3, 9-borabicyclo[3.3.1]nonane (9-BBN), or $HB(C_6F_5)_2$ (**12**). In the 1960s Ramp, DeWitt, and Trapasso reported the hydrogenation of select olefins in the presence of substoichiometric amounts of triisobutylborane with H_2 using 235 °C and 172 bar H_2 pressure.[32] These harsh conditions could be reduced as a result of the the excellent propensity of **12** to undergo hydroboration. This high reactivity was extensively used for the elegant synthesis of intramolecular FLPs[26b,27,33] or chiral boranes[23,34] for asymmetric imine hydrogenation. Also pentaarylboroles[35] or Lewis-acidic hydroboranes ($HB(Ar^F_2)$) can activate D_2 to afford the corresponding deuteroboranes.[36] The latter reaction can be understood as a σ-bond metathesis which is also observed in the synthesis of Piers' borane.[36b,37]

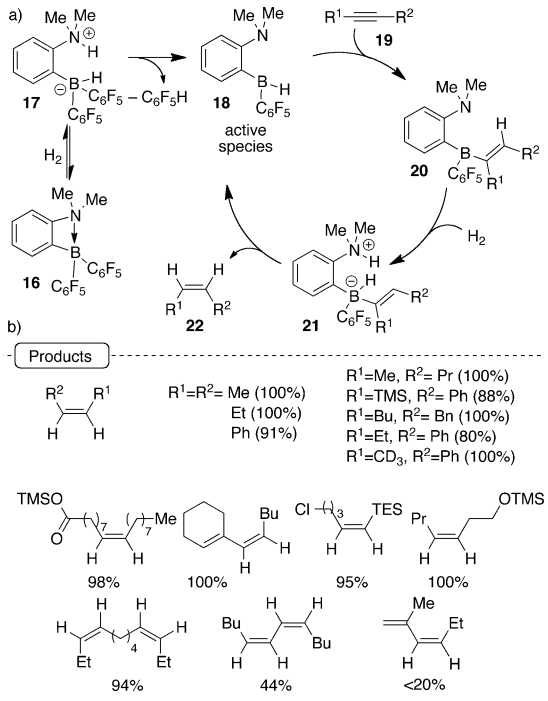
Such a process was anticipated for the hydrogenation of simple olefins (**13**; Scheme 7a):[38] first the hydroboration of the strongly Lewis-acidic borane **12** with the olefin **13** furnishes the diarylalkylborane **14** which subsequently undergoes σ-bond metathesis, thus liberating the saturated product **15** and recycling **12** as catalyst .

Kinetic investigations are consistent with an overall second-order rate law. In the transition state the H–H bond is significantly elongated to 1.06 Å (0.74 Å in free H_2) while both hydrogen atoms are located in close proximity (1.25 Å and 1.28 Å) to the boron atom (Scheme 7b). The natural bond-order analysis revealed significant charge transfer of the σ bond of H_2 to the empty *p* orbital of the boron. Simultaneously electron density is transferred from the σ alkyl–boron bond to the empty σ* bond of H_2. The hydrogenation proceeds under relatively mild reaction conditions (6 bar H_2, 140 °C) and provides good to excellent yields for a broad selection of substrates (Scheme 7c). Particularly higher substituted olefins, such as methylcyclohexene or 2,3-dimethylbut-2-ene, were hydrogenated in quantitative yields.

Only recently the highly selective FLP-catalyzed *cis* hydrogenation of alkynes was reported and proceeds through a protodeborylation step,[39] an alternative mechanism to the bond metathesis for cleaving an sp^3 or sp^2 carbon–boron bond to release an alkyl or alkene/aryl molecule (Scheme 6). The catalyst precursor consists of an intramolecular B/N FLP (**16**) which is activated in situ by exposure to an H_2 atmosphere at 80 °C. The FLP **16** exists as an intramolecular B–N adduct featuring a four-membered ring.[10a,e,11,26b,27,40] Because of the ring strain the B–N bond is relatively weak and reacts reversibly at room temperature with H_2 to give the ammonium hydridoborate **17** (Scheme 8a). At elevated temperatures **17** suffers from protodeborylation, thus yielding the catalytically active amino hydroborane **18** which hydroborates with the olefin **19**. The resulting vinyl borane **20** is sufficiently Lewis acidic to form the ammonium hydridoborate **21** by H_2 activation. The internal ammonium hydridoborate salt is perfectly setup for the final protodeborylation, thus releasing the product *cis*-**22** and regenerating the catalyst **18**. The method revealed an excellent substrate scope. A large number of alkynes (16 examples) were exclusively converted



Scheme 7. a) Proposed mechanism for the metal-free hydrogenation of olefins by σ-bond metathesis. b) Transition state of the σ-bond metathesis. c) Scope of the metal-free hydrogenation of simple olefins.[38]



Scheme 8. a) Mechanism of the FLP-catalyzed diastereoselective hydrogenation of alkynes. b) Selected products of the FLP-catalyzed hydrogenation of alkynes.[39] TES = triethylsilyl.

into *cis* olefins (Scheme 8b). Over-hydrogenation, a major problem in transition-metal-based hydrogenation, was not observed, and substrates bearing olefinic moieties were chemoselectively reduced. Terminal alkynes add directly to the borane to yield alkynylborates,[26b,41] which are inactive in H_2 splitting. However this limitation could be circumvented by TMS protection (TMS = trimethylsilyl) of the terminal alkyne. Similarly, TMS-protected alcohols or esters bearing an alkyne moiety were efficiently converted into the alkenes under the mild reaction conditions (2 bar, 80 °C to 120 °C).

4. Conclusions

Metal-free H_2 activation has experienced a dramatic evolution from a mere laboratory curiosity to a synthetically valuable method. The vast number of Lewis base and Lewis acid combinations allow the tailoring of an appropriate catalyst for a specific reaction. By exploiting this chemical reactivity the hydrogenation of unsaturated hydrocarbons has been realized for a field which has been traditionally associated with transition-metal chemistry. It will be very exciting to witness how the FLP technology will provide alternative catalytic processes for organic chemistry.

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