

FLP catalysis: the smart new approach to hydrogenation?

Could chemical industry's reliance on transition metals be vanquished by organo-catalysis? This article explores the field of frustrated Lewis pairs (FLP) catalysis which has been used to activate small molecules such as hydrogen or carbon dioxide, bears the advantage of avoiding costly rare earth noble metals such as Rhodium, Ruthenium, and Iridium, and has progressed to levels starting to rival conventional transition metals approaches. In an economic context setting out to build on circular hydrogen economy, FLP catalysed hydrogenation reactions are surely a key tool to the future fine chemical industry and hydrogen waste stream valorisation.

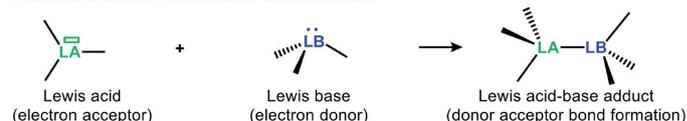
Noah Wright from the Greater Innovation for Smarter Materials Optimisation (GISMO) project at Lancaster University is conducting research into novel catalytic processes to develop a circular hydrogen economy and sets out the opportunities this presents.

Hydrogenation is an ever-present pillar in chemical industry. The materials science, polymer, pharmaceutical, agrochemical and foodstuffs industry all require catalytic hydrogenation systems for partial or full reduction of unsaturated bonds in their products. These transformations have been achieved in a variety of ways, however, as the 20th century saw such groundbreaking developments in transition metal (TM) hydrogenation chemistry the dogma meant that ultimately industry has almost exclusively used TMs to hydrogenate their compounds. The costs, toxicity and rarity of these precious TMs has led, since the turn of the century, to the development of new metal-free catalytic hydrogenation systems.

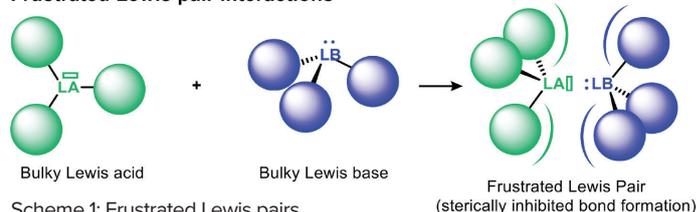
In 2006 Douglas Stephan and his group developed a reversible metal-free hydrogen activation system using $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_4)_2$. This sterically encumbered phosphine and borane combination (scheme 1) with the inability to quench one another is the reason for naming them 'frustrated' Lewis pairs (FLPs). It was quickly realised that the reactivity could be generalised to Lewis acid/Lewis base combinations given the steric constraints are sufficient to

prevent adduct formation and can emulate the TM electronic interactions. The last 15 years has seen major progressions in the field to the point where FLPs can start to compete with traditional TM catalysts. The scope of functional groups that have been reduced by various optimised FLP systems has seen rapid expansion from the initial imines in 2008 to now include N-protected nitriles, aziridines, enamines, alkenes, allenes, N-heterocycles, ketones, aldehydes, enones, ynones, polyaromatics and alkynes. A large number of studies have also probed the abilities of FLPs to activate a wide variety of small molecules as well as the original H_2 , these include CO_2 , CO , NO , SO_2 , and N_2O . Activation of these compounds has seen particular interest for industrial activation as this can lead to catalytic hydrogenation and capture of greenhouse gases. The last 5 years of FLP research has really seen a focus on heterogenous and asymmetric FLP catalysis with a range of approaches to achieve both.

Standard Lewis acid/base interactions



Frustrated Lewis pair interactions



Scheme 1: Frustrated Lewis pairs

Hydrogen is also becoming a much greater part of our energy consumption in order to phase out fossil fuels. The hydrogen economy is an envisioned future of hydrogen as a fuel for heat, vehicles and energy storage for long distance transport. With this in mind the goal of future projects should be to coordinate with industries already using hydrogenation and create a variety of novel FLP catalysts and develop these into optimised systems for application in their industry. The developments of new reactions using these new catalysts using hydrogen or hydrogen waste streams is key for the future of reducing energy consumption and achieving a more circular hydrogen economy.

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