In Silico Design and Synthesis of Novel, Metal-Free Systems for Bond Activation and Catalysis

Project Manager
Dr. Urs Gellrich

Researchers
Tizian Müller, Max Hasenbeck and Jama Ariai

Principal Investigator
Dr. Urs Gellrich

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Introduction

Our research focuses on the activation of stable bonds/small molecules. This is traditionally accomplished by transition metal complexes. However, in the course of sustainability and toxicity of the respective resources, the exploration of metal-free alternatives is demanding. Motivated by the rapid progress in the field of metal-free bond activation, we wish to expand this concept further. Therefore, we investigate, in a combined theoretical and experimental approach, novel potential catalysts to enable intricate chemical transformations in catalysis.

Methods

We use QM calculations, based on both density functional theory and wavefunction theory, to explore the potential energy surfaces of several bond activation processes by metal-free systems, thereby revealing the underlying reaction mechanisms. This rational design guides our synthetic work towards the development of efficient catalysts.

Results

The pyridone borane complex **3** liberates H2 under mild conditions (Scheme 1). The reverse reaction, heterolytic cleavage of the H−H bond, is achieved at room temperature under moderate H2 pressure.[1] DFT and DLPNO-CCSD(T) computations reveal that the active form, responsible for concerted H2 activation, is a boroxypyridine **2** being in equilibrium with its pyridonate borane complex **1**. Thus, the former can be regarded as a single-component frustrated Lewis pair.[2] Furthermore, in the course of hydrogenation, the boroxypyridine undergoes a chemical transformation to a neutral pyridone donor ligand akin to metal–ligand cooperation.[3] Hence, this metal-free system utilizes a novel mode of activation by incorporation of both frustrated Lewis pair reactivity and boron–ligand cooperation.

This concept can be applied in the reduction of benzaldehyde by the aforementioned pyridone borane complex (Scheme 2).[4] The resulting pyridone boronic ester complex **5** is stabilized by an intramolecular NH•••O hydrogen bond. The computations show that the hydrogenation step takes place in a concerted fashion, yielding a transient benzyl alcohol boroxypyridine complex **4** that undergoes barrierless O−H addition.

Outlook

QM calculations, combined with experimental in situ spectroscopic studies, are invaluable to gain more insights into the catalytic cycle and to unravel its elementary steps. These findings, in turn, allow to rationalize the mode of action and thereby improve the performance of the catalyst as well as to expand the substrate scope.

Publications

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