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Ammonia-borane dehydrogenation catalyzed by Iron pincer complexes: A concerted metal-ligand cooperation mechanism

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ABSTRACT

A quantum-chemical mechanistic investigation using density functional theory (DFT) on ammonia-borane dehydrogenation catalyzed by a series of iron bis(phosphinite) pincer complexes is reported. A metal-ligand cooperation mechanism has been proposed, in which the hydrogen atom of B–H moves to metal Fe and proton of N–H transfers to pincer ipso carbon simultaneously with the lowest activation barriers. DFT calculations and natural bond orbital (NBO) charge analysis suggest that Fe–POCOP complex with an electron-donating MeO group at the *para* position to the ipso carbon exhibits the highest catalytic activity. A plausible explanation of the observed catalytic activities is also given.

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Introduction

The ever-growing concerns on energy crisis have resulted in an urgent quest for the alternative renewable energy. Hydrogen is an ideal candidate as an energy carrier for fossil fuels if effective methods for its storage and release can be solved. Ammonia borane (NH₃BH₃, AB) is considered to be one of the most promising chemical hydrogen storage materials, which has received considerable attention in recent years due to the high gravimetric storage density (19.6 wt% of H₂) and high thermal stability. However, one of the challenges in the development of the hydrogen economy is to enhance the release rate and production of hydrogen released from AB [1–7]. Searching for efficient transition metal catalysts for

reversible H₂ release is still critical in dehydrogenation of AB. As a result, a myriad of catalysts for AB dehydrogenation have been investigated not only experimentally but also computationally in recent years [8–41]. Under reasonable conditions, transition metal based catalysts have provided the most potential for controlling both the rate and extent of H₂ release yet reported for AB dehydrogenation. Unfortunately, many of these catalysts use either relatively expensive metals (such as Ru [13,17,21,22], Rh [8,23,24], Pd [25,26], Ir [11,27,28] and Os [29], etc.) or suffer from instability under the reaction conditions (Ni [30], Pd [25]). Therefore, developing less expensive and earth abundant metal catalysts (Ti [9,31,32], Fe [20,33–36], Mo [37]) for AB dehydrogenation have attracted growing interest.

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Recently, a number of mechanistic studies have been carried out to explore the transition-metal-catalyzed dehydrogenation reaction of AB. Theoretical investigations by Paul and Musgrave [12] revealed that dehydrogenation of ammonia-borane (AB) using the Ir-pincer catalyst [(POCOP)Ir(H)₂] proceeds through a concerted N–H and B–H removal inner-sphere mechanism. Ohno and Luo [10] reported an intramolecular stepwise dehydrogenation process of Me₂NH·BH₃ catalyzed by Cp₂Ti in which N–H activation precedes B–H activation. Weller and coworker [38] suggested that ammonia borane dehydrogenation promoted by a Rh complex occurs via a B–H activation followed by the N–H activation. Oxidative addition of the B–H bond and then N–H β-elimination has also been explored by Douglas [39]. In contrast, Yang and Hall [15] demonstrated that the Ni(NHC)₂ catalyzed ammonia-borane dehydrogenation includes an initial NHC-ligand-assisted N–H proton transfer to ligated carbene carbon step. Fagnou's [13] bifunctional Ru catalysts undergo similar proton transfer to ligand nitrogen step, which they defined as ligand-assisted concerted dehydrogenation mechanism [18]. Meanwhile, our group investigated the catalytic AB dehydrogenation mechanism with Ir pincer complex [Ir(^tBu')₂]⁺ [40] and Ni(NHC)₂ catalyst [41], respectively, in which a proton transfer mechanism is also favored.

A more recent work by Guan's group [36] independently developed a catalytic system using a series of Fe–POCOP pincer complexes (Fig. 1) as catalytic precursors for the dehydrogenation of AB, which are best of few examples of first-row transition metal catalysts reported to date. This catalytic reaction can release 2.3–2.5 equiv. of H₂ per AB. Among the three Iron catalysts, iron bis(phosphinite) complex **M1** exhibits the highest activity in terms of both the rate and the extent of H₂ release [36]. As one of our ongoing research interests, we carried out theoretical modeling to investigate the mechanisms of the AB dehydrogenation catalyzed by Guan groups' Fe–POCOP pincer complexes (Cat-PMe, Cat-PPh, and **M1** shown in Fig. 1). Herein, the most activated complex, a prototype Iron pincer catalyst, [(MeO–POCOP^{Me})Fe] (**M1**), has been selected for full theoretical studies of AB dehydrogenation mechanism, in which the ⁱPr₂ were replaced by methyl substituents to save computational resources. According to our calculations, the optimized catalytic cycle for catalytic AB dehydrogenation is shown in Fig. 2.

Computational details

All calculations were conducted using density functional theory with the Gaussian09 suite of programs [42] at the M06 [43] level of theory. All main group elements were represented by means

of the 6-31G(d) [44,45] basis set along with the quasirelativistic Stuttgart Dresden pseudo potential SDD [46] for iron. For each optimized stationary point vibrational analysis was performed to establish its nature as a minimum (no imaginary frequencies) or saddle point (only one imaginary frequency). In addition, intrinsic reaction coordinate (IRC) [47,48] analysis was carefully carried out to confirm whether it connected the correct configurations of reactant and product on the potential energy surface. The single-point energy calculations with solvent effects (THF) were performed through the SMD continuum model [49] at the M06/6-311 + G (d,p) [50] level on gas phase-optimized configurations (Fig. S1). Energies reported in the text are based on the gas-phase free energies. Furthermore, for the sake of understanding the differences in catalytic activity of the three precatalysts, the natural bond orbital (NBO) [51] charge analysis was performed at the same level of theory. Optimized structures were visualized by the CYL view program [52].

Results and discussion

Our starting point in the dehydrogenation of AB is the dissociation of phosphine ligand *trans* to the hydride, which provides a vacant coordination site for AB activation and forms AB-bound complex **M2** easily (Fig. 2). In the catalytically active intermediate **M2**, the distance of Fe–H bond is 1.76 Å, B–H bond is 1.24 Å, leading to a η¹ sigma complex, involving a 3-center, 2-electron (3c-2e) Fe···H···B bridging bond (Fig. S2). However, the catalytically active species **M2** can undergo a geometric isomerization to yield **M2'**, placing the AB molecule *trans* to the *ipso* carbon. DFT calculations show that **M2'** is less stable than **M2** by 7.0 kcal/mol (Fig. S1), which is in good agreement with the experimental observations. As shown in Fig. 3, the dehydrogenation of AB catalyzed by Iron pincer complex **M1** may potentially occur through four possible reaction pathways, including no ligand-assisted (path 1 and path 2) and ligand-assisted (path 3 and path 4) AB dehydrogenation. At this point, the current catalytic reaction system is a good model to investigate competitions among various possible pathways in catalytic dehydrogenation of AB.

No ligand-assisted ammonia-borane dehydrogenation

At the beginning of our theoretical investigation, driven by the previous theoretical studies unveiled by Paul and Musgrave, we firstly examined the concerted N–H and B–H transfer inner phase mechanism. As depicted in Fig. 3 (path 1), the N–H and B–H bonds of AB simultaneous undergo oxidative addition to Fe center via a five-membered transition state **TS1**. In **TS1**, the distances of Fe–H1, B–H1, Fe–H2, and N–H2 are 1.67 Å, 1.30 Å,

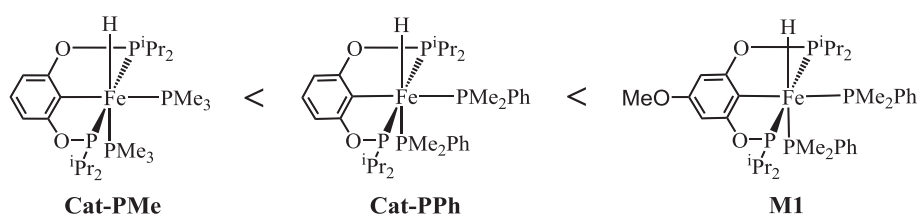


Fig. 1 – The increasing catalytic activities of Fe–POCOP pincer complexes [36].

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