Final Project Report: Time-Resolved XAFS Spectroscopic Studies of B-H and N-H Oxidative Addition to Transition Metal Catalysts Relevant to Hydrogen Storage

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Abstract

Successful catalytic dehydrogenation of aminoborane, H_3NBH_3, prompted questions as to the potential role of N-H oxidative addition in the mechanisms of these processes. N-H oxidative addition reactions are rare, and in all cases appear to involve initial dative bonding to the metal by the amine lone pairs followed by transfer of a proton to the basic metal. Aminoborane and its trimethylborane derivative block this mechanism and, in principle, should permit authentic N-H oxidative attrition to occur. Extensive experimental work failed to confirm this hypothesis. In all cases either B-H complexation or oxidative addition of solvent C-H bonds dominate the chemistry.

Background of the Proposed Research

Extensive work done by our collaborators at PNNL established the ability of several rhodium compounds to catalyze the loss of hydrogen from aminoborane, H_3NBH_3. Aminoborane is an attractive hydrogen storage material having 19.3 % hydrogen by weight. *Operando EXAFS* studies of these catalytic reactions determined that all of the rhodium starting materials produce the same tetrahedral Rh_4 cluster as the active catalyst.[i] EXAFS is unable to exactly distinguish between N and B bound to Rh, therefore computational studies were carried out to clarify the mechanism of reaction. These high level calculations suggest that rhodium undergoes an initial oxidative addition into the H-B bond to yield both terminal and bridging metal hydrides. Subsequent reaction of these hydrides with the slightly acidic N-H is projected to be responsible for hydrogen formation.

These results prompted us to ask under what circumstances would it be possible to insert a metal into an N-H bond? Energetically N-H bonds are weaker than C-H bonds (391 vs. 413 kJ/mole) and are, in fact somewhat weaker than Si-H bonds (395 kJ/mol) that are well known to undergo oxidative addition by transition metals. N-H bonds are more polar than C-H bonds and have the opposite polarity of Si-H bonds. As these fundamentals would seem to favor N-H oxidative addition, why are there only a handful of examples of apparent N-H oxidative addition.

Unlike carbon and silicon derivatives, nitrogen compounds have lone pairs that dominate the reactivity with electron deficient metals.

Reactions between ammonia and primary or secondary amines give rise to Lewis acid/base ammine complexes rather than to N-H oxidative addition. For those cases where N-H oxidative addition have been reported,[ii] computational studies suggest that the likely mechanism involves formation of a Lewis acid/base complex followed by transfer of an amine proton to the basic metal.[iii] This feature of N-H oxidative addition differs substantially from C-H oxidative additions that proceed through agostic interactions of the C-H bond with the metal. Lewis acid/base amine complexes, such as H_3NBH_3 in which the lone pair is bound up in a strong dative bond, in principle offer a more authentic platform to investigate N-H activation without the competition of the nitrogen lone pair.

Experimental Design

Building on the known C-H activation chemistry, we identified a series of metal complexes that were known to oxidatively add C-H. Our approach was to photochemically generate 16 electron intermediates with the expectation of observing N-H oxidative addition. H_3NBH_3 appeared to be an attractive platform with which to test these reactions.

We have already noted that H_3NBH_3 has been shown to undergo B-H oxidative addition with a variety of rhodium compounds. Reaction of aminoborane with a number of photochemically accessible 16 electron species yielded results that were consistent with σ-complexes in which the B-H end of the aminoborane is bound to the metal without B-H bond breaking. This result is not surprising in that tetrahydroborate, BH_4^{1-}, complexes of transition metals are well known.

To remove the competition between B-H and N-H bonds we shifted our attention to H_3NBMe_3, an inorganic analogue of neo-pentane, 2, 2-dimethylpropane. Neopentane has been shown to undergo C-H oxidative addition by CpM(CO) fragments where M = Rh and Ir.[iv] Additionally, $(R_3P)_2Pt(H)$(-neopentyl) compounds have been prepared.[v] These neopentyl complexes may be isolated but their rates of formation are slow relative to other hydrocarbons because of steric factors.

We have found that "$Fe(dmpe)_2$", formed from photolysis of $H_2Fe(dmpe)_2$, where dmpe is bis(dimethylphosphino)ethane, does not react with H_3NBMe_3 although reaction of this intermediate with amines has been shown to form $Fe(dmpe)_2(H)(NHR)$ derivatives. $H_2Fe(dmpe)_2$ has even been shown to react with methane in liquid Xe.[vi]

No reactions were observed upon photolysis of $M(CO)(PR_3)_2Cl$, where M = Rh and Ir, with H_3NBMe_3. In contrast, a thermal reaction between $(R_3P)_2Pt$(oxalate) and H_3NBMe_3 was found to break the N-B bond with release of BMe_3. The details of this reaction are not yet clear. Similarly, photolysis of $TpRh(CO)_2$, where Tp is tris(pyrazoyl)borate, with H_3NBMe_3 failed to yield characterizable products. $Cp'M(CO)_2$, where Cp' = Cp or Cp* and M = Rh or Ir, and (η^6-mesitylene)$Os(CO)H_2$ were examined.

In each case C-H oxidative addition with the hydrocarbon solvents was observed with no evidence of N-H reaction.

As can probably be understood from the above, This project that began with high hopes of finding authentic examples of N-H oxidative addition ended up with little to show for the effort. In reactions of aminoborane and substituted aminoboranes, R_2HNBH_3, the N-H bond appears to serve as a proton source for hydrogen liberation with no evidence for oxidative addition of N-H bonds. The introduction of BMe_3 to eliminate the possibility of B-H addition appears to create a steric barrier to N-H oxidative addition allowing solvent C-H oxidative addition to dominate.

Personnel

Two graduate students, Wyatt Thornley and Temple Warwick, worked full time on this project and an undergraduate, Bryce Sumner, was employed part time during the academic year and full time in the summers. Wyatt took on responsibility for proposed time-resolved step-scan FTIR studies while Temple, assisted by Bryce, focused on the synthesis of target compounds and solution studies. As the project progressed all three students were engaged in preparing reactive catalytic species and examining their reactions with the various aminoboranes. Both graduate students traveled regularly to PNNL to participate in group meetings. Temple completed his Ph.D. work and graduated in 2012. Temple now works for DOE at INL. Wyatt's progress was thrown off by a year of setbacks with the step-scan FTIR and will finish up in May, 2015. Bryce completed his BS in engineering and is now employed.

Products of the Research

Despite intensive effort, the research project yielded many negative results but little in the way of publishable data. A side study involving the formation and reactivity of Me_3BNH_2Li is continuing.

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