# Activation of hydrogen with bi-functional ambiphilic catalyst complexes

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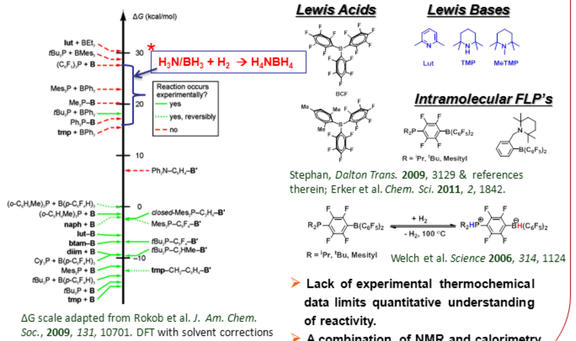
## Abstract

The objective of our research is to develop fundamental insight into small molecule activation in molecular complexes that will provide the basis for developing rational approaches in new catalysis design. Our focus is bi-functional – ambiphilic catalyst centers – molecular complexes comprised of both electron-rich and electron-poor sites. We are interested in the development of molecular structures capable of the heterolytic activation of hydrogen. We are developing new approaches to reaction calorimetry to obtain both kinetic and thermodynamic data, simultaneously, under in-situ or operando conditions to characterize the energy landscape of catalytic processes. Our research approach uses a combination of experimental spectroscopy and computational modeling approaches to study trends in structure-function relationships that control the thermodynamics and kinetics of small molecule activation.


## Introduction

*"Sterically demanding phosphine donors and Lewis acids generate an acid-base couple incapable of adduct formation, which opens alternate reaction pathways"* – Douglas Stephan *(Science, 2006)*



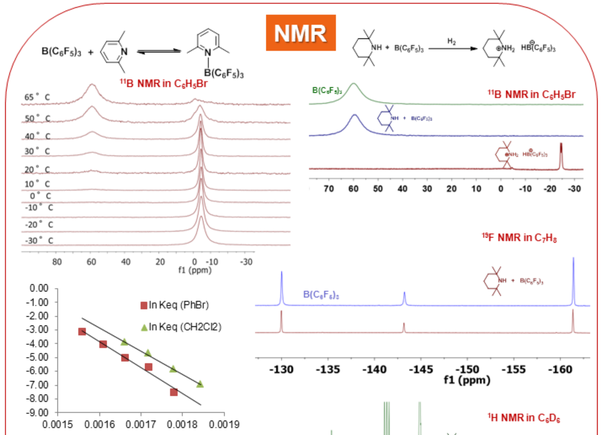

Stephan, *Dalton Trans.* **2009**, 3129 & references therein; Erker et al. *Chem. Sci.* **2011**, *2*, 1842.




ΔG scale adapted from Rokob et al. *J. Am. Chem. Soc.*, **2009**, *131*, 10701. DFT with solvent corrections
*AB + $H_2$ → ABH2 thermodynamics from Autrey et al. Faraday Discuss. **2011**, 151, 1157

- Lack of experimental thermochemical data limits quantitative understanding of reactivity.
- A combination of NMR and calorimetry is being used to address this gap.

## NMR

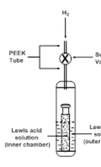



| kcal/mol 30 ° C | PhBr | $CH_2Cl_2$ |
|---|---|---|
| ΔH | -17.9 | -16.7 |
| ΔS | -49.2 | -47.3 |
| ΔG | -3.2 | -2.6 |
| $K_{eq}$ | 240 | 81 |

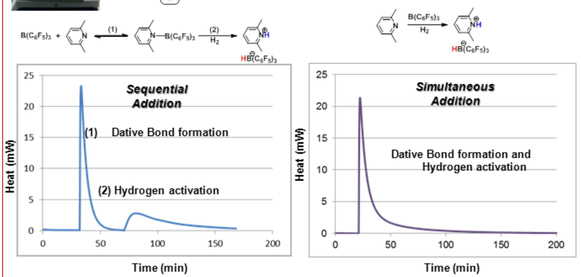
NMR spectroscopic signatures of FLPs. Nothing observed by $^{19}$F or $^{11}$B but shift of N-H in $^{1}$H NMR.

## Reaction Calorimetry: Thermodynamics

**Reaction calorimetry measures the heat flow, *q*, of the reaction.**




- Mixing cell under ambient $N_2$ atmosphere (loading cells in glove box) : ΔH observed (integrated area) is combination of enthalpy of dative bond and heats of dilution.
- Pressurize cell with $H_2$ to measure the heat of reaction of hydrogen activation by FLP.

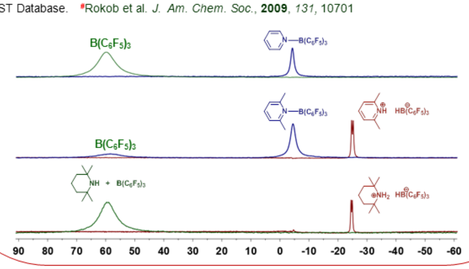



- The sum of the individual steps (dative bond formation and hydrogenation) equals the total heat released in Heterolytic splitting of $H_2$.
- Two methods (sequential and simultaneous) to determine $\Delta H_{H2}$

| Solvent = $C_6H_5Br$; $H_2$ pressure = 7 atm [LA and LB] = ~0.05M | Corrected $\Delta H_{Hydro.}$ (kcal/mol) | Exp PA-LB^ Calc. (PA-LB)# (kcal/mol) |
|---|---|---|
| $(tBu)_3P + B(C_6F_5)_3 \xrightarrow{+H_2} (tBu)_3\overset{\oplus}{P}H\ \overset{\ominus}{H}B(C_6F_5)_3$ | -31.4(±0.3) | -- (243) |
| $NH + B(C_6F_5)_3 \xrightarrow{H_2} \overset{\oplus}{N}H_2\ \overset{\ominus}{H}B(C_6F_5)_3$ | -31.5 (±0.2) | 235.9 (235) |
| $NMe + B(C_6F_5)_3 \xrightarrow{H_2} \overset{\oplus}{N}HMe\ \overset{\ominus}{H}B(C_6F_5)_3$ | -31.8 (±0.4) | -- (--) |
| $B(C_6F_5)_3 \rightleftharpoons \xrightarrow{H_2}$ | -23.4(±0.4) | 230.2 (229) |
| $P(C_6H_5)_3 + B(C_6F_5)_3 \xrightarrow{+H_2} (C_6H_5)_3\overset{\oplus}{P}H\ \overset{\ominus}{H}B(C_6F_5)_3$ | -12.1(±0.2) | -- *(233)* |

**Looking for correlation to predict reactivity. Sufficient driving force, back off on LA – e.g., Bis? BCCI? Alternatively back off on LB, TPP?**

^ NIST Database. #Rokob et al. *J. Am. Chem. Soc.*, **2009**, *131*, 10701




## Reaction Calorimetry: Kinetics

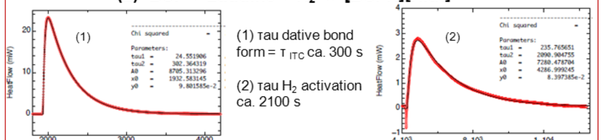
Mechanistic Kinetic Modeling (MKM) can yield detailed insight into reaction mechanism: $q(t) = \Delta H_{rxn} * volume * dC/dt$

$$\% \text{ conversion} = \int_{t_o}^{t} q(t) / \int_{t_o}^{t_f} q(t)$$

Need to minimize adjustable parameters:
Use $K_{eq}$ to set initial $H_2$(liq). measure independently when not available
Use Keq from NMR. measure $k_1$ & $k_{-1}$ from 2D NMR
Vary the [LA], [LB], $[H_2]$. determine kinetic order, KIE

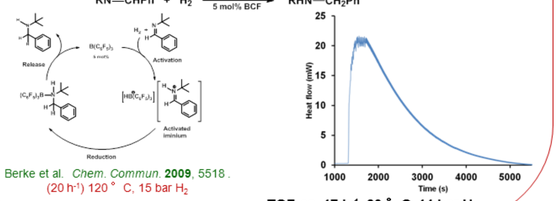
Blackmond et al. *Angew. Chem. Int. Ed.* **2005**, *44*, 4302.

**(1) BCF + Lutidine ⇔ BCF—Lut**
**(2) BCF + Lutidine + $H_2$ ⇔ [BCFH][Hlut]**




(1) τau dative bond form = $\tau_{ITC}$ ca. 300 s

(2) τau $H_2$ activation ca. 2100 s



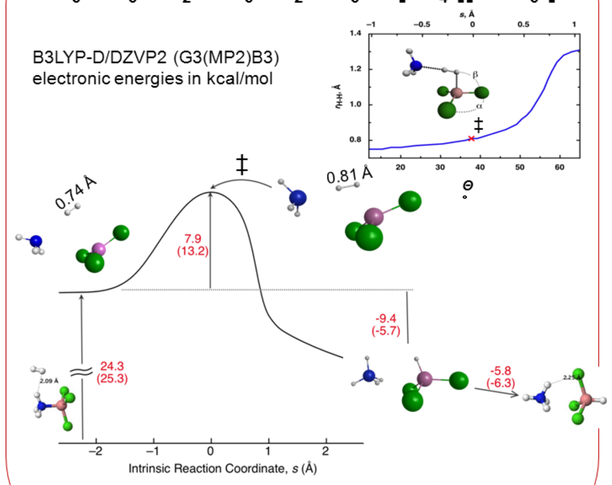

Berke et al. *Chem. Commun.* **2009**, 5518.
(20 $h^{-1}$) 120 ° C, 15 bar $H_2$

**TOF, ca. 17 $h^{-1}$, 80 ° C, 14 bar $H_2$.**

## Theoretical study of model reaction

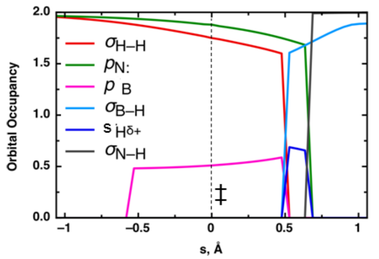
$$NH_3{\cdot}BCl_3 + H_2 \rightarrow H_3N{\cdot}H_2{\cdot}BCl_3 \rightarrow [NH_4^+][BHCl_3^-]$$

B3LYP-D/DZVP2 (G3(MP2)B3) electronic energies in kcal/mol




- Reaction coordinate s reflects distortion of $BCl_3$ from planarity
- H-H stretch remains strong at the S

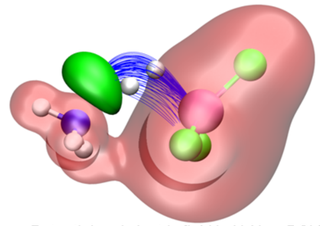
## Orbital analysis of $H_3N{\cdot}H_2{\cdot}BCl_3$




**3-stage mechanism**

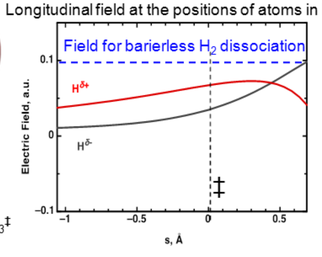
1. Weakening of $H_2$ and $BCl_3$ distortion
2. Breaking of $H_2$ and B-H bond formation
3. N-H bond formation

## Electric field along the MEP for $H_3N{\cdot}H_2{\cdot}BCl_3$



Potential and electric field in $H_3N$ --- $BCl_3$‡

Longitudinal field at the positions of atoms in $H_2$




## Energy decomposition for $H_3N{\cdot}H_2{\cdot}BCl_3$

| Interaction (kcal/mol) | $NH_3$-$H_2$-$BCl_3$ | $[NH_3$-$H_2$-$BCl_3]^‡$ |
|---|---|---|
| Electrostatic | -0.4 | -29.7 |
| Exchange | -2.4 | -41.6 |
| Repulsion | 10.1 | 137.9 |
| Polarization | -6.7 | **-59.1** |
| Dispersion | -2.6 | -9.9 |
| Total | -1.9 | -2.3 |

Polarization is the dominant stabilizing term:

Distortion of the orbitals (effect of the field): -8.1 kcal/mol

B-H and N-H bond formation: (effect of the orbital interaction): -51.0 kcal/mol

## Future Research

- Lewis Acids:
  - *Can we tune structure to decrease hydride affinity?*
  - *Can a stronger base compensate for a weaker acid?*
  - *How does the strength of acid and base effect kinetics?*
- Lewis Bases:
  - *How are solvent effects on proton affinity?*
  - *Is pKa scale expanded of compressed?*
  - *Is the reaction pathway different for P vs N base?*
- Geometrically considerations:
  - *What FLPs are better for catalysis, intra or intermolecular?*
  - *How do we determine the weak forces that hold an FLP together?*
  - *What is the optimized structure for splitting $H_2$? end-on, side on?*
  - *How does bond distortion effect kinetics?*
  - *What dominates the reactivity in an FLP? electric field? Bond distortion?*
  - *Does $H_2$ act as a 'wire' for charge transfer?*
- If we can start to answer some of these questions we will be able to rationally design catalyst structures to tune reactivity to optimize non-metal reduction pathways.

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