Smith Group Research

Invention of Catalytic Reactions

\[ \text{Catalyst} \quad \text{Product} \]

\[ \text{Z} = \text{BX}_2, \text{aryl, OH, ...} \]

Materials From Renewable Resources

\[ \text{HO}_2\text{C}-\text{CHOH} \quad \text{Polylactic Acid} \]

Commodity Materials

Biological Applications

Energy

Developing New Chemistry for Old Fuels
$upport

National Science Foundation

MERCK

ACS Green Chemistry Institute

BoroPharm, Inc.

National Institutes of Health

Michigan State University

Economic Development Corporation

Dow
C-H Activation: A Chemical “Holy Grail”


Iverson and Smith JACS 1999, 121, 7696.
Great Things Can Have Modest Beginnings

\[
\begin{align*}
&\text{[Ir(OMe)(COD)]}_2, \quad \text{HBPin,} \\
\text{[IrCl(COD)]}_2, \text{ or} \\
\text{(COD)} \\
\text{L} = \text{bisphosphine or bpy}
\end{align*}
\]

Boron is a Portal to Molecular Diversity

Aryl—B(OR)₂

Aryl—R

Aryl—NR₂

Aryl—SR

Aryl—X

Aryl—OH

Aryl—H + H—B(OR)₂

1. H-Bpin, 0.02 eq. (Ind) Ir(COD), dmpe, 150 °C, 3 h
2. aqueous Oxone, acetone, 25 °C, 10 min

one-pot, 79% yield

previous synthesis,
10 steps from TNT

Broad Scope of C–H Functionalization
Pyrrole Is The Biggest Outlier
N⋯H⋯O Bonding in the Transition State
Ligands have been shown to increase borylation rates, and dipyridyl ligands are more basic, which accounts for the pinacolate oxygens in complexes with more electron-rich ligands. Ortho selectivity (Figure 3) is enhanced by the use of directed H-bonding, where the H-bonding direction is in line with the electronic structure of the carbamate. The preference for reaction at the least hindered position (Table 1, entries 4 and 7 in Table 1) occurs because the selectivity diverges from that of 4-R (R = Me, CF3, or F) used to minimize diborylation. Converting Bpin products to their acetamide analog, which borylates ortho to CN exclusively. The comparison with D-protected anilines with a single meta substituent, where the H-bond direction is in line with the carbamate's electronic structure, produces a yield of 90:5:5 from entry 1. This is not an issue for 4-substituted substrates where the selectivity is high. Except for the acetamide analog, which borylates ortho to CN exclusively. The comparison with D-protected anilines with a single meta substituent, where the H-bond direction is in line with the carbamate's electronic structure, produces a yield of 90:5:5 from entry 1. This is not an issue for 4-substituted substrates where the selectivity is high. Except for the acetamide analog, which borylates ortho to CN exclusively. The comparison with D-protected anilines with a single meta substituent, where the H-bond direction is in line with the carbamate's electronic structure, produces a yield of 90:5:5 from entry 1.
Reaction Scope

\[
\begin{align*}
\text{NH}_2\text{R}_1\text{R}_2 & \quad + \quad \text{HBpin} \\
\text{NH}_2\text{BpinCl} & \quad \xrightarrow{0.25 \text{ mol}\% [\text{Ir(OMe)COD}]_2} \\
\text{NH}_2\text{R}_1\text{R}_2\text{BpinCl} & \quad \text{1.0 mol}\% \text{ tmphen} \\
\text{THF, 16h, 80 °C} & \quad \text{3.0 equiv} \\
\end{align*}
\]

Sean Preshlock and Don Plattner
Poly(lactic) Acid: A Renewable Commodity Plastic

poly(L-lactide) (PLLA)

poly(rac-lactide) (PLA)

crystalline ($T_m = 180 \, ^\circ C$)
glassy $T_g \,(\sim 55 \, ^\circ C)$:

Dehydration and Thermal Cracking

Fermentation

Hydrolysis

ROH

Metal catalyst

L-Lactide

PLLA
Degradable Single Molecule Micelles

Degradable Amphiphilic Polymer

Figure 17. TEM images of polymer nanomicelles (a) $M_n \sim 43,000$, diameter $\sim 10$ nm (b) $M_n \sim 260,000$, diameter $\sim 30$ nm.
Functional Nanoparticle Applications

Drug Screening (Labeling)
- Well-defined
- Easily Synthesized
- Controllable Release

Gene Delivery (Transfection--siRNA or DNA)
- Stimuli-responsive
- Degradable
- Cross-linkable
- Biocompatible

Diagnosis (Devices and Labeling)
- Diagnosis/Monitoring (Disease Markers)

Drug Delivery (Therapy)
- Detection (Imaging)

From Degradable to Nondegradable Nanomicelles

\[ \text{“Click”} \]

\[
\begin{align*}
\text{Degradable} & \quad \text{Nondegradable} \\
\end{align*}
\]

\[
\begin{align*}
\text{Marie Le Gaillard} & \quad 37-66 \% \text{ yield, 20 g scale} \\
\end{align*}
\]
A Simple Market Analysis

Membrane proteins are projected to have a $30 billion annual market...

...That buys a lot of beer.

Tween-80

Amphipol

Poorly degradable
Encapsulation of Non-Polar and Polar Species in Nanomicelles

10 kD PMMA

azobenzene headgroup

hydrophobic polymer in polymer micelle water soluble

Rhodamine B hydrocarbon indoluble

Charged dye in reverse polymer micelle hydrocarbon soluble
Enhancing Protein Solubility with Degradable and Tailorable Micelles
Sustainability is an Old Problem

By 1853 New York omnibuses carried 120,000 passengers per day.

In 2009, the New York Subway carries 4,300,000 passengers per day
Fossil Fuels: Key to 20th Century Sustainability

Growth is the biggest challenge to sustainability
The Energy Problem

By 2050 Earth’s population is predicted to increase by 50% while energy demand is predicted to increase by at least 100%
The Problem with CO$_2$ Recycling

Atmospheric CO$_2$ at Mauna Loa

3 Billion Years Ago

Today
Carbon-Free Fuels

Disadvantages of carbon-based fuels

CO$_2$ recycling required for carbon neutrality

Low CO$_2$ concentration hampers atmospheric recovery

Onboard CO$_2$ recovery impractical for transportation applications

One possible solution: Avoid carbon!
Carbon-Free Fuels

- N2
- O2
- CO2
- Other
Carbon Free Fuels: Research Team

MSU Research Team
Professor Thomas Hamann-Energy conversion chemistry
Professor Aaron Odom-Nitrogen chemistry, catalysis
Professor Viktor Poltavets-Solid-state chemistry, catalysis
Professor Milton Smith-Catalysis
Professor Daniel Nocera (Harvard/MSU)-Energy science

Dr. James Boncella (Los Alamos)-Fuel cells, nitrogen chemistry

Targeted agencies for center funding: DOE (ARPA-E), NSF
Ammonia: A Hydrogen Dense Fuel

Advantages

Haber-Bosch process is well-established and is the second largest industrial chemical process. Approximately 1-2% of global energy is dedicated to ammonia production.

1/2 N₂ + 3/2 H₂ $\rightarrow$ NH₃

$\Delta H^\circ_{\text{rxn}} = -11$ kcal/mol,

$\Delta S^\circ_{\text{rxn}} = -24$ cal/mol·K

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>7.1</td>
</tr>
<tr>
<td>160</td>
<td>1.0</td>
</tr>
<tr>
<td>450</td>
<td>0.01</td>
</tr>
</tbody>
</table>

NH₃ $\rightarrow$ 1/2 N₂ + 3/2 H₂

0.077 V

- By mass, liquid NH₃ energy density is 40% of gasoline, 94% of methanol
- Liquid NH₃ is an efficient H₂ carrier

2 NH₃ + 3/2 O₂ $\rightarrow$ N₂ + 3 H₂O

Releases 87% of the energy of H₂ oxidation!
Ammonia: A Hydrogen Dense Fuel
Ammonia: A Hydrogen Dense Fuel

Advantages

Synthesized from nitrogen, the most abundant gas in the atmosphere

Can be used as fuel in internal combustion engines

Produces less NOx emissions than gasoline

Ammonia is non-flammable
Ammonia: A Hydrogen Dense Fuel

Challenges

Carbon-neutral H$_2$ production does not meet energy needs

Current Haber-Bosch process requires high pressure of N$_2$ and H$_2$.

Like gasoline, ammonia is toxic.

Ammonia cracking to N$_2$ and H$_2$ is inefficient

Fundamental research is needed to address these challenges
Current Cracking Technology: Reverse Haber-Bosch

\[
\text{NH}_3 \xrightarrow{T > 500 \, ^\circ\text{C}} \text{catalyst} \quad \frac{1}{2} \text{N}_2 \; + \; \frac{3}{2} \text{H}_2
\]
New catalysts for ammonia synthesis

Improve current Haber-Bosch by synthesizing nano-structures that increase active sites for catalysis.

Develop ammonia synthesis where water is the hydrogen source instead of hydrogen gas.

\[
\begin{align*}
N_2 & + 3 \text{ H}_2\text{O} & + & \text{electrical energy} & \rightarrow & 2 \text{ NH}_3 & + & 3/2 \text{ O}_2
\end{align*}
\]
Ammonia Synthesis

\[
\begin{align*}
\text{Mo(III)} & \quad \text{Mo(NH}_3\text{)} & \quad \text{+ N}_2 & \quad \text{Mo(N}_2\text{)} & \quad \text{Mo(III)} \\
& \quad e^{\uparrow} & & \quad - \text{NH}_3 & \quad \downarrow H^+, e \\
\text{Mo(IV)} & \quad \{\text{Mo(NH}_3\text{)}\}^+ & \quad \text{Mo-N=N-H} & \quad \text{Mo(IV)} \\
& \quad H^+ & \downarrow & \downarrow H^+ & \\
\text{Mo(IV)} & \quad \text{Mo-NH}_2 & \quad \{\text{Mo=N-NH}_2\}^+ & \quad \text{Mo(VI)} \\
& \quad e^{\uparrow} & \downarrow & \downarrow e & \\
\text{Mo(V)} & \quad \{\text{Mo-NH}_2\}^+ & \quad \text{Mo=N-NH}_2 & \quad \text{Mo(V)} \\
& \quad H^+ & \downarrow & \downarrow H^+ & \\
\text{Mo(V)} & \quad \text{Mo=NH} & \quad \{\text{Mo=N-NH}_3\}^+ & \quad \text{Mo(V)} \\
& \quad e^{\uparrow} & \downarrow & \downarrow e & \\
\text{Mo(VI)} & \quad \{\text{Mo=NH}\}^+ & \quad \text{Mo=N+NH}_3 & \quad \text{Mo(VI)} \\
\end{align*}
\]

Fe surface with K$^+$
iron-nitride
ammonia release

$N_2$ $N$ $N$ $3 H_2$ $N\_3$ $N\_3$
Computational Studies of Haber-Bosch

New catalysts for ammonia synthesis

Improve current Haber-Bosch by synthesizing nano-structures that increase active sites for catalysis.
Carbon Free Fuels: Proposed Research

Figure 3. Hydrogen synthesis from ammonia feeding a hydrogen fuel cell.
Upgrading NH$_3$ by Selective Oxidation to Hydrazine

(1) $\text{NH}_3 + \text{V}^\text{V} = \text{V}^\text{VII}$

(2) $\text{V}^\text{VII} + \text{NH}_3 \rightarrow \text{V}^\text{V} + \text{NH}_4^+$

(3) Electron/proton transfer

(4) $\text{V}^\text{V} + \text{O}_2 \rightarrow \text{V}^\text{VII}$

Upgrading NH₃ by Selective Oxidation to Hydrazine

lower ignition temperature/
more efficient combustion
Proposed Research: Ammonia to Energy

Develop catalysts for ammonia oxidation

\[
\begin{align*}
\text{NH}_3 & \rightarrow 1/2 \text{N}_2 + 3 \text{H}^+ + 3 \text{e}^- \\
\text{H}_2\text{O} & \rightarrow 1/2 \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \\
\end{align*}
\]

- Design new ammonia fuel cells

![Diagram showing the process of ammonia to energy conversion](image-url)
Proposed Research: Ammonia to Energy

Electrolysis at 2 V potential!

A synthetic water splitting catalyst:

PS II OEC

Co-Pi

FIGURE 4. Proposed pathway for water splitting by Co-OEC. A PCET equilibrium proceeds the turnover-limiting O oxidation. The catalyst is selective for O evolution. The same conversion is also believed to be critical to turnover-limiting elementary step remain to be determined.

A BIDIRECTIONAL AND UNIDIRECTIONAL PCET IN A MOLECULAR MODEL OF A BIDIRECTIONAL AND UNIDIRECTIONAL PCET IN A MOLECULAR MODEL OF A

FIGURE 6.

Nocera and coworkers, J. Am. Chem. Soc. 2011, 133, 5174–5177
Proposed Research: Metal Catalyzed Oxidation
Proposed Research: Metal Catalyzed Oxidation

Figure 10. Crystal structure models of a) AMO₃ perovskite and b) AMO₃₋ₓ₋₀ₓ₋₀_N₀ₓ anion deficient oxynitride perovskite. The A cations are shown as light grey spheres, the B cations are situated in the octahedra and the square pyramids, and the O and N atoms are represented by red and green spheres respectively.
Impacts: Local and Global

Complements MSU’s efforts in Biofuels making us the leader in fuel research

Significant IP opportunities in energy and agricultural sectors

Elimination of CO$_2$ emission at the tailpipe of transportation vehicles

Hydrogen storage from Earth abundant feedstocks

Off-grid synthesis of fuel and fertilizer for third-world countries by converting electrical energy (from solar, wind, etc.) to fuel