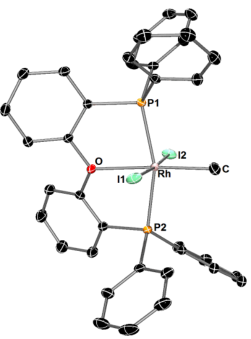
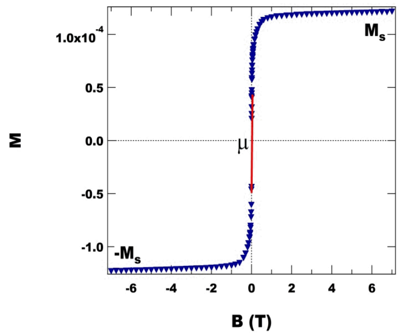
SAND2017-10378PE





Presentation to CNM college & career high school

Tyler E. Stevens

Some background- journey to become a scientist

- From Albuquerque
- High school interests
  - Music, science
- University of New Mexico
  - What to study?
    - Music? Pre-med?

Generally need science degree- biochemistry

Biochemistry as a path to med school

UNM HSC / Home / Education / Undergraduate Education

Why Study Biochemistry?

Undergraduate Education ▾

Undergraduate Program

How to Succeed

Course of Study

Research and Honors

Career Planning

Graduate Studies

Undergraduate Program Description

Biochemistry is an undergraduate major degree option in the UNM College of Arts & Sciences, making it one of the only undergraduate biochemistry programs in the nation housed in a School of Medicine. It trains pre-med, pre-pharmacy and pre-dental students, as well as students enrolled in the Combined BA/MD Program and students interested in MS and PhD degrees in the discipline.

Although the biochemistry major is offered by the College of Arts & Sciences, the Department of Biochemistry and Molecular Biology is organizationally and physically part of the School of Medicine, located just across Lomas Boulevard from UNM's main campus. Some courses are offered on the main campus, while more advanced courses and senior research are conducted in two modern, excellently equipped buildings in the medical school complex.

Both BA and BS degrees are available. Students seeking to major in Biochemistry must first be accepted into the College of Arts & Sciences.

The Biochemistry degree meets or exceeds all of the curricular recommendations from both the American Chemical Society and the American Society of Biochemistry and Molecular Biology. The program is also consistent with current national recommendations for 21st century educational practices.

Admission Requirements

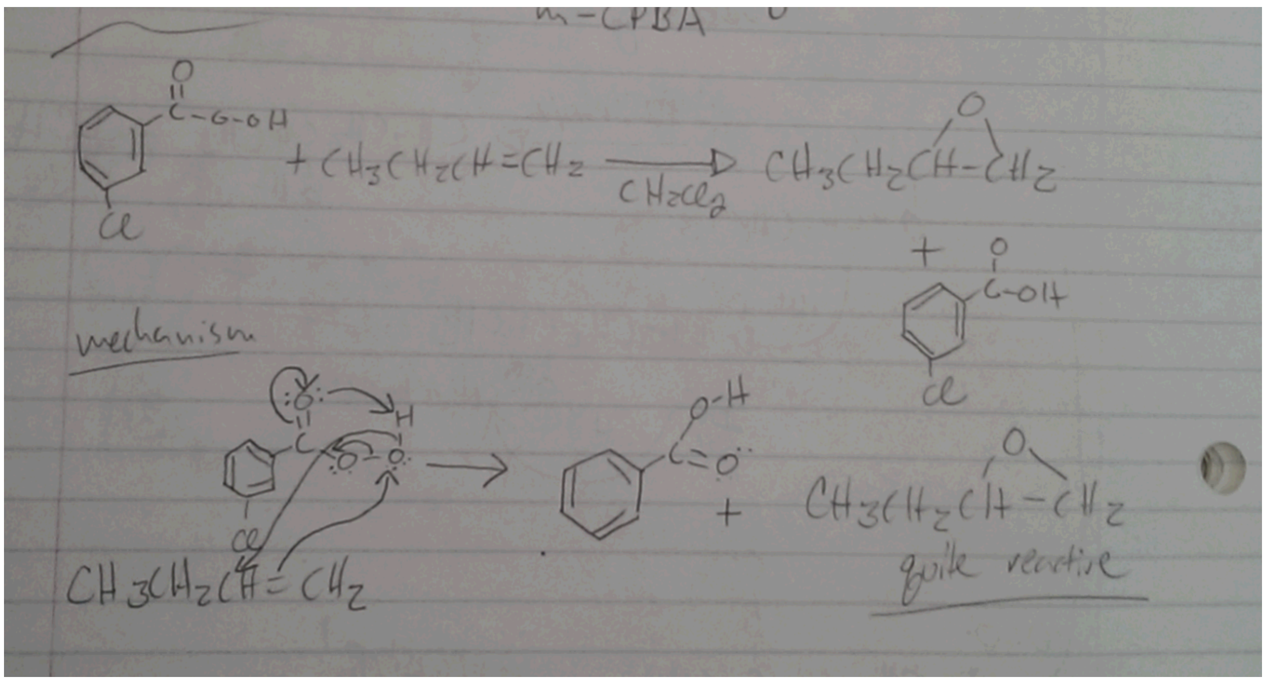
- Read the College of Arts and Sciences and Biochemistry Major Undergraduate Admission Requirements
- Elective choices for a Biochemsitry Degree

http://bmb.unm.edu/education/undergraduate/index.html

Chemistry research

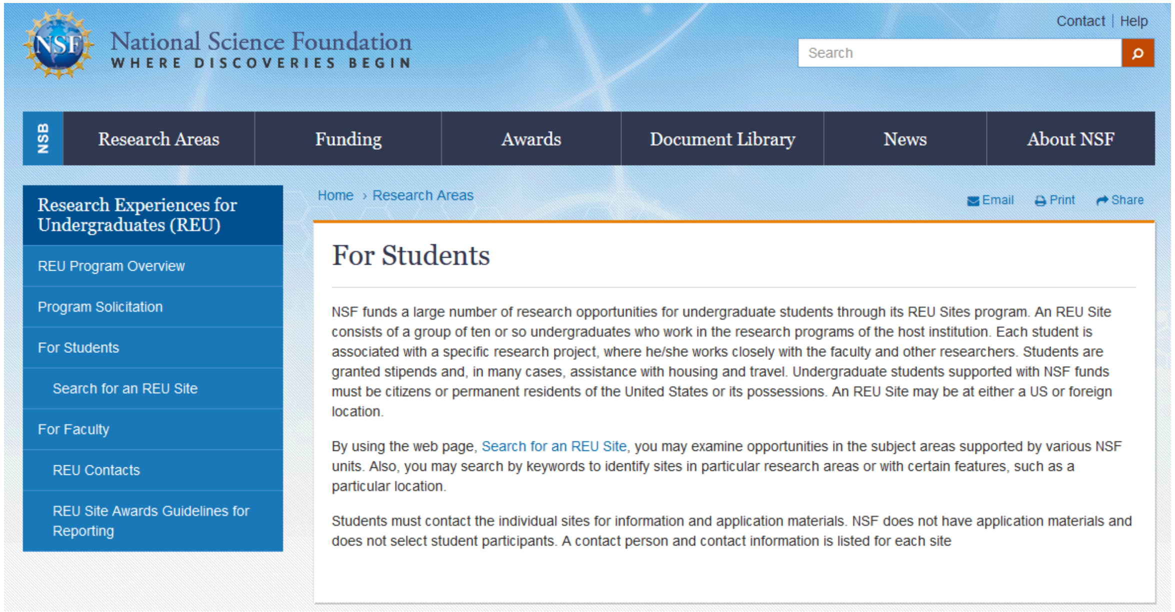
Biochemistry- many pre-requisite courses in chemistry and biology

Chemistry was exciting (after gen chem!)
Reaction mechanisms



Undergraduate research possibilities

- Many options
  - At school of study
  - REU
  - Internship



What next?

Sandia National Laboratories

- Graduate School
  - Great option, but where to go?
  - I applied to four schools:

UNIVERSITY of WASHINGTON

Boulder

TEXAS
The University of Texas at Austin

UCSB

University of Washington was best fit for me

Sandia National Laboratories

UNIVERSITY *of* WASHINGTON

Chemistry

DEPARTMENT OF CHEMISTRY
UNIVERSITY *of* WASHINGTON

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Faculty by Research Area
- Analytical Chemistry
- Biological Chemistry
- Catalysis / Synthesis
- Inorganic Chemistry
- Materials, Polymers and Nanoscience
- Organic Chemistry
- Physical Chemistry / Chemical Physics
- Theoretical Chemistry

Description of Research Areas

Centers & Institutes

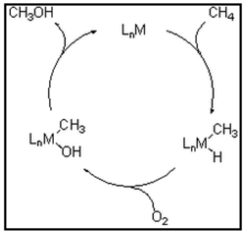
Karen I. Goldberg

Professor and Nicole A. Boand Endowed Chair in Chemistry
Director, Center for Enabling New Technologies through Catalysis
Ph.D. University of California at Berkeley, 1988
(Organometallic and Inorganic Chemistry)
(206) 616-2973
Email: **goldberg@chem.washington.edu**
Goldberg group website
Center for Enabling New Technologies through Catalysis website

Research Interests

One of the most important applications of organometallic chemistry has been the use of organotransition metal catalysts in the commercial production of chemicals, pharmaceuticals and organic materials. The reaction steps in the catalytic cycles are typically general, or so called fundamental reactions in organometallic chemistry, such as oxidative addition, reductive elimination, migratory insertion and beta-hydride elimination. Understanding the mechanisms of these basic reaction steps is key to the improvement of current catalysts and to the design of new catalytic systems. The Goldberg group focuses on developing detailed mechanistic understanding of these fundamental reactions with the goal of creating catalysts for desirable and challenging transformations.

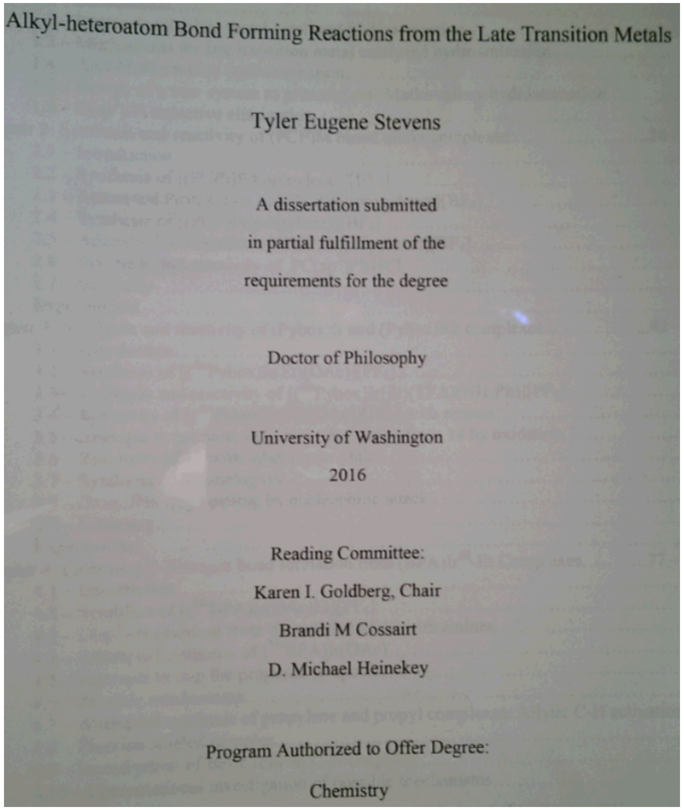
As an example, in one particular project in the group, the reaction steps that could be involved in the selective oxidation of alkanes to alcohols are being studied. Shown below is an idealized catalytic cycle for converting methane to methanol – oxidative addition of the C-H bond forms a metal alkyl hydride, insertion of oxygen into the metal hydride bond forms a metal alkyl hydroxide species, and finally C-O reductive elimination forms the alcohol product and regenerates the catalyst. Understanding how each step proceeds, what type of MLn fragment (geometry and ligand set) is needed, and what type of solvent system will promote that reaction step provides insight and direction to efforts to rationally design catalysts that will carry out such transformations. Some other transformations for which we are trying to develop catalysts are anti-Markovnikov hydration and hydroamination of olefins, oxidation of olefins with molecular oxygen and the release of hydrogen from amine boranes and other viable hydrogen storage materials.



Ph.D. students working on projects in the Goldberg group are trained in syntheses, characterization and mechanistic analysis using a variety of experimental, spectroscopic and analytical methods. These include the manipulation of air-sensitive compounds by Schlenk and vacuum line techniques, high field multinuclear NMR, IR and UV-visible spectrometry, mass spectrometry, and x-ray crystallography.

Graduate school experience

- Depends on school, but most are similar
  - UW Chemistry
    - 6 classes + research (4-5+ years)
    - 2 oral exams, each 2+ hours with 4-5 professors
    - Dissertation, Defense
  - Generally TA or RA



Alkyl-heteroatom Bond Forming Reactions from the Late Transition Metals

Tyler Eugene Stevens

A dissertation submitted

in partial fulfillment of the

requirements for the degree

Doctor of Philosophy

University of Washington

2016

Reading Committee:

Karen I. Goldberg, Chair

Brandi M Cossairt

D. Michael Heinekey

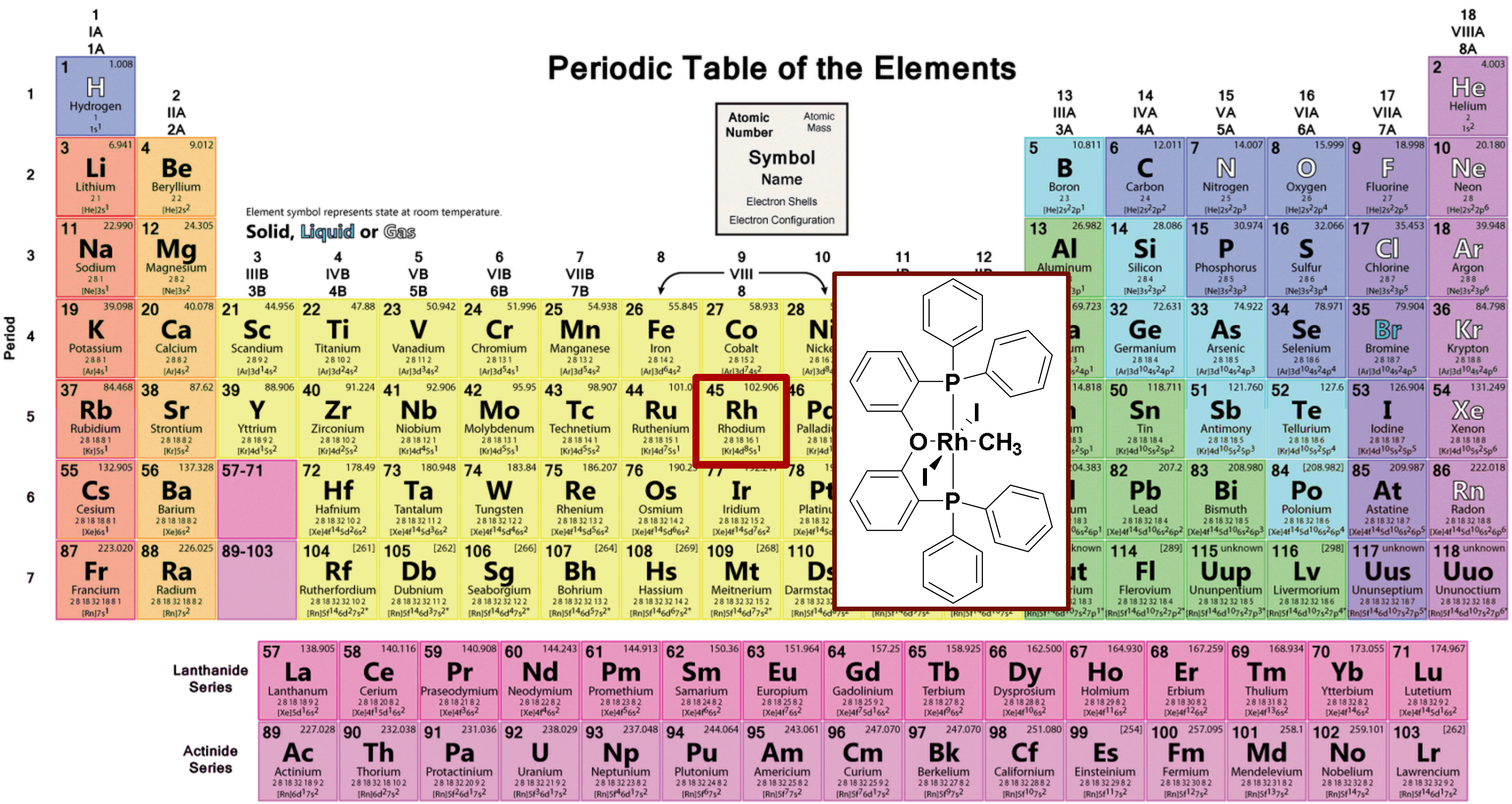
Program Authorized to Offer Degree:

Chemistry

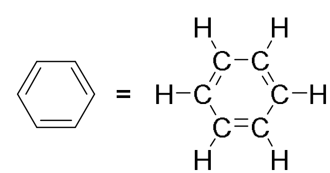
Graduate school experience

- Not all work...

Organometallic (OM) chemistry

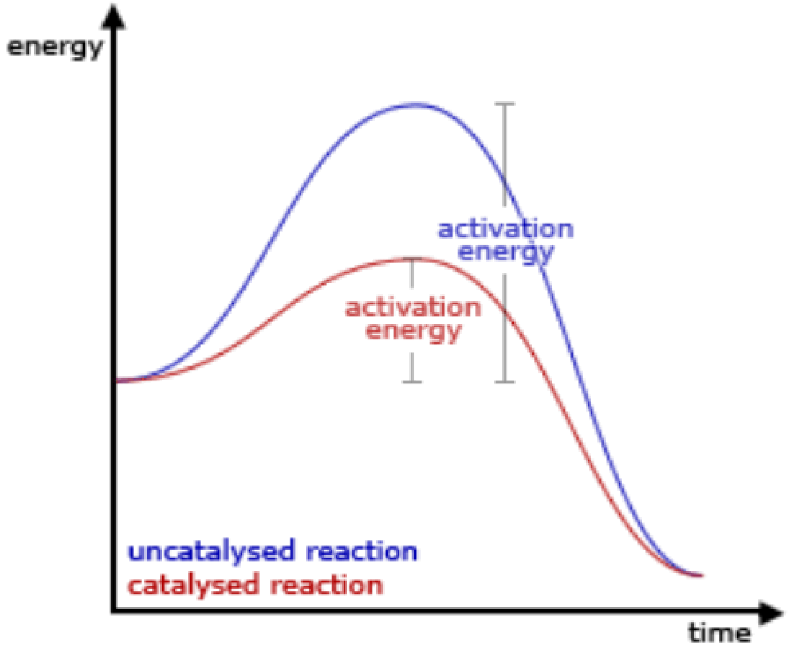


- Must have at least one metal-carbon bond



Application of OM complexes: Catalysis

Sandia National Laboratories



http://ch302.cm.utexas.edu/images302/Catalyst_effect.pn
g

CENTC

CENTER FOR ENABLING NEW TECHNOLOGIES THROUGH CATALYSIS

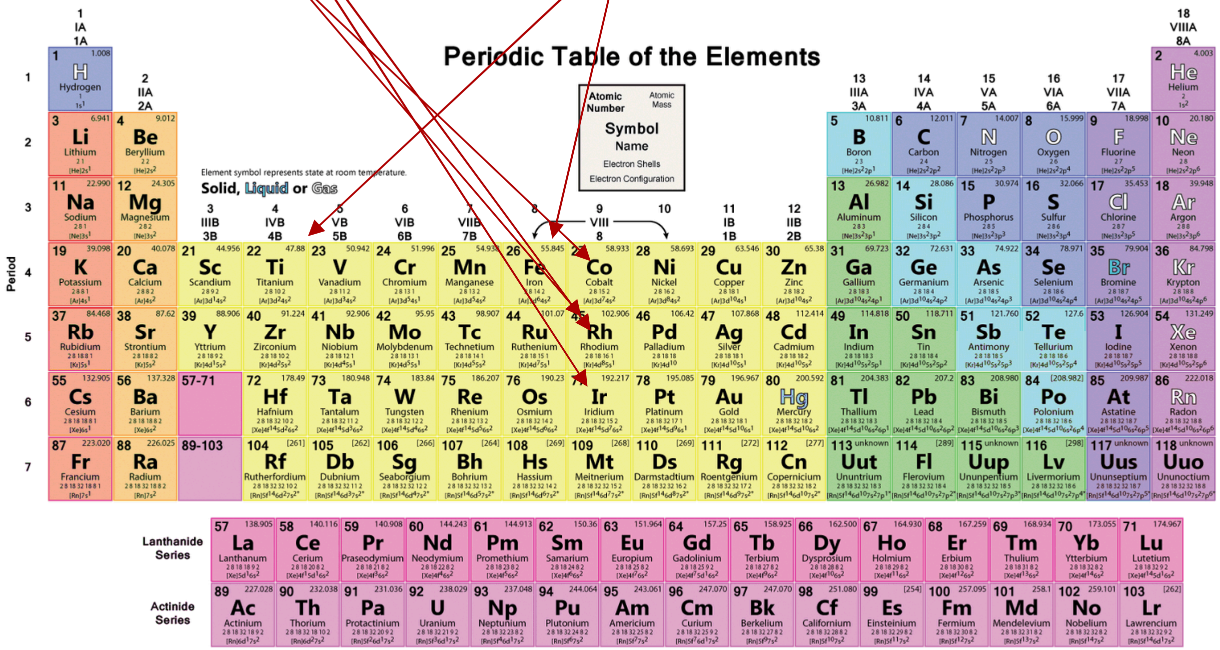
A NSF CENTER FOR CHEMICAL INNOVATION

Industrial uses of catalysts

- Both homogeneous and heterogeneous catalysts are used
  (same phase) (different phase)

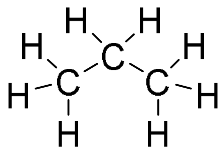
- Acetic acid
- Oxo process

- Haber-Bosch
- Olefin polymerization

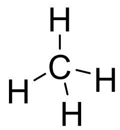


Some challenges for OM chemistry

- Hydrocarbons- many uses

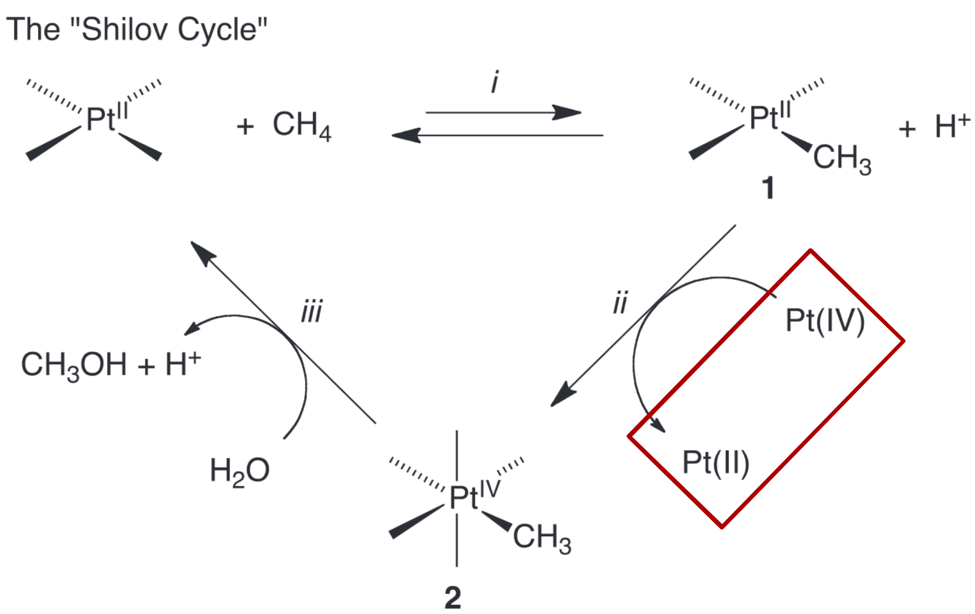


- What happens when we can't easily use them (i.e. methane)?



Converting methane into something that we can use is challenging

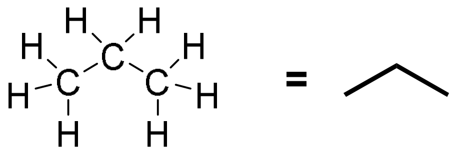
- C-H bonds are strong!
- What if we could selectively break the bond?



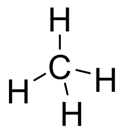
Labinger & Bercaw *JOMC* **2015**, *793*, 47.

Some challenges for OM chemistry

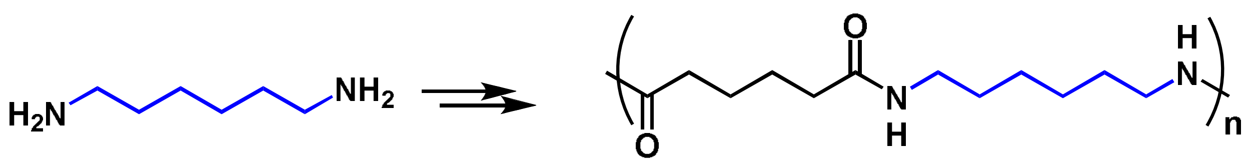
- Hydrocarbons- many uses



- What happens when we can't easily use them (i.e. methane)?



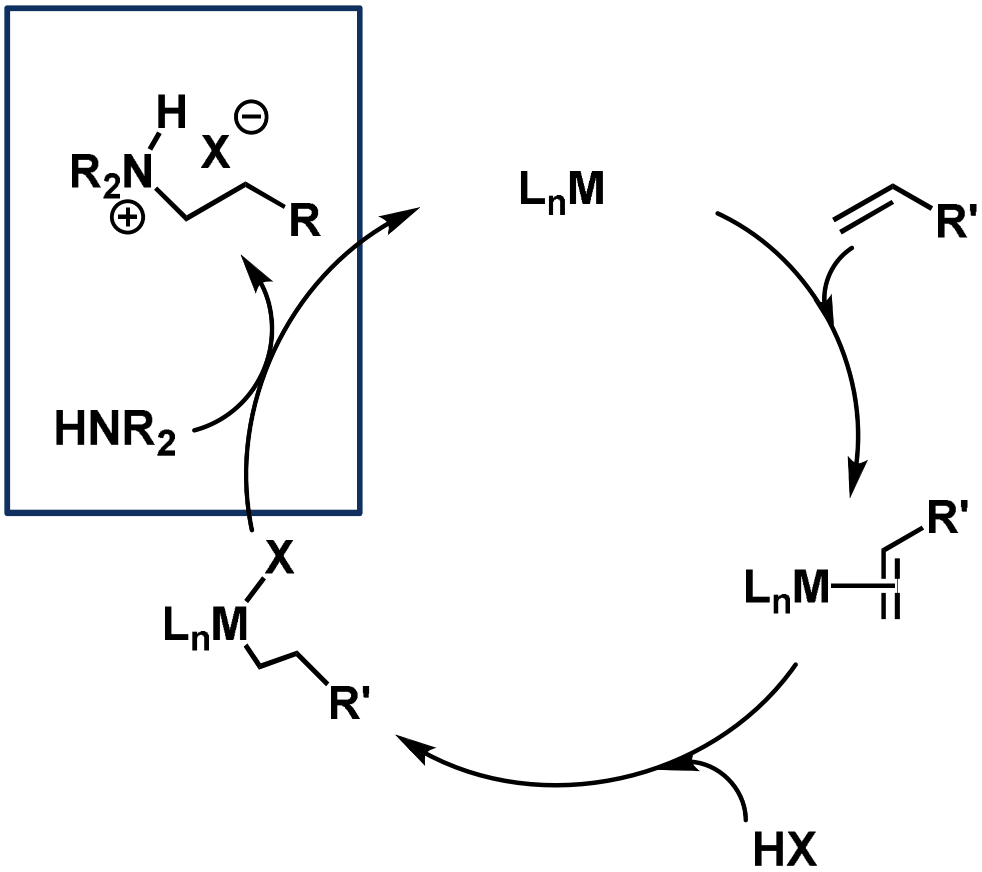
- Or if many steps are required to synthesize?



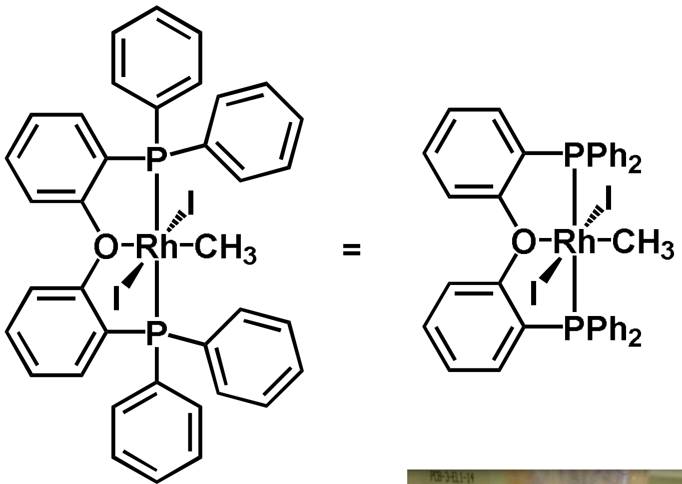
Nylon 6,6
~2 million tons/ year

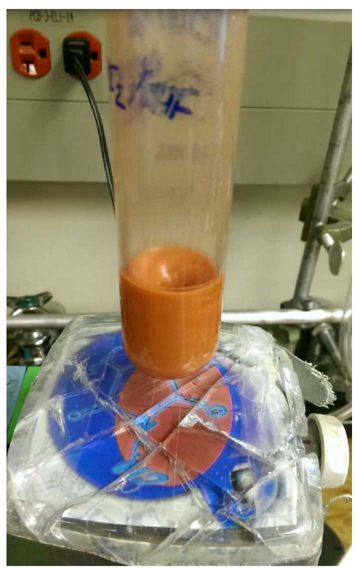
Lawrence, S. A. *Amines: Synthesis, Properties and Applications*; Cambridge University Press, New York, **2004**.
Eller, K.; Henkes, E.; Rossbacher, R.; & Hoke, H. "Aliphatic Amines" in Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, **2012**, pp647-692.

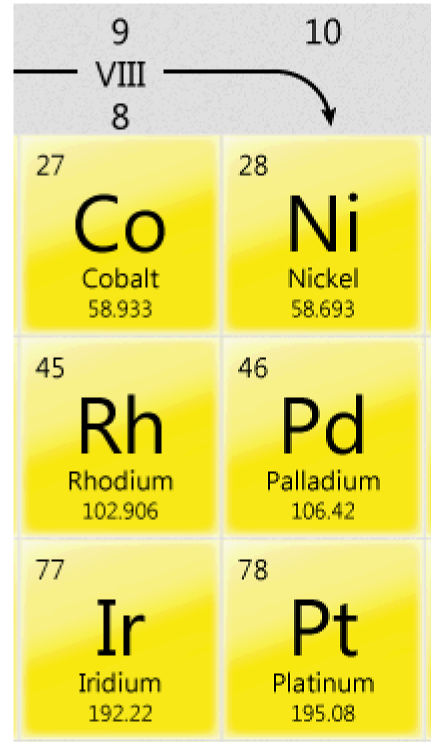
Can we develop a catalyst to produce alkylamines?



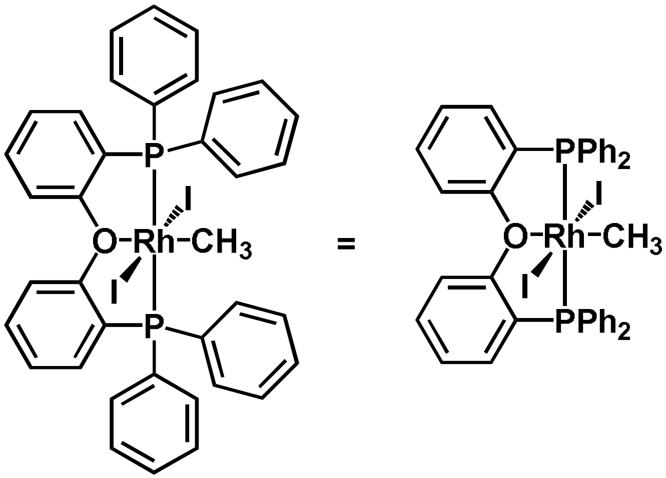
Synthesis of model complexes

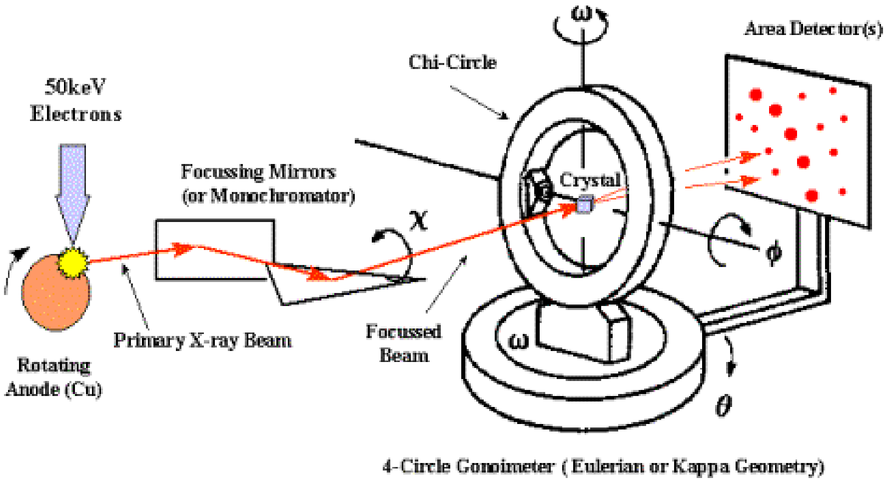




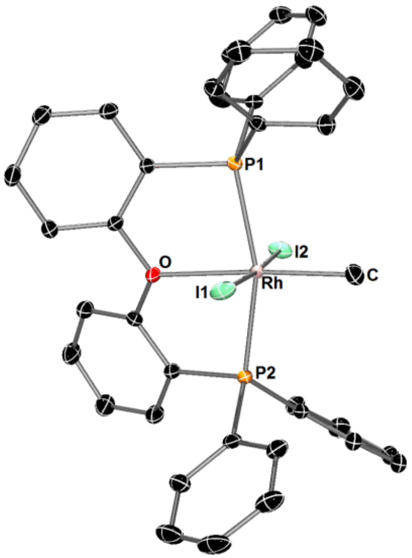


Characterization of new complexes





http://pruffle.mit.edu/atomiccontrol/education/xray/xray_diff_files/image006.gif

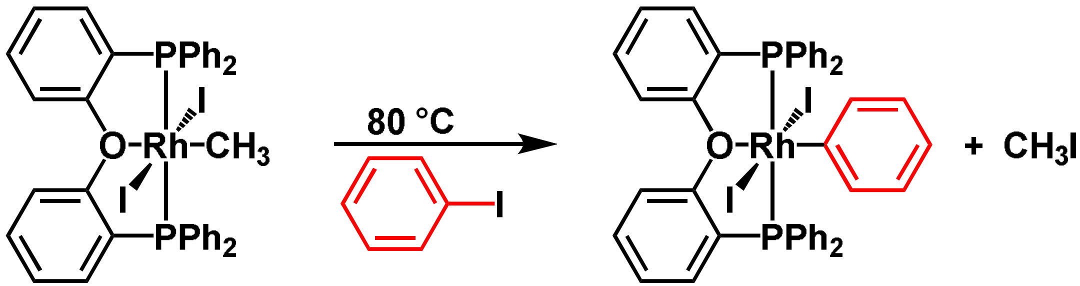


Nuclear Magnetic Resonance (NMR)

Image source: Bruker

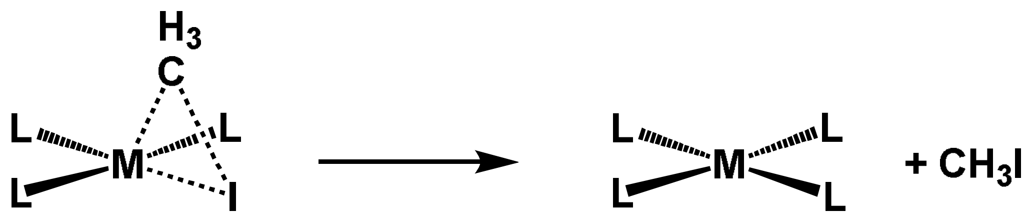
Image source: Philips

What happens if we heat?

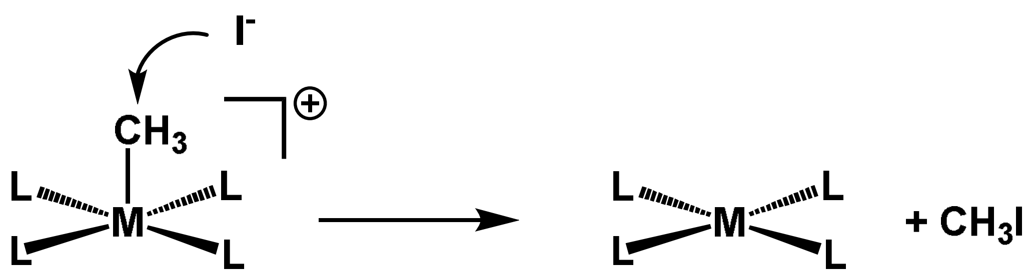


- How does this happen (mechanism)?

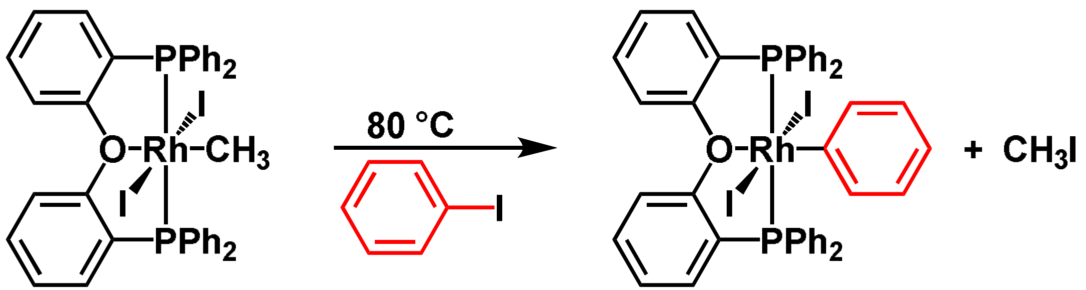
Concerted

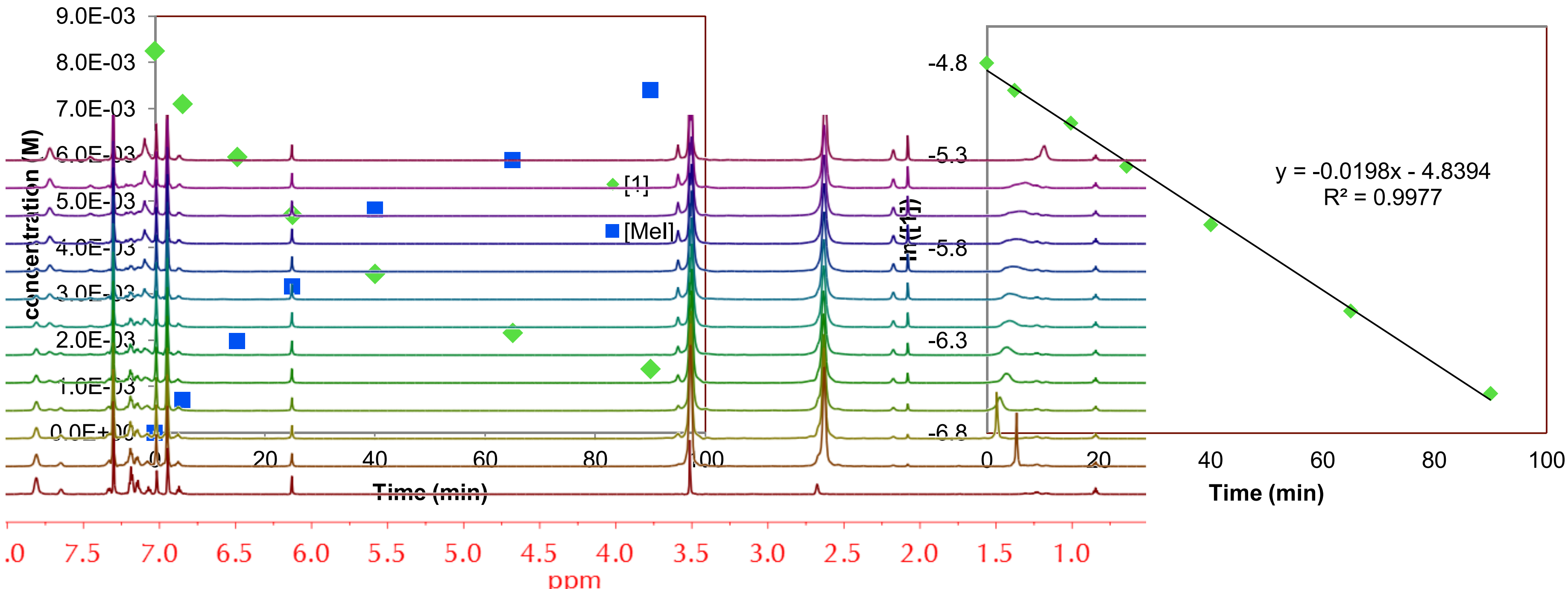


S_N2

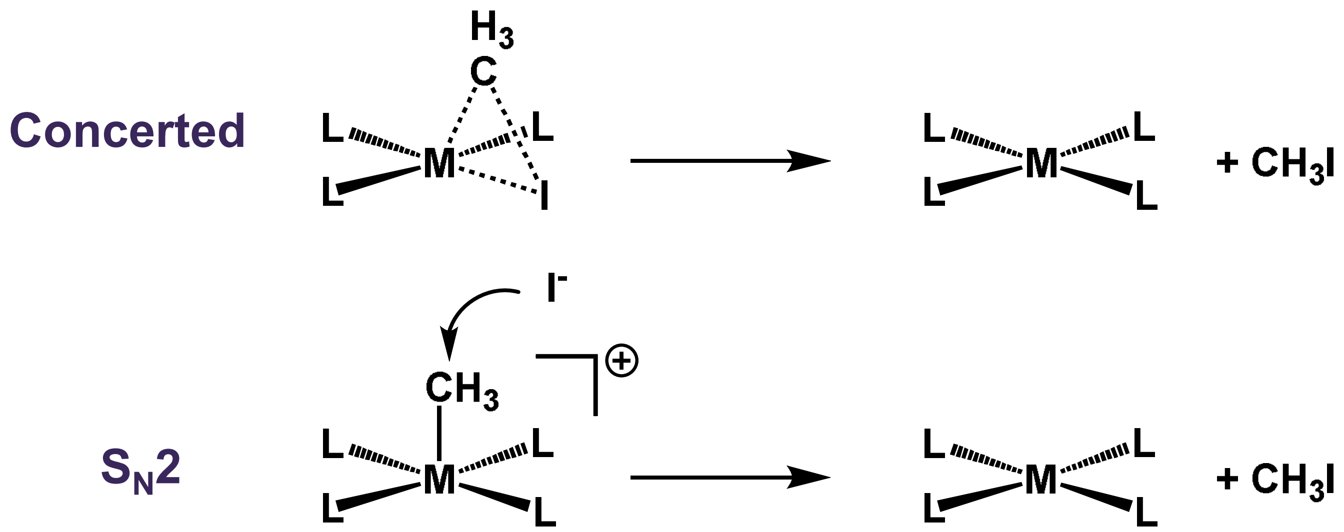


Reaction progress





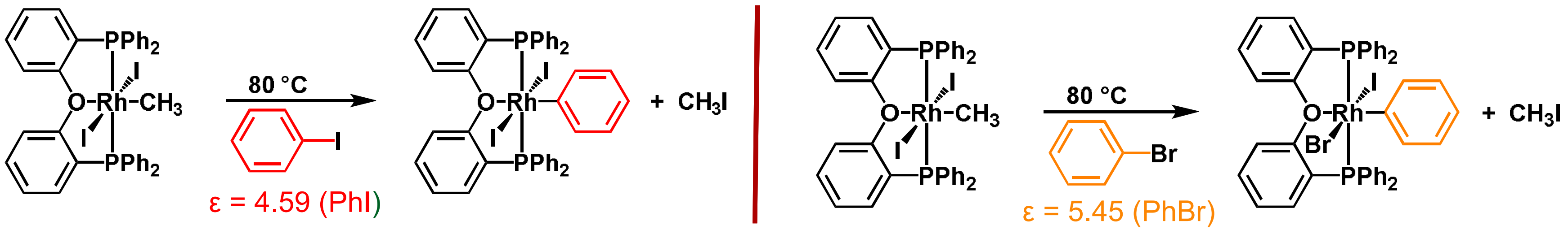
1st order reaction

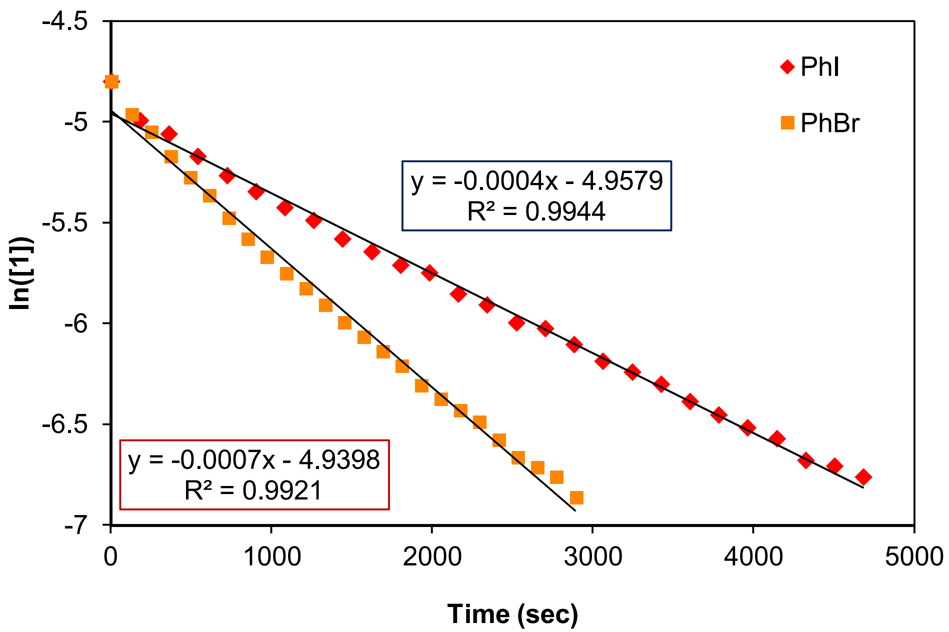


- Need more experiments to rule out mechanisms

Vary conditions- one at a time

- Formation of charged species should be more favored in more polar solvent
- Polarity should not have significant effect on concerted pathway



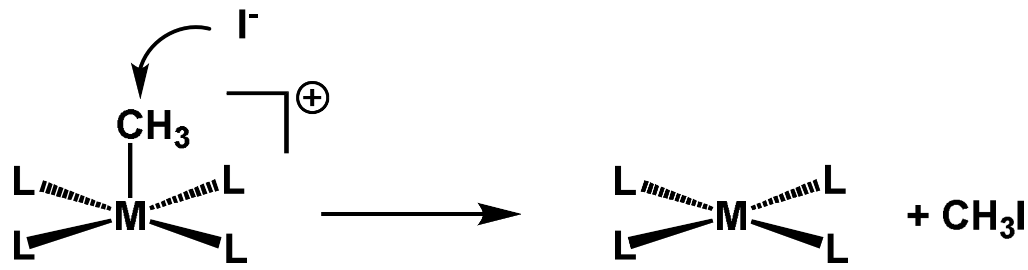


- k_{obs} = 4.0 ± 0.1 × 10^{-4} s^{-1} (PhI)
- k_{obs} = 6.6 ± 0.1 × 10^{-4} s^{-1} (PhBr)
- k_{obs} is 1.7x faster in PhBr

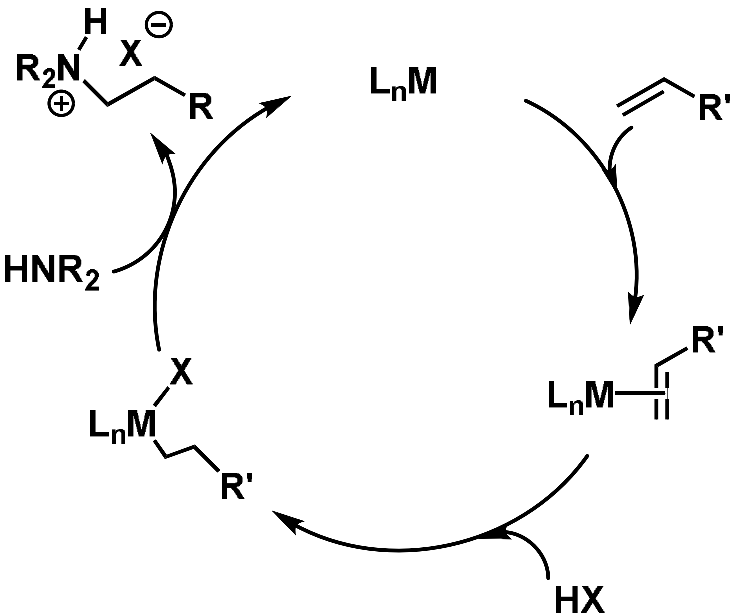
W. M. Haynes, ed., *CRC Handbook of Chemistry and Physics*, 97th Edition (Internet Version **2017**), CRC Press/Taylor & Francis, Boca Raton, FL.

After many more experiments…

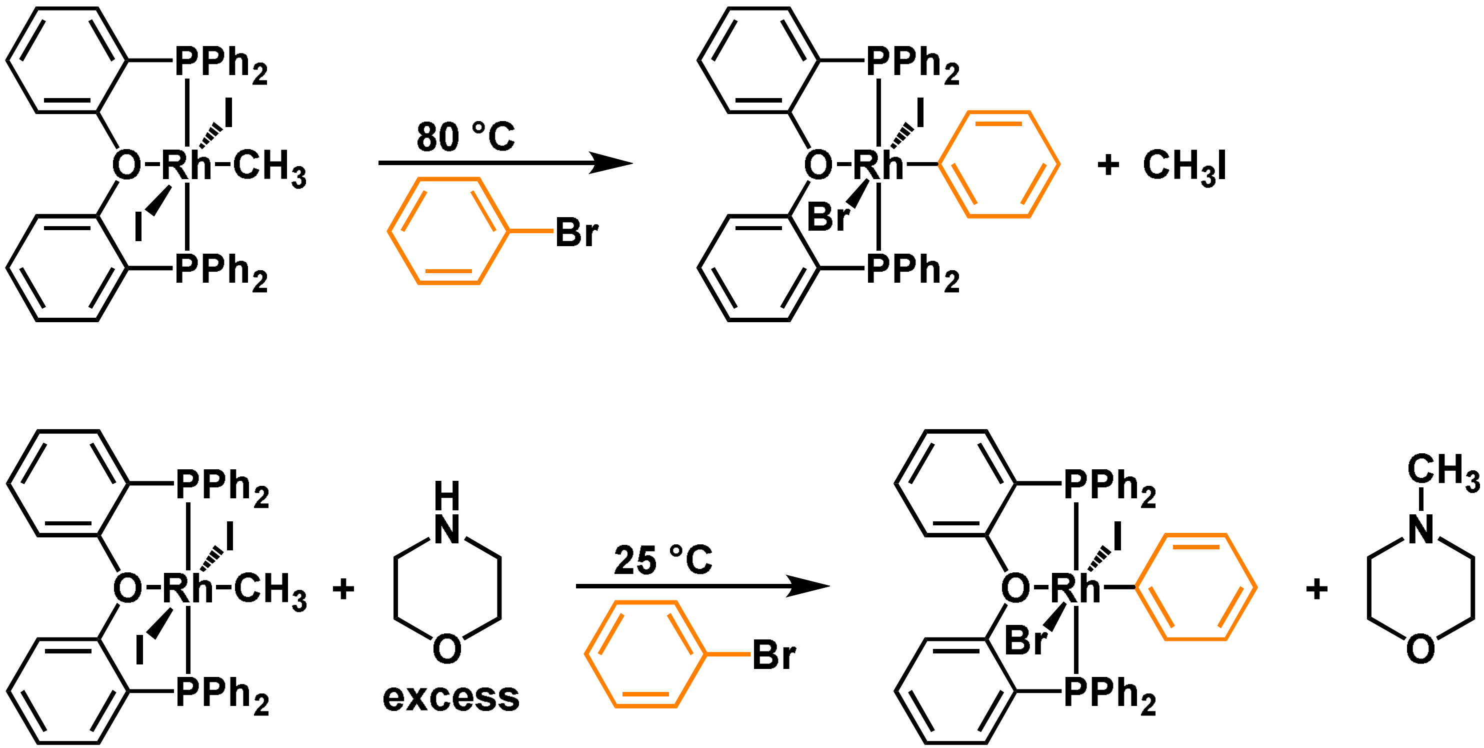
S_N2



- Two path mechanism (second path not shown)



Reaction with amines results in C-N bond formation



What do we do with the results?

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Communication

‹ Previous Article | Next Article › | Table

Direct Formation of Carbon(sp^3)–Heteroatom Bonds from Rh^{III} To Produce Methyl Iodide, Thioethers, and Alkylamines

Tyler E. Stevens, Karena A. Smoll, and Karen I. Goldberg*
Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195, United States

J. Am. Chem. Soc., **2017**, *139* (23), pp 7725–7728
DOI: 10.1021/jacs.7b04169
Publication Date (Web): June 2, 2017

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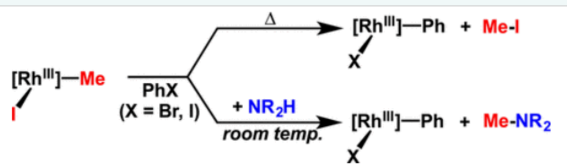
*goldberg@chem.washington.edu

Abstract



Thermolysis of the Rh^{III}–Me complex (DPEphos)$RhMeI_2$ (**1**) results in reductive elimination of MeI. Mechanistic studies are consistent with S_N2 attack by I^- at the Rh^{III}–Me group via *two separate* competing paths. Addition of sulfur and nitrogen nucleophiles allows effective competition and formation of C(sp^3)–S and C(sp^3)–N coupled products in high yields. C(sp^3)–N bond formation is second-order in amine, consistent with amine substitution of iodide at the metal followed by nucleophilic attack at carbon by a second amine.

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Communication
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Direct Formation of Carbon(sp^3)–Heteroatom Bonds from Rh^{III} To Produce Methyl Iodide, Thioethers, and Alkylamines

Tyler E. Stevens, Karena A. Smoll, and Karen I. Goldberg*

Department of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195, United States

Supporting Information

ABSTRACT: Thermolysis of the Rh^{III}–Me complex (DPEphos)$RhMeI_2$ (**1**) results in reductive elimination of MeI. Mechanistic studies are consistent with S_N2 attack by I^- at the Rh^{III}–Me group via *two separate* competing paths. Addition of sulfur and nitrogen nucleophiles allows effective competition and formation of C(sp^3)–S and C(sp^3)–N coupled products in high yields. C(sp^3)–N bond formation is second-order in amine, consistent with amine substitution of iodide at the metal followed by nucleophilic attack at carbon by a second amine.

Reductive elimination, a fundamental organometallic reaction, is the product release step in numerous catalytic processes.[1] Reactions that form carbon–heteroatom (C–X) bonds via reductive elimination are particularly valuable, as new functionality is introduced into the product. For example, arylamines are formed by C(sp^2)–N reductive elimination from Pd^{II} in the product release step in Buchwald–Hartwig cross-coupling reactions.[2] Strikingly less prevalent in both catalytic and stoichiometric reactions are reductive eliminations involving alkyl groups to form C(sp^3)–X bonds[3] and in particular C(sp^3)–N bonds.[4,5] Access to such couplings to form C(sp^3)–N bonds would be a tremendous asset in rational design efforts for catalytic systems. For example, a C(sp^3)–N bond-forming reaction could be used to produce alkylamines via olefin hydroamination or direct alkane oxidation.

In the few reported examples of C(sp^3)–X coupling reactions (X = N, O, S, halide), high-valent metal centers such as Rh^{III}[3e,k−m] and Pt^{IV}[3b−d,g,i,j,4b] are primarily employed. Recently, examples of C(sp^3)–N reductive elimination from Pd^{IV} and Ni^{IV} have also been observed.[4e,f] However, sulfonamides were employed for these reactions, and C(sp^3)–N reductive elimination to produce alkylamines has rarely been documented.[4d] Both concerted reductive elimination and S_N2-type mechanisms have been proposed for C(sp^3)–X coupling reactions,[3,4] with both pathways occurring through coordinately unsaturated metal centers. We now report a well-characterized example of C(sp^3)–I reductive elimination from Rh^{III} along with mechanistic studies that indicate the involvement of two competing pathways of S_N2 attack in the presence of excess iodide. Similar competitive behavior has not previously been observed in reductive elimination reactions, and the presence of the second pathway provides access to incorporation of external nucleophiles. This second pathway allows for the formation of C(sp^3)–S and C(sp^3)–N bonds *at room temperature*. Furthermore, mechanistic studies of the C(sp^3)–N coupling point to an unprecedented path involving coordination of the amine to the metal center followed by C–N bond formation via external attack at the Rh–Me group by a second amine equivalent.

The Rh^{III}–Me complex (DPEphos)RhMe$(I)_2$ (**1**) was prepared in high yield by addition of excess MeI to $(DPEphos)_2Rh_2Cl_2$.[6] Complex **1** in THF-d_8 exhibits a doublet at 13.2 ppm (J_{Rh-P} = 103.8 Hz) in the ^{31}P NMR spectrum. The methyl group bound to Rh gives rise to a doublet of triplets in the ^1H NMR spectrum at 2.22 ppm (J_{Rh-H} = 4.9 Hz, J_{P-H} = 2.6 Hz). The solid-state structure of **1** (Figure S1) shows octahedral geometry about Rh with meridional DPEphos and trans iodide ligands. The Rh–Me (2.0769(19) Å) and Rh–I (2.6633(4) Å and 2.6379(4) Å) bond lengths are similar to those reported for other Rh^{III} octahedral bisphosphine complexes.[3k,7]

Thermolysis of **1** in iodobenzene at 80 °C resulted in quantitative formation of MeI and a new Rh species. The ^{31}P NMR resonance of the new Rh product appeared only slightly downfield at 15.4 ppm with a similar J_{Rh-P} coupling constant (106.4 Hz). On this basis, we speculated that it was also a Rh^{III} complex, and given that the reaction was performed in iodobenzene, we proposed that the product was (DPEphos)-RhPh$(I)_2$ (**2**). Overlap of the ^1H NMR aromatic resonances made characterization of the product challenging, and attempts to obtain crystals were unsuccessful. To establish the identity of the Rh product, **1** was thermolyzed in *p*-bromotoluene. The ^{31}P NMR chemical shift and J_{Rh-P} coupling constant of the corresponding product (18.6 ppm, J_{Rh-P} = 105.5 Hz) were similar to those of the product from thermolysis in iodobenzene. Now, however, the ^1H NMR spectrum contained an upfield singlet (2.18 ppm, 3H), consistent with a bound *p*-tolyl moiety. Furthermore, the solid-state structure (Figure S2) confirmed that the solvent had added to rhodium, yielding (DPEphos)Rh-(tolyl)IBr (**3**). The production of tolyl complex **3** by thermolysis of **1** in *p*-bromotoluene substantiates the proposed formation of phenyl complex **2** by thermolysis of **1** in iodobenzene. Thus, the overall thermolysis reaction involves the formation of a C(sp^3)–I bond with the reductive elimination of MeI and the cleavage of a C(sp^2)–X bond with the oxidative addition of aryl halide.

On the basis of literature precedent for mechanisms of reductive elimination, six potential pathways for MeI elimination from **1** are proposed in Scheme 1. Routes C_1–C_3 involve concerted formation of the C(sp^3)–I bond. In path C_1, MeI is eliminated directly from the six-coordinate complex **1**. In path C_2, the formation of a five-coordinate species prior to concerted C–I coupling is proposed, with the DPEphos ligand changing

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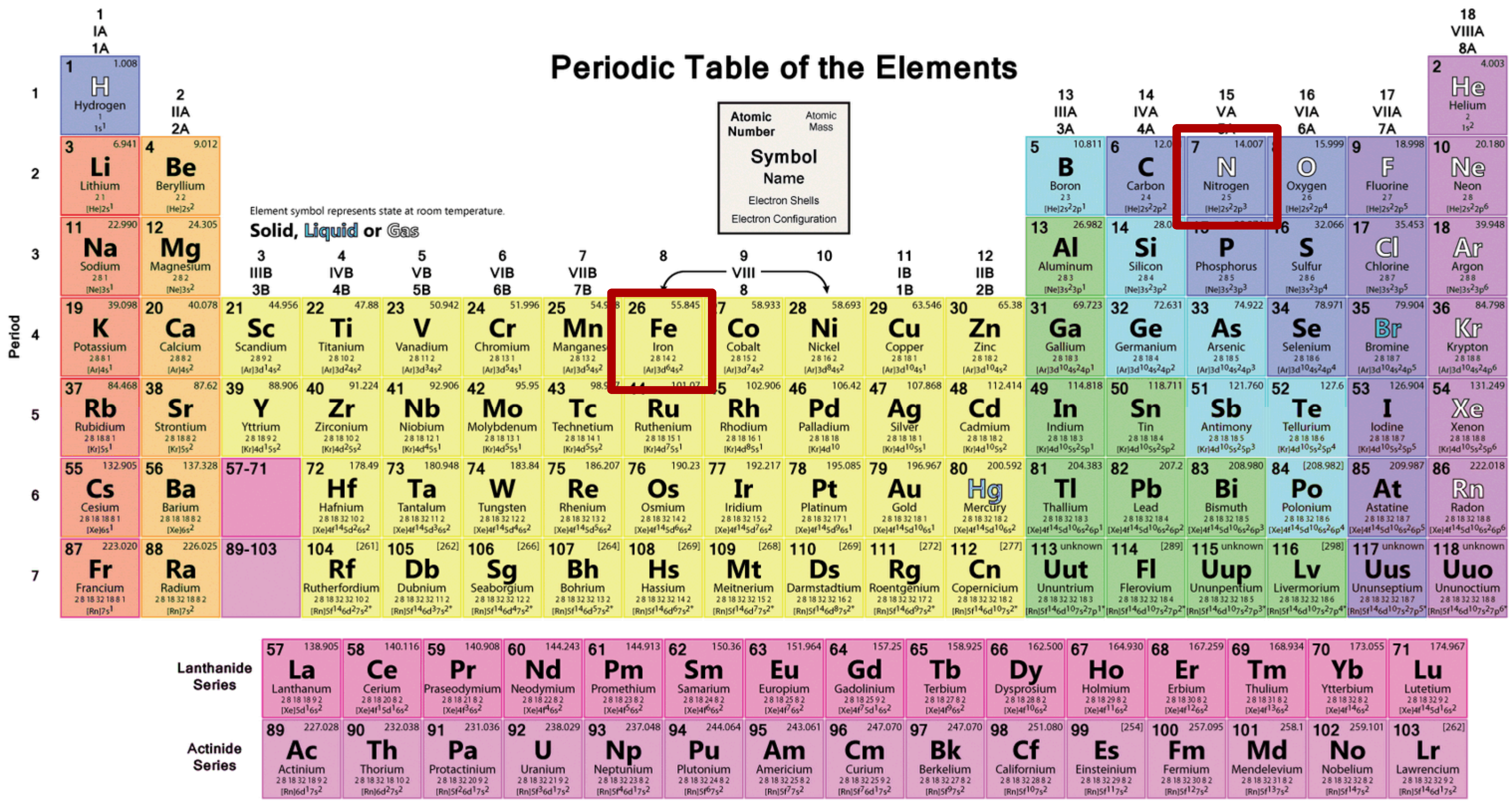
Published: June 2, 2017

Transition to inorganic materials

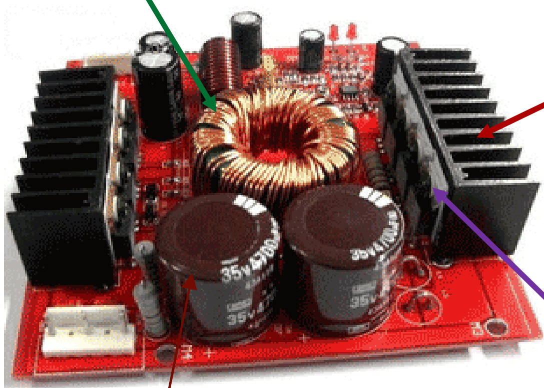


- Iron nitride

Magnetic components are large!

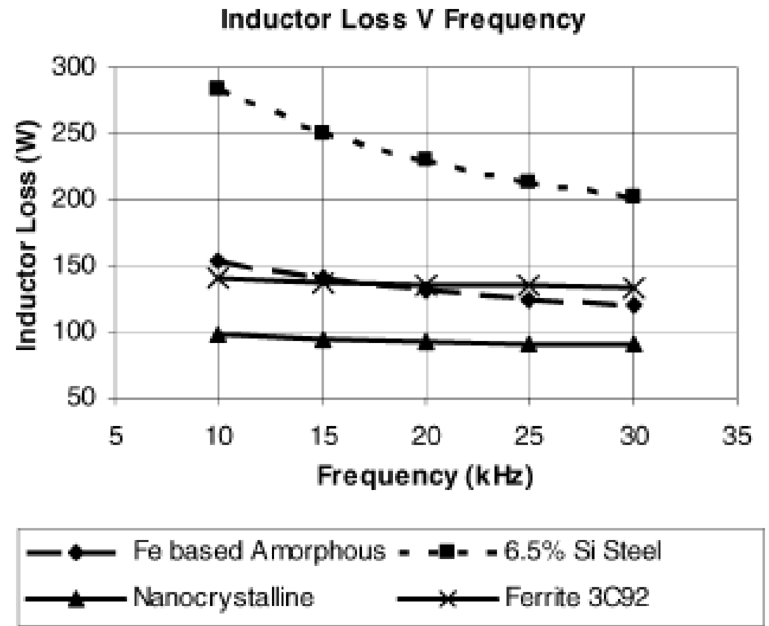
Magnetics

Thermal management



Capacitors

Semiconductor switches

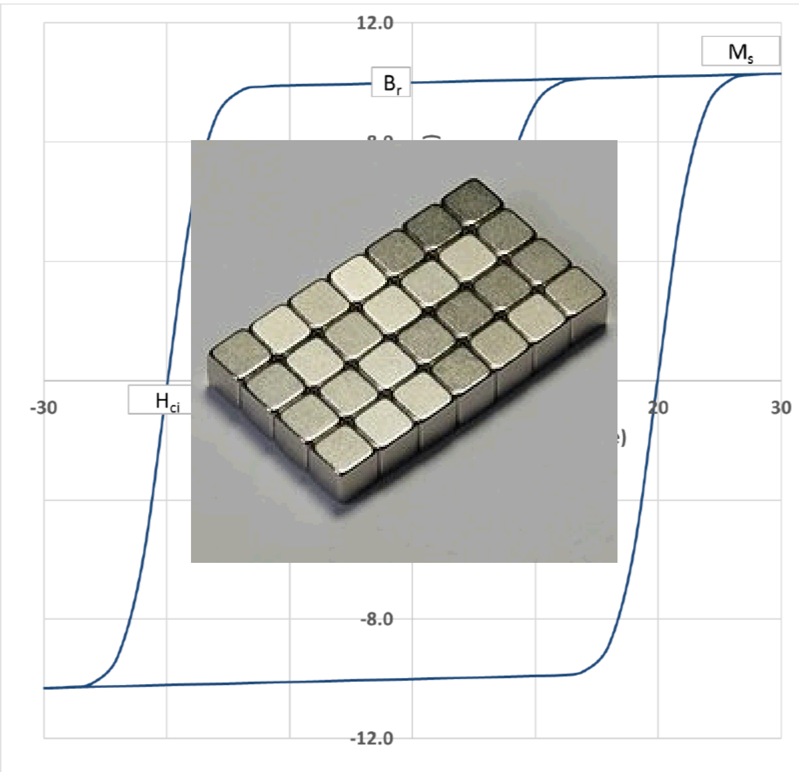


B.J. Lyons, J.G. Hayes, M.G. Egan, Magnetic Material Comparisons for High-Current Inductors in Low-Medium Frequency DC-DC Converters, *IEEE*, **2007**, 71.

- New soft magnetic materials could enable smaller/ more portable power electronics

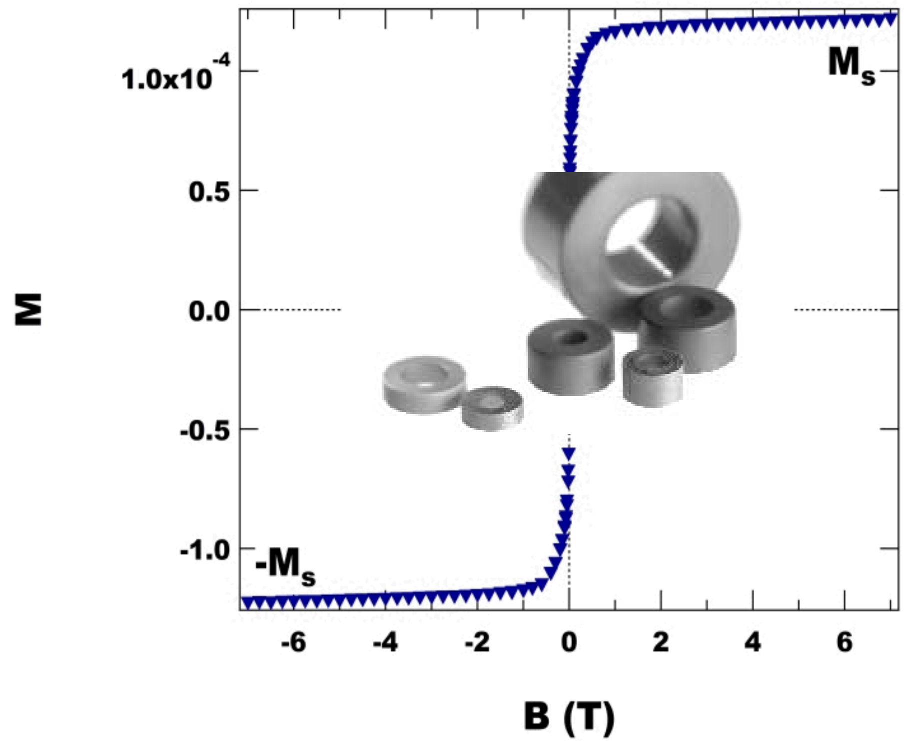
What is a soft magnet???

Hard (permanent)magnet



Spontaneous Materials

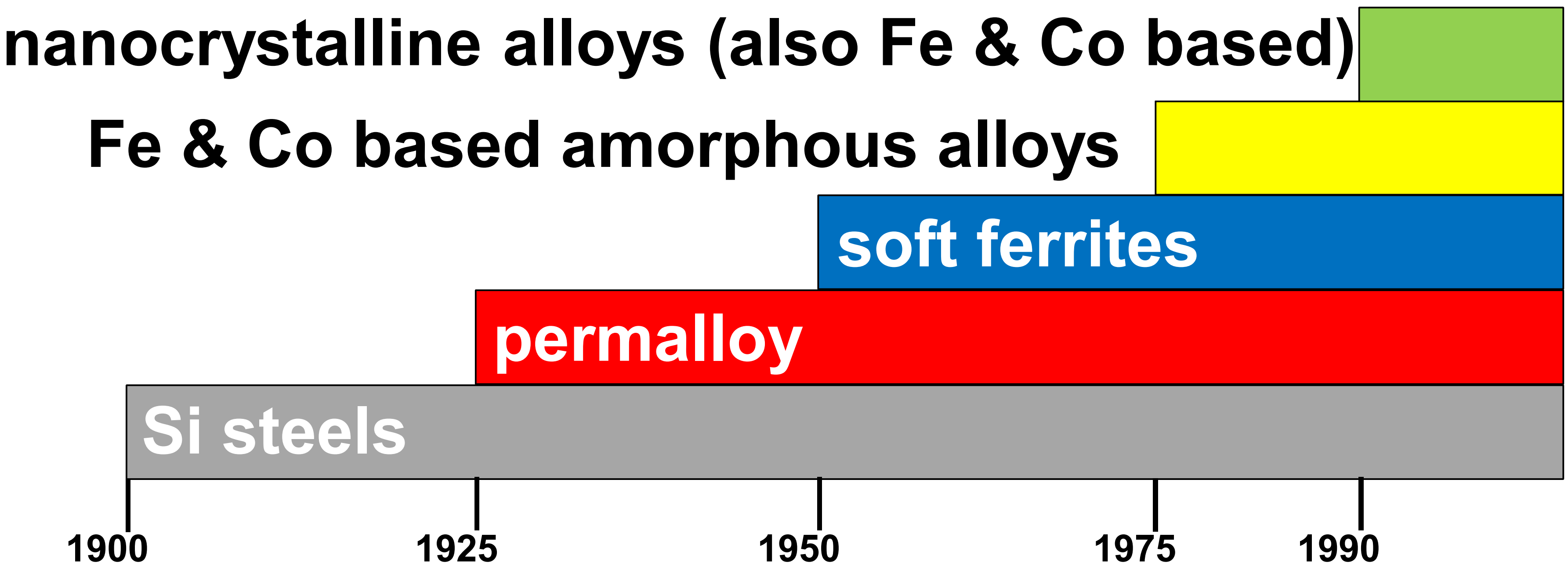
Soft magnet



M_s = saturation magnetization, B_r = magnetic remnance
H_c = coercivity, μ = permeability

Development of soft magnetic materials

Sandia National Laboratories



Adapted from: L.A. Dobrzański, M. Drak, B. Ziębowicz, Materials with specific magnetic properties, *Journal of Achievements in Materials and Manufacturing Eng.* **2006**, *17*, 37.

γ'-Fe_4N meets all of the requirements

Magnetic Material	J_s (T)	$\rho(\mu\Omega\cdot m)$	Cost
VITROPERM (Vacuumschmelze)	1.20	1.15	High
Metglas 2605SC	1.60	1.37	High
Ferrite (Ferroxcube)	0.52	$5x10^6$	Low
Si steel	1.87	0.05	Low
γ'-Fe_4N	1.89	> 200	Low

Possible careers for an OM chemist

- Universities
  - Professor, research assistant, lecturer, etc.

- Industry

- National Labs & other govt. agencies

Questions???