

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN • ANN ARBOR, MI 48109
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NATHANIEL K. SZYMCZAK

APPOINTMENTS

Associate Professor of Chemistry. University of Michigan Ann Arbor, Michigan	2017-present
Dow Corning Assistant Professor of Chemistry. University of Michigan Ann Arbor, Michigan	2012-2017
Assistant Professor of Chemistry. University of Michigan Ann Arbor, Michigan	2010-2017

PROFESSIONAL PREPARATION

California Institute of Technology Postdoctoral Associate Advisor: Jonas Peters	2009-2010
Massachusetts Institute of Technology Postdoctoral Associate Advisor: Jonas Peters	2007-2009
University of Oregon Ph. D. in Chemistry Advisor: David Tyler	2002-2007
University of Illinois-Urbana-Champaign B.S. in Chemistry Advisor: Thomas Rauchfuss	1998-2002

HONORS AND AWARDS

<i>Class of 1923 Memorial Teaching Award</i>	2017
<i>Camille Dreyfus Teacher-Scholar Award</i>	2016
<i>Emerging Investigator – ACS Virtual Issue in Bioinorganic</i>	2015
<i>Distinguished Lectureship Award – KAIST</i>	2014
<i>Alfred P. Sloan Research Fellowship</i>	2014-2016
<i>NSF-CAREER Award</i>	2014-2019
<i>Dow Corning Assistant Professor of Chemistry</i>	2012-2014
<i>Young Investigator Award – ACS Division of Inorganic Chemistry</i>	2006
<i>IGERT Graduate Fellowship – National Science Foundation</i>	2004-2006

PUBLICATIONS

*denotes Principal Investigator, underline denotes undergraduate co-author, † denotes shared authorship

- 30) Hale, L. V. A.; Szymczak, N. K.* Hydrogen Transfer Catalysis Beyond the Primary Coordination Sphere. *ACS Catalysis*. **2018**, *invited perspective in revision*.
- 29) Dahl, E. W.; Dai, H. T.; T.; Szymczak, N. K.* Phenylamino Derivatives of Tris(2-pyridylmethyl)amine: Hydrogen-Bonded Peroxodicopper Complexes. *Chem. Comm.* **2018**, *54*, 892-895.
- 28) Kiernicki, J. J.; Zeller, M.; Szymczak, N. K.* Hydrazine Capture and N-N Bond Cleavage at Iron Enabled by Flex-ible Appended Lewis Acids. *J. Am. Chem. Soc.*, **2017**, *139*, 18194-18197.
- 27) Geri, J. B.; Wade Wolfe, M. M.; Szymczak, N. K.* Borazine-CF₃⁻ Adducts for Rapid, Room Temperature, and Broad Scope Trifluoromethylation *Angew. Chem., Int. Ed.*, **2018**, *57*, 1-7 *Featured in *Chemical & Engineering News*, **2018**, Jan. 1.
- 26) Geri, J. B.; Szymczak, N. K.* Recyclable Trifluoromethylation Reagents from Fluoroform. *J. Am. Chem. Soc.*, **2017**, *139*, 9811-9814. *Featured in *JACS Spotlights August 1, 2017*.
- 25) Geri, J. B.; Shanahan, J. P.; Szymczak, N. K.* Testing the Push-Pull Hypothesis: Lewis Acid Augmented N₂ Activation at Iron. *J. Am. Chem. Soc.*, **2017**, *139*, 5952-5956.
- 24) Dahl, E. W.; Louis-Goff, T.; Szymczak, N. K.* Second sphere ligand modifications enable a recyclable catalyst for oxidant-free alcohol oxidation to carboxylates. *Chem. Comm.* **2017**, *53*, 2287-2289.
- 23) Hale, L. V. A.; Szymczak, N. K.* Stereoretentive Deuteration of α -Chiral Amines with D₂O. *J. Am. Chem. Soc.*, **2016**, *138*, 13489-13492.
- 22) Tseng, K-N T.; Kampf, J.; Szymczak, N. K.* Modular Attachment of Appended Boron Lewis Acids to a Ruthenium Pincer Catalyst: Metal-Ligand Cooperativity Enables Selective Alkyne Hydrogenation. *J. Am. Chem. Soc.*, **2016**, *33*, 10378-10381.
- 21) Hale, L. V. A.;[†] Malakar, T.;[†] Tseng, K-N T.; Zimmerman, P. M.; Paul, A.;* Szymczak, N. K.* The Mechanism of Acceptorless Amine Double Dehydrogenation by *N,N,N*-Amide Ruthenium (II) Hydrides: A Combined Experimental and Computational Study. *ACS Catalysis*, **2016**, *6*, 4799-4813.
- 20) Moore, C. M.; Bark, B.; Szymczak, N. K.* Simple Ligand Modifications with Pendent OH Groups Dramatically Impact the Activity and Selectivity of Ruthenium Catalysts for Transfer Hydrogenation: the Importance of Alkali Metals. **2016**, *ACS Catalysis*, *6*, 1981-1990.
- 19) Tseng, K-N T.; Lin, S.; Kampf, J.; Szymczak, N. K.* Upgrading Ethanol to 1-Butanol with a Homogeneous Air-Stable Ruthenium Catalyst. *Chem. Comm.* **2016**, *52*, 2901-2904. *Featured in *Chemistry World (1-13-2016)*
- 18) Dahl, E. W.; Szymczak, N. K.* Hydrogen Bonds Dictate the Coordination Geometry of Copper: Characterization of a Square Planar Cu(I). *Angew. Chem., Int. Ed.*, **2016**, *55*, 3101-3105.
- 17) Geri, J. B.; Szymczak, N. K.* A Proton-Switchable Bifunctional Ruthenium Complex that Enables Catalytic Nitrile Hydroboration. . *J. Am. Chem. Soc.*, **2015**, *137*, 12808-12814.
- 16) Carter, T. J.; Heiden, Z. M.;* Szymczak, N. K.*; Discovery of Low Energy Pathways to Metal-Mediated B=N bond Reduction Guided by Computation and Experiment. *Chem. Sci.* **2015**, *6*, 7258-7266.

- 15) Tseng, K-N T.; Kampf, J.; Szymczak, N. K.*. Mechanism of N,N,N-Amide Ruthenium(II) Hydride Mediated Acceptorless Alcohol Dehydrogenation: Inner-Sphere β -H Elimination vs. Outer-Sphere Bifunctional Metal-Ligand Cooperativity. *ACS Catalysis*, **2015**, *5*, 5468-5485.
- 14) Moore, C. M.; Szymczak, N. K.*. Nitrite Reduction by Copper Through Ligand-Mediated Proton and Electron Transfer. *Chem. Sci.*, **2015**, *6*, 3373-3377
- 13) Tseng, K-N T.; Kampf, J.; Szymczak, N. K.*. Regulation of Iron-Catalyzed Olefin Hydroboration by Ligand Modifications at a Remote site. *ACS Catalysis*, **2015**, *5*, 411-415.
- 12) Moore, C. M.; Szymczak, N. K.*. Beyond H₂: Exploiting 2-Hydroxypyridine as a Design Element from [Fe]-Hydrogenase for Energy-Relevant Catalysis *Curr. Opin. Chem. Biol.*, **2015**, *25*, 9-17. *Invited contribution.
- 11) Moore, C. M.; Szymczak, N. K.*. Redox-induced Fluoride Ligand Dissociation Stabilized by Intramolecular Hydrogen Bonding. *Chem. Comm.*, **2015**, *51*, 5490-5492. *Selected for Journal Cover
- 10) Tseng, K-N T.; Szymczak, N. K.*; Dehydrogenative Oxidation of Primary Amines to Nitriles. *Synlett (Synfacts)*. **2014**, *25*, 2385-2389
- 9) Carter, T. J.; Wang, J. Y.; Szymczak, N. K.*; Manganese-Mediated Hydride Delivery to a Borazine by Stepwise Reduction and Protonation. *Organometallics*, **2014**, *33*, 1540-1543.
- 8) Moore, C. M.; Quist, D. A.; Kampf, J. W.; Szymczak, N. K.*. A 3-Fold-Symmetric Ligand Based on 2-Hydroxypyridine: Regulation of Ligand Binding by Hydrogen Bonding. *Inorg. Chem.*, **2014**, *53*, 3278 - 3280. *Selected as a Highlighted Manuscript on the Inorganic Chemistry homepage.
- 7) Tseng, K-N T.; Rizzi, A.; Szymczak, N. K.*; Oxidant-Free Conversion of Primary Amines to Nitriles. *J. Am. Chem. Soc.*, **2013**, *135*, 16352-16355. Featured in the Organic Chemistry Portal: <http://www.organic-chemistry.org/Highlights/2014/19May.sht>.
- 6) Moore, C. M.; Szymczak, N. K.*. Approaches for the Incorporation of Appended Functionality in Pincer Ligands. In Pincer and Pincer-type Complexes – Application in Organic Synthesis and Catalysis; 1st Ed. Szabó, K. J.; Wendt, O. F., Ed. Wiley-VCH: Weinheim, Germany, **2014**; 117-147.
- 5) Tseng, K-N T.; Kampf, J. W.; Szymczak, N. K.*; Base-Free, Acceptorless, and Chemoselective Alcohol Dehydrogenation Catalyzed by an Amide-Derived NNN-Ruthenium(II) Hydride Complex. *Organometallics*, **2013**, *32*, 2046-2049. *Top 10 Most Read Articles: April-June 2013.
- 4) Tutusaus, O.; Ni, C.; Szymczak, N. K.*; A Transition Metal Lewis Acid-Base Triad System for Cooperative Substrate Binding. *J. Am. Chem. Soc.*, **2013**, *135*, 3403-3406. *Featured in Chemical & Engineering News, **2013**, *91*, 29.
- 3) Moore, C. M.; Szymczak, N. K.*. 6,6'-Dihydroxy Terpyridine: A Proton-Responsive Bifunctional Ligand and its Application in Catalytic Transfer Hydrogenation of Ketones. *Chem. Comm.*, **2013**, *49*, 400 - 402.
- 2) Carter, T. J.; Kampf, J. W.; Szymczak, N. K.*. Reduction of Borazines Mediated by Low-Valent Chromium Species. *Angew. Ch., Int. Ed.*, **2012**, *51*, 13168-13172. *Featured in Advances in Engineering
- 1) Moore, C. M.; Szymczak, N. K.*. A Tris(2-quinolylmethyl)amine Scaffold that Promotes Hydrogen Bonding within the Secondary Coordination Sphere. *Dalton Trans.*, **2012**, *41*, 7886-7889. Invited contribution for "New Talent: The Americas." - *Top ten most accessed articles in May 2012*

- 17) McCrory, C. C. L.; Szymczak, N. K.; Peters, J. C.* Evaluating Activity for Hydrogen-Evolving Cobalt and Nickel Complexes at Elevated Pressures of Hydrogen and Carbon Monoxide. *Electrocatalysis*, **2016**, *7*, 87-96.
- 16) Bayram, Ercan; Linehan, John C.*; Fulton, John L.; Szymczak, Nathaniel K.; Finke, Richard G.*; Determination of the Dominant Catalyst Derived from the Classic $[\text{RhCp}^*\text{Cl}_2]_2$ Precatalyst System: Is it Single-Metal Rh_1Cp^* -Based, Subnanometer Rh_4 Cluster-Based, or $\text{Rh}(\text{O})_n$ Nanoparticle-Based Cyclohexene Hydrogenation Catalysis at Room Temperature and Mild Pressures? *ACS Catalysis*, **2015**, *5*, 3876-3886.
- 15) Ercan, B.; Linehan, J.; Fulton, J.; Roberts, J.; Szymczak, N.; Smurthwaite, T.; Ozkar, S.; Balasubramanian, M.; Finke, R. Is It Homogeneous or Heterogeneous Catalysis Derived from $[\text{RhCp}^*\text{Cl}_2]_2$? In Operando-XAFS, Kinetic and Crucial Kinetic Poisoning Evidence for Subnanometer Rh_4 Cluster-Based Benzene Hydrogenation Catalysis. *J. Am. Chem. Soc.*, **2011**, *133*, 18889-18902.
- 14) Neiner, D.; Karkamamkar, A.; Bowden, M.; Choi, Y. J.; Luedtke, A.; Holladay, J.; Fisher, A.; Szymczak, N.; Autrey, T. Kinetic and Thermodynamic Investigation of Hydrogen Release from Ethane 1,2-Di-Amineborane. *Energy Environ. Sci.*, **2011**, *4*, 4187-4193
- 13) Szymczak, N. K.; Berben, L. A.; Peters, J. C. Redox-Rich Dicobalt Macrocycles as Templates for Multi-Electron Transformations. *Chem. Comm*, **2009**, 6729-6731
- 12) Szymczak, N. K.; Braden, D. A.; Crossland, J. L.; Turov, Y.; Zakharov, L. N.; Tyler, D. R. Aqueous Coordination Chemistry of H_2 . Why is Coordinated H_2 Inert to Substitution by Water in *trans*- $\text{Ru}(\text{P}_2)_2(\text{H}_2)\text{H}^+$ -type Complexes (P_2 = a Chelating Phosphine)? *Inorg. Chem.*, **2009**, *48*, 2976-2984
- 11) Yelle, R. B.; Crossland, J. C.; Szymczak, N. K.; Tyler, D. R. Theoretical Studies of N_2 Reduction to Ammonia in $\text{Fe}(\text{dmpe})_2\text{N}_2$. *Inorg. Chem.*, **2009**, *48*, 861-871
- 10) Pons, V; Baker, R. T.; Szymczak, N. K.; Heldebrant, D. J.; Linehan, J. C.; Matus, M. H.; Grant, D. J.; Dixon, D. A. Coordination of Aminoborane, NH_2BH_2 , Dictates Selectivity and Extent of H_2 Release in Metal-Catalysed Ammonia Borane Dehydrogenation. *Chem. Comm.*, **2008**, *48*, 6597 - 6599
- 9) Shaw, W. J; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Baker, R. T.; Autrey, T. In Situ Multinuclear NMR Spectroscopic Studies of the Thermal Decomposition of Ammonia Borane in Solution. *Angew. Ch., Int. Ed.*, **2008**, *120*, 7603-7606
- 8) Szymczak, N. K.; Tyler, D. R. Aspects of Dihydrogen Coordination Chemistry Relevant to Reactivity in Aqueous Solution. *Coord. Chem. Rev.*, **2008**, *252(1-2)*, 212-230
- 7) Fulton, J. L.; Linehan, J. C.; Autrey, T.; Balasubramanian, M.; T.; Chen, Y.; Szymczak, N. K.. When is a Nanoparticle a Cluster? An Operando EXAFS Study of Amine Borane Dehydrocoupling by Rh_4 Clusters. *J. Am. Chem. Soc.*, **2007**, *129*, 11936-11949
- 6) Gilbertson, J. D.; Szymczak, N. K.; Crossland, J. C.; Miller, W. K.; Lyon, D. K.; Foxman, B. M.; Davis, J.; Tyler, D. R. Water-Soluble Transition Metal Phosphine Complexes: Investigation of the Aqueous Binding and Activation of H_2 and N_2 in *trans*- $\text{Fe}^{\text{II}}(\text{P}_2)_2\text{X}_2$ -type Complexes (P_2 = a Chelating Phosphine). *Inorg. Chem.*, **2007**, *46*, 1205-1214
- 5) Szymczak, N. K.; Zakharov, L. N.; Tyler, D. R. Solution Chemistry of a Water-Soluble η^2 - H_2 Complex: Evidence for H_2 acting as a Hydrogen Bond Donor. *J. Am. Chem. Soc.* **2006**, *128*, 15830-15835
- 4) Szymczak, N. K.; Oelkers, A. B.; Tyler, D. R. Detection of Hydrogen Bonding in Solution: A ^2H Nuclear Magnetic Resonance Method Based on Rotational Motion of a Donor/Acceptor Complex. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4002-4008

- 3) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. Reduction of N₂ to Ammonia and Hydrazine Utilizing H₂ as the Reductant. *J. Am. Chem. Soc.*, **2005**, *127*, 10184-10185
- 2) Szymczak, N. K.; Han, F.; Tyler, D. R. Arrested Chloride Abstraction from *trans*-RuCl₂(DMeOPrPE)₂ with TIPF₆; Formation of a 1-D Coordination Polymer having Unusual Octahedral Coordination around Thallium(I). *J. Chem. Soc., Dalton Trans.*, **2004**, 3941-3942
- 1) Gilbertson, J. D.; Szymczak, N. K.; Tyler, D. R. H₂ Activation in Aqueous Solution: Formation of *trans*-[Fe(DMeOPrPE)₂H(H₂)]⁺ via the Heterolysis of H₂ in Water. *Inorg. Chem.*, **2004**, *43*, 3341-3343

INVITED PRESENTATIONS

upcoming:

University of Pennsylvania
University of Minnesota, MN
Organometallics Gordon Research Conference, Salve Regina, RI

2018:

2018 ACS Meeting, New Orleans

2017:

West Virginia University, September, 2017
Institute of Chemistry, Chinese Academy of Sciences, Beijing, China
Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences, Beijing, China
Tsinghua University, Beijing, China
Michigan State University, MI
Telluride Science Research Center Proton and Electron Transfer Workshop, Telluride, CO
University of Wisconsin-Madison, WI
Princeton, NJ

2016:

USC, CA
UNC-Chapel Hill, NC
University of Chicago, IL
ACS-Central Regional Meeting, KY
Los Alamos National Laboratory, NM
Kaohsiung Medical University, Taiwan
Telluride Science Research Center Small Molecule Activation Workshop, Telluride, CO
IONiC VIPER Workshop, Ann Arbor, MI
International symposium of homogeneous catalysis (ISHC-20), Kyoto, Japan
International Symposium on Precisely Designed Catalysts with Customized Scaffolding, Osaka, Japan
Kyoto University, Japan
University of Utah, UT
Boston University, MA
MIT, MA
UCLA, CA
UC Irvine, CA
Caltech, CA
University of Oregon, OR
Iowa State University, IA

2015:

Pacificchem 2015 (2 invited talks), HI
 UC Berkeley, CA
 Nara Institute of Science and Technology, Japan
 University of Wisconsin LaCrosse, WI
 Washington State University, WA
 Pacific Northwest National Laboratory, WA
 Indiana University, IN
 University of Illinois at Urbana-Champaign, IL
 Texas A&M University, TX
 Inorganic Reaction Mechanisms Gordon Research Conference, Galveston, TX
 University of Washington, WA
 University of New Hampshire, NH.

2014:

University of Tulsa, OK
 University of Louisville, KY
 Dow Corning, Midland, MI
 41st International Conference on Coordination Chemistry, Singapore
 KAIST International Inorganic Chemistry Symposium, Korea
 Korea Advanced Institute of Science and Technology Korea
 Western Washington University, WA
 Kenyon College, OH
 University of Cincinnati, OH.

2013:

245th ACS Meeting New Orleans (2 invited talks)

2012:

University of Minnesota Duluth, MN
 Truman State University, MO
 Oakland University, MI

PRODUCTS

Sigma-Aldrich Prod. No. 794414. $HRu(bmpi)(PPh_3)_2$
 Sigma-Aldrich Prod. No. 794406. $Ru(bmpi)(PPh_3)Cl$

Patent Pending Serial number: 62/353,928. *Complexes for Nucleophilic, Radical, and Electrophilic Polyfluoroalkylation.* Nathaniel K. Szymczak (PI), Jacob B. Geri

Provisional Patent (11-16-2015). *Formation of High-Molecular Weight Polyethylene from a Sterically Unencumbered Iron-Based Catalyst.* Nathaniel K. Szymczak (co-PI), Jeffery A. Byers (co-PI), Jeffrey A. Kehl, Kuei-Nin T. Tseng.

PROFESSIONAL AFFILIATIONS

Michigan Memorial Phoenix Energy Institute – Faculty Fellow	2010 – present
Society of Biological Inorganic Chemistry – Member	2010 – present
American Chemical Society – Member	2002 – present

American Association for the Advancement of Science – Member

2001 – present

ACADEMIC SERVICE

To the Community:

Symposium Organizer: 2014 Ohio Inorganic Weekend, Nov. 14-15 at the University of Michigan. ~130 attendees

251st ACS Meeting, Philadelphia, *Secondary Coordination Sphere Influences: Stability, Reactivity, and Everything in Between*. Aug. 21-25, 2016.

Advisory: International Advisor for Student Symposium, NAIST, Japan, Nov. 9-10, 2015

Manuscript Reviewer: ACS Catalysis, AIMS Environmental Science, Catalysis Science and Technology, ChemComm, Chemistry, a European Journal, Chemical Science, Current Opinion in Chemical Biology, Dalton Transactions, Energy and Environmental Science, Inorganic Chemistry, Journal of the American Chemical Society, Journal of Organic Chemistry, Journal of Inorganic Biochemistry, Organic Chemistry Frontiers, Organometallics, Science Advances

Proposal Reviewer: Air Force Office of Scientific Research, DOE-SCGF, ACS-PRF, NSF, SDE/GWIS, NIH SBCA *ad hoc* (2018)

Session Moderator: 2012 Ohio Inorganic Weekend, 245th ACS Meeting, New Orleans, 2013 (3 sessions), 41st International Conference on Coordination Chemistry, Singapore. 2014, 47th Central Regional ACS Meeting, Covington, KY 2016.

Editorial: Volume co-editor for Comprehensive Coordination Chemistry

To the University of Michigan:

ADVANCE Panelist on running a research lab	December, 2017
CSIE UM Panelist on managing conflict in the lab	May 2017
Speaker for Chemistry REBUILD Symposium	March 2016
CSIE UM Panelist on hiring postdoctoral candidates	February 2016
Speaker for Provost's seminar workshop: REBUILDing STEM Education at Michigan"	October 2014
Dept. of Chemistry Executive Committee	2017 – present
Dept. of Chemistry Graduate Committee	2014 – 2017
Dept. of Chemistry Safety Committee	2014 – present
Dept. of Chemistry Curriculum Committee	2013 – 2016
Dept. of Chemistry Recruiting Committee	2010 – 2013
Dept. of Chemistry Graduate Student Admissions Committee	2011 – 2016
Graduate Thesis Committees (16)	2010 – present
Chemistry Rotation Students (>20)	2010 – present