Editor-in-Chief
Rick L. Danheiser
Department of Chemistry, Rm 18-298
Massachusetts Institute of Technology
Cambridge, MA 02139
Tel. 617 253-1842
Fax 617 252-1504
danheisr@mit.edu

Associate Editor
Charles K. Zercher
Department of Chemistry
University of New Hampshire
Durham, NH 03824
Tel. 603 862-2697
Fax 603 862-4278
org.syn@unh.edu

Organic Syntheses Summer Research Grant Program

Application Cover Sheet

Name Allegra Liberman-Martin

Mailing Address Keck Science Center
450 N. Center St.
Orange, CA 92866

Email Address libermanmartin@chapman.edu

Phone Number (714)-516-5586

Website http://www.allegraliberman-martin.com/
https://www.chapman.edu/our-faculty/allegra-liberman-martin

Title of Proposed Research Synthesis and Catalytic Applications of Carbodiphosphoranes

Applications should be submitted as email attachments by November 1, 2020 to the office of the Editor in Chief at ospui@mit.edu. Complete applications must include

- This cover sheet
- Curriculum vitae including list of publications, indicating which papers represent research by undergraduate coworkers.
- List of most recent undergraduate coworkers (5-10 maximum) including their first position after graduation and current employment (if known).
- Description of proposed research (maximum 3 pages including figures, schemes, and references).
- Letter of support from the Chair of your department confirming the availability of space, equipment, and administrative support for the proposed research and confirming that undergraduate researchers will receive appropriate training in laboratory safety.

Allegra L. Liberman-Martin

Assistant Professor of Chemistry and Biochemistry
Chapman University
One University Drive
Orange, CA 92866
Phone: (714) 516-5586
Email: libermanmartin@chapman.edu
Website: www.allegraliberman-martin.com

Education

University of California, Berkeley 2010 – 2015

Ph.D. in Chemistry

with Profs. T. Don Tilley and Robert G. Bergman

Lewis Acid Mediated Reactions: Electronic Modification of Platinum Complexes and Metal-Free Catalysis

Scripps College, Claremont, CA 2006 – 2010

B.A. in Chemistry, summa cum laude with honors in chemistry

with Prof. Nancy S. B. Williams (2008–2010, Scripps College)

Aryl Orientation Preferences during Reductive Elimination from Platinum Complexes

with Prof. Alan S. Goldman (Summer 2009, Rutgers University)

Iridium-Catalyzed Transfer Dehydrogenation of Cyclic Alkyl Ether Substrates

with Prof. Kathleen L. Purvis-Roberts (2007 – 2008, Scripps College)

Analysis of Amines in Air and Smog Chamber Samples by Ion Chromatography

Professional Appointments

Chapman University, Orange, CA 2018 – present

Assistant Professor of Chemistry & Biochemistry

Main Group Catalysis for Sustainable Organic and Polymer Synthesis

California Institute of Technology, Pasadena, CA 2016 – 2018

Resnick Sustainability Institute postdoctoral fellow

with Prof. Robert H. Grubbs

Investigation of Brush Polymers as Stimuli-Responsive Photonic Crystals

Publications

* denotes corresponding authorship

‡ denotes equal contribution

Underlining denotes undergraduate coauthor

(15) **Liberman-Martin, A. L.**;*‡ Ogba, O. M.*‡ Midsemester Transition to Remote Instruction in a Flipped College-Level Organic Chemistry Course. *J. Chem. Educ.* **2020**, *97*, 3188–3193. (special issue on "Insights Gained While Teaching Chemistry in the Time of COVID-19")

(14) Chu, C. K.; Lin, T.-P.; Shao, H.; **Liberman-Martin, A. L.**; Liu, P.; Grubbs, R. H. Disentangling Ligand Effects on Metathesis Catalyst Activity: Experimental and Computational Studies of Ruthenium–Aminophosphine Complexes. *J. Am. Chem. Soc.* **2018**, *140*, 5634–5643.

(13) **Liberman-Martin, A. L.**; Grubbs, R. H. Ruthenium Olefin Metathesis Catalysts Featuring a Labile Carbodicarbene Ligand. *Organometallics* **2017**, *36*, 4091–4094.

(12) Chang, A. B.; Lin, T.-P.; Thompson, N. B.; Luo, S.-X.; **Liberman-Martin, A. L.**; Chen, H.-Y.; Lee, B.; Grubbs, R. H. Design, Synthesis, and Self-Assembly of Polymers with Tailored Graft Distributions. *J. Am. Chem. Soc.* **2017**, *139*, 17683–17693.

(11) Suslick, B. A.; **Liberman-Martin, A. L.**; Wambach, T. C.; Tilley, T. D. Olefin Hydroarylation Catalyzed by (Pyridyl-Indolate)Pt(II) Complexes: Catalytic Efficiencies and Mechanistic Aspects, *ACS Catal.*, **2017**, *7*, 4313–4322.

(10) **Liberman-Martin, A. L.**; Chu, C. K.; Grubbs, R. H. Application of Bottlebrush Block Copolymers as Photonic Crystals. *Macromol. Rapid Commun.* (special issue on "Polymers and Light"), **2017**, DOI: 10.1002/marc.201700058.

- Featured in *Advanced Science News*
- A "Most Accessed" article of 2017 on the *Macromol. Rapid Commun.* website

(9) Lin, T.-P.; Chang, A. B.; Chen, H.-Y.; **Liberman-Martin, A. L.**; Bates, C. M.; Voegtle, M.; Bauer, C. A.; Grubbs, R. H. Control of Grafting Density and Distribution in Graft Polymers by Living Ring-Opening Metathesis Copolymerization. *J. Am. Chem. Soc.* **2017**, *139*, 3896–3903.

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(7) **Liberman-Martin, A. L.**; Levine, D. S.; Ziegler, M. S.; Bergman, R. G.; Tilley, T. D. Lewis Acid-Base Interactions between Platinum(II) Diaryl Complexes and Bis(perfluorophenyl)zinc: Strongly Accelerated Reductive Elimination Induced by a Z-Type Ligand. *Chem. Commun.* **2016**, *52*, 7039–7042.

(6) Lipke, M. C.; **Liberman-Martin, A. L.**; Tilley, T. D. Significant Cooperativity Between Ruthenium and Silicon in Catalytic Transformations of an Isocyanide. *J. Am. Chem. Soc.* **2016**, *138*, 9704–9713

(5) **Liberman-Martin, A. L.**; Ziegler, M. S.; DiPasquale, A. G.; Bergman, R. G.; Tilley, T. D. Functionalization of an Iridium–Diamidocarbene Complex by Ligand-Based Reactions with Titanocene and Zirconocene Sources. *Polyhedron* (special issue dedicated to Malcolm L. H. Green) **2016**, *116*, 111–115.

(4) **Liberman-Martin, A. L.**; Levine, D. S.; Liu, W.; Bergman, R. G.; Tilley, T. D. Biaryl Reductive Elimination Is Dramatically Accelerated by Remote Lewis Acid Binding to a 2,2′-Bipyrimidyl–Platinum Complex: Evidence for a Bidentate Ligand Dissociation Mechanism. *Organometallics* **2016**, *35*, 1064–1069.

- Featured as cover article
- A "Most Read" article from January–April 2016 on the *Organometallics* website

(3) **Liberman-Martin, A. L.**; Bergman, R. G.; Tilley, T. D. Lewis Acidity of Bis(perfluorocatecholato)silane: Aldehyde Hydrosilylation Catalyzed by a Neutral Silicon Compound. *J. Am. Chem. Soc.* **2015**, *137*, 5328–5331.

- Featured in *Synfacts*, 2015; 11(7): 0764.
- Featured in *ChemInform*, 46: DOI: 10.1002/chin.201538046

(2) **Liberman-Martin, A. L.**; Bergman, R. G.; Tilley, T. D. A Remote Lewis Acid Trigger Dramatically Accelerates Biaryl Reductive Elimination from a Platinum Complex. *J. Am. Chem. Soc.* **2013**, *135*, 9612–9615.

(1) Erupe, M. E.; **Liberman-Martin, A. L.**; Silva, P. J.; Malloy, Q. G. J.; Yonis, N.; Crocker, D. R.; Purvis-Roberts, K. L. Determination of Methylamines & Trimethylamine-N-oxide in Particulate Matter by Non-suppressed Ion Chromatography. *J. Chromatogr. A.* **2010**, *1217*, 2070–2073.

Manuscripts in Preparation

Liberman-Martin, A. L.; Chang, A. B.; Chu, C. K.; Siddique, R. H.; Lee, B.; Grubbs, R. H. Processing Effects on the Self-Assembly of Brush Block Polymer Photonic Crystals. (will be submitted to *ACS Macro Letters*)

Thammavongsy, Z.; **Liberman-Martin, A. L.*** Catalytic Applications of Low Valent Group 14 Compounds. (will be submitted to *Coordination Chemistry Reviews*)

Liberman-Martin, A. L.; van Vleet, M.; Zapeda, E.; Roleder, C.; Stephens, E. N.; Cave, R. J.; Williams, N. S. B. Aryl Orientation Preferences in Csp^2–Csp^3 Reductive Elimination from Platinum (IV) Complexes. (will be submitted to *Organometallics*)

Grants and Awards Received

• American Chemical Society Petroleum Research Fund Undergraduate New Investigator Program "Carbodiphosphoranes as Organocatalysts for Carbodiimide and Isocyanate Reduction" ($55,000)	2021–2023
• Chapman Pedagogical Innovation Award and Grant ($5,000) "Development of a Concept Video Library and Class Demonstrations for an Advanced Organic Chemistry Course"	2020–2021
• Chapman Grant Writers Bootcamp Grant ($5,000)	2019–2021
• Chapman University Faculty Opportunity Fund Grant ($15,000)	2019–2021
• Hamilton Syringe Grant ($1,000)	2019
• Resnick Sustainability Institute Postdoctoral Fellowship	2016 – 2018
• Outstanding Poster Award, Division of Polymer Chemistry 253rd American Chemical Society National Meeting, San Francisco, CA	2017

- Benjamin Boussert Memorial Award (UC-Berkeley, Department of Chemistry) 2016
  Award for exemplifying commitment to social or environmental change
- Margaret Jorgenson Memorial Prize Travel Grant (UC-Berkeley) 2013
- Graduate Division Conference Travel Grant (UC-Berkeley) 2013 and 2015
- Barbara McClintock Award for Best Senior Thesis in the Sciences (Scripps College) 2010
- ACS Division of Inorganic Chemistry Undergraduate Award (Scripps College) 2009
- Undergraduate Summer Research Fellowship (Rutgers University) 2009
  Center for Enabling New Technologies through Catalysis
- Norris Foundation Summer Research Fellowship (Scripps College) 2008

Professional Activities

Professional affiliations:

- American Chemical Society
- Council on Undergraduate Research
- Phi Beta Kappa
- Sigma Xi Scientific Research Honor Society

Peer reviewer:

- *Journal of the American Chemical Society*
- *Chemical Science*
- *Chemical Communications*
- *Journal of Chemical Education*

Conference session chair: *New Synthesis & Characterization of Polymers*, Division of Polymer Chemistry, 254th American Chemical Society National Meeting, Washington DC, August 2017.

Teaching Experience

Chapman University

- CHEM 230: Organic Chemistry I 2018, 2019
- CHEM 230L: Organic Chemistry I Laboratory 2018, 2019
- CHEM 331: Organic Chemistry II 2019, 2020
- CHEM 331L: Organic Chemistry II Laboratory 2019

California Institute of Technology

- Ch101: "Revolutionary Inorganic Molecules" (co-instructor) 2017
- Research Mentor, Jayce Miller, Undergraduate Student 2016 – 2018

University of California, Berkeley

- Graduate Student Instructor
  - Organometallic Chemistry (Prof. T. Don Tilley) 2011, 2015
  - NMR Spectroscopy (Dr. Chris Canlas) 2013
  - Physical Organic Chemistry (Prof. Robert G. Bergman) 2012
  - General Chemistry (Prof. John Arnold) 2010

- Research Mentor

Jana Schmitt, Visiting Graduate Student	2013 – 2014
Myles Walden, High School Student	Summer 2012

Supervised Undergraduate Research Students at Chapman University

Daniel Chang (Chemistry '19, Chapman University) (2018–2020)

- NSF Graduate Research Fellowship recipient (2020)
- Ronald M. Huntington Award recipient (campus-wide award for research accomplishments)
- Poster presenter at the SoCal Undergraduate Chemistry Research Symposium, July 2019
- Poster presenter at the Fall 2019 American Chemistry Society National Meeting, San Diego, CA. August 2019
- Awarded a Spring 2019 Student Scholarly Research/Creative grant ($1,000)

Tamara Elenberger (Biochemistry '21, Chapman University) (2020–present)

Cara Fleener (Biochemistry '21, Chapman University) (2019 – present)

- Awarded a 2019 Chapman Summer Undergraduate Research Fellowship ($4,000)
- Awarded a Spring 2020 Student Scholarly Research/Creative grant ($1,000)

Vanna Kizirian (Chemistry '21, Chapman University) (2020–present)

Ali Mahmoud (transferred from Chapman University to the University of Washington) (Spring 2020)

- Received Honorable Mention for 2020 Chapman Summer Undergraduate Research Fellowship

Roxanne Naumann (Chemistry '21, Chapman University) (2019 – present)

- Awarded a 2019 Chapman Summer Undergraduate Research Fellowship ($4,000)
- Awarded a Fall 2019 Student Scholarly Research/Creative grant ($1,000)

Liam Sullivan (Chemistry '21, Chapman University) (2020–present)

Alexa Wilson (Chemistry '22, Chapman University) (2020–present)

Service and Outreach

Chapman University

• Schmid College of Science & Technology Discussion Leader on "Flipped Classrooms"	2020
• Co-founder and co-director of the Chemistry & Biochemistry Seminar Series	2018 – present
• Member of Search Committee for Assistant Professor of Mathematics	2019 – 2020
• Organic Chemistry curriculum development	2018 – present
• Faculty Internship advisor for Zubair Lakhia (through KGI)	Summer 2020
• Invited speaker to University of California, Berkeley's Science, Leadership, and Management Seminar Series on "Mentoring and Working with Undergraduates"	2019
• Panelist in the CHEM 100 / BCHM 100 Introduction to the Chemistry and Biochemistry Majors and Career Paths course	2019 and 2020
• Judge for the California Junior Science and Humanities Symposium (JSHS)	2019
• Invited speaker to the Chapman TriBeta Biological Honor Society Presented on "Pathways to a Ph.D. in Science"	2018

California Institute of Technology

- Speaker on "Interviewing for Faculty Positions" Panel 2018
  Caltech Project for Effective Teaching event
- Caltech Teaching Conference Organizing Committee 2017
  Facilitated a conference session on authoring problem sets and exams
- Women Mentoring Women Program 2016 – 2018
  Peer mentor for a female graduate student

University of California, Berkeley

- Student Chair, Chemical Sciences Division Catalysis Group, 2013 – 2015
  Lawrence Berkeley National Laboratory
  - Organized a monthly interdisciplinary seminar series
- Department of Chemistry volunteer 2010 – 2015
  - Peer advisor for first-year graduate students
  - Presenter to undergraduate chemistry students on research opportunities
  - Speaker on "Choosing a Research Group" panel (through Iota Sigma Pi, National Honor Society of Women in Chemistry)
- Bay Area Scientists in Schools classroom volunteer 2010 – 2015
  - "Be a Scientist" pilot program mentoring 7th grade students' scientific investigations over a two-month period
  - "Science of Soap" and "Water and Carbon Dioxide" classes for 5th graders

Scripps College

- Alumna interviewer 2012 – 2015
- Co-director of the Chemistry Mentor Program 2009 – 2010
  - Program provided all general chemistry students with a peer mentor.
- Chemistry mentor for six general chemistry students 2008 – 2010

Presentations (* denotes Chapman University undergraduate co-authors)

Liberman-Martin, A. L.; Chang, D. K.*; Fleener, C. R.* Hydroboration by a Cyclic Carbodiphosphorane Organocatalyst. Organometallics Gordon Research Conference, Newport, RI, July 2019. (poster)

Liberman-Martin, A. L. Metal-Free Catalysis for Organic and Polymer Synthesis. Chapman University Summer Undergraduate Research Fellowship (SURF) Seminar Series. Orange, CA, July 2019.

Liberman-Martin, A. L.; Grubbs, R. H. Ruthenium Olefin Metathesis Catalysts Featuring Carbodicarbene and Carbodiphosphorane Ligands. Organometallics Gordon Research Conference, Newport, RI, July 2018. (poster)

Liberman-Martin, A. L. Stimuli-Responsive Molecules: From Inorganic Complexes to Light-Reflecting Polymers. Chemistry Department Seminar, Reed College, Portland, OR, September 2017.

Liberman-Martin, A. L.; Chu, C. K.; Grubbs, R. H. Synthesis and Self-Assembly of Brush Block Copolymers with Low T_g Side Chains. 254th American Chemical Society National Meeting, Washington, DC, August 2017.

Liberman-Martin, A. L.; Chu, C. K.; Chang, A. B.; Grubbs, R. H. Self-Assembly of Brush Block Copolymer Photonic Crystals Featuring Low T_g Side Chains. 253rd American Chemical Society National Meeting, San Francisco, CA, April 2017. (poster)

Liberman-Martin, A. L. Side Chain Design in Brush Block Copolymer Photonic Crystals. Resnick Foundation Seminar, California Institute of Technology, Pasadena, CA, March 2017.

Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. Activation of Platinum Complexes by Ligand-Based Reactions with Lewis Acids. Organometallics Gordon Research Conference and Seminar, Newport, RI, July 2015. (poster at GRC, speaker at GRS)

Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. Aldehyde Hydrosilylation Catalyzed by a Neutral Bis(perfluorocatecholato)silicon Compound. 46th Silicon Symposium, Davis, CA, June 2015.

Liberman-Martin, A. L. Activation of Platinum Complexes by Ligand-Based Reactions with Lewis Acids. University of California, Berkeley, Berkeley, CA, February 2015. *Invited seminar for prospective graduate students.

Liberman-Martin, A. L. Activation of Platinum Complexes by Ligand-Based Reactions with Lewis Acids. Inorganic Division Seminar, University of Washington, Seattle, WA, January 2015.

Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. Remote Triggers for the Activation of Unreactive Bonds by Late Metal Complexes. 248th American Chemical Society National Meeting, San Francisco, CA, August 2014.

Liberman-Martin, A. L.; Bergman, R. G.; Tilley, T. D. Platinum Complexes Activated by Ligand-Based Reactions with Lewis Acids. 245th American Chemical Society National Meeting, New Orleans, LA, April 2013.

Undergraduate Researchers Supervised at Chapman University

Name	Major (Graduation Year)	Time in Research Group	First Position After Graduation and Current Employment
Daniel Chang	Chemistry (2019)	Fall 2018–Spring 2020	• First position: research assistant in Liberman-Martin group (Summer 2019–Summer 2020) • Current employment: Chemistry Ph.D. program at Caltech (started Fall 2020) • NSF Graduate Research Fellow
Cara Fleener	Biochemistry (2021)	Spring 2019–present	N/A (intends to attend medical school)
Roxanne Naumann	Chemistry (2021)	Summer 2019–present	N/A (intends to pursue Chemistry Ph.D.)
Liam Sullivan	Chemistry (2022)	Spring 2020–present	N/A (intends to pursue Chemistry Ph.D.)
Vanna Kizirian	Chemistry (2022)	Spring 2020–present	N/A (intends to pursue Chemistry Ph.D.)
Tamara Elenberger	Biochemistry (2022)	Spring 2020–present	N/A (intends to pursue Biochemistry Ph.D.)
Alexa Wilson	Chemistry (2022)	Spring 2020–present	N/A (undecided future plans)

Synthesis and Catalytic Applications of Carbodiphosphoranes

Background and Significance

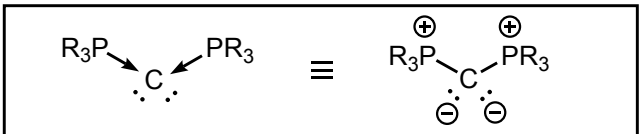

Figure 1. Two carbodiphosphorane representations.

There has been significant recent interest in the use of carbon nucleophiles as organocatalysts. Most prominently, *N*-heterocyclic carbenes (NHCs) have emerged as widely used catalysts for a range of organic transformations.[1] Other classes of carbon nucleophiles have more recently emerged as organocatalysts, including *N*-heterocyclic olefins[2] and phosphorus ylides.[3] Robust synthetic methods for the preparation of these compounds enables their widespread use as ligands for transition metal and their application as organocatalysts.

Carbodiphosphoranes (CDPs) constitute an interesting class of molecules featuring a two-coordinate carbon center that is formally zerovalent and possesses two lone pairs (**Figure 1**).[4] As a result, the central carbon of the CDP is strongly nucleophilic. There has been significant interest in CDPs as ligands for transition metal complexes,[5] as CDPs are more strongly donating than NHC ligands.[6] However, despite their rich coordination chemistry, *to our knowledge, there are no previous reports using carbodiphosphoranes as organocatalysts*. We believe this represents an opportunity to investigate the catalytic potential of these overlooked compounds and gain deeper insight into their nucleophilic properties.

This proposal describes efforts to: (i) apply previously reported cyclic and acyclic CDPs as catalysts for imine hydroboration, and (ii) synthesize novel chiral CDPs for use in enantioselective catalysis. This work is designed to be completed by an undergraduate researcher during Summers 2021 and 2022.

Aim 1: Synthesis and Imine Hydroboration Catalysis by Reported Carbodiphosphoranes

To make the proposed project accessible for undergraduate researchers, initial CDP targets have been selected that (i) can be synthesized from commercially available precursors in two reaction steps, and (ii) are indefinitely stable when stored as solids under inert atmosphere. To date, undergraduates in my research group have successfully synthesized CDP derivatives **1** and **3** in a nitrogen-atmosphere glovebox (**Figure 2**). The acyclic $(MePh_2P)_2C$ and six-membered cyclic CDP were first reported by Schmidbaur and coworkers in the 1970s.[7] Both syntheses involve alkylation of bis(diphenylphosphino)methane, followed by deprotonation using methylenetrimethylphosphorane, Me_3PCH_2; however, *detailed reaction conditions and yields for the preparation of CDPs **1**, **3**, and **4** have not been reported.*

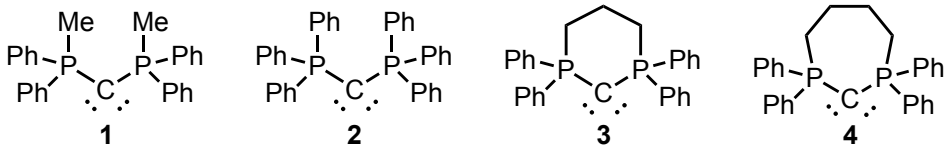

Figure 2. Target carbodiphosphoranes for synthesis during Summer 2021.

One goal for Summer 2021 is to generate reliable, detailed synthetic procedures for known CDPs **1–4** (**Figure 2**). There are no previous reports of carbodiphosphorane preparation in *Organic Syntheses*, and we believe there is an opportunity to enable more widespread use of these compounds by providing detailed synthetic methods. Our group currently performs both alkylation and deprotonation steps within a nitrogen-atmosphere glovebox. During Summer 2021, we will determine if the alkylation reactions or the workup for the alkylation step can be performed under air. We will also attempt the deprotonation procedure using a Schlenk line. Our goal is to generate reproducible and detailed procedures for CDP synthesis that are suitable for publication in *Organic Syntheses*.

All CDPs that are successfully synthesized will be tested as catalysts for imine hydroboration reactions. Imine hydroboration is a convenient method to synthesize amine products,[8] which are important in pharmaceutical, agrochemical, and materials chemistry applications.[9] Current metal-free catalysts for imine reduction are primarily Lewis acids, which can be inhibited by the presence of coordinating functional groups, including the imine nitrogen itself.[10] We anticipate that Lewis basic CDP catalysts can offer complementary or broader functional group compatibility in imine reduction reactions.

We have preliminary results demonstrating that cyclic CDP **3** can catalyze imine hydroboration using pinacolborane (HBPin) at room temperature (**Figure 3**). During Summer 2021, we will expand the imine substrate scope for hydroboration reactions and compare CDP catalysts **1**–**4** for these transformations. A series of *para*-substituted imine substrates featuring cyano, methoxy, and dimethylamino substituents will be investigated, as these functional groups are poorly tolerated by Lewis acid catalysts.[10] The influence of nitrogen substitution will be determined by comparing hydroboration rates and yields for *N*-phenyl, *N*-benzyl, and *N*-methyl substituents.[11] All reactions will be performed in triplicate and products will be characterized by ^{1}H (quantitative), ^{13}C, and ^{11}B NMR spectroscopy and mass spectrometry.

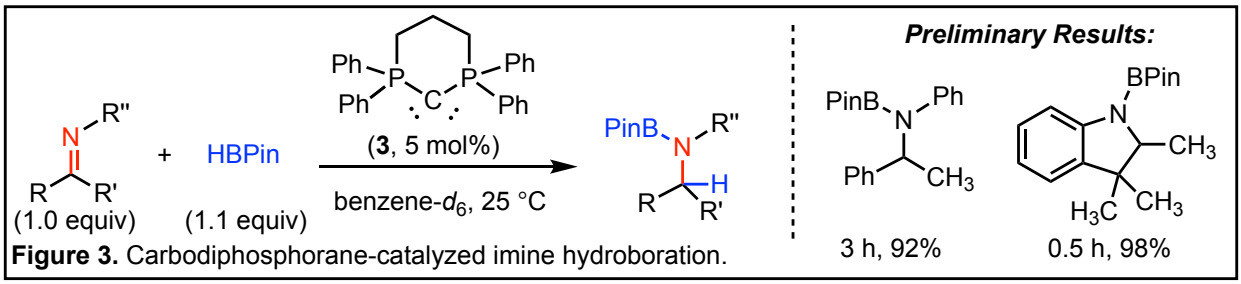

Figure 3. Carbodiphosphorane-catalyzed imine hydroboration.

Aim 2. Synthesis of Chiral Carbodiphosphoranes and Imine Hydroboration Catalysis

The development of chiral phosphines and NHCs has enabled a wide range of enantioselective catalytic transformations.[12] We believe that chiral carbodiphosphoranes have the potential to be both a new class of asymmetric nucleophilic catalysts and a new chiral ligand motif for transition metal catalysts. *To our knowledge, chiral carbodiphosphoranes have not been previously reported.*

During Summer 2022, an undergraduate researcher will prepare a series of novel chiral carbodiphosphoranes (**5**–**8**, **Figure 4**), with the goal of publishing these detailed synthetic procedures in *Organic Syntheses*. For ease of synthesis, chiral CDP targets were selected that utilize commercially available bis(phosphine) motifs. To prepare chiral CDPs **5**–**8**, chiral bis(phosphine) compounds will be alkylated with diiodomethane, and the resulting cyclic bis(phosphonium) compounds will be deprotonated using potassium bis(trimethylsilyl)amide or benzyl potassium. All chiral CDPs will be characterized by ^{1}H (quantitative), ^{13}C, and ^{31}P NMR spectroscopy, X-ray crystallography, and elemental analysis.

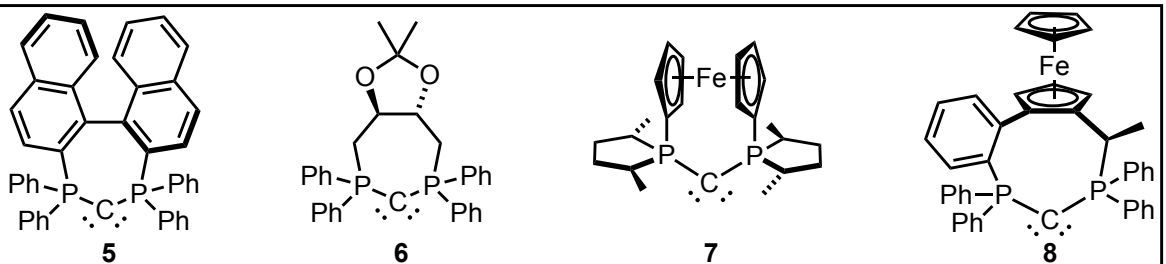

Figure 4. Target chiral carbodiphosphorane compounds for synthesis during Summer 2022.

Chiral CDPs that are successfully synthesized will be examined as catalysts for enantioselective imine hydroboration (**Figure 5**), as the preparation of enantioenriched amines is desirable for pharmaceutical applications.[13] A substrate scope containing both cyclic and acyclic

prochiral imines has been selected for hydroboration studies. Amine products will be characterized by ^{1}H (quantitative) and ^{13}C NMR spectroscopy, mass spectrometry, and HPLC to determine enantiomeric excess.

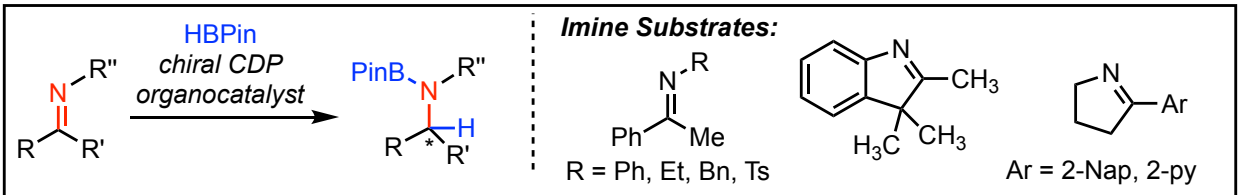

Figure 5. Asymmetric imine hydroboration by chiral carbodiphosphorane catalysts.

Conclusion

The research plan described above will advance the field of nucleophilic organocatalysis while simultaneously providing a highly mentored research experience for an undergraduate student. The detailed procedures for carbodiphosphorane synthesis generated from this work will be broadly applicable methods for other researchers, and the fundamental knowledge gained from imine hydroboration studies will contribute to the development of new catalytic methods.

Investigator and Institutional Context

I began my independent career in 2018 as an Assistant Professor at Chapman University. Chapman University is a medium sized, private liberal arts college. The Chemistry and Biochemistry Department at Chapman University serves solely undergraduates. The combined number of Chemistry and Biochemistry majors is approximately 90–110 at any given time.

The top priority of my research group is the education and training of undergraduate researchers. To empower undergraduate researchers to make new scientific discoveries, projects are structured such that each student takes intellectual ownership of a small piece of a project, including performing literature searches, planning and executing experiments, analyzing results, and troubleshooting. My research group currently consists of seven undergraduate researchers and Dr. Zachary Thammavongsy, a Teacher-Scholar Postdoctoral Fellow who provides research support on an unrelated project and additional mentoring for students.

References

1. Flanigan, D. M.; Romanov-Michiailidis, F.; White, N. A.; Rovis, T. *Chem. Rev.* **2015**, *115*, 9307–9387.
2. Crocker, R. D.; Nguyen, T. V. *Chem. Eur. J.* **2016**, *22*, 2208–2213.
3. (a) Toda, Y.; Sakamoto, T.; Komiyama, Y.; Kikuchi, A.; Suga, H. *ACS Catal.* **2017**, *7*, 6150–6154; (b) Wu, W.-B.; Zeng, X.-P.; Zhou, J. *J. Org. Chem.* **2020**, DOI: 10.1021/acs.joc.9b03347
4. Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. *Angew. Chem. Int. Ed.* **2006**, *45*, 8038–8042.
5. Petz, W.; Frenking, G. Carbodiphosphoranes and Related Ligands. In *Transition Metal Complexes of Neutral η^1-Carbon Ligands*; Chauvin, R., Canac, Y., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2010; Vol. 30, pp 49–92.
6. Petz, W.; Weller, F.; Uddin, J.; Frenking, G. *Organometallics* **1999**, *18* (4), 619–626.
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CHAPMAN UNIVERSITY

Schmid College of Science and Technology
One University Drive, Orange, California 92866
(714) 628-7318 **Chapman.edu/science**

schmidcollege@chapman.edu

October 26, 2020

RE: *Organic Syntheses* Summer 2021-2022 Research Grant for Faculty at PUIs

I am writing to express my enthusiastic support for the *Organic Syntheses* Summer 2021-2022 Research proposal being submitted by Dr. Allegra Liberman-Martin, Assistant Professor of Chemistry in the Department of Chemistry & Biochemistry at Chapman University. Dr. Liberman-Martin is a recognized scholar in the field of homogeneous catalysis for sustainable organic and polymer synthesis, and she is submitting the research proposal for the *Synthesis and Calalytic Applications of Carbodiphosphoranes.*

In the short time since Dr. Liberman-Martin has joined our faculty, she has made substantive contributions to the mentorship of eight undergraduates conducting research in chemistry. Embodying the role of the consummate teacher-scholar, Dr. Liberman-Martin has challenged students with little research experience to learn how to formulate hypotheses and design experiments, to analyze and answer important questions of interest and relevance to the students, and to perform complex experiments requiring intricate techniques and utilization of sophisticated instrumentation. Creating a collaborative and inclusive team environment, Dr. Liberman-Martin encourages student self-efficacy. In support of students' professional development, Dr. Liberman-Martin has encouraged and mentored students to apply for grants, present at conferences, and publish. Recent funding by the American Chemical Society Petroleum Research Fund Undergraduate New Investigator Program will allow Dr. Liberman-Martin to further expand her mentorship of undergraduate research in chemistry.

Chapman University offers undergraduate only, B.S. in Chemistry and B.S. Biochemistry & Molecular Biology degree programs. The Department of Chemistry & Biochemistry fully supports and encourages sustained deep and meaningful research experiences for our undergraduates. Each undergraduate is required to complete a senior capstone research project for their B.S. degree.

Dr. Liberman-Martin's research will be conducted in our new Keck Center of Science & Engineering, completed in 2018. About 80% of the Keck Center science space, is dedicated to the Chemistry, Biochemistry, and Biology programs, including 14 research labs and 11 modern teaching labs that are fully equipped for research and advanced teaching. Significantly, research-quality and advanced teaching instrumentation is housed in 5 shared suites, including 400 MHz NMR, GPC, Confocal Microscope, SEM, AFM, CD, Raman, GC/MS, GC w/FID and ECD, ICP-OES, Fluorometer, and FT-IR. Moreover, the Keck Center is infused with a diversity of meeting, collaboration, and ideation spaces that permit the type of unstructured interactions that lead to interdisciplinary synergies.

Dr. Liberman-Martin's students will conduct research in a 450 square feet research space, equipped with three 4-foot wide fume hoods, containing three custom-made Schlenk lines for air-free experiments; a MBraun LabstarPro glove box (four gloves): outfitted with a cold well, solvent removal system, purge functionality, and freezer for the synthesis of air- and moisture-sensitive compounds; a JCMeyer solvent purification system (dispenses six anhydrous and degassed solvents); two rotary evaporators; and a group computer. Moreover, Dr. Liberman-Martin's students will be using the Keck Center 400 MHz NMR (with variable temperature and heteronuclear capabilities) and the two attenuated-total reflectance (ATR) IR spectrometers, as well as the X-ray diffractometer housed on Chapman's Rinker Campus.

A FT Lab Operations & Safety Director oversees safety trainings for the College of Science. All students conducting research complete online courses in basic laboratory safety. Additionally, each

student in Dr. Liberman-Martin's group specifically receives the following extensive safety training and supervision:

- Hands-on fire extinguisher training
- Awareness of the nearby safety shower, eye wash, first aid kit, Class ABC and Class D fire extinguisher, and telephone locations
- All students in Dr. Liberman-Martin's group are provided copies of Standard Operating Procedures (SOPs) for Schlenk line use, cryogen handling, and pyrophorics handling. Dr. Liberman-Martin goes over these documents with each student and supervises the student until proficiency in each area is established.
- If pyrophoric reagents are required, Dr. Liberman-Martin oversees the use of these chemicals regardless of the experience level of the student.

Under the supervision of the Lab Operations & Safety Director, staff are available for hands-on equipment and instrumentation trainings. A FT instrumentation technician oversees instrumentation maintenance. Furthermore, a FT administrative assistant dedicated to the Chemistry & Biochemistry department manages purchases and administration for the department.

The Department of Chemistry & Biochemistry fully endorses the *Organic Syntheses* Summer 2021-2022 Research proposal being submitted by Dr. Allegra Liberman-Martin. Dr. Allegra Liberman-Martin has developed a vibrant, undergraduate-focused research program of the highest caliber which will positively impact student outcomes in the Chemistry Program at Chapman University.

Respectfully submitted,

Elaine Benaksas Schwartz, Ph.D.
Associate Professor of Chemistry
Co-Director of Chemistry & Biochemistry
Assistant Dean of External Relations
Schmid College of Science and Technology