



16th Boron Chemistry Meeting in the Americas  
June 26 - 30, 2018 at Boston College



# Program and Abstracts



## WELCOME

It is our distinct pleasure to welcome you to the 16th Boron Chemistry Meeting in the Americas here at Boston College. We hope that you will enjoy the historic city of Boston as well as the four-day program filled with exciting talks and stimulating discussions.

Delegates from all over the world (North-, Central-, and South America, Europe, and Asia), and from diverse backgrounds (academia, industry, and government) are coming together at this conference to learn about the latest developments in boron chemistry. Thus, we hope that this gathering will not only promote scientific exchange and collaboration but also provide an opportunity for participants to make new connections and to reconnect with old friends.

In organizing the program, the vision we had was to highlight the versatility of the element boron in four specific areas (medicinal chemistry, organic synthesis, materials chemistry, fundamental chemistry). This four-pronged thematic focus is represented by our conference logo with four infinity symbols surrounding the boron and is reflected by the scientific program.

One of the highlights of the program will be the poster session on Wednesday evening. This will be a great opportunity to chat about the latest research while enjoying small bites and drinks. Another highlight is the conference banquet, which will take place on Thursday evening at the exquisite State Room with unparalleled views of the city and the Boston waterfront from the 33<sup>rd</sup> floor in the heart of downtown Boston. During the banquet we will celebrate Prof. Narayan Hosmane's 70<sup>th</sup> birthday and honor his service to the BORAM organization as a founding member and long-time chairman. Many of you are traveling from afar, and we would like to give you the opportunity to explore the city of Boston on your own during the scheduled free time on Friday afternoon/evening. The conference will close on Saturday, which includes another highlight of the conference: winners of the poster presentation awards presenting their exciting work to the full audience.

Of course, we need to give a big shout-out to all of our sponsors, which are listed in this program book as well as on the conference website. The organization of this event would be simply impossible without their generous support.

Finally, we would like to wish you a wonderful time at BORAM XVI!

Professor Shih-Yuan Liu  
Conference Chair

Organizing Committee:

Dale Mahoney, Prof. Jianmin Gao, Prof. Jeff Byers, Prof. Masayuki Wasa, Lori St. Peter

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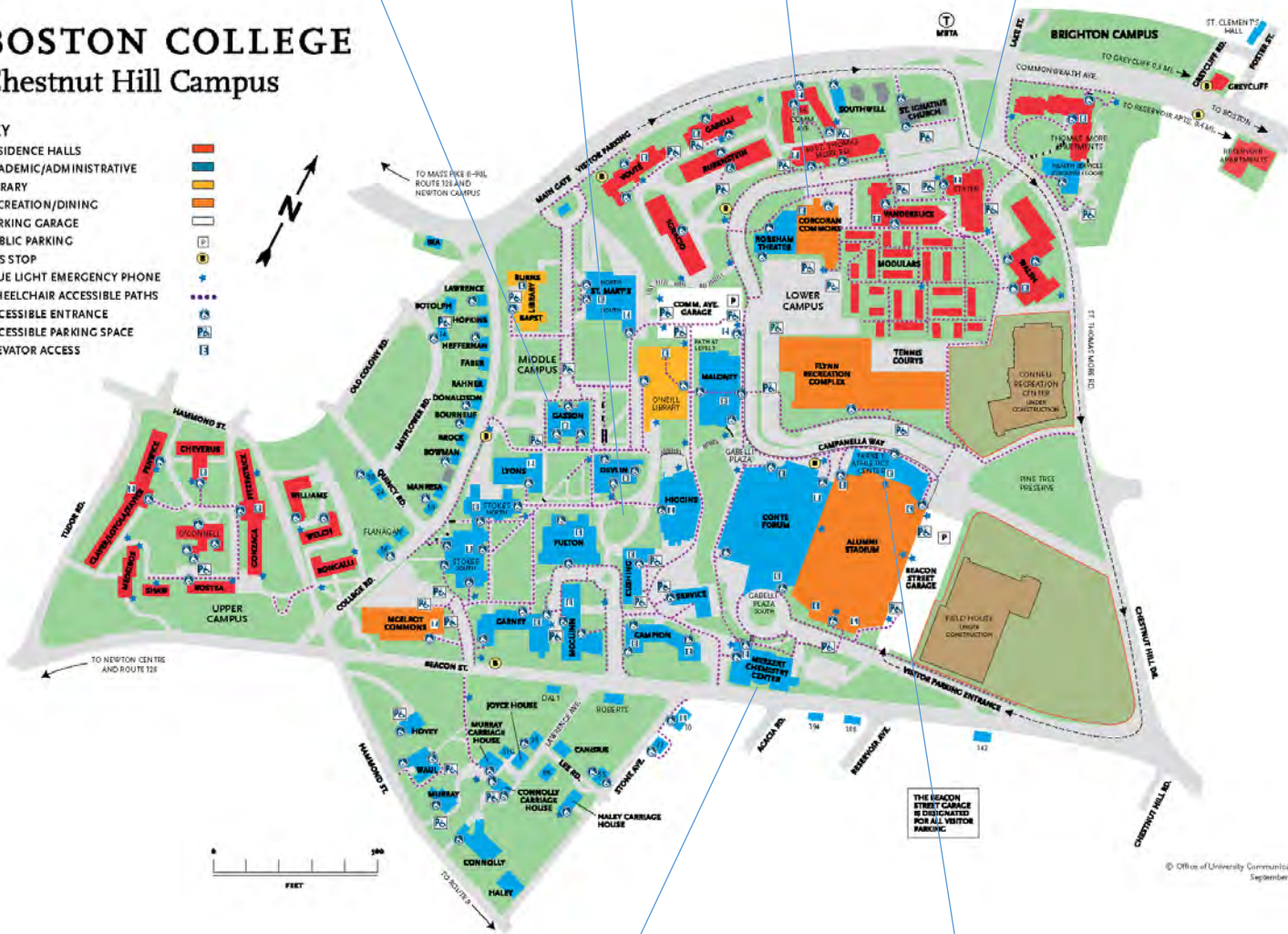


	Tuesday, June 26th	Wednesday, June 27th	Thursday, June 28th	Friday, June 29th	Saturday, June 30th
	7:30		Breakfast		
		S2 Chair: Matthias Wagner	S6 Chair: Douglas Stephan	S9 Chair: Zuowei Xie	Breakfast
	8:20	OP5 Joe Gilroy	OP20 Imre Papai	OP32 Sundargopal Ghosh	S12 Chair: Alex Spokorny
	8:45	OP6 Suning Wang	OP21 Gerhard Erker	OP33 Rei Kinjo	SP19 Mariusz Uchman
	9:10	SP1 Piotr Kaszynski	SP9 Russel Fritzeimer	SP15 Bruce King	OP44 Chunming Cui
	9:20	SP2 Kanglei Liu	OP20 Alexander Speed	SP16 Michael Beckett	OP45 Anna Chrostowska
	9:30	OP7 Sang Ook Kang	OP22 Masayuki Wasa	OP34 Hermann Wegner	SP20 Xuguang Liu
	9:55	OP8 Frieder Jäkke (ad 1)	OP23 Rebecca Melen (ad4)	OP35 Francois Gabbai	OP46 Caleb Martin
	10:20		Coffee Break		
		S3 Chair: Frieder Jäkke	S7 Chair: Jeffery Byers	S10 Chair: Dennis Hall	S13 Chair: Webster Santos
	10:40	OP9 Zuowei Xie	OP24 Andrew Weller	OP36 Michael Ingleson	OP47 Mitch Smith
	11:05	OP10 Matthias Wagner	OP25 Tom Autrey	OP37 Ching-Wen Chiu	OP48 Andrei Yudin
	11:30	SP3 Soren Mellerup	SP11 Angelina Gigante	SP17 Cameron McConnell	SP21 TBD (poster award)
	11:40	SP4 Siyuan Liu	SP12 Tom Stennett	SP18 Michael Crockett	SP22 TBD (poster award)
	11:50	OP11 Holger Bettinger (ad 2)	OP26 Xuenian Chen	OP38 Cathleen Crudden	SP23 TBD (poster award)
	12:15		Lunch		
		S4 Chair: James Morken	S8 Chair: Masayuki Wasa	S11 Chair: Paul Jellis	S14 Chair: Shih-Yuan Liu
13:30	13:30	OP12 Michinori Sugimoto	OP27 Hajime Ito	OP39 Suzanne Blum	OP49 Lai-Sheng Wang
	13:55	OP13 Sebastian Torke	OP28 Senmiao Xu	OP40 Josef Michl	OP50 Andreas Lorbach
	14:20	SP5 Zaozao Qiu	SP13 Lu Yan	OP41 Dmitry Peryshkov	OP51 Vincent LaVallo
	14:30	SP6 Marvin Kischkewitz	SP14 Ryan Morrison	OP42 Yangjian Quan	OP52 John Soderquist
	14:40	OP14 Mark Taylor	OP29 Silvina Pellegrinet	OP43 Simon Duttwyler	
	15:05	OP15 Dennis Hall (ad3)	OP30 Makoto Yamashita	FREE TIME	Concluding Remarks
	15:30	Coffee Break	OP31 Alexander Spokorny		
		S5 Chair: Jianmin Gao	Conference Photo		
16:00	15:50	OP16 Matthew Perry			
	16:15	OP17 Paul Jellis			
	16:40	SP7 Soriano Antonio	FREE TIME		
	16:50	SP8 Samantha Cambray			OP: Oral presentation
	17:00	OP18 Pedro Gois			SP: Short presentation
17:50	17:25-17:50	OP19 Webster Santos	Busses depart for banquet		
	18:00	POSTER SESSION	Cocktail Hour		
18:00			Dinner		
18:30					
19:00					
19:30-20:00	20:30		Bus returns		



# BOSTON COLLEGE Chestnut Hill Campus

- KEY**
- RESIDENCE HALLS
  - ACADEMIC/ADMINISTRATIVE
  - LIBRARY
  - RECREATION/DINING
  - PARKING GARAGE
  - PUBLIC PARKING
  - BUS STOP
  - BLUE LIGHT EMERGENCY PHONE
  - WHEELCHAIR ACCESSIBLE PATHS
  - ACCESSIBLE ENTRANCE
  - ACCESSIBLE PARKING SPACE
  - ELEVATOR ACCESS



Corcoran Commons  
Lecture Hall and  
Dining

Stayer Hall Dormitory

Welcome Reception – Gasson 100

Group Photo Location

Merkert Chemistry Center  
Conference Registration

Yawkey Athletics Center  
Murray Function Room – 4<sup>th</sup> floor  
Poster Session

You must register your laptop and/or mobile device on the Boston College network to access the Internet. The BC wireless network is available in residence halls, campus buildings, and some outdoor areas.

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## Conference Schedule

### Tuesday, June 26th

13:30 - 16:00	Registration Opens	Merkert Chemistry Center Foyer
16:00 - 17:50	Welcome Reception	Gasson Hall 100
17:50 - 18:00	Opening Remarks	Corcoran Commons Heights Room

#### Session 1      Session Chair: Shih-Yuan Liu

18:00 - 18:30	<b>OP1 - James P. Morken</b> Boston College, USA <i>Enantioselective Catalysis with Organoboron Reagents</i>
18:30 - 19:00	<b>OP2 - Douglas W. Stephan</b> University of Toronto, Canada <i>The Broadening Reach of FLP Chemistry</i>
19:00 - 19:30	<b>OP3 - Evamarie Hey-Hawkins</b> Leipzig University, Germany <i>Carboranes in Medicinal Chemistry</i>
19:30-20:00	<b>OP4 - Shigehiro Yamaguchi</b> Nagoya University, Japan <i>Planarized Boron-Containing <math>\pi</math>-Electron Materials</i>

### Wednesday, June 27th

7:30-8:15      **Breakfast, Corcoran Commons**

#### Session 2      Session Chair: Matthias Wagner

8:20 - 8:45	<b>OP5 - Joe P. Gilroy</b> The University of Western Ontario, Canada <i>Multifunctional BN Heterocycles Derived from Formazanate Ligands</i>
8:45 - 9:10	<b>OP6 - Suning Wang</b> Queen's University, Canada <i>New Stimuli Responsive Donor-Acceptor Systems</i>
9:10 - 9:20	<b>SP1 - Piotr Kaszynski</b> Middle Tennessee State University, USA <i>Intermolecular Charge Transfer in Ionic Liquid Crystals Derived from the [closo-B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> anion</i>
9:20 - 9:30	<b>SP2 - Kanglei Liu</b> Rutgers University, USA <i>Borane-functionalization at the Periphery of Polycyclic Aromatic Hydrocarbons</i>
9:30 - 9:55	<b>OP7 - Sang Ook Kang</b> Korea University, Korea <i>Reversible Stimuli-Induced Mechanofluorochromism by Molecular Assembly of o-Carborane</i>



9:55 - 10:20 **OP8 - Frieder Jäkle**  
Rutgers University, USA  
*Organoboron Polymers as Functional Hybrid Materials*

10:20 - 10:24 Sponsor Featurette 1

10:24-10:40 **Coffee Break, Corcoran Commons**

**Session 3** **Session Chair: Frieder Jäkle**

10:40 - 11:05 **OP9 - Zuowei Xie**  
The Chinese University of Hong Kong, China  
*Monovalent Boron Compounds: A Class of Metallomimetics*

11:05 - 11:30 **OP10 - Matthias Wagner**  
Goethe Universität Frankfurt, Germany  
*Nucleophilic Behavior and C–H-Activation Reactions of a B=B System*

11:30 - 11:40 **SP3 - Soren K. Mellerup**  
Queen's University, Canada  
*Metal-Free C-X Bond Scission (X=S, O, N) via Base-Stabilized Boriranes as a Facile Route to Novel B,X-Heterocycles*

11:40 - 11:50 **SP4 - Siyuan Liu**  
Universität Würzburg, Germany  
*A New Path to Unusual Boron Compounds – Borylene Reactivity with Chalcogens*

11:50 - 12:15 **OP11 - Holger F. Bettinger**  
Universität Tübingen, Germany  
*Photoreactivity of B-N Containing Molecules: Boryl Azides, Azaborinines, and Nanoscaled Polycyclic Aromatics*

12:15 - 12:19 Sponsor Featurette 2

12:19 - 13:30 **Lunch, Corcoran Commons/ Poster Set-Up**

**Session 4** **Session Chair: James Morken**

13:30 - 13:55 **OP12 - Michinori Suginome**  
Kyoto University, Japan  
*Directed Catalytic C-H Activation Using Boronyl-Based Directing Groups*

13:55 - 14:20 **OP13 - Sebastian Torker**  
Boston College, USA  
*Stereochemical Integrity of Cu-Alkyl and Cu-Allenyl Intermediates: Mechanistic Implications Regarding Enantioselective Transformations*

- 14:20 - 14:30 **SP5 - Zaozao Qiu**  
Shanghai Institute of Organic Chemistry, China  
*Enantioselective Synthesis of Chiral-at-Cage o-Carboranes via Pd-Catalyzed Asymmetric B-H Substitution*
- 14:30 - 14:40 **SP6 - Marvin Kischkewitz**  
Wesfälische Wilhelms-Universität Münster, Germany  
*Exploring the Scope of Radical-Polar Crossover Reactions of Vinyl Boron Ate Complexes in Three Component Couplings*
- 14:40 - 15:05 **OP14 - Mark S. Taylor**  
University of Toronto, Canada  
*Exploiting Reversible Covalent Interactions of Boron Compounds in Reactivity and Catalysis*
- 15:05 - 15:30 **OP15 - Dennis G. Hall**  
University of Alberta, Canada  
*Boronic Acid Catalysis: Hydroxyl Activation Using Reversible B–O Bonds*
- 15:30 - 15:34 Sponsor Featurette 3
- 15:34 - 15:50 **Coffee Break: Corcoran Commons**
- Session 5** **Session Chair: Jianmin Gao**
- 15:50 - 16:15 **OP16 - Matthew A. Perry**  
Pfizer, USA  
*Boron as a Pharmacophore in Drug Discovery*
- 16:15 - 16:40 **OP17 - Paul A. Jelliss**  
Saint Louis University, USA  
*Rhenacarborane Complexes for Peptide Delivery Across the Blood-Brain Barrier (BBB)*
- 16:40 - 16:50 **SP7 - Soriano Ursúa Marvin Antonio**  
Escuela Superior de Medicina del Instituto Politécnico Nacional, Mexico  
*Advances in Pharmacodynamics and Pharmacokinetics of Boron-Containing Compounds*
- 16:50 - 17:00 **SP8 - Samantha Cambray**  
Boston College, USA  
*Facile Labeling of Bacterial Pathogens via Diazaborine Formation of Semicarbazide*
- 17:00 - 17:25 **OP18 - Pedro M. P. Gois**  
Universidade de Lisboa, Portugal  
*BComplexes: Functional Linkers for Targeted Delivery*
- 17:25-17:50 **OP19 - Webster L. Santos**  
Virginia Tech, USA  
*Molecular Recognition and in vitro Activity of Branched Peptide Boronic Acids against HIV-1 Rev Response Element RNA*
- 18:00-20.30 **Poster Session - Yawkey Athletic Center, Murray Function Room 4th floor**

7:30-8:15 **Breakfast - Corcoran Commons**

**Session 6** **Session Chair: Douglas Stephan**

8:20 - 8:45 **OP20 - Imre Pápai**  
Hungarian Academy of Sciences, Hungary  
*On the Origin of Enantioselectivity in Asymmetric Hydrogenation of Imines Catalyzed by Chiral Boranes*

8:45 - 9:10 **OP 21 - Gerhard Erker**  
Organisch-Chemisches Institut der Universität Münster, Germany  
*New Pathways in Frustrated Lewis Pair Chemistry*

9:10 - 9:20 **SP9 - Russell Fritzsche**  
Virginia Tech, USA  
*Organocatalytic Trans-Hydroboration of Internal Alkynes*

9:20 - 9:30 **SP10 - Alexander W. H. Speed**  
Dalhousie University, Canada  
*Asymmetric Imine Hydroboration Using Diazaphospholene Catalysts*

9:30 - 9:55 **OP22 - Masayuki Wasa**  
Boston College, USA  
*Cooperative Enantioselective Catalysis with Frustrated Acid/Base Complexes*

9:55 - 10:20 **OP23 - Rebecca Melen**  
Cardiff University, UK  
*Modern Alchemy: Turning Boron into Gold*

10:20 - 10:24 Sponsor Featurette 4

10:24 - 10:40 **Coffee Break: Corcoran Commons**

**Session 7** **Session Chair: Jeffery Byers**

10:40 - 11:05 **OP24 - Andrew S. Weller**  
University of Oxford, UK  
*[Rh(Xantphos-alkyl)] Catalysts for the Efficient Dehydropolymerization of Amine-boranes. Mechanistic Insight through a Systemic Study*

11:05 - 11:30 **OP25 - Tom Autrey**  
Pacific Northwest National Laboratory, USA  
*An Experimental and Computational Study of Intermediates Formed in the Release of Hydrogen from  $Mg(BH_4)_2$*



- 11:30 - 11:40 **SP11 - Angelina Gigante**  
University of Geneva, Switzerland  
*A Safe Synthesis of Alkali Metal Triboranes ( $M(B_3H_8)_2$ ) in Relation to Their Role as Intermediates for Hydrogen Storage in  $M(BH_4)_2$  ( $M = Mg, Ca$ )*
- 11:40 - 11:50 **SP12 - Tom E. Stennett**  
Julius-Maximilians-Universität Würzburg, Germany  
*Synthesis and Reactivity of Diborenes based on a Benzylphosphine Chelate*
- 11:50 - 12:15 **OP26 - Xuenian Chen**  
Henan Normal University, China  
*Synthesis and Formation Mechanism of Lithium and Sodium Octahydrotriborate*
- 12:15 - 13:30 **Lunch, Corcoran Commons**
- Session 8** **Session Chair: Masayuki Wasa**
- 13:30 - 13:55 **OP27 - Hajime Ito**  
Hokkaido University, Japan  
*Copper-Catalyzed Asymmetric Borylative Dearomatization for Optically Active Heterocyclic Compounds*
- 13:55 - 14:20 **OP28 - Senmiao Xu**  
Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China  
*Novel Chiral Boryl ligands Enabled Iridium-Catalyzed Asymmetric C-H Activation Borylation*
- 14:20 - 14:30 **SP13 - Lu Yan**  
Boston College, USA  
*Mechanistic Insight on Carbohydrate Catalyzed Alkene Diboration Reaction*
- 14:30 - 14:40 **SP14 - Ryan J. Morrison**  
Boston College, USA  
*Differentially Protected Vicinal Amino Alcohols by Catalytic, Enantioselective Additions of MEMO-Substituted Allylboron Compounds to Phosphinoylimines*
- 14:40 - 15:05 **OP29 - Silvina C. Pellegrinet**  
Universidad Nacional De Rosario, Argentina  
*Recent Advances in the Development of Diels-Alder Reactions of Unsaturated Organoboron Compounds*
- 15:05 - 15:30 **OP30 - Makoto Yamashita**  
Nagoya University, Japan  
*Reactivity of B-B Bond in Highly Lewis Acidic Diborane(4)*
- 15:30-15:55 **OP31 - Alexander M. Spokoyny**  
University of California, Los Angeles, USA  
*A Boron Cluster-Based Approach to Nucleophilic Borylation*

16:00-16:20	<b>Conference Photo</b>
16:20 - 17:15	<b>Free Time</b>
17:15 - 18:00	<b>Buses depart from the Crowne Plaza, Courtyard Marriott Hotels and Stayer Hall for the State Room</b>
18:00 - 19:00	<b>Cocktail Hour</b>
19:00 - 22:00	<b>Dinner</b>
22:00	<b>Buses depart</b>

**Friday, June 29th**

7:30 - 8:15      **Breakfast: Corcoran Commons**

**Session 9      Session Chair: Zuowei Xie**

8:20 -8:45      **OP32 - Sundargopal Ghosh**

Indian Institute of Technology Madras, India

*Transition Metal Complexes of Diborane(4) and Diborene(2)*

8:45-9:10      **OP33 - Rei Kinjo**

Nanyang Technological University, Singapore

*Formation and Property of Asymmetric B=B Bond*

9:10-9:20      **SP15 - R. Bruce King**

University of Georgia, USA

*Imbedding Metal Triangles in Polyhedral Borane Matrices: A Theoretical Study*

9:20-9:30      **SP16 - Michael A. Beckett**

Bangor University, UK

*Cobalt(3+), Copper(2+) and Zinc(2+) Complexes with Hydroxyoxidoborates*

9:30 - 9:55      **OP34 - Hermann A. Wegner**

Julius-Maximilians-Universität Giessen, Germany

*Interplay of Boron and Nitrogen – A Stable Organic Neutral Diradical via Reversible Coordination*

9:55 - 10:20      **OP35 - François P. Gabbaï**

Texas A & M University, USA

*"Large Bite" Diboranes for the Complexation of Diatomic Anions and Molecules*

10:20 - 10:40      **Coffee Break: Corcoran Commons**

**Session 10      Session Chair: Dennis Hall**

10:40 - 11:05      **OP36 - Michael J. Ingleson**

University of Manchester, UK

*C-B Bond Formation Using Boron Lewis Acids and Alkynes or Alkenes*

- 11:05 - 11:30 **OP37 - Ching-Wen Chiu**  
National Taiwan University, Taiwan  
*Reactivity and Catalytic Activity of Boron Cations*
- 11:30 - 11:40 **SP17 - Cameron McConnell**  
Boston College, USA  
*Electronic Asymmetry of 1,2-Azaborine Leads to Differential Reactivity of C(4) and C(5) Borylated Isomers*
- 11:40 - 11:50 **SP18 - Michael P. Crockett**  
Boston College, USA  
*Development of an Iron-Catalyzed Suzuki-Miyaura Cross-Coupling Reaction Between Alkyl Halides and Unactivated Aryl Boronic Esters*
- 11:50 - 12:15 **OP38 - Cathleen Crudden**  
Queen's University, Canada  
*Boron in Catalysis: Borenum Ions and Cross-Coupling Transformations of Multiply Borylated Molecules*
- 12:15 - 13:30 **Lunch: Corcoran Commons**
- Session 11** **Session Chair: Paul Jelliss**
- 13:30 - 13:55 **OP39 - Suzanne A. Blum**  
University of California, Irvine, USA  
*Borylative Heterocyclization: Oxyboration, Aminoboration, and Thioboration*
- 13:55 - 14:20 **OP40 - Josef Michl**  
University of Colorado, USA  
*Anodic Oxidation of  $CB_{11}H_{12}$  (-) Derivatives*
- 14:20 - 14:45 **OP41 - Dimitry V. Peryshkov**  
University of South Carolina, USA  
*Carborane Cluster Architectures Featuring Multiple Metal-Boron Interactions: Boranes, Boryls, and Carborynes*
- 14:45 - 15:10 **OP42 - Yangjian Quan**  
The Chinese University of Hong Kong, China  
*Directing Group Guided Transition Metal Catalyzed Carboranyl B-Heteroatom Bond Construction*
- 15:10-15:35 **OP43 - Simon Duttwyler**  
Zhejiang University, China  
*Selective Catalytic Functionalization of Anionic Boron Clusters*
- 15:35 **Free Time**



**Saturday, June 30th**

7:55 - 8:40 **Breakfast: Cororan Commons**

**Session 12 Session Chair: Alex Spokoyny**

8:45 - 8:55 **SP19 - Mariusz Uchman**

Charles University Prague, Czechia

*Phenylboronic Ester as a Sensitive Block Linkage in Block Copolymer Micelles. Lactic Acid- and Glucose-Responsive Nanoparticles*

8:55 - 9:20 **OP44 - Chunming Cui**

Nankai University, China

*Catalytic Approaches to New Types of Polycyclic BN Compounds*

9:20 - 9:45 **OP45 - Anna Chrostowska**

Université de Pau et des Pays de l'Adour, France

*The Synergy Between Theory and Experiment in Developing the Basic Science of New BN Heteroaromatics*

9:45 - 9:55 **SP20 - Xuguang Liu**

Tianjin University of Technology, China

*Synthesis, Characterization and Properties of Bis-BN Ullazines*

9:55 - 10:20 **OP46 - Caleb Martin**

Baylor University, USA

*9-Borafluorenes: Reagents to Access Inorganic Doped Polycyclic Aromatic Hydrocarbons*

10:20 **Coffee Break: Corcoran Commons**

**Session 13 Session Chair: Webster Santos**

10:40 - 11:05 **OP47 - Milton R. Smith III**

Michigan State University, USA

*C-H Borylation/Hydrogenation of Aromatic and Heteroaromatic Substrates*

11:05 - 11:30 **OP48 - Andrei K. Yudin**

University of Toronto, Canada

*Boroscan – a Suite of Technologies to Enable Synthesis and Evaluation of Bioactive Boron-Containing Molecules*

11:30 - 11:45 **SP21 TBD (Poster Award)**

11:45 - 12:00 **SP22 TBD (Poster Award)**

12:00-12:15 **SP23 TBD (Poster Award)**

12:15 - 13:30 **Lunch: Corcoran Commons**

<b>Session 14</b>	<b>Session Chair: Shih-Yuan Liu</b>
13:30 - 13:55	<p><b>OP49 - Lai-Sheng Wang</b>            Brown University, USA  <i>Recent Progress in the Investigation of Size-Selected Boron Clusters:            From Borophenes to Metallo-Borophenes</i></p>
13:55 - 14:20	<p><b>OP50 - Andreas Lorbach</b>            University of Konstanz, Germany  <i>Boron-Based Spiro Compounds as TADF Emitters</i></p>
14:20 - 14:45	<p><b>OP51 - Vincent LaVallo</b>            University of California, Riverside USA  <i>Beyond Acidic Transition Metal Hydrides: The Direct Heterolytic Cleavage of Dihydrogen            to Produce a Super Acid</i></p>
14:45-15:10	<p><b>OP52 - John Soderquist</b>            University of Puerto Rico, USA  <i>Chirality Transfer with the Borabicyclodecanes</i></p>
15:15	<b>Concluding Remarks</b>



## ORAL PRESENTATION ABSTRACTS



## Enantioselective Catalysis with Organoboron Reagents

James P. Morken

*Author Affiliation, Boston College, Chestnut Hill, MA 02467 USA  
morken@bc.edu*



### ABSTRACT

Chiral organoboron compounds are well known as versatile intermediates for chemical synthesis. Not only are these compounds stable under a variety of reaction conditions, they are generally non-toxic and can be transformed with minimal generation of hazardous waste. An important feature of aliphatic organoboronic esters is that the boron atom may be replaced with an array of different functional groups through efficient, stereospecific transformations. This seminar will present new strategies for the construction of these compounds in a catalytic enantioselective fashion. Particular attention will be placed on recently developed methods that allow for practical and economical borylation reactions, as well as the development of methods that allow for their application in streamlined organic synthesis.

## The Broadening Reach of FLP Chemistry

Douglas W Stephan

*Douglas Stephan, Department of Chemistry, University of Toronto,  
80 St. George St., Toronto, Ontario, Canada M5S3H6  
Email: douglas.stephan@utoronto.ca*



### ABSTRACT

We have previously exploited Frustrated Lewis pair (FLP) chemistry for the activation of H<sub>2</sub>, hydrogenation catalysis and the capture of small molecules.<sup>1-4</sup> We now extend the use of FLPs to trap reaction intermediates, access novel air stable radicals<sup>5-6</sup> and heterocycles<sup>7-9</sup> and target main group-N<sub>2</sub> chemistry.<sup>10</sup> We have also shown that FLP chemistry can be derived from systems that are seemingly not “frustrated” and in addition we have developed one electron FLP chemistry. Examples of each of these new aspects of FLP chemistry will be discussed.

### REFERENCES

1. Stephan, D. W., *Science* **2016**, *354*, aaf7229.
2. Stephan, D. W.; Erker, G., *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441.
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5. Longobardi, L. E.; Zatsepin, P.; Korol, R.; Liu, L.; Grimme, S.; Stephan, D. W., *J. Am. Chem. Soc.* **2017**, *139*, 426-435.
6. Longobardi, L. E.; Liu, L.; Grimme, S.; Stephan, D. W., *J. Am. Chem. Soc.* **2016**, *138*, 2500-2503.
7. Tsao, F. A.; Stephan, D. W., *Chem. Commun.* **2017**, *53*, 6311-6314.
8. Tsao, F. A.; Stephan, D. W., *Dalton Trans.* **2015**, *44*, 71-74.
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10. Tang, C. N.; Liang, Q. M.; Jupp, A. R.; Johnstone, T. C.; Neu, R. C.; Song, D. T.; Grimme, S.; Stephan, D. W., *Angew. Chem. Int. Ed.* **2017**, *56*, 16588-16592.

## Carboranes in Medicinal Chemistry

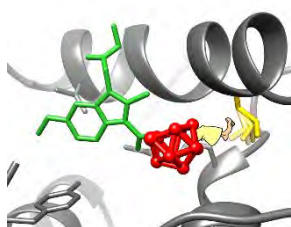
Evamarie Hey-Hawkins,<sup>a,\*</sup> Robert Kuhnert,<sup>a</sup> Stefan Saretz,<sup>a</sup> Antonio Buzharevski,<sup>a</sup> Menyhárt-Botond Sárosi<sup>a</sup>

<sup>a</sup>*Institute of Inorganic Chemistry, Leipzig University, Johannisallee 29, D-04103 Leipzig, Germany. hey@uni-leipzig.de*



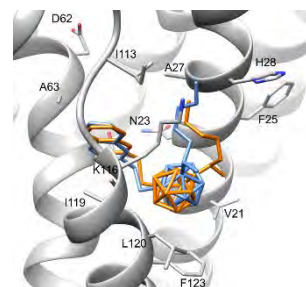
### ABSTRACT

Since the discovery of polyhedral carboranes more than fifty years ago, their potential for various applications has been unlocked. Mainly, their use as pharmacophores is due to their remarkable biological stability and hydrophobicity. The cage framework of these clusters can be easily modified with a variety of substituents both at the carbon and at the boron atoms. It has been shown that the implementation of the carboranyl moiety, as a phenyl mimetic, in biologically active molecules results in compounds that can exhibit improved biological stability and activity in comparison to their generic paradigms. However, up to now, the use of carboranes as pharmacophores is limited to just a few examples.<sup>[1]</sup> Our research focuses on several types of enzyme inhibitors, such as cyclooxygenase (COX) or lipoxygenase (LOX) inhibitors.



A highly coveted approach in the design of novel nonsteroidal anti-inflammatory drugs that are applied in the treatment of various inflammatory processes is achieving cyclooxygenase (COX) 2 selectivity. By implementing a carboranyl moiety in the structures of known COX inhibitors more selective and robust COX-2 inhibitors were obtained.<sup>[2]</sup>

5-Lipoxygenase (5-LOX) is an enzyme of the extracellular matrix and plays a role in increased metastasis and angiogenesis. Numerous reports show the overexpression of 5-LOX in several cancer cell lines. For the activation of 5-LOX, the 5-LOX-activating protein (FLAP) is necessary.<sup>[3]</sup> Therefore, inhibition of 5-LOX or FLAP could inhibit tumour growth and angiogenesis. Replacement of phenyl rings in selected 5-LOX inhibitors by carboranes resulted in a similar enzymatic inhibitory behaviour but markedly increased cytotoxicity against several melanoma and colon cancer cell lines.<sup>[4]</sup> Selected examples will be presented.



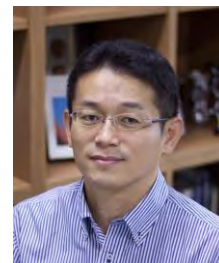
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## Planarized Boron-Containing $\pi$ -Electron Materials

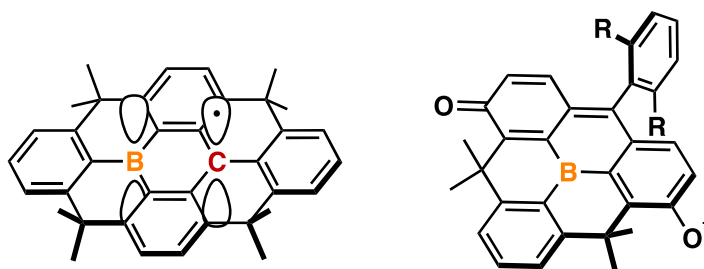
Shigehiro Yamaguchi

*Institute of Transformative Bio-molecules (ITbM), Nagoya University, Nagoya University, Furo, Chikusa, Nagoya 464-8602, Japan  
yamaguchi@chem.nagoya-u.ac.jp*



### ABSTRACT

Incorporation of main group elements into  $\pi$ -conjugated skeletons is a powerful strategy to develop new optoelectronic organic materials with unusual properties. Representative design principles are to make use of an orbital interaction between a  $\pi$  skeleton and a main group element moiety. Conformational constraint often plays a crucial role to gain an optimal orbital interaction. In addition, this is also important to gain high chemical and/or photo-stability. Based on this strategy, we have so far synthesized various types of functional  $\pi$ -electron materials. In this presentation, we would like to report recent progress in the development of planarized boron-containing  $\pi$ -electron materials.<sup>[1]</sup> In particular, we have recently succeeded in the synthesis of a boron-stabilized triphenylmethyl radical, which shows ambipolar charge carrier transport properties.<sup>[2]</sup> We have also developed a new fluorescein-type dye that can show absorption and fluorescence in the near infrared region by introducing a boron atom into a planarized xanthene framework.



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## Multifunctional BN Heterocycles Derived from Formazanate Ligands

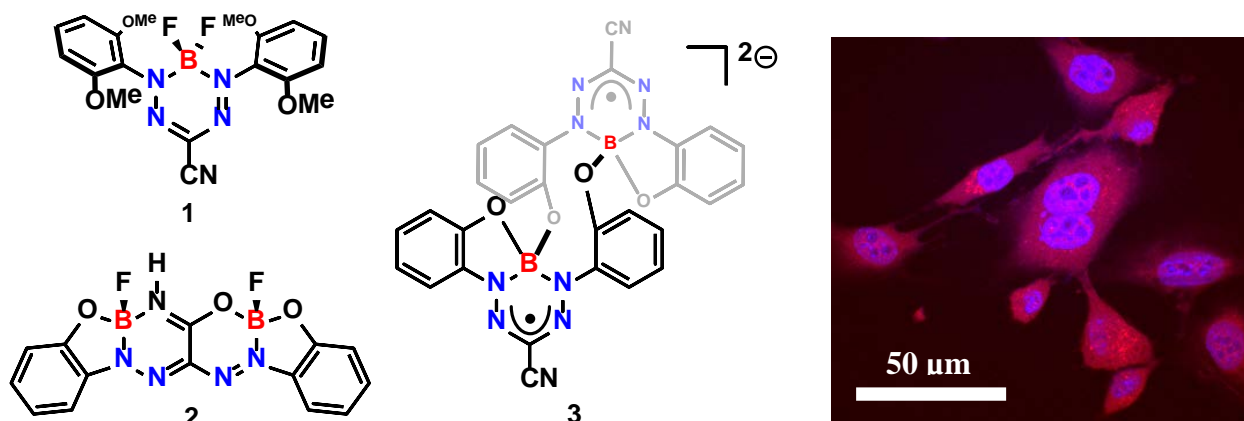
Stephanie M. Barbon, Ryan R. Maar, Joe B. Gilroy\*

*Department of Chemistry, The University of Western Ontario,  
1151 Richmond St. N., London, ON, Canada N6A 5B7  
joe.gilroy@uwo.ca*



### ABSTRACT

Boron difluoride (BF<sub>2</sub>) complexes of *N*-donor ligands represent a diverse class of molecular materials that have shown utility as sensors, light-harvesting materials, and cell-imaging agents.<sup>[1]</sup> Given their widespread application, there is a pressing need for the discovery of new examples that can be produced by straightforward synthetic methods from low cost starting materials. BF<sub>2</sub> formazanates, derived from formazans (R<sup>1</sup>-NH-N=CR<sup>3</sup>-N=N-R<sup>5</sup>), are readily accessible heterocycles that exhibit tunable absorption, emission, and redox properties and potentially address this need. This presentation will highlight our recent work surrounding the chemical functionalization of BF<sub>2</sub> formazanates *en route* to examples that exhibit aggregation-induced emission (e.g., **1**),<sup>[2]</sup> show utility as cell-imaging agents,<sup>[3]</sup> and act as precursors to a range of unusual BN heterocycles (e.g., **2** & **3**).<sup>[4]</sup>



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## New Stimuli Responsive Donor-Acceptor Systems

Suning Wang,<sup>a,b\*</sup> Yonggang Shi,<sup>b</sup> Soren Mellerup,<sup>a</sup> Junwei Wang,<sup>b</sup> Haijun Li<sup>a</sup>

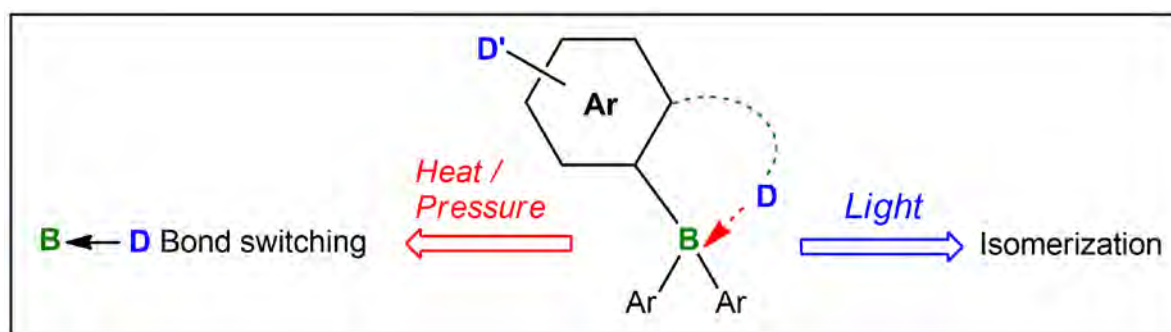
<sup>a</sup>Department of Chemistry, Queen's University, Kingston, Ontario, K7L 3N6, Canada

<sup>b</sup>School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, China  
sw17@queensu.ca



### ABSTRACT

Donor and acceptor appended organoboron systems have versatile applications in materials chemistry with many interesting examples demonstrated in the literature.<sup>[1]</sup> Our recent endeavor in further exploring this research field has led to the discovery of several unexpected stimuli responsive systems that change color/luminescence with either light, temperature or pressure. The location of the donor/acceptor group and the degree of molecular aggregation have been found to play a critical role in modulating the nature of the structural change and the type of molecular response toward external stimuli. Representative examples from our recent investigation will be presented.



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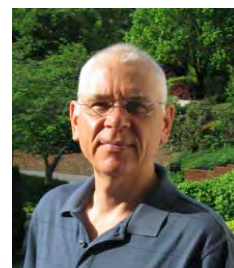
## Intermolecular Charge Transfer in Ionic Liquid Crystals Derived from the [closo-B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> anion

Edyta Rzeszotarska,<sup>a</sup> Piotr Paluch,<sup>a</sup> Jakub Wojciechowski,<sup>b</sup>  
Piotr Kaszyński<sup>a,b,c \*</sup>

<sup>a</sup> Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90-363 Łódź, Poland.

<sup>b</sup> Department of Chemistry, Middle Tennessee State University, Murfreesboro, TN, 37130, USA.

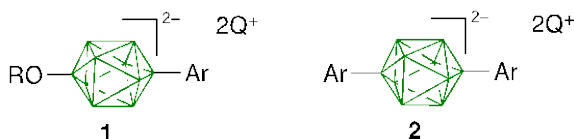
<sup>c</sup> Faculty of Chemistry, University of Łódź, 91-403 Łódź, Poland.  
 Piotr.Kaszynski@mtsu.edu



### ABSTRACT

Self-organizing ionic liquids are of interest for applications in contemporary technologies, such as energy storage and energy harvesting.<sup>[1]</sup> In the context of the latter, we have focused our interest in ionic liquid crystalline derivatives of closo-boranes<sup>[2]</sup> on photo-active ionic materials derived from the [closo-B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> anion. Initially, we developed a convenient and efficient synthetic access to iodo derivatives, [closo-B<sub>10</sub>H<sub>9</sub>-1-I]<sup>2-</sup> and [closo-B<sub>10</sub>H<sub>8</sub>-1-2I]<sup>2-</sup>,<sup>[3]</sup> which through functional group interconversion yielded 1-aryl and 1,10-diaryl derivatives **1** and **2**.

Judicious choice of the aryl group Ar and the counterion Q<sup>+</sup> led to induction of lamellar phases in these derivatives and appearance of intermolecular charge-transfer bands. Synthesis, thermal and photophysical properties of these derivatives will be presented.



This work was supported by the FNP (TEAM/2016-3/24) and NSF (DMR-1611250) grants.

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## Borane-functionalization at the Periphery of Polycyclic Aromatic Hydrocarbons

Kanglei Liu<sup>a</sup>, Roger A. Lalancette<sup>a</sup> and Frieder Jäkle<sup>a,\*</sup>

<sup>a</sup> *Department of Chemistry, Rutgers University-Newark  
73 Warren Street, Newark, NJ 07102, USA*

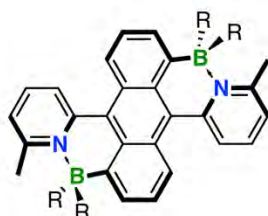
*Email: [kanglei.liu@rutgers.edu](mailto:kanglei.liu@rutgers.edu); [fjaekle@rutgers.edu](mailto:fjaekle@rutgers.edu)*



### ABSTRACT

The incorporation of main-group elements (i.e., B, Si, P, Se) into  $\pi$ -conjugated oligomers, polymers and polycyclic aromatic hydrocarbons (PAHs) presents an efficient strategy to create novel materials with remarkable optoelectronic properties.<sup>1</sup> Especially embedding boron atoms into fused structures has attracted increasing attention due to the unusual optical and electronic properties that can be achieved. These organoboranes have been studied in many different applications, including light emitting diodes, field effect transistors, organic solar cells, in sensing and biological imaging, and as photoresponsive materials.<sup>2</sup>

We have recently developed a new class of BN-substituted polycyclic aromatic hydrocarbons that are readily obtained by directed electrophilic borylation.<sup>3</sup> The B-N Lewis pair formation in the periphery of anthracene results in unique structural features and electronic properties. We also discovered that these new conjugated materials undergo self-sensitized uptake of singlet oxygen and subsequent controlled release by thermolysis, opening the possibility for new applications in photodynamic therapy (PDT) and sensing. We are also currently exploring their utility in optoelectronic device applications.



- Highly Twisted Structure
- Low-lying "Quinoid" LUMOs
- Strong Luminescence
- EPOs without Sensitizer

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## Reversible Stimuli-Induced Mechanofluorochromism by Molecular Assembly of *o*-Carborane

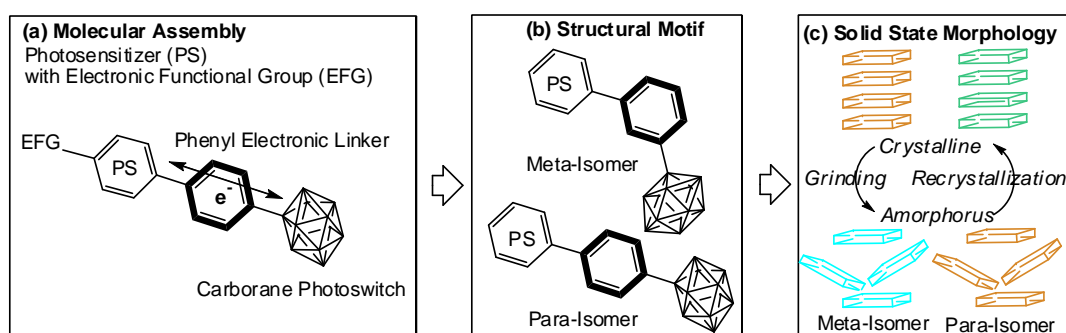
Yang-Jin Cho, So-Yoen Kim, Jie-Won Lee, Chul Hoon Kim, Ho-Jin Son, and Sang Ook Kang\*



*Department of Advanced Materials Chemistry, Korea University, Sejong-city 30019, South Korea, sangok@korea.ac.kr*

### ABSTRACT

In recent years, there reported diverse solid state photochromisms and among them reversible mechanofluorochromism brought special attention due to its potential applications involving sensors, memory devices, and optical devices.<sup>1</sup> Along the line, we found a unique mechanofluorochromism associated with *o*-carborane (Cb) upon forming a linear molecular array with an organic photosensitizer (PS). As shown in Scheme 1, Cb starts to build a molecular assembly with a photofunctional group and depending on its coordination sites at the connecting phenyl unit two positional isomers were produced, meta- (**PS-*m*-Cb**) and para- (**PS-*p*-Cb**) isomers. (Scheme 1) Crystals of each isomer cast out distinctive photoemissions; yellow and blue emissions for meta- and para-isomer, respectively. When crystals were grinded to powders, each isomer changed its color to blue and yellow, indicating that mechanical force caused the change of intermolecular interactions in the solid states. The grinded powders were recrystallized back from solvent evaporation; such a grinding-recrystallization process was repeated without discernable decomposition.



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## Organoboron Polymers as Functional Hybrid Materials

Frieder Jäkle\*

*Department of Chemistry, Rutgers University-Newark  
73 Warren Street, Newark, NJ 07102, USA  
fjaekle@newark.rutgers.edu*



### ABSTRACT

The incorporation of main group elements into polymeric materials frequently results in new properties and enables new functions.<sup>[1]</sup> Organoborane polymers in particular have emerged as an important class of organic-inorganic hybrid material with applications ranging from supported reagents and catalysts to sensing and detection of anions and biologically relevant species, self-healing, and organic electronic materials.<sup>[2]</sup> These desirable characteristics are enabled by the electron-deficient character of boron and the ensuing Lewis acidic properties of tricoordinate organoborane compounds.<sup>[3]</sup>

This presentation outlines some of our recent efforts on the efficient preparation borane-functionalized polymers, the unique properties that are achieved, and their diverse applications. Specifically, polyolefins containing Lewis acidic tricoordinate borane groups are explored in supramolecular chemistry, as sensory and stimuli-responsive materials, and in catalysis.<sup>[4]</sup> On the other hand, conjugated polymers that contain electron-deficient borane moieties embedded into their backbone are applied in electronic devices, for instance as luminescent and photovoltaic materials.<sup>[5]</sup>

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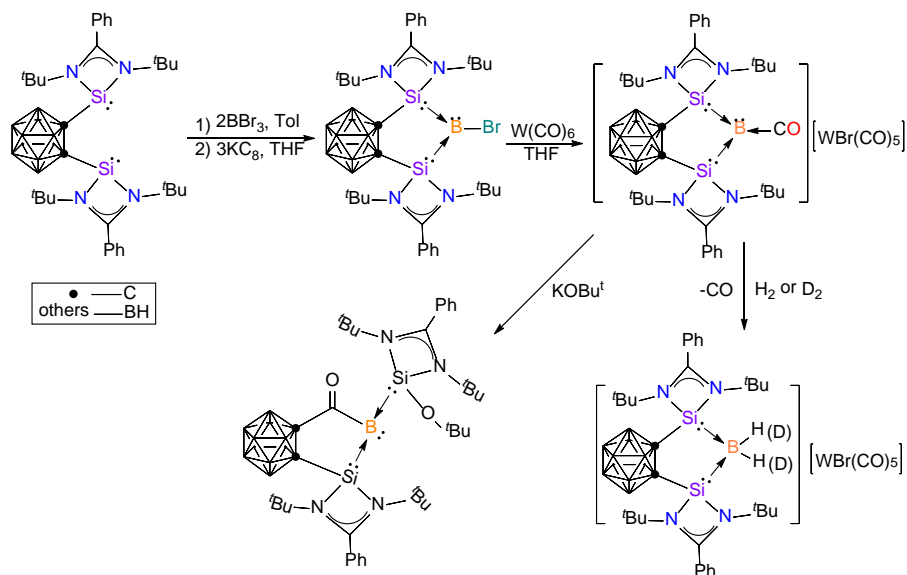
## Monovalent Boron Compounds: A Class of Metallomimetics

Zuowei Xie\*

Department of Chemistry, The Chinese University of Hong Kong  
Shatin NT, Hong Kong, China  
E-mail: zxie@cuhk.edu.hk



Monovalent boron compounds (borylenes; R-B:), featuring one lone pair of electrons and two vacant p orbitals, are typically highly reactive species, which can only be transiently prepared and spectroscopically characterized. In fact, free borylenes (R-B:) have never been isolated as stable compounds thus far. These reactive species can, however, be stabilized by either coordination to transition metal fragments or Lewis bases. Over the past several years, a series of borylene-transition-metal complexes, and Lewis base-stabilized borylenes have been synthesized and structurally characterized. Among the latter, carbenes are the commonly used Lewis bases which serve as  $\sigma$  donors and  $\pi$  acceptors. In contrast, silylenes, the silicon analogues of carbenes, have not been used for the stabilization of low-valent boron compounds. We have very recently found that *o*-carborane-based bis(silylene) can stabilize borylenes and their cations. These monovalent boron species exhibit transition-metal like properties such as activation of dihydrogen and small molecules. The results will be discussed in my lecture.<sup>[1-3]</sup>



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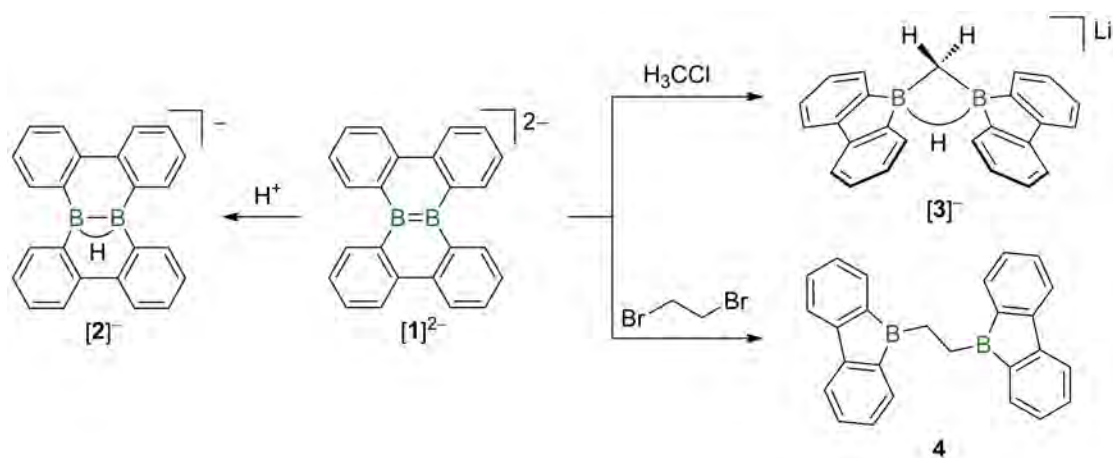
## Nucleophilic Behavior and C–H-Activation Reactions of a B=B System

Thomas Kaese<sup>a</sup>, Timo Trageser<sup>a</sup>, Hendrik Budy<sup>a</sup>, Matthias Wagner<sup>a\*</sup><sup>a</sup>Goethe-Universität Frankfurt, 60438 Frankfurt am Main, Germany  
matthias.wagner@chemie.uni-frankfurt.de

## ABSTRACT

Tricoordinate organoboranes possess a vacant boron  $p_z$  orbital and are therefore archetypal electrophiles. Upon reduction, however, this orbital can be filled with up to two electrons, such that the boron center ultimately acquires an electron lone pair. Information regarding the reactivity of dianions  $[\text{Ar}_3\text{B}]^{2-}$  is scarce, mainly due to their limited synthetic accessibility. As one of few examples, doubly reduced 9,10-dihydro-9,10-diboraanthracenes have been shown to efficiently activate small molecules such as  $\text{H}_2$ .<sup>[1]</sup> Our group has recently reported a doubly boron doped analog  $[\mathbf{1}]^{2-}$  of dibenzo[*g,p*]chrysene,<sup>[2,3]</sup> in which two excess electrons are shared between two adjacent boron atoms to give a B=B double-bonded compound.  $[\mathbf{1}]^{2-}$  undergoes quantitative protonation to afford the B-H-B-bridged species  $[\mathbf{2}]^-$ .<sup>[4]</sup> Switching from the electrophilic proton to the electrophilic organohalide  $\text{H}_3\text{CCl}$  leads to skeletal rearrangement, B=B-bond cleavage and C–H activation with formation of  $[\mathbf{3}]^-$ . When the ditopic electrophile  $\text{BrCH}_2\text{CH}_2\text{Br}$  is used, no C–H activation occurs and ethylene-bridged 9-borafluorenes are obtained ( $\mathbf{4}$ ).

Herein, we propose a mechanistic scenario that explains the above-mentioned observations and is based on deuterium-labelling experiments, trapping reactions of key intermediates, and quantum-chemical calculations.



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## Metal-Free C-X Bond Scission (X = S, O, N) via Base-Stabilized Boriranes as a Facile Route to Novel B,X-Heterocycles

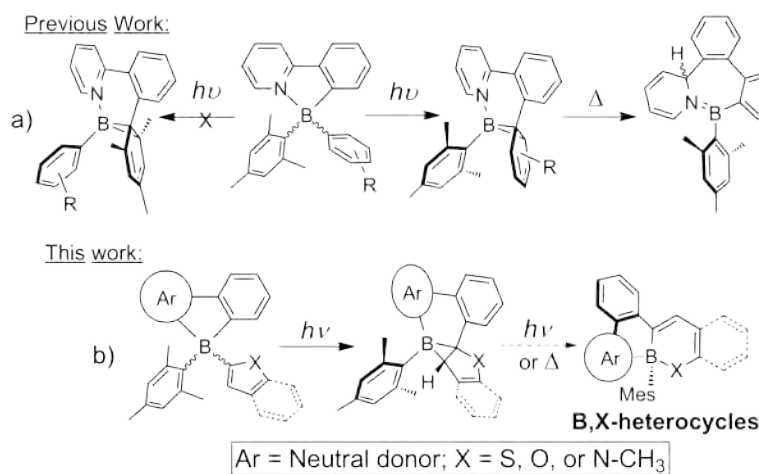
Soren K. Møllerup<sup>a</sup>, Cally Li<sup>a</sup>, Xiang Wang,<sup>a</sup> Suning Wang<sup>a,\*</sup>

<sup>a</sup>Queen's University, 90 Bader Lane, Kingston, ON, CA, K7L 3N6  
[13sm4@queensu.ca](mailto:13sm4@queensu.ca), [suning.wang@chem.queensu.ca](mailto:suning.wang@chem.queensu.ca)



### ABSTRACT

Boron-containing  $\pi$ -systems have long been known to possess interesting and unique properties compared to their all-carbon analogues. One pertinent example is the photochromic behaviour of four coordinated N,C-organoboron chelates (Figure 1),<sup>1</sup> which our group has been studying for a number of years. Very recently, we have been able to demonstrate the significance of the aryl groups on boron for the first time by preparing unsymmetric (chiral) analogues.<sup>2,3</sup> This presentation will focus on current efforts to exploit the reactivity of such systems bearing two different aryl groups, with particular emphasis on our ability to generate unprecedented B,X-heterocycles via C-X bond activation/insertion by H-functionalized boriranes.



**Figure 1.** (a) Regioselective photoisomerization and H-atom migration of chiral N,C-chelate organoboranes; (b) Proposed C-X bond cleavage reactions of boriranes adjacent to C-X bonds.

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## A New Path to Unusual Boron Compounds – Borylene Reactivity with Chalcogens

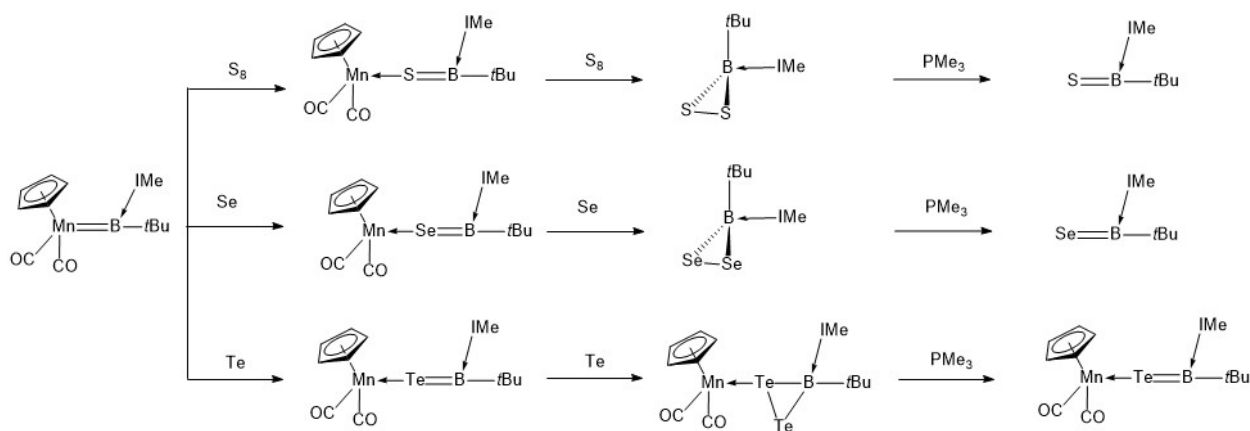
Siyuan Liu, Marc-André Légaré, Holger Braunschweig\*

Department of Chemistry  
Universität Würzburg  
97074 Würzburg, Germany  
Emails: [siyuan.liu@uni-wuerzburg.de](mailto:siyuan.liu@uni-wuerzburg.de)  
[h.braunschweig@uni-wuerzburg.de](mailto:h.braunschweig@uni-wuerzburg.de)



Despite years of study on boron, the knowledge surrounding well-defined boron-chalcogen interactions remain sparse. Indeed, the difficulty of attaining selective multiple bond formation between boron and the chalcogens has severely hampered the isolation and investigation of compounds that feature B-E (E = O, S, Se, Te) multiple bonds. [1,2,3,4] In this context, we have recently disclosed a method that allowed us to selectively synthesized novel complexes of borachalcones [(IMe)*t*BuB=E] by the direct insertion of the chalcogen in a manganese borylene complex. [5]. By this pathway, we were able to structurally characterize the first boron-tellurium double bond.

We now present recent developments in the use of this method to generate a variety of unusual boron compounds from [Cp(CO)<sub>2</sub>Mn=B(IMe)*t*Bu] with elemental chalcogens. By varying the stoichiometry of starting materials and through the use of Lewis bases, we managed to selectively prepare and characterize a series of novel [L(*t*Bu)B=E] and [L(*t*Bu)B(η<sup>2</sup>-E<sub>2</sub>)] (E= S, Se, Te) complexes as well as better define the chemistry of metal borylene complexes.



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## Photoreactivity of B-N Containing Molecules: Boryl Azides, Azaborinines, and Nanoscaled Polycyclic Aromatics

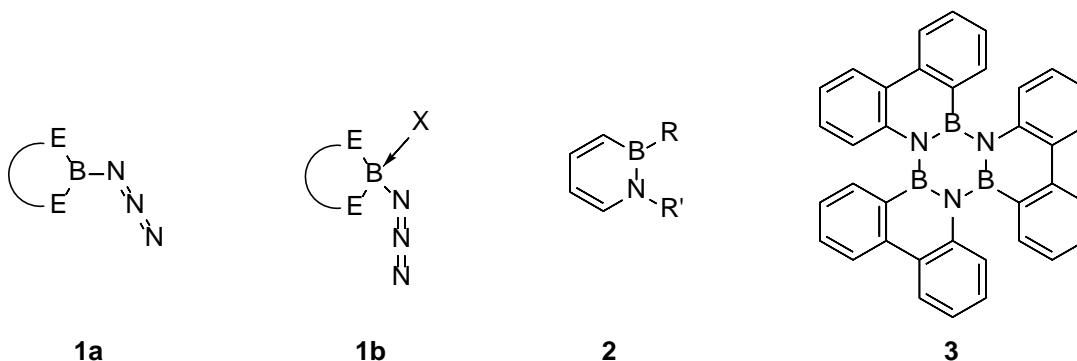
Holger F. Bettinger<sup>a,\*</sup>

<sup>a</sup>Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18,  
72076 Tübingen, Germany  
holger.bettinger@uni-tuebingen.de



### ABSTRACT

Organoboron compounds that feature B-N bonds display an intriguing and rich photochemistry that allows access to novel chemical entities. Systems of interest include boryl azides **1a** and **1b** that yield highly electrophilic boryl nitrenes<sup>[1]</sup> or BN-arynes,<sup>[2]</sup> 1,2-dihydro-1,2-azaborinines **2** that isomerize to Dewar structures,<sup>[2]</sup> and polycyclic aromatic hydrocarbons with internal borazine cores such as **3** that can undergo photocyclization.<sup>[3]</sup>



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## Directed Catalytic C-H Activation Using Boronyl-Based Directing Groups

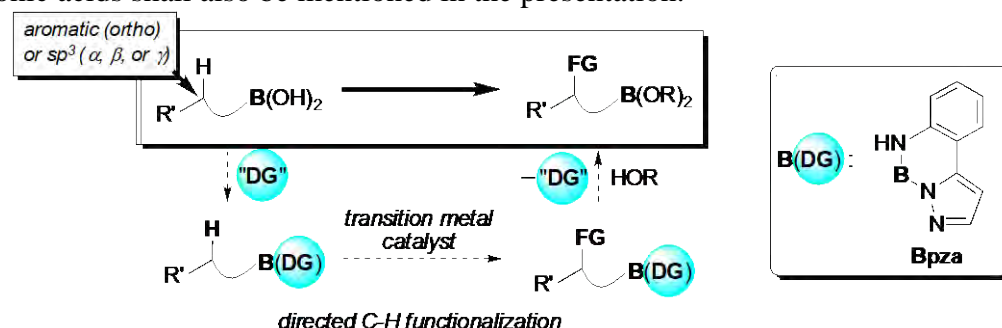
Michinori Suginome

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan



## ABSTRACT

Much attention has been focused on transition-metal-catalyzed, directed C-H bond activation, as it provides highly atom-economical, chemoselective, and straightforward synthetic accesses to highly functionalized organic molecules. Particular effort has been devoted to the development of "traceless" or "convertible" directing groups to facilitate synthetic applications, while conventional directing groups significantly limit the substrate scope. From this point of view, use of boron-based functional groups as directing groups in C-H bond functionalization is highly attractive by virtue of a wide variety of boronyl-based transformations.<sup>[1]</sup> Herein, the author describes boryl-directed C-H bond functionalization reactions, which are enabled by introduction of a 2-pyrazol-5-ylaniline (pza)-based temporary modifier as a removable directing group on the boron atom of aryl and alkylboronic acids. Iridium-catalyzed *ortho*-C-H borylation<sup>[2]</sup> and rhodium-catalyzed *o*-C-H addition to alkynes<sup>[3]</sup> are demonstrated with arylboronic acids. In addition, borylation of otherwise unreactive C(sp<sup>3</sup>)-H bond of various alkylboronic acids shall also be mentioned in the presentation.<sup>[4]</sup>



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## Stereochemical Integrity of Cu–Alkyl and Cu–Allenyl Intermediates: Mechanistic Implications Regarding Enantioselective Transformations

Sebastian Torker<sup>a,\*</sup>, Youming Huang<sup>a</sup>, Juan del Pozo<sup>a</sup>, Amir H. Hoveyda<sup>a,\*</sup>

<sup>a</sup>Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467, USA  
[torker@bc.edu](mailto:torker@bc.edu), [hoveyda@bc.edu](mailto:hoveyda@bc.edu)

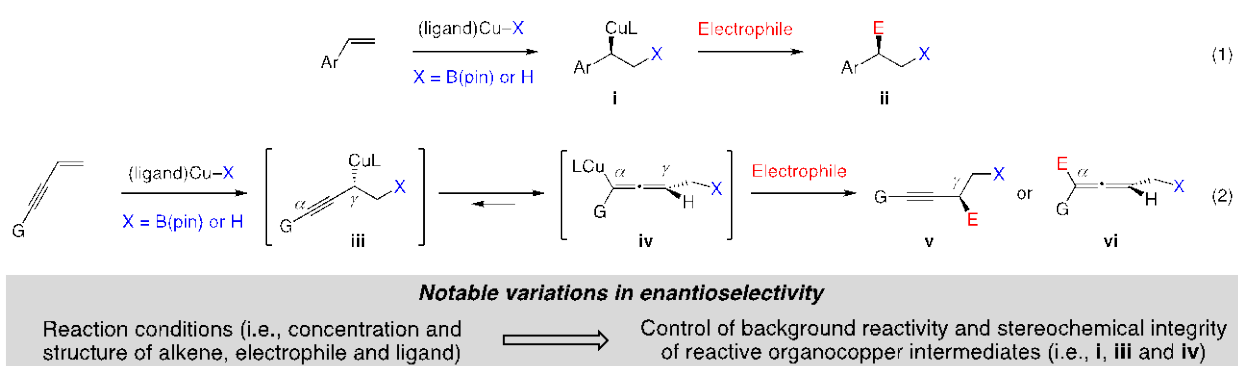


### ABSTRACT

Catalytic reactions involving stereodefined Cu–alkyl or Cu–allenyl intermediates are among a rapidly emerging set of transformations.<sup>[1],[2]</sup> The reactive organocopper entities are commonly generated by catalytic enantioselective addition of *in situ* generated Cu–boryl or Cu–hydride species to olefins. Attaining high efficiency and high levels of enantioselectivity can often be challenging due to the simultaneous presence of multiple components [H–B(pin)/B<sub>2</sub>(pin)<sub>2</sub>, alkene, electrophile, ...], which requires careful tuning of relative reaction rates.

Some of our recently obtained key findings that allow for control of the reaction outcome will be elucidated with the help of the transformations shown in Scheme 1.<sup>[1],[2]</sup> It will be discussed how reaction conditions (concentration and structure of alkene, electrophile and ligand) can influence both, background reactivity as well as the stereochemical integrity of organocopper intermediates, leading to notable variations in enantioselectivity.

Scheme 1. Enantioselective reactions via chiral Cu–alkyl and Cu–allenyl intermediates



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## Enantioselective Synthesis of Chiral-at-Cage *o*-Carboranes via Pd-Catalyzed Asymmetric B–H Substitution

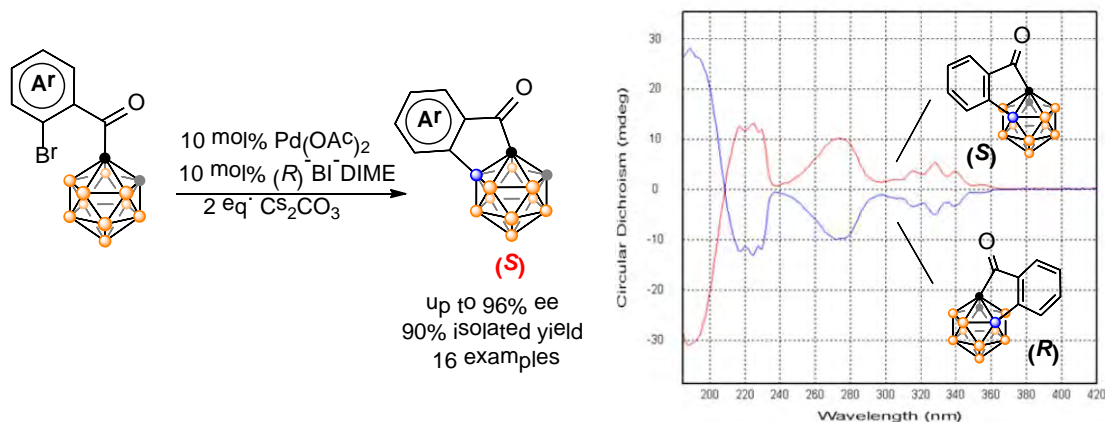
Zaozao Qiu<sup>a,\*</sup>

<sup>a</sup>Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, 345 Lingling Rd, Shanghai 200032, China  
qiuzz@sioc.ac.cn



### ABSTRACT

Transition-metal-catalyzed enantioselective reaction is a promising strategy to obtain enantiomerically enriched compounds to support the ever-growing needs of pharmaceutical industry. Although carborane has been found many important applications in medicinal and materials chemistry, the study of chiral-at-cage carboranes is still a blank field due to the lack of asymmetric synthetic methods. Icosahedral carboranes can be viewed as three-dimensional analogues to benzene, whose chirality is determined by the substitution patterns on the polyhedron.<sup>[1]</sup> Introduction of new chirality at the boron clusters can result in novel chiral-at-cage carborane ligands as well as important potential chiral drug building blocks. Here, we use the palladium-catalyzed asymmetric B–H substitution strategy generating chiral-at-cage *o*-carboranes with high efficiency and enantioselectivity. This is the first step toward new type of molecular design in boron cage inherent chirality, which will enhance our fundamental understanding of carboranes chemistry.



**Scheme 1** Palladium-catalyzed Asymmetric Intramolecular B–H Arylation of *o*-Carborane

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## Exploring the Scope of Radical-Polar Crossover Reactions of Vinyl Boron Ate Complexes in Three Component Couplings

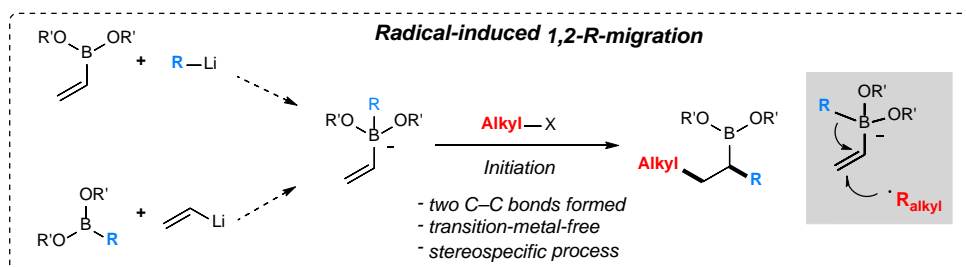
Marvin Kischkewitz, Armido Studer\*

Organisch-Chemisches Institut, Westfälische Wilhelms-Universität,  
Corrensstraße 40, 48149 Münster, Germany  
marvin.kischkewitz@wwu.de, studer@wwu.de



### ABSTRACT

Vinylboronic esters are highly important building blocks for C–C bond formations in the *Suzuki-Miyaura* coupling.<sup>[1]</sup> Importantly, vinyl boron ate complexes can be also used in three component coupling reactions, in which two new bonds are formed and the valuable boronic ester moiety remains in the product. The general strategy is based on the ability of boronic esters to form vinyl boron ate complexes with carbon nucleophiles, which further can undergo a 1,2-metalate rearrangement induced by different electrophilic trigger mechanisms.<sup>[2,3]</sup> Along these lines, we demonstrated that *in situ* prepared vinyl boron ate complexes react efficiently with electrophilic alkyl radicals generated from alkyl iodides. The resulting radical anions undergo a radical-polar crossover reaction and a 1,2-alkyl/aryl shift from boron to the  $\alpha$ -carbon  $sp^2$ -center provides valuable secondary and tertiary alkyl boronic esters.<sup>[4]</sup>



Notably, the cascade proceeds without the help of any transition metal and uses commercial starting materials allowing a readily construction of molecular complexity. The reaction tolerates  $\alpha$ - and  $\beta$ -substituted vinyl boronic esters and the scope of the radical precursor includes perfluoroalkyl iodides,  $\alpha$ -iodo esters, iodoacetonitriles,  $\alpha$ -iodo phosphonates and  $\alpha$ -iodo sulfonates. Initiation of the chain reaction can be either achieved by catalytic amounts of  $BEt_3$ <sup>[4]</sup>, by photo-<sup>[5]</sup> or photoredox initiation.<sup>[6]</sup> Furthermore, we recently demonstrated that vinyl boron ate complexes of enantioenriched secondary alkyl pinacolboronic esters undergo stereospecific radical induced 1,2-migration in radical polar crossover reactions.<sup>[6]</sup>

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## Exploiting reversible covalent interactions of boron compounds in reactivity and catalysis

Mark S. Taylor\*

*Department of Chemistry, University of Toronto  
80 St. George St., Toronto, ON M5S 3H6 Canada  
mtaylor@chem.utoronto.ca*



### ABSTRACT

Reversible covalent interactions of organoboron compounds have been applied extensively in molecular recognition and chemical sensing. My group has developed reactions that take advantage of the strength and selectivity of these interactions.<sup>[1]</sup> This approach has led to the discovery of methods for selective functionalization of carbohydrate derivatives,<sup>[2]</sup> regio- and stereoselective glycosylations,<sup>[3]</sup> polymerizations of sugar-derived feedstocks,<sup>[4]</sup> as well as ring-opening and rearrangement reactions of epoxy alcohols.<sup>[5]</sup> Mechanistic studies of these processes will be discussed.

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## Boronic Acid Catalysis: Hydroxyl Activation Using Reversible B–O Bonds

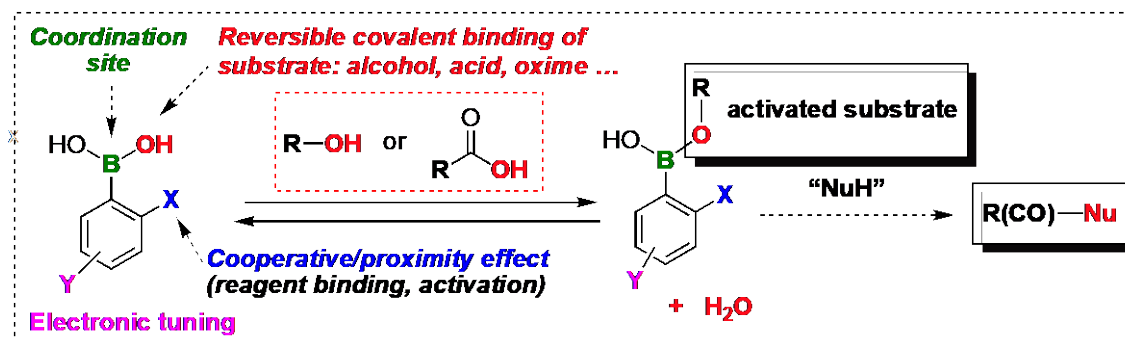
Dennis G. Hall\*

Department of Chemistry, Centennial Centre for Interdisciplinary Science  
University of Alberta,  
Edmonton, AB, T6G 2G2, Canada  
dennis.hall@ualberta.ca



### ABSTRACT

Although boronic acids are recognized primarily for their utility in cross-coupling chemistry, other applications are emerging, including their use as catalysts in a concept coined “Boronic Acid Catalysis” (BAC).<sup>[1]</sup> By exploiting the reversibility of B–O bonds, BAC provides a unique strategy for the organocatalytic activation of hydroxyl functional groups. It features mild conditions, without the need for stoichiometric amounts of activating groups and reagents, leading to the direct transformation of alcohols and carboxylic acids into useful products with water as the sole by-product. One of the first successful applications of BAC is the direct amidation of carboxylic acids and amines. Furthermore, boronic acids have the ability to form reversible covalent bonds with hydroxyl groups, exploiting the selective electrophilic activation of pi-activated alcohols to form carbocation intermediates. The most active catalyst to date is a ferrocenium boronic acid salt that is thought to ionize alcohols through a novel ion-redistribution mechanism. This unique mode of catalysis was applied in the direct Friedel-Crafts alkylation of arenes with readily available benzylic and allylic alcohols.<sup>[2]</sup> In a promising evolution of this concept, dual catalysis combining BAC with chiral amine catalysis allowed enantioselective enamine alkylation to generate optically enriched quaternary carbon centers.<sup>[3]</sup> Recently, the scope of BAC was extended to the activation of N–OH units to facilitate the Beckmann rearrangement of oximes into amides. These reaction processes and other ongoing applications of BAC will be described.



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**Boron as a Pharmacophore in Drug Discovery**

Matthew A. Perry<sup>a,\*</sup>

*<sup>a</sup>Pfizer Inc, WWMD, I&I, 445 Eastern Point Rd, Groton CT 06340  
matthew.perry@pfizer.com*

**ABSTRACT**

A broad look at the use of boron as a key pharmacophore in drug discovery and development will be presented. Topics will include the physicochemical properties of boron-based compounds, the types of binding modes observed by X-ray crystallography, and examples on the use of boron containing compounds in various therapeutic areas.

## Rhenacarborane Complexes for Peptide Delivery Across the Blood-Brain Barrier (BBB)

Daniel G. Pruitt<sup>a</sup>, Kristin Bullock<sup>b</sup>, William A. Banks<sup>b</sup>, Paul A. Jelliss<sup>a,\*</sup>

<sup>a</sup> Dept. of Chemistry, Saint Louis University, St Louis, MO 63103.

<sup>b</sup> Dept. of Internal Medicine, University of Washington, Seattle, WA.

paul.jelliss@slu.edu

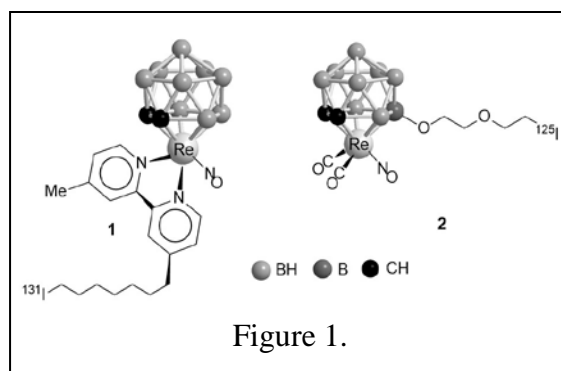


### ABSTRACT

The search for non-invasive neural therapeutics is a problematic pursuit often hindered by the blood-brain barrier (BBB), a gatekeeper of endothelial cells and tight junctions closely regulating exchange between the bloodstream and brain tissue. A study of the complex [3-NO-3,3- $\kappa^2$ -(2,2'-N<sub>2</sub>C<sub>10</sub>H<sub>6</sub>(Me))((CH<sub>2</sub>)<sub>7</sub><sup>131</sup>I)-4,4')-*closo*-3,1,2-ReC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] (**1**) (Figure 1) demonstrated its ability to not only safely pass through the BBB but also cleanly efflux out of neural tissue, suggesting potential use as a drug-delivery vehicle for Central Nervous System (CNS) infiltration.<sup>[1]</sup> However, due to the practical difficulty of asymmetric modification of the bipyridyl ligand, a more direct synthetic approach of carborane cage vertex adaptation has been investigated with the hope of utilizing such species for CNS therapeutics.<sup>[2]</sup> A second prototype of [3,3-(CO)<sub>2</sub>-3-NO-*closo*-Re(8-O(CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub><sup>125</sup>I)-3,1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)] (**2**) (Figure 1) was rapidly absorbed into the bloodstream from the subcutaneous site of injection and displayed a 1 %Inj/g for peak brain uptake, which rapidly stabilized to 0.1 while the previous complex **1** merely peaked at 0.1 %Inj/g.<sup>[3]</sup> It was also determined that peak brain uptake of 15 mL/g was higher than lung and liver tissues, suggesting that the brain is somehow specifically targeted, while the exact rationale for selectivity remains to be explored. Recent experiments (NMR and mass spectroscopy) suggest that peptidyl coupling with both amino acids (tyrosine) and oligopeptides (methionine-enkephalin) has been successful. The latter bioorganometallic conjugate is designed to target opiate receptors in the brain.

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## Advances in Pharmacodynamics and Pharmacokinetics of Boron-Containing Compounds

Soriano Ursúa Marvin Antonio<sup>a,\*</sup>, Trujillo-Ferrara José G.<sup>a</sup>, Farfán-García Eunice D.<sup>a</sup>

<sup>a</sup>*Departments of Physiology and Biochemisty. Sección de Estudios de Posgrado e Investigación. Escuela Superior de Medicina del Instituto Politécnico Nacional, Plan de San Luis y Diaz Mirón s/n, Col. Casco de Santo Tomás, Del. Miguel Hidalgo, Mexico City, México*

*Email: [soum13mx@gmail.com](mailto:soum13mx@gmail.com)*



### ABSTRACT

Albeit maybe the origin of species is linked to boron presence,<sup>[1]</sup> boron-containing compounds (BCCs) are now in ‘increasing’ contact with living organisms, due to the increasing identification and synthesis of many new BCCs. Just in the last century, research is elucidating the detailed behavior for interactions between boron-containing compounds found in nature or those synthesized and living organisms.<sup>[2]</sup> These interactions can be analyzed in two ways: By describing how the BCCs act on biological targets to induce responses (pharmacodynamics), and by analyzing how the BCCs moves through -or is transformed- in a living organism (pharmacokinetics).

In this work, we compiled data of pharmacodynamics of BCCs. Recently, advances are clear for explaining reported effects of boric acid on plant and animals.<sup>[1,3]</sup> But also, for probing the action of designed synthetic BCCs on specific biological targets. Interactions of BCCs on enzymes, membrane receptors and cytoplasmic receptors are recently reported with atomic details.<sup>[4]</sup> These advances let us to propose the rational addition of boron to new molecules which can act as potential drugs, preventive or diagnostic tools with application in many diseases.<sup>[1]</sup>

Besides, we collected and analyzed data of pharmacokinetics of BCCs. Absorption, distribution, metabolism and excretion of BCCs is different for each BCCs as is for boron-free compounds.<sup>[5]</sup> The movement of natural BCCs is well-known in plants, but lesser is known in animals. The stability of BCCs is questionable and seems to be related to the chemical environment of boron in the analyzed molecule.<sup>[5,6]</sup>

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## Facile Labeling of Bacterial Pathogens via Diazaborine Formation of Semicarbazide

Samantha Cambray<sup>a</sup> and Jianmin Gao<sup>a\*</sup>

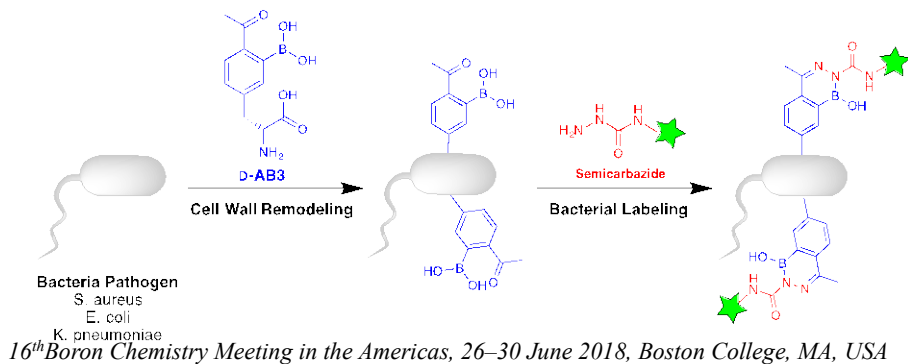
<sup>a</sup>Department of Chemistry, Boston College, 2609 Beacon Street, Chestnut Hill, MA

cambray@bc.edu, jianmin.gao@bc.edu



### ABSTRACT

Bioorthogonal conjugation chemistry is an important chemical tool, which facilitates the study of exceptionally complex biological systems. The current landscape of bioorthogonal reactions includes a wide array of chemistries, most of which are sub-optimal for one or more reasons, including slow kinetics, off-target reactivity, generation of toxic side reactions, formation of non-stable products, or the requirement of toxic reagents or catalysts. However, we have discovered that conjugation of a hydrazine-containing small molecule, semicarbazide, to an aryl aldehyde or ketone with an *ortho*-boronic acid moiety is both fast ( $>10^3 \text{ M}^{-1}\text{s}^{-1}$ ) and meets the aforementioned optimal characteristics for biocompatibility. The *ortho*-boronic acid substituent accelerates diazaborine formation to enable rapid kinetics, and the conjugation reaction is both compatible with and non-toxic towards both blood serum and cell lysates, and shows minimal interference from abundant biomolecules. Upon establishing biocompatibility, it was determined that diazaborine formation can be applied for facile labeling of several important bacterial pathogens via cell wall remodeling with suitably designed unnatural amino acids. Varied bacterial selectivity was observed for these synthetic cell wall modifiers. For example, D-AB3, which presents a 2-acetylphenylboronic acid moiety as its side chain, was found to most efficiently incorporate into *E. coli* over other bacterial species. Furthermore, we have developed fluorogenic versions of the diazaborine conjugation reaction, which allows fluorescent labeling of bacteria under no-wash conditions, demonstrating the wide adaptability of this facile, bioorthogonal chemistry.





## BComplexes: Functional Linkers for Targeted Delivery

Pedro M. P. Gois\*

Research Institute for Medicines (iMed.Ulisboa)

Faculty of Pharmacy, Universidade de Lisboa

Lisbon (Portugal)

pedrogois@ff.ulisboa.pt



### ABSTRACT

Targeting drug conjugates, emerged as a powerful class of chemotherapeutic agents that are capable of sparing healthy tissues by liberating the cytotoxic payload only upon specific antigen recognition. The approval of two new antibody drug conjugates (Kadclyla<sup>®</sup> and Adcetris<sup>®</sup>) triggered much interest in designing novel formats of conjugates combining the lethality of potent cytotoxic drugs with biomolecules with high affinity for well characterized antigens overexpressed in cancer cells and tumors.<sup>[1]</sup> A considerable body of work in this field highlighted that targeting drug conjugates therapeutic efficacy, correlates well with the conjugate homogeneity and activation of the drug at the diseased site. Therefore, the linker technology used to connect both functions contributes decisively to the therapeutic usefulness of these constructs, by enabling the biomolecule functionalization without altering its pharmacokinetic properties and by maintaining the conjugate integrity in circulation and triggering the release of the active drug only upon reaching the target.<sup>[1,2]</sup> In this communication will be presented the use of boron based complexes as functional linkers in the design of cancer cell targeting conjugates (Fig. 1).<sup>[3]</sup>

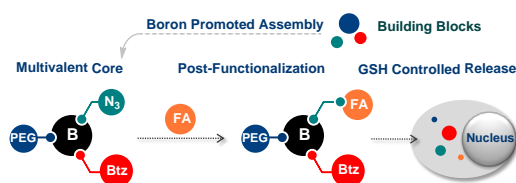


Fig. 1 – Example of a BComplexes used as a functional linker delivery of Btz to cancer cells

**Acknowledgment:** FCT - Gants: PTDC/QEQ-QOR/1434/2014; SAICTPAC/0019/2015

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## Molecular Recognition and *in vitro* Activity of Branched Peptide Boronic Acids against HIV-1 Rev Response Element RNA

Webster L. Santos\*

Virginia Tech, Department of Chemistry, Blacksburg, VA 24061, USA  
santosw@vt.edu



### ABSTRACT

Targeting RNA remains to be a formidable challenge. To develop compounds as possible RNA therapeutics, our laboratories are focused on molecular recognition of the three-dimensional architecture of conserved RNAs present in HIV-1 Rev response element (RRE). Using a library of branched peptides composed of unnatural amino acids—some with boronic acids, potent and selective binders of RRE RNA were discovered.[1-7] Binding of Rev to RRE is essential for the transport of full length RNA transcripts to the cytoplasm, which is a key step in the viral replication process. Hence, inhibitors of this interaction have the potential as therapeutics. We will discuss the synthesis of the library, high throughput screen, and biophysical characterization of hit peptides. We discovered inhibitors in the nanomolar range against RRE RNA: peptide branching and formation of reversible covalent bonds with boronic acids and 2'-hydroxyl group of RNA are key intermolecular interactions. Selective 2' hydroxyl acylation analyzed by primer extension (SHAPE) analysis reveal binding sites with full length RNA and *in vitro* studies suggest inhibition of viral replication in a Rev-RRE RNA interaction dependent manner.

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## On the Origin of Enantioselectivity in Asymmetric Hydrogenation of Imines Catalyzed by Chiral Boranes

Imre Pápai<sup>a,\*</sup>, Andrea Hamza<sup>a</sup>, Dénes Berta<sup>a</sup>, Kristina Sorochkina<sup>b</sup>, Konstantin Chernichenko<sup>b</sup>, Timo Repo<sup>b</sup>

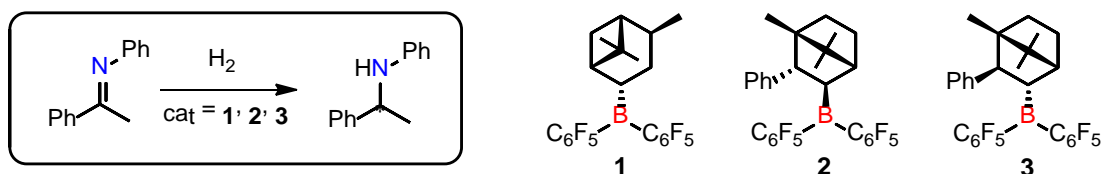
<sup>a</sup> Research Centre for Natural Sciences, Hungarian Academy of Sciences,  
Magyar tudósok körútja 2, H-1117, Budapest, Hungary

<sup>b</sup> Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O.  
Box 55, 00014 Helsinki, Finland  
papai.imre@ttk.mta.hu



### ABSTRACT

The asymmetric hydrogenation of unsaturated bonds using chiral boranes as catalysts has been of continuous interest since the introduction of the concept of frustrated Lewis pairs (FLPs). Using different chiral inter- and intramolecular FLP combinations and molecular hydrogen as a reducing agent, the asymmetric hydrogenation of imines, enamines, silyl enol ethers and N-heteroarenes could be achieved with moderate to excellent stereoselectivities.<sup>[1]</sup> However, our understanding regarding the factors that govern the stereoselectivity in these metal-free catalytic hydrogenation processes is quite limited. Our preliminary computational analysis revealed a subtle balance between steric repulsion and non-covalent stabilization in the key hydride transfer step.<sup>[2]</sup> To gain further insight into the nature and the importance of these interactions, we examined computationally a series of imine reduction processes described in seminal papers from Klankermayer (see scheme below).<sup>[3]</sup>



The experimentally observed stereoselectivities could be reasonably reproduced and rationalized by the computational approach. Based on the new insights, modifications in the camphor-derived boranes were proposed to improve the enantioselectivity, which could be demonstrated experimentally.<sup>[4]</sup>

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## New Pathways in Frustrated Lewis Pair Chemistry

Gerhard Erker

Organisch-Chemisches Institut der Universität Münster  
Corrensstr.40, Münster, Germany  
erker@uni-muenster.de

**ABSTRACT**

Frustrated Lewis pair (FLP) chemistry has seen a steep development in the recent years. Some new developments in this area shall be presented, which involve sequences of hydroboration, carboboration or halogenoboration reactions using suitable X-B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> reagents (X = H-, hydrocarbyl- or halogen-). Examples include the reactions of bulky aryl(divinyl)phosphanes to give various types of cyclic reaction products. The cyclic P/B FLPs undergo some novel types of cycloaddition reactions with various organic π-reagents, which will be presented and whose consequences will be discussed. Some new reactions of the X-B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> reagents with acetylenes shall also be presented.

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## Organocatalytic *trans* hydroboration of internal alkynes

Russell Fritzscheier<sup>a</sup>, Ashley Gates<sup>a</sup>, Xueying Guo<sup>b</sup>, Zhenyang Lin<sup>b</sup>, Webster Santos<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA

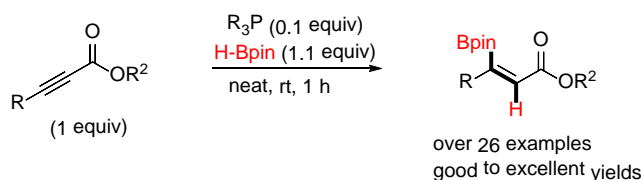
<sup>b</sup>Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China  
rgf004@vt.edu, santosw@vt.edu\*



### ABSTRACT

Vinylboronates represent an invaluable class of synthetic intermediate as demonstrated by their ability to undergo a wide variety of useful transformations. [1-3] In addition to use as synthetic intermediates, boronic acids have recently garnered interest due to biological and medicinal applications. [4-5] As such, our laboratory has devoted significant efforts towards the development of efficient and environmentally friendly synthetic methods for the preparation of vinylboronates.

We report the phosphine catalyzed *trans* hydroboration of internal alkynes. The transition metal-free reaction proceeds efficiently under mild conditions with complete regio- and stereoselectivity to afford the corresponding (*Z*)- $\beta$ -borylacrylates. A wide substrate scope is demonstrated as well as a unique application in the efficient synthesis of oxaboroles. Mechanistic insights into the selectivity and catalysis are demonstrated through DFT and mechanistic studies.



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## Asymmetric Imine Hydroboration Using Diazaphospholene Catalysts

Alexander W. H. Speed<sup>a\*</sup>, Matt R. Adams<sup>a</sup>, Chieh-Hung Tien<sup>a</sup>

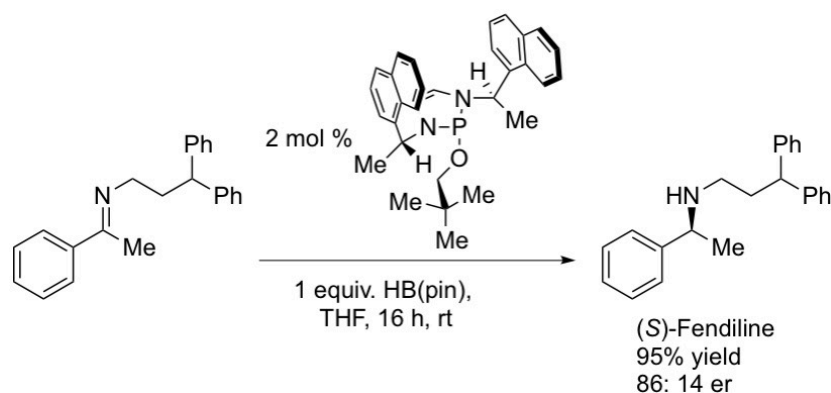
<sup>a</sup>*Dalhousie University, Department of Chemistry, 6274 Coburg Road,  
Halifax, Nova Scotia, Canada B3H 4R2*

*aspeed@dal.ca*



### ABSTRACT

Diazaphospholenes are an emerging class of catalyst for reductive transformations of carbonyls, imines, carbon dioxide, and pyridines. Boron-based reductants have been particularly successful in enabling diazaphospholene catalysis.<sup>[1]</sup>



Our group's development of catalytic imine and conjugate reductions employing diazaphospholenes and pinacolborane will be described. Dearomatization of substituted pyridines through hydroboration provides mechanistic insight into the hydroboration of imines. The optimization of asymmetric reductive chemistry employing chiral pseudo-C<sub>2</sub> symmetric diazaphospholene precatalysts has provided enantioselectivities of up to 88:12 in imine hydroboration.<sup>[2]</sup> New strategies to enhance enantioinduction employing second-generation dissymmetric catalysts will be described.

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## Cooperative Enantioselective Catalysis with Frustrated Acid/Base Complexes

Masayuki Wasa

*Author Affiliation, Boston College, Chestnut Hill, MA 02467 USA  
wasa@bc.edu*



### ABSTRACT

The application of frustrated Lewis pairs (FLPs), consisting of hindered and electronically disparate boron-based Lewis acids and various Lewis bases, has emerged as an attractive strategy for activation of otherwise unreactive molecules. However, such strategies are yet to be successfully applied to catalytic and enantioselective C–C bond forming transformations. In this seminar, we describe the development of highly diastereo- and enantioselective C–C bond forming transformation by implementing the cooperative action of  $B(C_6F_5)_3$  and chiral Mg–PyBOX complexes that possess overlapping functions. We illustrate that by proper tuning of different features of structurally and electronically different Lewis acids and substrates, the ability of Lewis acid catalysts to serve as a hydride acceptor from amines, or an activator of  $\alpha,\beta$ -unsaturated compounds, can be adjusted. The principles outlined herein serve as a conceptual framework for the development of new processes that demand separate and independently operational Lewis acidic co-catalysts whose functions might easily overlap and the simultaneous use of which might initially seem to have a negative impact on enantioselectivity.



## Modern Alchemy: Turning Boron into Gold

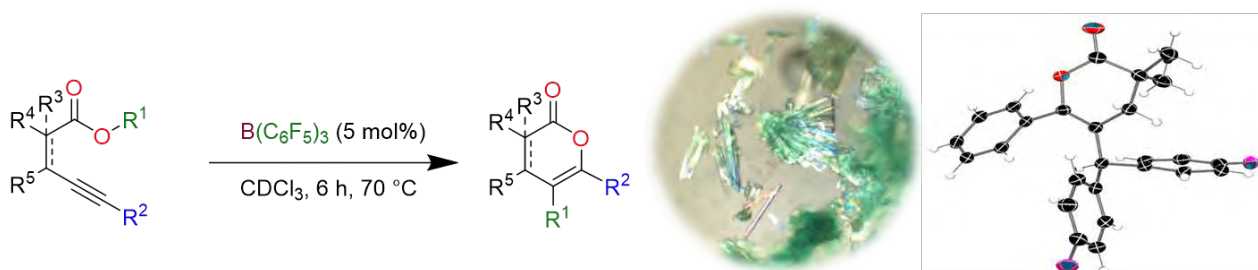
Rebecca L. Melen<sup>a,\*</sup>

<sup>a</sup>Cardiff University, School of Chemistry, Main Building, Park Place, Cardiff,  
CF10 3AT, UK.

MelenR@Cardiff.ac.uk



As main-group chemistry, in particular boron chemistry, has expanded and developed over the past 20 years, one reagent has risen to prominence as well. Tris(pentafluorophenyl)borane,  $B(C_6F_5)_3$  (commonly known as BCF), has demonstrated extensive applications in a wide variety of reactions, including borylation, hydrogenation, hydrosilylation, frustrated Lewis pair (FLP) chemistry, Lewis acid catalysis, and more.<sup>[1]</sup> Recent developments in the Melen group have investigated new directions in metal free catalysis to provide new openings in both the synthesis and applications of main group compounds. Our contributions to the field of main group mediated organic transformations include the exploration of Lewis acidic main group compounds as reagents for enabling transformations which are typically promoted or catalyzed by heavier d-block metals such as Au(I). This includes the use of Lewis acidic boranes to generate a range of pharmaceutically important heterocycles which will be discussed in this talk.<sup>[2]</sup>



**Figure 1.** Borane catalysis.

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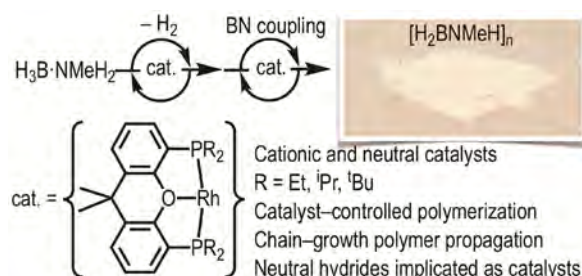
## [Rh(Xantphos-alkyl)] catalysts for the efficient dehydropolymerization of amine–boranes. Mechanistic insight through a systemic study.

Andrew S. Weller

*Department of Chemistry, University of Oxford, UK.  
Andrew.weller@chem.ox.ac.uk*

Polyaminoboranes, a class of main group backbone polymer isoelectronic with societally ubiquitous polyolefins, are a potentially very important class of macromolecule with essentially unexplored properties, that also offer opportunities to act as precursors to BN-containing materials (e.g. hexagonal boron nitride). Metal-catalysed dehydropolymerization routes to their formation offer the potential to control kinetics and chain propagation/termination events that, as elegantly shown by many for polyolefins, could ultimately lead to the synthesis “to order” of BN-polymeric materials with tuned properties. However, to date, detailed insight into the overall mechanism of dehydropolymerization is limited.

In this contribution a detailed study into role played by catalyst structure (variation of ligand) and overall charge on the metal center in amine–borane dehydropolymerization is discussed with regard to {Rh(Xantphos–R)} catalysis. This allows for a holistic consideration of: catalyst structure, dehydrogenation and polymer growth kinetics, degrees of polymerization, characterization of polymer, detailed catalyst speciation studies and mechanistic insight from catalyst kinetics (including isotopic labelling studies that require new synthetic routes to the corresponding d-labelled amine boranes).



An overall model for dehydropolymerization is suggested that comes from these studies that invokes hydride transfer, boronium formation and classical chain growth processes as being central to productive catalysis. This model provides a framework that is also transferable to other catalyst systems, and potentially offers a testable set of fundamental catalytic steps for the community to investigate and harness in future work.

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## An Experimental and Computational Study of Intermediates Formed in the Release of Hydrogen from $\text{Mg}(\text{BH}_4)_2$ .

Iffat Nayyar, Marina Chong, and Tom Autrey\*  
Pacific Northwest National Laboratory, Richland, WA 99352

*tom.autrey@pnl.gov*



### ABSTRACT

Recently we demonstrated the ability to cycle between  $\text{Mg}(\text{BH}_4)_2$  and  $\text{Mg}(\text{B}_3\text{H}_8)_2$  under relatively mild conditions of temperature and hydrogen pressure.<sup>[1]</sup> This was one of the first examples of reversible  $\text{H}_2$  storage at temperatures below 300 °C in complex metal hydrides. Subsequently a computational study was published that questioned the formation of  $\text{Mg}(\text{B}_3\text{H}_8)_2$  intermediate at these temperatures based on DFT calculations. The reaction enthalpy for the decomposition of  $\text{Mg}(\text{BH}_4)_2$  to  $\text{Mg}(\text{B}_3\text{H}_8)_2$  was predicted to be higher, by an order of magnitude, than for  $\text{MgB}_2$  and  $\text{MgB}_{12}\text{H}_{12}$ . However, the distinctive  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectrum of  $\text{B}_3\text{H}_8$  anion in our experimental study was unambiguous.

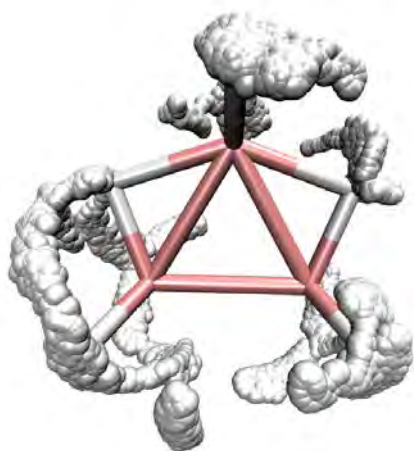


Figure 1. AIMD simulation of  $\text{B}_3\text{H}_8$  anion showing motion of H.

To address the apparent discrepancy between the experimental observations of  $\text{Mg}(\text{B}_3\text{H}_8)_2$  and the theoretical predictions we have revisited the thermodynamics calculations – extending the earlier studies to include vibrational and thermal corrections to calculate the free energy for  $\text{Mg}(\text{B}_3\text{H}_8)_2$  using supercell approach. Figure 1 summarizes the results for the calculated enthalpy ( $\Delta\text{H}$ ) of formation for possible intermediates ( $\text{MB}_x\text{H}_y$  species,

$\text{Mg}(\text{B}_3\text{H}_8)_2$ ;  $\text{Mg}_3(\text{B}_3\text{H}_6)_2$ ,  $\text{MgB}_2\text{H}_6$ ,  $\text{MgB}_{10}\text{H}_{10}$ ,  $\text{MgB}_{12}\text{H}_{12}$ ,  $\text{MgB}_2$ ) in the thermal decomposition of  $\text{Mg}(\text{BH}_4)_2$ . With this new insight we suggest a possible mechanism for the

selective reversible formation of  $\text{Mg}(\text{B}_3\text{H}_8)_2$  from the hydrogenation of  $\text{Mg}(\text{BH}_4)_2$ .

**Acknowledgements.** Research support from the Hydrogen Materials - Advanced Research Consortium (HyMARC), established as part of the Energy Materials Network under the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office is gratefully acknowledge. All of the quantum chemical calculations were performed at EMSL, a DOE Office of Science user facility. EMSL is a DOE Office of Science User Facility sponsored by the Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, a multi-program national laboratory operated by Battelle for the U.S. Department of Energy. The authors thank Gary Edverson, Bojana Ginovska, Craig Jensen, Mark Bowden, Abhi Karkamkar for insightful discussion.

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## A safe synthesis of alkali metal triboranes ( $M(B_3H_8)_2$ ) in relation to their role as intermediates for hydrogen storage in $M(BH_4)_2$ ( $M=Mg, Ca$ )

Angelina Gigante<sup>a</sup>, Romain Moury<sup>a</sup>, Tom Autrey<sup>b</sup>, Mark Bowden<sup>b</sup>, and Hans Hagemann<sup>a,\*</sup>

<sup>a</sup>*Department of Physical Chemistry, University of Geneva, Quai E. Anserment 30, CH-1211 Geneva 4, Switzerland.*

<sup>b</sup>*Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, WA 99352 USA.*

*angelina.gigante@unige.ch*

*\*Hans-Rudolf.Hagemann@unige.ch*



### ABSTRACT

Borohydride compounds are a fascinating class of materials that have attracted the interest of the scientific community for the last 2 decades owing to their high hydrogen content (up to 14.9 and 9.6 wt %  $H_2$  for  $Mg(BH_4)_2$  and  $Ca(BH_4)_2$  respectively) and have been considered as potential materials for hydrogen storage<sup>[1,2]</sup>.

Recently, it has been reported that the system  $Mg(B_3H_8)_2 \cdot 2THF$  and  $MgH_2$  can be rehydrogenated to  $Mg(BH_4)_2$  under moderate conditions (200°C and 5 MPa  $H_2$ ). However, the presence of the solvent (like THF) can affect the reaction pathways, the mechanism of reaction, and the kinetics of reversible hydrogenation<sup>[3]</sup>. For this reason, it is important to prepare pure (solvent-free) samples for mechanistic and kinetic studies.

Until now, the synthesis methods reported in the literature have employed expensive and unfriendly routes, which require toxic and not readily available compounds like  $B_2H_6$ . Our efforts are focused on the design of an efficient, cheap and safe way, starting from the cheapest metal borohydrides available, namely sodium borohydride  $NaBH_4$ <sup>[4]</sup>.

In this presentation I report the synthesis and characterization of unsolvated  $M(B_3H_8)_2$  ( $M=Mg$  and  $Ca$ ). We have developed a reproducible process to convert  $BH_4^-$  into  $B_3H_8^-$  on a large laboratory scale. The synthesis of the deuterated species  $Mg(B_3D_8)_2$  and  $Ca(B_3D_8)_2$  will be also presented. Kinetic isotope effects provide more insight about the characterization and understanding of the intermediates pathways during the hydrogenation of the triborane to  $Mg(BH_4)_2$ .

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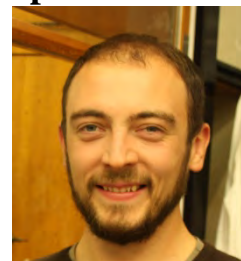
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## Synthesis and Reactivity of Diborenes based on a Benzylphosphine Chelate

Tom E. Stennett,<sup>a</sup> James D. Mattock,<sup>b</sup> Leanne Pentecost,<sup>b</sup> Ivonne Vollert,<sup>a</sup>  
Alfredo Vargas<sup>b</sup> and Holger Braunschweig\*<sup>a</sup>.

<sup>a</sup>Institut für anorganische Chemie, Julius-Maximilians-Universität  
Würzburg, Am Hubland, 97074 Würzburg, Germany

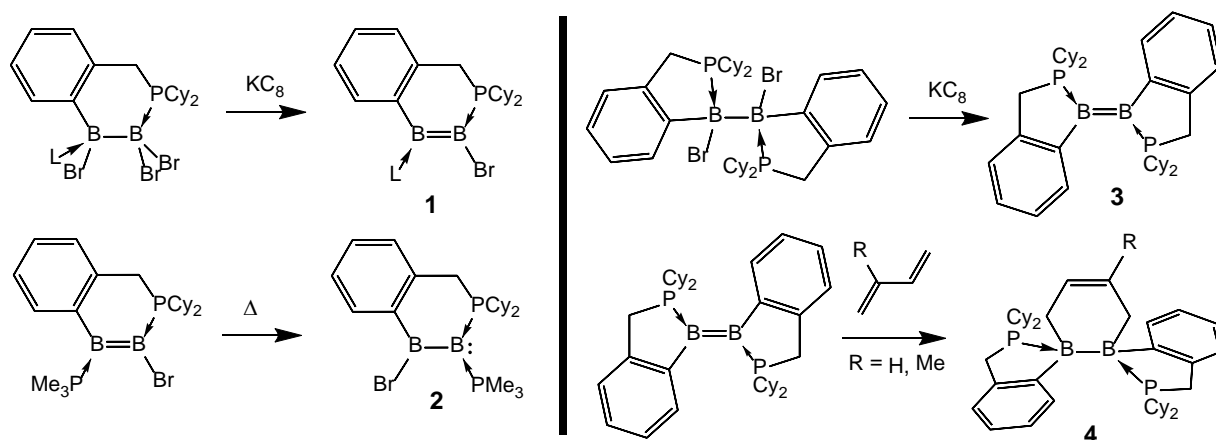
<sup>b</sup>Department of Chemistry, University of Sussex, BN1 9QJ, Brighton, UK  
[thomas.stennett@uni-wuerzburg.de](mailto:thomas.stennett@uni-wuerzburg.de), [h.braunschweig@uni-wuerzburg.de](mailto:h.braunschweig@uni-wuerzburg.de)



### ABSTRACT

Since their discovery in 2007, base-stabilised diborenes have become a cornerstone of low-valent boron chemistry.<sup>1</sup> A range of covalently bound substituents (H, X, Ar, Alkyl, Fc etc.) and Lewis bases (carbenes, phosphines) are now accessible, and reactivity includes coordination to transition metals, hydroboration, oxidative insertion of chalcogens, and coordination/insertion of CO. Alongside *trans*-diborenes, examples of the *cis*-isomer and one *gem*-isomer have been isolated. Recently, the first unsymmetrical diborenes were developed.<sup>2</sup>

We have prepared diborenes based on a chelating benzylphosphine group. Different synthetic approaches allowed selective introduction of one or two of these units to diboranes, after which reduction yielded a series of diborenes. Unsymmetrical *trans*-diborene **1** underwent a thermal rearrangement to borylborylene **2**, whereas doubly-1,1-chelated diborene **3** was shown to convert to its 1,2-isomer upon heating in the presence of a catalytic halide source. The diborenes show interesting optical properties owing to conjugation of the B=B bond with the aryl substituent, and display high reactivity towards small molecules. Several established and novel reaction types will be presented, including Diels-Alder reactions with dienes to form 4,5-dibora-1-cyclohexenes (**4**).



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## Synthesis and Formation Mechanism of Lithium and Sodium of Octahydrotriborate

Xi-Meng Chen, Nana Ma, Xin-Ran Liu, Xiao-Ge Feng, Xuenian Chen\*

School of Chemistry and Chemical Engineering,  
Henan Key Laboratory of Boron Chemistry and Advanced Energy Materials  
Henan Normal University, Xingxiang, Henan, 453007, China

Email: xnchen@htu.edu.cn



### ABSTRACT

The alkali salts of octahydrotriborate anion is a hot topic of recent research due to its high hydrogen content derivatives, such as  $\text{NH}_3\text{B}_3\text{H}_7$  and  $\text{NH}_4\text{B}_3\text{H}_8$ ,<sup>1,2</sup> are considered as potential chemical hydrogen storage materials. Although the preparation of the alkali salts of octahydrotriborate can be dated back to Stock's work in the 1920s,<sup>3</sup> its synthetic methods has been continually improved in the past century.<sup>4</sup> The improvement of the synthetic methods has been mainly focused on using other boranes to replace the flammable and toxic diborane or dispersing alkali metal on other media, instead of using alkali metal amalgam, which poses health and safety issues. In this presentation, we report a direct reaction between  $\text{MBH}_4$  ( $\text{M} = \text{Li}$  and  $\text{Na}$ ) and  $\text{THFBH}_3$  solution to produce lithium and sodium of octahydrotriborate with high yield. The formation mechanism of  $\text{MB}_3\text{H}_8$  will also be discussed in combination of experimental results and theoretical work (Fig. 1).

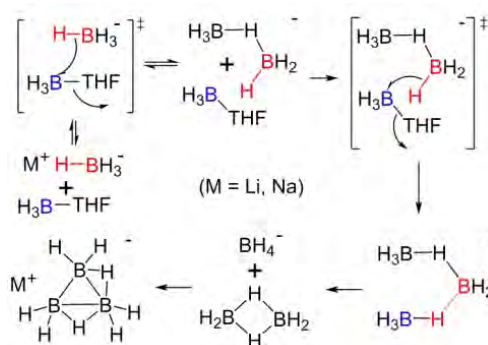


Fig. 1. Proposed the formation mechanism of  $\text{MB}_3\text{H}_8$

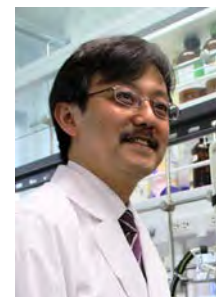
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## Copper-Catalyzed Asymmetric Borylative Dearomatization for Optically Active Heterocyclic Compounds

Hajime Ito\*

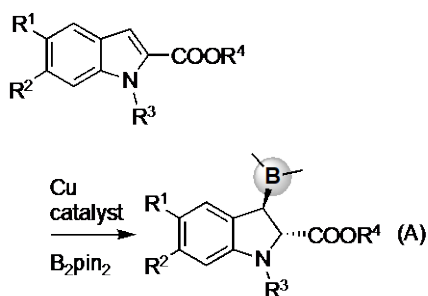
*<sup>a</sup>Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan.  
hajito@eng.hokudai.ac.jp*



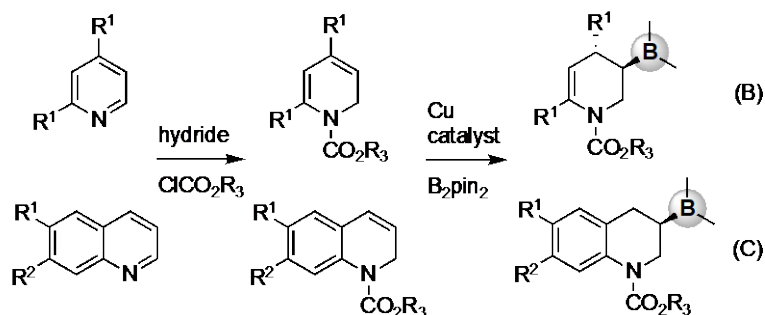
### ABSTRACT

Chiral *N*-heterocyclic organoboronates are useful intermediates for the preparation of various bioactive and pharmaceutical compounds. We recently reported the first asymmetric dearomative borylation of indoles using copper-catalysis with diboron (A).<sup>[1]</sup> We further developed sequential dearomatization/enantioselective borylation reaction. Enantio-enriched 3-boryl-tetrahydropyridines via the copper(I)-catalyzed regio-, diastereo- and enantioselective borylation of 1,2-dihydropyridines, which were prepared by the partial reduction of the pyridine derivatives (B).<sup>[2]</sup> This dearomatization borylation sequence provided direct access to chiral piperidines derivatives from various pyridines in combination with the stereospecific transformation of a stereogenic C–B bond. We also developed the synthesis of chiral boryl-tetrahydroquinolines from quinolines via this sequential dearomative reduction/borylation reaction (C).<sup>[3]</sup> These reactions can provide useful tools for the enantioselective synthesis of chiral *N*-heterocyclic organoboronates.

#### Asymmetric dearomative borylation



#### Dearomatization/enantioselective borylation



### REFERENCES

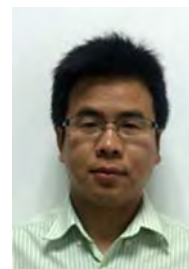
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## Novel Chiral Boryl ligands Enabled Iridium-Catalyzed Asymmetric C-H Activation Borylation

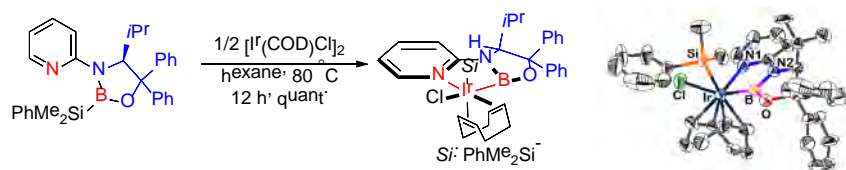
Xiaoliang Zou, Haonan Zhao, Senmiao Xu\*

*Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,  
Lanzhou 73000, China  
senmiaoxu@licp.cas.cn*



### ABSTRACT

Anionic boryl ligand (i.e., an  $sp^2$ -hybridized boron with the transition metal fragment as one of its three substituents) has been widely used in the transition-metal-catalyzed borylation of organic substrates.<sup>[1]</sup> Although metalloboryl complexes have been structurally evidenced as early as 1990s, boryl as supporting ligand in transition-metal catalysis remains a great challenge due to its lability. However, its intrinsic strong  $\sigma$  donating ability makes itself an attractive candidate in ligand design. To ameliorate challenges associated with its high reactivity, multidentate ligands are usually required to stabilize metalloboryl complexes.<sup>[2]</sup> Some of them could be applied in catalytic transformations.<sup>[2d,2e,3]</sup> Despite the fact, boryl as supporting ligand in asymmetric catalysis has not been touched. This is surprising in view of tremendous opportunities for achieving new reactivity and selectivity in asymmetric catalysis that electronic properties of boryl ligands could potentially provide. Herein, we present the concise synthesis of chiral boryl ligands with readily available backbones and their application in iridium-catalyzed asymmetric C-H activation borylation of aromatic C-H bonds.



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## Mechanistic Insight on Carbohydrate Catalyzed Alkene Diboration reaction

Lu Yan<sup>a</sup>, James. P. Morken<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

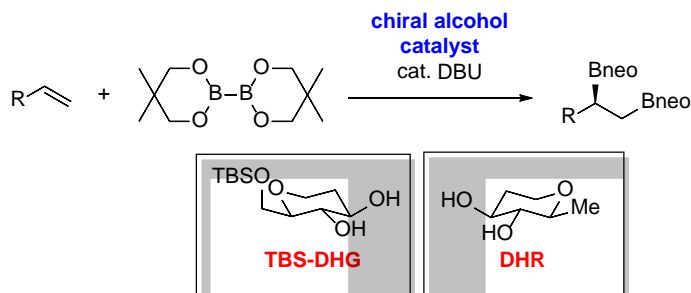
[yanlu@bc.edu](mailto:yanlu@bc.edu); [morken@bc.edu](mailto:morken@bc.edu)



### ABSTRACT

Catalytic enantioselective 1,2-diboration of alkenes is a useful way for transforming alkenes into a variety of functionalized compounds.<sup>1</sup> Most often, this process is facilitated by transition metal catalysis. Alternatively, Fernandez made the remarkable report that alkene 1,2-diboration reaction can be catalyzed by alkaline metal alkoxides.<sup>2</sup> Although Fernandez make efforts on rendering the metal-free alkene diboration reaction enantioselective, only modest enantioselective (40% ee) was achieved by using 2.0 equivalents of chiral alcohol.<sup>3</sup> In 2016, we described an enantioselective alkene diboration reaction catalyzed by carbohydrate-derived glycols (Scheme 1).<sup>4</sup>

Scheme 1. Glycol-Catalyzed Alkene Diboration



While preliminary studies revealed an operating system works with terminal alkenes with decent yield and good enantioselectivity, they also exposed to several limitations: long reaction time and restricted substrate scope (insufficient reaction with other than terminal alkenes). To allow for a deeper understanding of the glycol-catalyzed alkene diboration reaction system, detailed mechanistic study such as kinetic studies, DOSY NMR studies, and DFT calculations were applied. These studies provide an understanding of the origin of stereoselectivity and also reveal a strategy for enhancing reactivity and broadening the substrate scope.<sup>5</sup>

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## Differentially Protected Vicinal Amino Alcohols by Catalytic, Enantioselective Additions of MEMO-Substituted Allylboron Compounds to Phosphinoylimines

Ryan J. Morrison, Amir Hoveyda\*

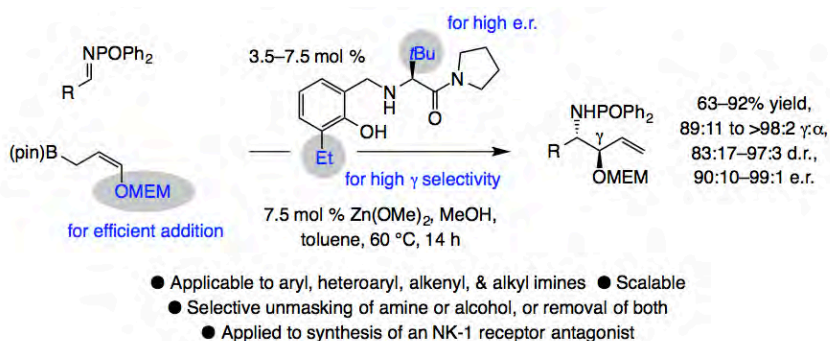
Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill 02467

ryan.morrison.4@bc.edu; amir.hoveyda@bc.edu



### ABSTRACT

A method for catalytic,  $\gamma$ -, diastereo-, and enantioselective addition of MEMO-substituted allyl B(pin) compounds to phosphinoylimines (MEM = methoxyethoxymethyl, pin = pinacolato) is presented. The identity of the optimal protecting group for the organoboron reagent and that of the catalyst was determined by consideration of the steric and electronic requirements at different stages of the catalytic cycle; namely, generation of the chiral allylboronate, the subsequent 1,3-borotropic shift, and the addition. Aryl-, heteroaryl-, alkenyl-, and alkyl-substituted, and differentially protected, vicinal amino alcohols were accessed in 43 – 92% yield, 89:11 to >98:2  $\gamma$ : $\alpha$  selectivity, 83:17 – 97:3 diastereomeric ratio, and 90:10 – 99:1 enantiomeric ratio. The method is scalable; the phosphinoyl and MEM groups can be removed selectively or simultaneously. Utility is highlighted by an enantioselective formal synthesis of an NK-1 receptor agonist.



## Recent Advances in the Development of Diels-Alder Reactions of Unsaturated Organoboron Compounds

Noelia S. Medrán, Federico Dezotti, Juan M. Ramos Marchena, Gustavo O. Terrestre, Sebastián O. Simonetti and Silvina C. Pellegrinet\*

*Instituto de Química Rosario (CONICET), Facultad de Ciencias Bioquímicas y Farmacéuticas, Universidad Nacional de Rosario, Suipacha 531, Rosario, Argentina*  
*pellegrinet@iquir-conicet.gov.ar*



### ABSTRACT

The Diels-Alder (DA) reactions of unsaturated boron compounds are fascinating transformations with great synthetic potential and interesting mechanistic features.<sup>1,2</sup> In 2010, we reported that the DA reactions of vinylboronates occurred readily under microwave irradiation.<sup>2a</sup> Later, we described the DA reactions of a variety of pinacol alkenylboronic esters.<sup>2d</sup> More recently, we proved that  $\alpha$ -hydroxyacids accelerate the DA reaction of dibutyl vinylboronate with cyclopentadiene.<sup>2e</sup> Theoretical calculations and NMR studies indicated that ligand exchange gives rise to the reactive acyloxyborane species. In the past years we have been devoted to rationally design improved organocatalysts in terms of catalytic activity and enantioselectivity by introducing diverse substituents in the  $\alpha$ -hydroxyacid and to extend the scope of the reaction. Also, we have ventured into the development of new DA reactions of other unsaturated organoboron compounds. Along these lines, we have found that boron-containing heterocyclic compounds participate in DA reactions. The effect of the substitution pattern has been investigated with experimental and theoretical tools.

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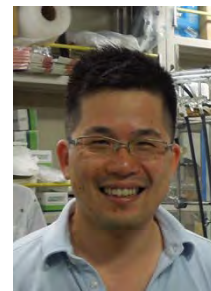
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## Reactivity of B–B Bond in Highly Lewis Acidic Diborane(4)

Makoto Yamashita\*

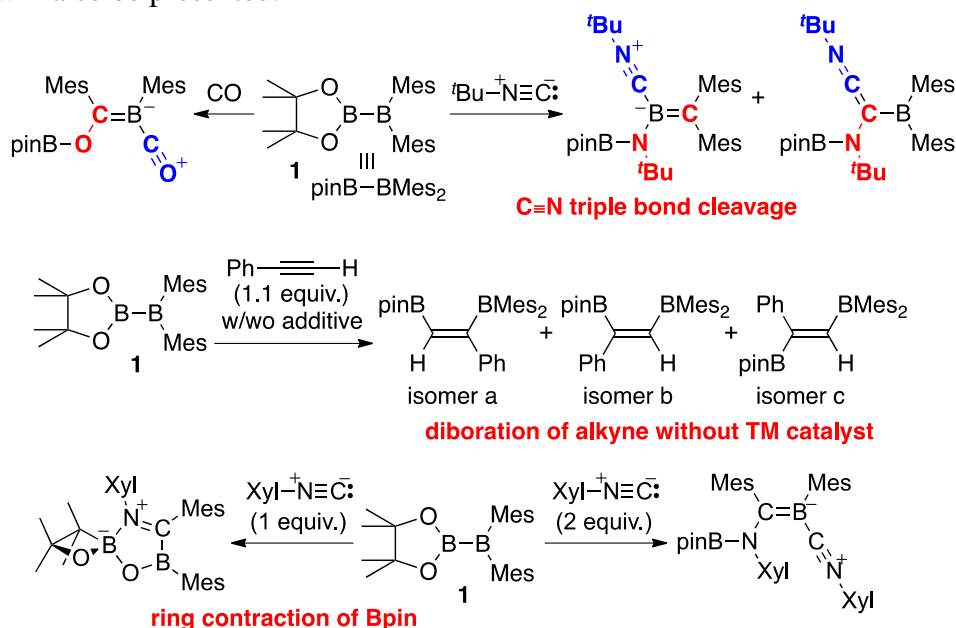
Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

makoto@oec.chembio.nagoya-u.ac.jp



### ABSTRACT

Recently, we reported easy and scalable synthesis of novel unsymmetrical diborane(4), pinB-BMes<sub>2</sub> (**1**). This compound showed unique reactivity towards C≡O and C≡N triple bond in carbon monoxide and *tert*-butylisocyanide.<sup>[1]</sup> The latter reaction involved a cleavage of C≡N triple bond of isocyanide in the absence of transition metal reagent or catalyst. The strong Lewis acidity of **1** was originated from lowering LUMO level due to overlapping two vacant p-orbitals of pinB and BMes<sub>2</sub> groups as supported by DFT calculation.<sup>[2]</sup> The unsymmetrical diborane(4) **1** also exhibited reactivity toward C≡C triple bond of alkynes to form diborylalkenes having diarylboryl unit.<sup>[3]</sup> In the lecture, complicated mechanisms of these unique reactions and the related diborane(4) chemistry will also be presented.



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## A Boron Cluster-Based Approach to Nucleophilic Borylation

Alexander M. Spokoyny<sup>a,\*</sup>

<sup>a</sup>*Department of Chemistry and Biochemistry and the California Nanosystems Institute (CNSI), University of California, Los Angeles, Los Angeles, CA 90095.  
Email: [spokoyny@chem.ucla.edu](mailto:spokoyny@chem.ucla.edu)*



### ABSTRACT

Functionalization of organic substrates by means of creating boron-carbon bonds has emerged as one of the most powerful tools in synthetic chemistry over the past several decades. Most of these methods normally rely on reagents where a boron site formally behaves as an electron-poor Lewis acid. Recently, several classes of isolable compounds where boron can be rendered electron-rich and nucleophilic have been discovered. Despite these efforts, the synthetic utility of these nucleophilic boron reagents has been limited given the multistep protocols needed for their synthesis as well as their poor stability to air and moisture. Furthermore, sterically encumbering ligand scaffolds with high molecular weight are often needed to stabilize a highly reactive nucleophilic boron site, which renders these systems less practical as stoichiometric reagents.

In this presentation, we will showcase recent work from our laboratory focused on addressing these challenges. Specifically, we developed a conceptually different approach toward generating a source of nucleophilic boron via three-dimensional delocalization instead of steric protection. We discovered that the reaction of small and air-stable boron clusters with benzyl and alkyl halides as well as pseudohalides under mild conditions affords compounds featuring B-C bonds. Importantly, unlike the dodecaborate ( $B_{12}$ -based) cluster system, which is well known to resist degradation even under exceedingly harsh conditions, electrochemical studies of these clusters reveal an irreversible one-electron oxidation, indicating degradative cage rupture. Our preliminary results suggest that this redox instability may be harnessed to conveniently prepare benzyl and alkyl pinacol boron ester derivatives by controlled cage decomposition in good yields. The nucleophilic character of the small boron clusters may also be applied to main-group electrophiles (e.g.,  $Me_3SiCl$ ,  $R_2PCl$ ) to generate the corresponding compounds in nearly quantitative yields.

We are currently developing this chemistry further in the context of late-stage functionalization of complex molecules. We envision subsequent transfer and/or addition chemistry using these reagents to be a highly valuable addition to the chemist's synthetic arsenal.



## Transition Metal Complexes of Diborane(4) and Diborene(2)

Sundargopal Ghosh

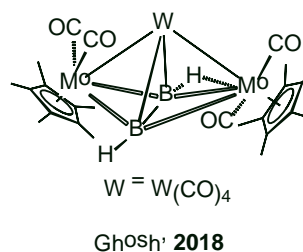
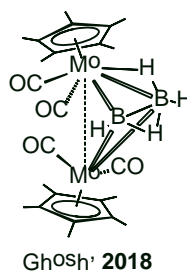
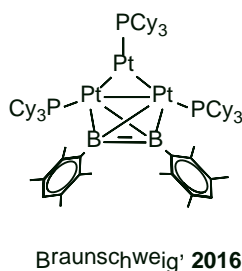
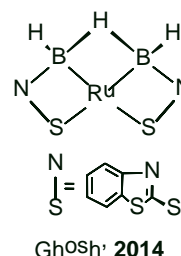
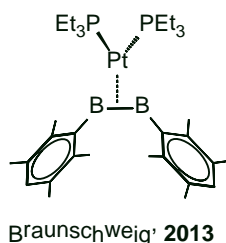
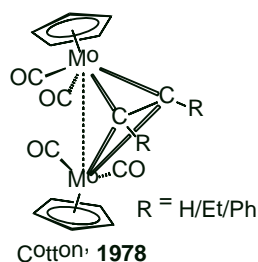
Department of Chemistry, Indian Institute of Technology Madras, Chennai 600  
036, India

Email: sghosh@iitm.ac.in



### ABSTRACT

The field of transition metal boron chemistry that signifies the compounds with highest vertices to single boron has experienced rebirth during the past several decades. Amid the several boranes known, the chemistry of diborane compounds, particularly the derivatives of  $B_2H_6$  and  $B_2H_4$  been extensively explored for the broad understanding of the chemical bonding and catalysis. Furthermore, diborane(4) compounds have been utilized as relevant starting materials to generate electron precise metal–boron bonds<sup>[1]</sup>. Diborane(4) can act as a bridging ligand between two transition metals with an unbroken B–B bond<sup>[2]</sup>. Based on the progress of the structures of hydrogen-substituted diborane compounds, shown below in Chart<sup>[3]</sup>, it appears rather surprising that the search for the simple bimetallic transition metal diborane(4) species met with very little success. As a result, the synthesis, chemistry and detailed bonding description of such species became of interest. The key results of this work will be presented.



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## Formation and Property of Asymmetric B=B Bond

Rei KINJO<sup>a,\*</sup>

<sup>a</sup>Nanyang Technological University, 21 Nanyang Link SPMS-CBC 06-20,  
Singapore, 637371

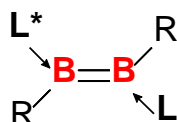
rkinjo@ntu.edu.sg



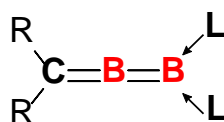
### ABSTRACT

In 2007, Robinson and co-workers demonstrated that by employing N-heterocyclic carbenes (NHCs) as the supporting ligands, a metal free and neutral diborene IDip·HB=BH·IDip (IDip = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) can be synthesized.<sup>[1]</sup> Since this milestone, a variety of diborenes supported by Lewis bases have been developed and structurally characterized.<sup>[2]</sup> The extant isolable diborenes are limited to the symmetric derivatives involving the same Lewis base on each B atom, and the study of asymmetrically supported diborene derivatives has remained unexplored thus far.<sup>[3]</sup>

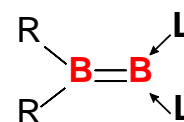
In this presentation, synthesis, X-ray diffraction analysis, computational studies and reactivity of various organoboron derivatives involving the asymmetric boron-boron double bond<sup>[4-6]</sup> will be described. The relevant recent results will also be presented.



**Asymmetric diborene**



**Allenic diborene**



**gem-diborene**

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## Imbedding Metal Triangles in Polyhedral Borane Matrices: A Theoretical Study

R. Bruce King<sup>a</sup>, Amr A. A. Attia,<sup>b</sup> and Alexandru Lupan<sup>b</sup>

<sup>a</sup>Department of Chemistry and Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602, USA

<sup>b</sup>Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca, Romania



### ABSTRACT

The syntheses and structural characterization of the capped octahedral complexes  $\text{Cp}^*_3\text{M}_3\text{B}_4\text{H}_4$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ ;  $\text{Cp}^* = \eta^5\text{-Me}_5\text{C}_5$ ) and the unusual 11-vertex tungsten hydride  $\text{Cp}^*_3\text{W}_3(\mu\text{-H})\text{B}_8\text{H}_8$  (Figure 1) indicate the feasibility of imbedding metal triangles into polyhedral borane matrices. In order to provide a better understanding of such species the systems  $\text{Cp}_3\text{M}_3\text{B}_{n-3}\text{H}_{n-3}$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ ),  $\text{Cp}_3\text{Re}_3\text{B}_{n-3}\text{H}_{n-3}$ , and  $\text{Cp}_3\text{W}_3(\text{H})\text{B}_{n-3}\text{H}_{n-3}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) have been investigated by density functional theory.

For the group 9 metal systems ( $\text{M} = \text{Co}, \text{Rh}, \text{Ir}$ ) the experimentally observed 7-vertex capped octahedral  $\text{Cp}_3\text{M}_3\text{B}_4\text{H}_4$  structures have the lowest energies. The unknown 8-, 9-, and 11-vertex systems are predicted to have *closo* structures whereas the 10-vertex system, known experimentally in  $\text{Cp}^*_3\text{Rh}_3\text{B}_7\text{H}_7$ , is predicted to have an *isocloso* structure in accord with experiment. More interestingly, the 12-vertex  $\text{Cp}_3\text{M}_3\text{B}_9\text{H}_9$  systems are predicted not to have icosahedral structures but instead structures with a central alternative 12-vertex deltahedron having two degree 6 vertices balanced by two degree 4 vertices.

For the early transition metals, the five lowest energy structures for the 11-vertex  $\text{Cp}_3\text{W}_3(\text{H})\text{B}_8\text{H}_8$  gratifyingly have the same central  $\text{W}_3\text{B}_8$  deltahedron as the experimental structure. They differ only by the location of the “extra” hydrogen atom. Other  $\text{Cp}_3\text{W}_3(\text{H})\text{B}_{n-3}\text{H}_{n-3}$  systems exhibit related low-energy structures having tungsten atoms at degree 5 to 7 vertices and boron atoms at degree 3 to 5 vertices. The trirhenium  $\text{Cp}_3\text{Re}_3\text{B}_{n-3}\text{H}_{n-3}$  systems lacking the “extra” hydrogen atom follow a similar pattern. In these tungsten and rhenium trimetallaboranes with  $\text{M}_3$  triangles imbedded into a polyhedral borane matrix, M–M bonds on the surface of the polyhedron of lengths  $\sim 2.6$  to  $2.7$  Å are typically shorter than the M–M bonds of lengths  $\sim 2.8$  to  $3.0$  Å through the interior of the  $\text{M}_3\text{B}_{n-3}$  deltahedron.

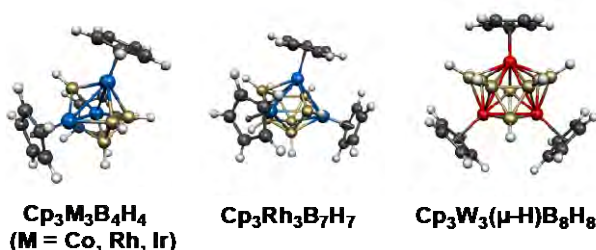


Figure 1. Experimentally known trimetallaborane structures.

## Cobalt(3+), copper(2+) and zinc(2+) complexes with hydroxyoxidoborates

Mohammed A. Altahan<sup>a</sup>, Michael A. Beckett<sup>a\*</sup>, Peter N. Horton<sup>b</sup>

<sup>a</sup> School of Chemistry, Bangor University, Bangor, LL57 2SX, UK

<sup>b</sup> School of Chemistry, Southampton University, Southampton, S017 1BG, UK  
m.a.beckett@bangor.ac.uk



### ABSTRACT

Hydroxyoxidoborates are anionic boron species with boron atoms solely bound to oxygen atoms; such compounds are commonly referred to as ‘borates’. The hydroxyoxidoborate name is more informative and avoids confusion with hydridoborates which are also commonly referred to borates.

Hydroxyoxidopolyborates are readily synthesized by solvothermic methods or from the addition of B(OH)<sub>3</sub> to a basic aqueous solution containing templating cations.<sup>[1]</sup> Generally, the hydroxyoxidopolyborate salts obtained from aqueous solution contain discrete, insular anions. This occurs since boric acid in basic aqueous solution exists as a dynamic combinatorial library of many such polyborate anions. Pentaborate(1-) salts, containing the [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sup>-</sup> anion, are most readily formed and this is because these salts have a very strong H-bonded anionic lattice that is able to accommodate many small-sized to medium-sized cations.<sup>[2]</sup> Salts containing other polyborate anions are known but are less commonly encountered.<sup>[1]</sup>

We are interested in the synthesis of structurally novel hydroxyoxidopolyborate anions and have adopted a strategy of templating such species by the use of either sterically demanding and/or highly charged transition-metal complexes. We have recently reported the synthesis of several salts containing isolated polyborate anions partnered with transition-metal complexes and have describe the synthesis and structures of two novel isolated polyborate anions *viz.* heptaborate(3-)<sup>[3]</sup> and octaborate(2-).<sup>[4]</sup> We now report some novel species containing copper(2+)<sup>[5]</sup> and zinc(2+)<sup>[6]</sup> centers with ‘isolated’ polyborate anions *e.g.* pentaborate(1-), hexaborate(2-), dodecaborate(6-), within their primary coordination shell.

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## Interplay of Boron and Nitrogen – A Stable Organic Neutral Diradical via Reversible Coordination

Hermann A. Wegner,<sup>\*a</sup> Zhenpin Lu,<sup>a,b</sup> Henrik Quanz<sup>a</sup>

<sup>a</sup> Institut für Organische Chemie, Justus-Liebig-Universität,  
Heinrich-Buff-Ring 17, 35392 Giessen, Germany

<sup>b</sup> Present Addresses: University of Cambridge, Department of Chemistry,  
Lensfield Road, Cambridge, CB2 1EW UK  
[hermann.a.wegner@org.chemie.uni-giessen.de](mailto:hermann.a.wegner@org.chemie.uni-giessen.de)



### ABSTRACT

As organic diradicals are deemed fleetingly existent it is generally rather difficult to prepare and trap them to study their unique structures.<sup>[1]</sup> In the presentation the formation of a stable neutral diboron diradical simply by coordination of an aromatic dinitrogen compound to an *ortho*-phenyldiborane is demonstrate.<sup>[2]</sup> The diradical has been characterized *inter alia* by X-ray analysis, NMR, IR, UV-spectroscopy and its structure supported by computations. This process is reversible upon addition of pyridine. Computations are consistent with an open-shell triplet diradical with a very small singlet-triplet energy gap that is indicative of the electronic disjointness of the two radical sites. This opens a new way of generating stable radicals with fascinating electronic properties useful for a large variety of applications.

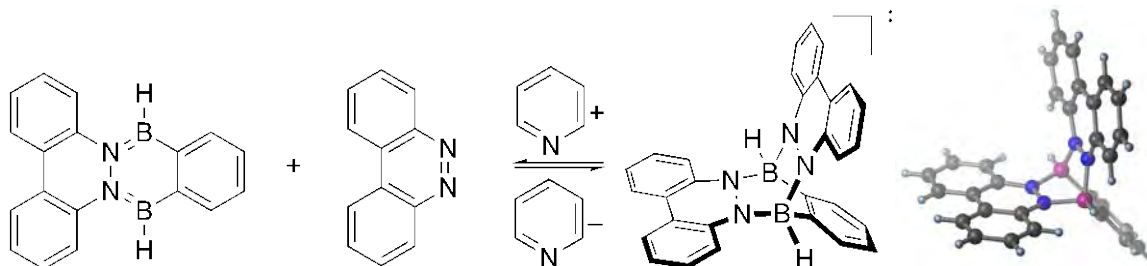


Figure 1. Reversible formation of the diradical upon coordination with pyridine and solid state structure (right).

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## “Large Bite” Diboranes for the Complexation of Diatomic Anions and Molecules

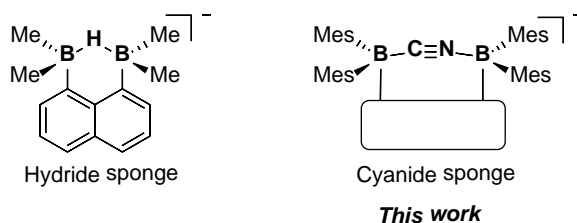
François P. Gabbai

Department of Chemistry, Texas A&M University, College Station, Texas  
77843-3255, United States  
francois@tamu.edu



### ABSTRACT

The chemistry of main group-based polydentate Lewis acids continues to be a vibrant field of research because of applications in catalysis, anion transport, and anion sensing. Diboranes featuring the rigid 1,8-naphthalenediyl or *ortho*-phenylene backbone have been extensively investigated. Owing to the short distance separating the two boron atoms, these diboranes are well-suited for the chelation of monoatomic anions or polyatomic anions amenable to the  $\mu(1,1)$  coordination mode. Bearing in mind that this selectivity could be altered by modification of the backbone architecture, we have recently become interested in bidentate Lewis acids that display a large spacing between the Lewis acidic centers.<sup>1,2</sup> By analogy with the pioneering work of Katz on the hydride sponge,<sup>3</sup> it occurred to us that such systems could behave as sponges toward diatomic anions. In this presentation, we will introduce a new family of diboranes in which the two boron atoms are connected by the 1,8-biphenylenediyl and 1,8-triptycenediyl backbones.<sup>4</sup> In addition to reporting on the electrochemical and spectroscopic properties of these compounds, we will also describe their anion binding properties and their affinity for the cyanide anion which is accommodated within the diboron pocket in a  $\mu(1,2)$  fashion. We will also show that these diboranes can sequester neutral, dibasic molecules.



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## C-B Bond Formation Using Boron Lewis Acids and Alkynes or Alkenes

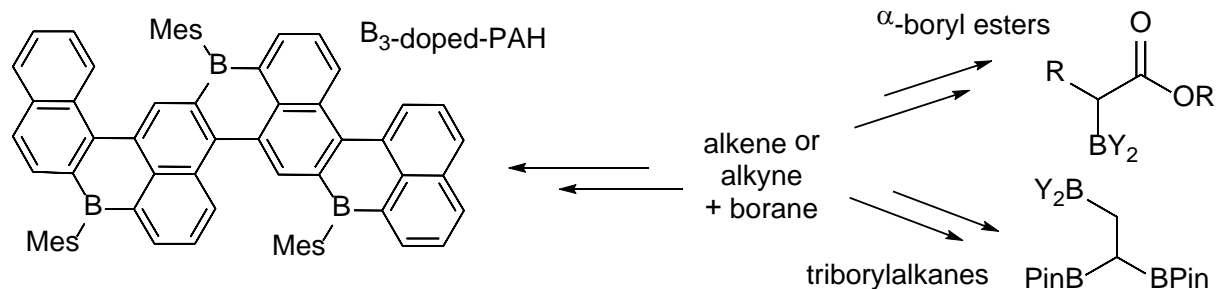
Michael J. Ingleson\*

School of Chemistry, University of Manchester, Manchester, UK, M13 9PL  
 michael.ingleson@manchester.ac.uk



## ABSTRACT

The functionalisation of alkynes and alkenes using boron Lewis acids is a well-established field, with many venerable examples, most notably hydroboration, and “named” reactions such as the Zweifel and Wrackmeyer reactions (amongst others).<sup>[1]</sup> Despite this long history new reactions, or modifications on established reactions, have recently been reported that represent useful ways to generate new C-B bonds. We and others have explored the borylative cyclisation<sup>[2]</sup> reaction as a simple way to concomitantly form C-B and C-Y (Y = O, N, S, C) bonds thereby provide access to (i) a range of synthetically desirable boronic acid derivatives,<sup>[3]</sup> and (ii) when borylative cyclisation is coupled with the boron-Friedel Crafts reaction, boron containing polycyclic aromatic hydrocarbons (PAHs).<sup>[4]</sup> This talk will discuss latest results functionalizing alkenes and alkynes with boron electrophiles, including a selection from our studies on forming B-doped-PAHs,  $\alpha$ -boryl esters and 1,1,2-triborylalkanes by a borane initiated Zweifel reaction.



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## Reactivity and Catalytic Activity of Boron Cations

Ching-Wen Chiu\*

Department of Chemistry, National Taiwan University, No. 1, Section 4,  
Roosevelt Road, Taipei, Taiwan 10617  
cwchiu@ntu.edu.tw



### ABSTRACT

The avidity of tricoordinate boron atom towards electron densities has rendered neutral and cationic boron derivatives versatile reagents in organic synthesis. In addition to stoichiometric reactions, electron deficient perfluorinated boranes are also effective catalysts for reactions including hydrogenation, hydroboration, and hydrosilylation. As the utility of borane catalyst is continuously expanding in the past few years, boron cation catalyst has also received considerable interests.<sup>[1]</sup> Besides the well-established oxazaborolidine-type catalysts, carbene and pyridine stabilized borenium cations were also proven to be active in hydrogenation of imine,<sup>[2]</sup> hydrosilylation of carbonyl compounds,<sup>[3]</sup> and hydroboration of alkene.<sup>[4]</sup> However, catalytic activity of borinium cation, a ligand-free di-coordinate boron cation, has never been explored. To stabilize the highly electron deficient boron center of borinium cation, we decided to introduce the electronically and coordinatively flexible substituent to the system. Thus, we have prepared the Cp\*-substituted hypercoordinated borinium cations and investigated their catalytic performance.<sup>[5]</sup> In this presentation, the catalytic hydrosilylation of carbonyl compounds using the newly prepared hypercoordinated borinium cations will be discussed. Mechanistic studies revealed that two independent reaction pathways leading to two different products were involved. Since the two reaction pathways are close in energy, the product distribution is highly sensitive to the steric and electronic properties of carbonyl compound.

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## "Electronic Asymmetry of 1,2-Azaborine Leads to Differential Reactivity of C(4) and C(5) Borylated Isomers"

Cameron McConnell, Shih-Yuan Liu\*

Department of Chemistry, Boston College

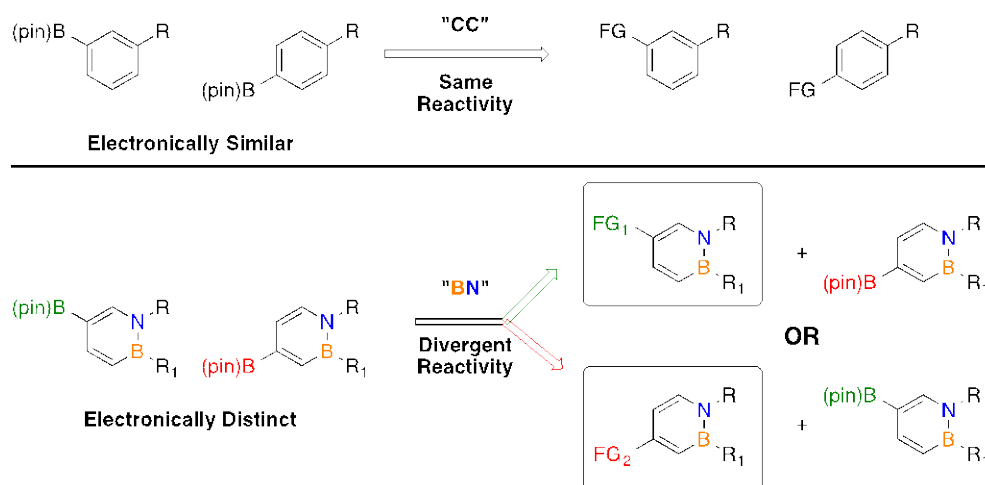
2609 Beacon St. Chestnut Hill, MA 02467

cameron.mcconnell@bc.edu; shihyuan.liu@bc.edu



### ABSTRACT

Examples of differential reactivity of positional isomers of borylated arenes in the literature are very rare.<sup>1</sup> The inherent electronic asymmetry of BN/CC isosterism provides a unique opportunity to discriminate between all six positions on the azaborine ring, allowing for the creation of libraries of biologically relevant compounds.<sup>2</sup> Chemical separation of the C(4)-Bpin and C(5)-Bpin positional isomers of 1,2-azaborine is made possible by their distinctive electronic properties. Treatment of a 1:1 mixture of the two isomers with NMO results in a kinetic resolution where the C(4) position is oxidized while the C(5)-Bpin remains untouched. Conversely, the C(5)-Bpin reacts preferentially to the C(4) isomer when subjected to Ir-catalyzed proto-deborylation with methanol. Reaction with diethanolamine results in an equilibrium process that completely favors the C(4) transesterified product which can be separated from the C(5)-Bpin. This work provides a practical route to divergent, regioselective functionalizations of the synthetically challenging C(4) and C(5) positions of 1,2-azaborines. Detailed kinetic studies of the aforementioned reactions provide insight into the electronic properties of the two positions.



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## Development of an Iron-Catalyzed Suzuki-Miyaura Cross-Coupling Reaction Between Alkyl Halides and Unactivated Aryl Boronic Esters

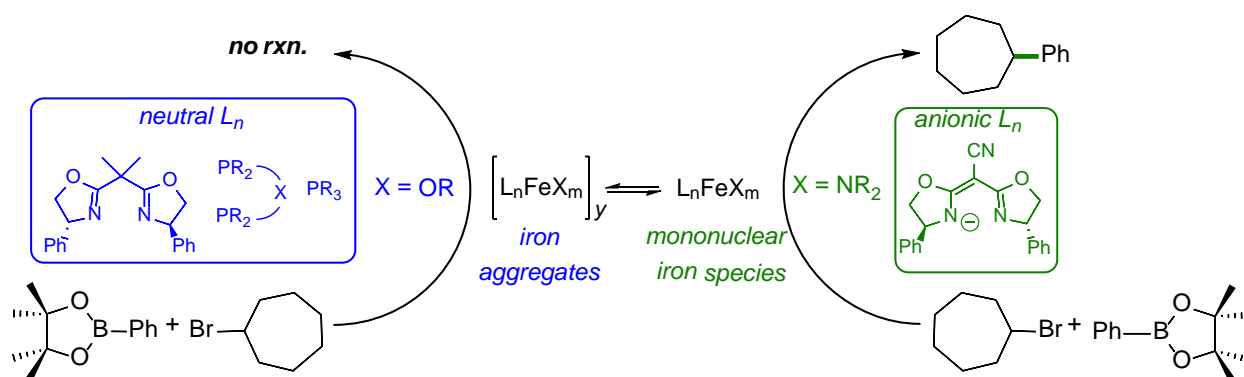
Michael P. Crockett<sup>a</sup>, Chet C. Tyrol<sup>a</sup>, Alexander S. Wong<sup>a</sup>, Jeffery A. Byers<sup>a\*</sup>

<sup>a</sup>Boston College, Department of Chemistry, Chestnut Hill, MA 02467  
Michael Crockett – [crockemi@bc.edu](mailto:crockemi@bc.edu) Jeffery Byers – [byersja@bc.edu](mailto:byersja@bc.edu)



### ABSTRACT

An iron-catalyzed Suzuki-Miyaura cross-coupling reaction between alkyl halides and aryl boronic acids was developed. Unlike previous iron-catalyzed Suzuki-Miyaura reactions, this method does not rely on preactivation of the boronic ester starting material. Using mechanistic insight into palladium-catalyzed Suzuki Miyaura as a guide, amide bases (instead of alkoxides) were found to be effective in facilitating iron-catalyzed cross-coupling reactions. Iron complexes comprised of deprotonated cyanobis(oxazoline) ligands were most suitable to obtain high yields in catalytic cross-coupling reactions. Yields up to 85% were obtained for cross-coupling reactions with a variety of primary and secondary alkyl bromides, chlorides, and iodides. Additionally, electron rich and electron deficient aryl boronic esters were tolerated. Initial mechanistic investigations suggest the presence of radical intermediates and the critical importance of avoiding conditions that lead to iron aggregates, which hinder catalytic turnover.



## **Boron in catalysis: Borenium ions and cross-coupling transformations of multiply borylated molecules**

Cathleen Crudden

*Queen's University, Kingston, Ontario, Canada  
cruddenc@chem.queensu.ca*

### **ABSTRACT**

The use of boron-cations, specifically borenium ions, as catalysts for organic transformations will be presented. Our group has found that the use of meso-ionic boranes as supporting ligands for borocations results in catalysts that are highly robust and can be used for hydrogenations without rigorous exclusion of moisture. Further efforts to increase their robustness by the use of hemilabile ligands will be addressed.

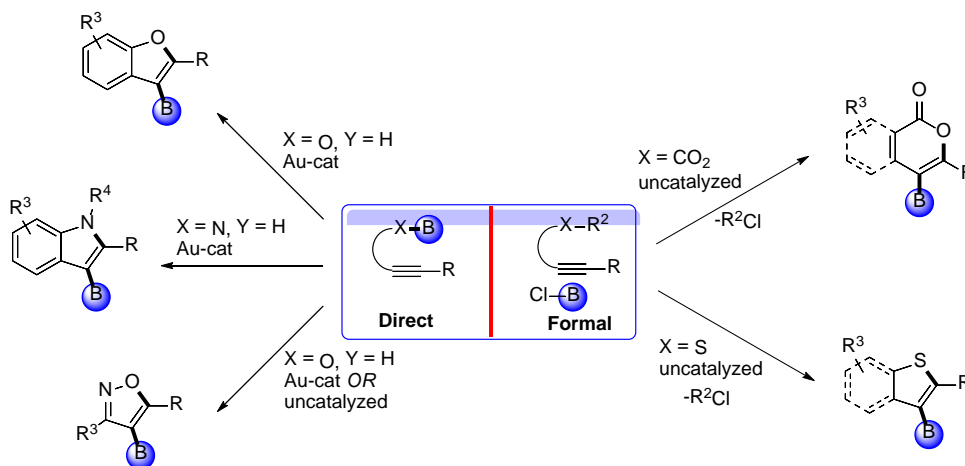
The use of boron in cross coupling chemistry as a reagent is well preceded and our group has shown that molecules with multiple boron substituents can be orthogonally coupled by virtue of transmetalation activity. In this talk, we will present new cross coupling reactions of organoboranes with multiple boron substituents on a single atom.

## Borylative Heterocyclization: Oxyboration, Aminoboration, and Thioboration

Suzanne A. Blum\*

Chemistry Department, University of California, Irvine,  
Irvine CA 92697-2025

Organoboron compounds and heterocycles are powerful building blocks and precursors for organic synthesis, including for drug discovery, and for agrochemical and material synthesis. The common strategy for the synthesis of borylated heterocycles involves two separate synthetic steps: first, synthesis of the heterocyclic core, and second, borylation of the core through established methods such as transition metal-catalyzed C–H or C–X activation/borylation or lithiation/borylation. We describe our laboratory's development of borylative heterocyclization reactions that access the heterocyclic core and install boron in one synthetic step.<sup>1</sup> These methods provide complementary bond disconnections, regiochemistry, and functional-group compatibility to current methods. We describe our methods with two categories: A direct borylation method that refers to addition reactions starting from a preformed B–element  $\sigma$  bond, which are essential in the mechanistic route to product formation, and a formal borylation method that refers to addition reactions that do not require formation of a B–element bond but instead, proceed through carbon–carbon  $\pi$  bond activation by an electrophilic boron source.



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## Anodic Oxidation of $\text{CB}_{11}\text{H}_{12}(-)$ Derivatives

Jiří Kaleta<sup>a</sup>, Jiří Ludvík<sup>b</sup>, Josef Michl<sup>b,c,\*</sup>

<sup>a</sup> *Institute of Organic Chemistry and Biochemistry AS CR, Flemingovo nám. 2, 16610 Prague 6, Czech Republic*

<sup>b</sup> *J. Heyrovský Institute of Physical Chemistry, Dolejškova 3, 18223 Prague, Czech Republic*

<sup>c</sup> *Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, U.S.A.  
Josef.Michl@colorado.edu*



### ABSTRACT

We shall describe products of anodic oxidation of  $\text{CB}_{11}\text{H}_{12}(-)$  derivatives in acetonitrile, which range from simple ones to very complex ones, and shall consider possible mechanisms. An example of a simple process is the one-step formation of stable derivatives of the  $\text{CB}_{11}\text{H}_{12}(\cdot)$  radical, and an example of a complicated multistep process is the formation of highly alkylated anions formed by decarboxylation of 1-COOH- $\text{CB}_{11}\text{Me}_{11}(-)$ .

## Carborane Cluster Architectures Featuring Multiple Metal-Boron Interactions : Boranes, Boryls, and Carborynes

Dmitry V. Peryshkov\*

*Department of Chemistry and Biochemistry, University of South Carolina,  
631 Sumter St., Columbia, South Carolina 29208, United States.  
peryshkov@sc.edu*



### ABSTRACT

Development of novel molecular architectures capable of enforcing unique electronic and geometric environments of reactive metal centers is an important avenue of homogeneous catalysis. The unusual three-dimensional structure of icosahedral carborane is utilized in our research for the synthesis of metal complexes with novel bonding arrangements.

First examples of (BB)-carboryne complexes containing three-membered (BB)>M metallacycles, which are inorganic boron-based analogs of metal benzyne complexes, were synthesized.<sup>[1]</sup> Facile interconversion between carborane, carboranyl, and carboryne bonding modes plays an important role in reactivity of these metal complexes and leads to cooperative activation of organic substrates.<sup>[1]</sup> The role of metal-boron interactions in reactivity pathways for activation of organic substrates will be discussed.<sup>[2]</sup>

The three-dimensional structure of carboranes and strong electron-donating ability of their boron atoms led us to the selective synthesis of heterobimetallic complexes by the unique expansion of three-membered (BB)>Ru metallacycle by insertion of Lewis acidic cations.<sup>[3]</sup> The resulting complexes feature unusual B–M···Ru interactions that are isolobal to bridging borane coordination.

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## Directing Group Guided Transition Metal Catalyzed Carboranyl B-Heteroatom Bond Construction

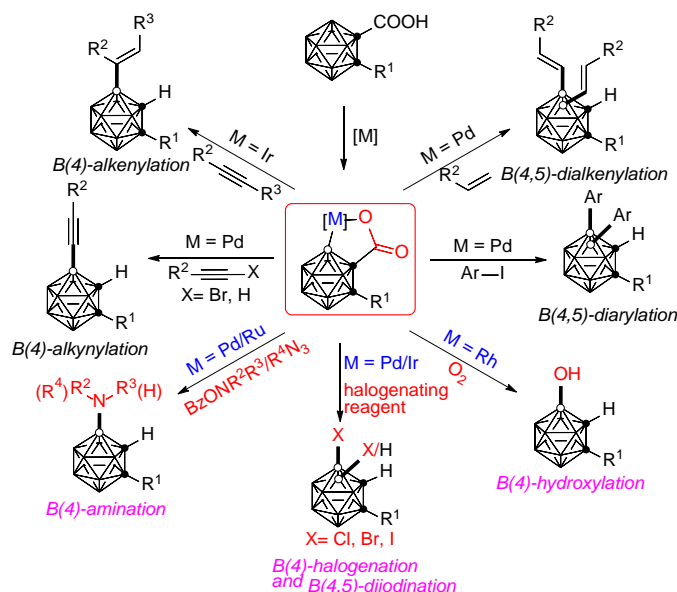
Yangjian QUAN\* and Zuwei XIE

*Department of Chemistry and State Key Laboratory of Synthetic Chemistry,  
The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China  
E-mail: yjquan@cuhk.edu.hk*



### ABSTRACT

To tackle the challenging regioselectivity issue resulting from chemically very similar ten BH vertices in *o*-carborane, we have introduced the directing group strategy into carborane chemistry. Subsequently, several efficient methods have been developed to construct cage B-C ( $sp^2$  and  $sp^3$ ) bonds via transition metal catalyzed selective and straightforward B-H activation.<sup>[1]</sup> On the basis of these achievements and in view of the valuable applications of heteroatom-containing carborane derivatives in coordination chemistry and medicine, we conceive to extend our research to B-heteroatom bond formation. Recently, transition metal catalyzed straightforward and efficient cage B-H amination, hydroxylation and halogenation have been realized with the help of  $-COOH$  directing group.<sup>[2]</sup> The in-situ removed carboxyl directing group plays an important role not only in controlling site-selectivity but also in regulating the degree of functionalization.



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## Selective Catalytic Functionalization of Anionic Boron Clusters

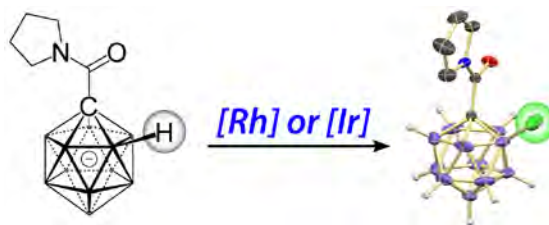
Yunjun Shen<sup>a</sup>, Furong Lin<sup>a</sup>, Yuanbin Zhang<sup>a</sup>, Simon Duttwyler<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Zhejiang University,  
38 Zheda Road, 310027 Hangzhou, P.R. China  
duttwyler@zju.edu.cn



### ABSTRACT

Boron cage compounds based on the dicarba-*closo*-dodecaborane  $C_2B_{10}H_{12}$ , monocarba-*closo*-dodecaborate  $[CB_{11}H_{12}]^-$  and *closo*-dodecaborate  $[B_{12}H_{12}]^{2-}$  scaffolds are icosahedral cluster compounds which feature sphere-like delocalization of electron density, leading to remarkable chemical and thermal stability. The past decade of research has revealed their potential for applications in areas such as coordination, supramolecular and medicinal chemistry, as well as fluorescence/phosphorescence and materials science.<sup>[1,2]</sup> In order to take advantage of boron clusters as useful products or building blocks, new methodologies that allow for selective functionalization are highly desirable.



B–H activation as a strategy to convert unfunctionalized vertices to B–X bonds (X = C, N, O, halogen) has been shown to be a step-economic way to prepare tailor-made clusters.<sup>[3]</sup> On the other hand, transition metal-catalyzed derivatization of the anionic cages  $[CB_{11}H_{12}]^-$  or  $[B_{12}H_{12}]^{2-}$  is a young field of research.<sup>[4]</sup> Recently, our group has demonstrated the feasibility of direct B–H activation of these clusters mediated by rhodium and iridium complexes.<sup>[5–7]</sup> The synthetic methodologies, X-ray crystal structures of products and reactive intermediates as well as applications will be discussed.

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## Phenylboronic Ester as a Sensitive Block Linkage in Block Copolymer Micelles. Lactic Acid- and Glucose-Responsive nanoparticles.

Mariusz Uchman<sup>a\*</sup>, David Vrbata<sup>a</sup>

<sup>a</sup> *Soft Matter Group, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, 12843 Prague, Czechia*

*Email: uchman@natur.cuni.cz*



### ABSTRACT

The present study describes the synthesis, self-assembly and responsiveness to glucose and lactic acid of biocompatible and biodegradable block copolymer micelles using phenylboronic ester as the linker between hydrophobic poly( $\epsilon$ -caprolactone) (PCL) and hydrophilic poly(ethylene oxide) (PEO). The PCL block with pendant phenylboronic acid (PCLBA) was synthesized by combining  $\epsilon$ -caprolactone ( $\epsilon$ -CL) ring-opening polymerisation (ROP), using 4-hydroxymethyl(phenylboronic) acid pinacolate as the initiator. The glucose-terminated PEO (PEOGlc) was obtained by 1,3-dipolar, Cu(I)-catalysed, alkyne-azide cycloadding  $\alpha$ -methoxy- $\omega$ -propargyl poly(ethylene oxide) and 1-azido-1-deoxy-D-glucopyranose. PCLBA and PEOGlc blocks were linked in NaOH acetone solution, which was confirmed by ARS fluorescence and by <sup>1</sup>H NMR spectroscopy. Dialysis against water induced the self-assembly of PCLBA-*b*-PEOGlc nanoparticles, which were characterised by light scattering and by cryogenic transmission electron microscopy. Furthermore, the microscopic properties of the charged interface between the hydrophobic PCLBA core and the hydrophilic PEOGlc shell were examined by electrophoretic light scattering and fluorescence spectroscopy using the fluorescent probe 5-(*N*-dodecanoyl)aminofluorescein as pH indicator. Subsequently, the nanoparticles were transferred to a PBS buffer solution supplemented with different concentrations of glucose, to simulate the physiological conditions in blood, or lactic acid, to simulate acidic cytosolic or endosomal conditions in tumour cells. Thus, this novel block copolymer may contribute to the field of selective, lactic acid- and/or glucose-responsive drug delivery vehicle design under both pathological and physiological conditions.

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## Catalytic Approaches to New Types of Polycyclic BN Compounds

Chang Kailun<sup>a</sup>, Huanan Huang<sup>a</sup>, Chunming Cui<sup>a,b\*</sup>

[Please underline the name of the presenting author and indicate the corresponding author using \*]

<sup>a</sup>State Key Laboratory of Elemento-Organic Chemistry, Nankai University,  
Tianjin 300071, China

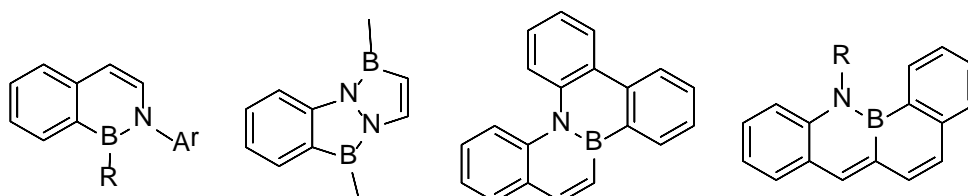
<sup>b</sup>Collaborative Innovation Center of Chemical Science and Engineering,  
Tianjin 300072, China  
cmcui@nankai.edu.cn



### ABSTRACT

Replacement of C=C bonds in poly-aromatic compounds by isoelectronic B-N bonds could effectively tune their electronic properties, leading to the discovery of new materials with improved photophysical properties. In this presentation, the catalytic approaches based on C-H activation for the efficient synthesis of new types of polycyclic BN aromatic compounds will be discussed.

In the past several years, our group has developed several efficient synthetic routes based on C-H cyclization of imines and transition metal catalyzed cyclization reactions for the synthesis of new types of mono and polycyclic BN aromatic compounds (Scheme 1). These compounds have been studied by UV-vis and fluorescent spectroscopic methods and DFT calculations. In addition, the chemistry of these compounds has also been studied. The results indicated that these compounds exhibited unique properties and chemistry.



**Scheme 1. The Structures of Representative Compounds Synthesized in the Group**

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## The synergy between theory and experiment in developing the basic science of new BN heteroaromatics

Anna Chrostowska<sup>a\*</sup>, Clovis Darrigan<sup>a</sup>, Alain Dargelos<sup>a</sup>, Alain Graciaa<sup>b</sup>,  
Shih-Yuan Liu<sup>c\*</sup>

<sup>a</sup>Université de Pau et des Pays de l'Adour, IPREM, UMR CNRS 5254; Av. de l'Université, 64 000 Pau, France. <sup>b</sup>Université de Pau et des Pays de l'Adour, LFC-R, UMR CNRS TOTAL 5150; Av. de l'Université, 64 000 Pau, France.

<sup>c</sup>Department of Chemistry, Boston College, Chestnut Hill, Massachusetts, USA  
[anna.chrostowska@univ-pau.fr](mailto:anna.chrostowska@univ-pau.fr); [liusd@bc.edu](mailto:liusd@bc.edu)



### ABSTRACT

The problem that all chemists encounter more and more often concerns the choice of the most promising target molecule for a given set of specifications. The direct application of difficult, time-consuming, and expensive syntheses, without a deep prior analysis, is oftentimes not optimal. The constant back-and-forth dialectic between computations and experiments creates useful connections between theoretical knowledge and practical use of scientific achievements. This synergistic approach between high-level theory and experiment is now being applied more frequently to enhance our comprehension and conceptualization of new systems. We present our recent work on boron(B)-nitrogen(N)-containing heteroaromatics<sup>[1-7]</sup> and highlight the synergy between computational electronic structure analysis and experimental physical characterization to develop a fundamental comprehension of physical and chemical properties of this emerging family of compounds.

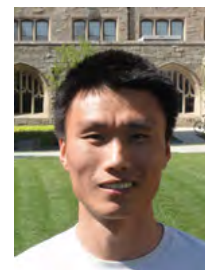
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## Synthesis, Characterization and Properties of Bis-BN Ullazines

Chenglong Li<sup>a</sup>, Jinyun Zhang<sup>a</sup>, Zhe Sun<sup>a</sup>, Yuming Liu<sup>a</sup>, Xuguang Liu<sup>a\*</sup>

<sup>a</sup>Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, People's Republic of China.  
xuguangliu@tjut.edu.cn



### ABSTRACT

Ullazine is polycyclic aromatic hydrocarbons containing a conjugated 16  $\pi$ -system with one nitrogen atom in the center, isoelectronic to pyrene. It was first synthesized by Balli and Zeller in 1983.<sup>[1]</sup> Ullazine has received extensive interest in the field of photovoltaic and particularly in dye-sensitized solar cells (DSCs).<sup>[2]</sup>

In this presentation, we will present the synthesis and property investigation of bis-BN-ullazines. Our synthesis is based on a highly efficient two-fold Friedel-Crafts-type electrophilic borylation reaction. A series of bis-BN ullazine derivatives, including the parent species, were synthesized in a small number of steps from commercially available materials. X-ray crystallographic analysis revealed that bis-BN ullazines have rigid and planar frameworks. The absorption and emission bands of these ullazines are blueshifted compared to those of their carbonaceous ullazine analogs. In addition, solvent-induced switching between two emitting states (the  $\pi, \pi^*$  state and the charge-transfer state) was observed for the as-synthesized bis-BN ullazines.<sup>[3]</sup>

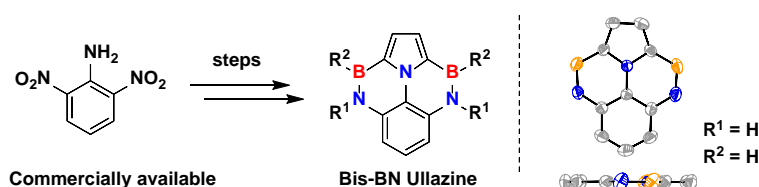


Figure 1. Bis-BN Ullazines

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## 9-Borafluorenes: Reagents to Access Inorganic Doped Polycyclic Aromatic Hydrocarbons

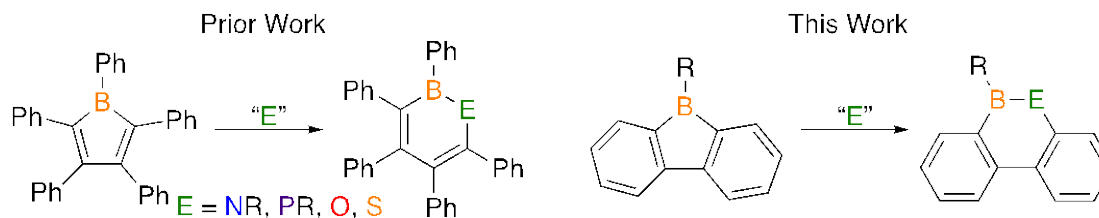
Caleb D. Martin<sup>a,\*</sup>

<sup>a</sup>Baylor University, One Bear Place #97348, Waco, TX 76798  
caleb\_d\_martin@baylor.edu



### ABSTRACT

The concept of inorganic doping by substituting boron and a lone-pair bearing heteroatom in place of a C=C unit in carbon-based aromatics is an attractive method to alter the electronic properties. Our group has been working on developing a facile route to access monocyclic inorganic/organic hybrid aromatic species via ring insertion reactions with anti-aromatic BC<sub>4</sub> heterocycles, namely boroles.<sup>[1]</sup> The insertion chemistry has been effective for the preparation of 1,2-azaborine,<sup>[2]</sup> 1,2-phosphaborine,<sup>[3]</sup> 1,2-oxaborine,<sup>[4]</sup> and 1,2-thiaborine<sup>[5]</sup> heteroarenes. Our efforts are now focused on extending conjugation in these inorganic/organic hybrid arenes to enhance their electronic properties. The strategy is to utilize a borole-based starting materials with two fused aryl groups, specifically 9-borafluorenes. The reactivity of the two anti-aromatic boracycles will be compared and the photophysical properties of the boron doped polycyclic aromatic hydrocarbon products analyzed.



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## IrC–H Borylation/Hydrogenation of Aromatic and Heteroaromatic Substrates

Timothy M. Shannon, Ryan M. Fornwald, Robert E. Maleczka, Jr., and  
Milton R. Smith, III\*

*Department of Chemistry, Michigan State University, East Lansing, MI 48824*  
*smithmil@msu.edu*



### ABSTRACT

Catalytic transformations of C–H bonds are now common. This wasn't always the case. Building from the first thermal, catalytic coupling of a borane and a hydrocarbon, our research group developed highly active iridium catalysts that exhibit unique regioselectivities for arene substitution and remarkable chemoselectivity for C–H functionalization.<sup>[1-4]</sup> For example, sp<sup>2</sup>-C–X bonds (X = Cl, Br, and I) that are commonly cleaved in reactions with late transition metal complexes are remarkably inert to the Ir catalysts. From the roadmap we created many other groups in academia and industry have made important contributions to C–H borylations. Extensions to heterocyclic substrates and development of one-pot, catalytic reactions where the C–B bonds that result are further transformed make C–H borylation particularly attractive to synthetic chemists. Unusual mechanistic aspects of C–H borylations will be discussed in the context of identifying and developing directing effects to add to the synthetic toolbox.<sup>[5]</sup> In addition, recent approaches to saturated, and partially saturated, cyclic and heterocyclic boronate esters will be presented. Specifically, this approach involves C–H borylation of C(sp<sup>2</sup>)–H bonds in aromatic and heteroaromatic compounds, followed by reductions with H<sub>2</sub> for borohydrides. The regioselectivities and relative stereochemistries of the saturated borylated compounds complement those typically seen for C–H borylations of C(sp<sup>3</sup>)–H bonds.

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## ***Boroscan – a Suite of Technologies to Enable Synthesis and Evaluation of Bioactive Boron-Containing Molecules***



Andrei K. Yudin\*

*Chemistry Department, University of Toronto  
80 St. George Street, Toronto, ON, M5S 3H6  
ayudin@chem.utoronto.ca*

### **ABSTRACT**

Boron is an abundant element on earth yet, despite its availability, C-B bonds are not present in the structures of natural products. This, however, does not mean that boron has no utility in chemical biology and drug discovery. On the contrary, there are numerous examples of bioactive molecules that contain C-B bonds in their structures. Similar to the synthetic utility of organoboron compounds, the biological activity of boron-containing molecules is based on reversible covalent interactions with nucleophiles. I will present the foundational principles of *Boroscan* – an enabling method to construct boron-containing bioactive molecules using amphoteric molecules.

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## Recent Progress in the Investigation of Size-Selected Boron Clusters: From Borophenes to Metallo-Borophenes

Lai-Sheng Wang

Department of Chemistry, Brown University, Providence, Rhode Island 02912

E-mail: Lai-Sheng\_Wang@brown.edu



### ABSTRACT

Photoelectron spectroscopy in combination with computational studies has shown that small boron clusters possess planar structures,<sup>[1]</sup> in contrast to that of bulk boron, which is dominated by three-dimensional polyhedral building blocks. The propensity for planarity has been found to be a result of both  $\sigma$  and  $\pi$  electron delocalization over the molecular plane, giving rise to concepts of  $\sigma$  and  $\pi$  multiple aromaticity.<sup>[2]</sup> Because of its electron deficiency, boron cannot form graphene-like structures with a honeycomb hexagonal framework. Computational studies suggested that extended boron sheets with partially filled hexagonal vacancies are stable. We found that the  $B_{36}$  cluster has a highly stable quasi-planar structure with a central hexagonal vacancy, providing the first experimental evidence that single-atom boron-sheets with hexagonal vacancies, or borophenes, are viable.<sup>[3]</sup> Borophenes have since been synthesized on Ag(111) surfaces, forming a new class of 2D materials.<sup>[4]</sup> Recent studies of metal-doped boron clusters have shown that transition metals can be doped into the plane of boron clusters,<sup>[5,6]</sup> suggesting the possibility of metallo-borophenes.<sup>[7]</sup> Finally, I will also discuss recent progresses in the investigation on the structures and bonding of lanthanide-doped boron clusters.<sup>[8]</sup>

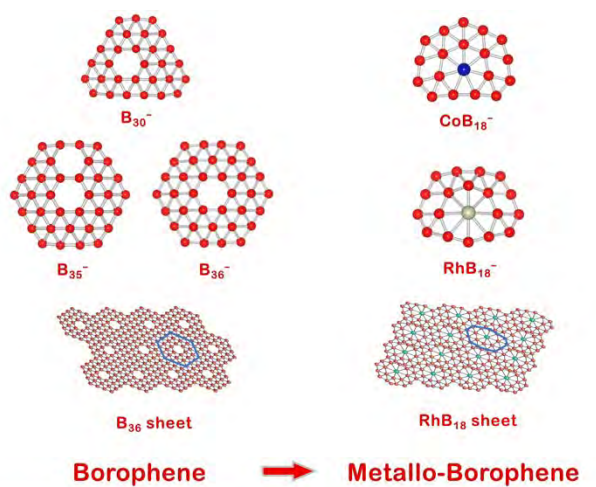


Fig. 1. From borospherenes to metallo-borophenes.

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## Boron-Based Spiro Compounds as TADF Emitters

Andreas Lorbach\*, Marco Stanoppi

University of Konstanz, Universitätsstr. 10, 78464 Konstanz, Germany  
andreas.lorbach@uni-konstanz.de



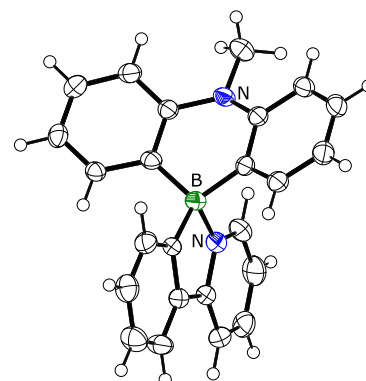
### ABSTRACT

Luminescent materials that exhibit thermally activated delayed fluorescence (TADF) are attractive OLED emitters since TADF minimizes the energy loss caused by the population of non-radiative triplet states.<sup>[1]</sup>

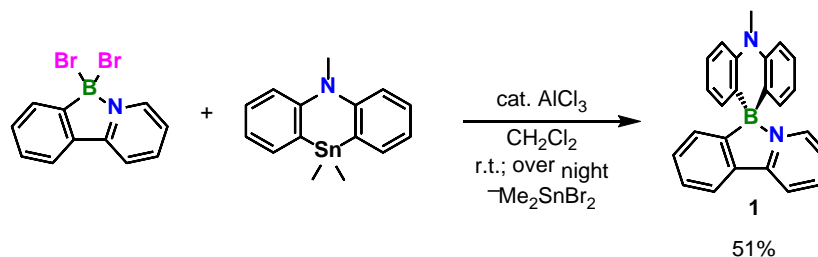
Rigid donor-spiro-acceptor compounds with spatially separated frontier orbitals facilitate TADF and a variety of such spiro compounds was successfully utilized in OLEDs. Recently, Wu et al. demonstrated that electron-poor borylated phenylpyridines can act as efficient acceptors and show TADF even in non-spiro compounds when electron-rich aryl substituents are attached to the boron center.<sup>[2]</sup>

Combining both approaches, we synthesized novel donor-spiro-acceptor compounds such as **1**, based on a tetracoordinate boron atom acting as the spiro center. For the synthesis of **1**, an AlCl<sub>3</sub>-catalyzed arylation protocol described by Ingleson et al. was applied.<sup>[3]</sup>

**1** is a weak emitter in toluene solution (orange) but exhibits green photoluminescence with a quantum yield of 43% in thin films (PMMA matrix). In both cases, time-dependent photoluminescence spectroscopy indicates the presence of TADF. We also demonstrated that the strength of the donor unit directly affects the emission wavelength of these TADF materials.



Solid-state structure of **1**.



Synthesis of **1** based on a protocol of Ingleson et al.<sup>[3]</sup>

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## Beyond Acidic Transition Metal Hydrides: The Direct Heterolytic Cleavage of Dihydrogen to Produce a Super Acid

Vincent LaVallo<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry, UCR  
Riverside, CA 92521 USA  
vincentl@ucr.edu*



### ABSTRACT

Transition metal hydrides and dihydrogen complexes can act as strong Bronstead acids. Some of these systems can provide deliverable protons with Bronstead acidities in the range of super acids. However, all of the known super acidic hydrides and dihydrogen complexes are always formed via the utilization of a super acid (e.g. fluoro sulfonic acid, triflic acid) or super electrophile (e.g. silylium cation). Here we will show that in an appropriately weakly coordinating solvent it is possible to form a trizwitterionic Ir cluster, supported by perchlorinated carboranyl phosphine ligands, which readily cleaves dihydrogen into a dichloroethane solvated proton and a hydride ligand. It is hypothesized that this direct heterolytic activation of dihydrogen is achieved via polarization of a capping metal hydride bond via the simultaneous and cooperative action of three electrophilic Ir(III) centers. Time permitting, the synthesis of a water stable, dianionic, metal free NHC, featuring two perchlorinated CB<sub>9</sub>Cl<sub>9</sub> clusters, will be discussed.



## Chirality Transfer with the Borabicyclodecanes

John A. Soderquist\*

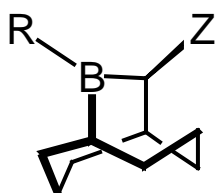
University of Puerto Rico, Department of Chemistry, San Juan, PR,  
USA 00931

*jasoderquist@yahoo.com*



### ABSTRACT

The stereoselective additions of reagents containing the chiral 10-substituted-9-borabicyclo[3.3.2]decane (BBD) moiety to aldehydes, ketones, aldimines and ketimines will be described. The rigid and robust nature of these systems permits a wide variety of organoborane conversions to not only be conducted in a highly enantioselective manner, but also, it facilitates the recovery of the chiral borane by-product which can be recycled through simple operations. Moreover, numerous chemical conversions can be performed on these organoboranes providing remarkable new reagents for organic synthesis.<sup>[1-9]</sup> The origin of the observed selectivities will be presented and discussed in terms of the compact chiral reaction centers provided by the BBD systems. The implications of specific structural features of the reagent-substrate interactions will be considered to provide the clearly predictable chemistry of these compact asymmetric reagents.



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## POSTER PRESENTATION ABSTRACTS



## Alkylated bis(quaternary ammonium) cation polyborates

Michael A. Beckett<sup>a\*</sup>, Peter N. Horton<sup>b</sup>, Thomas A. Rixon<sup>a</sup>

<sup>a</sup>*School of Chemistry, Bangor University, Bangor, LL57 2SX, UK*

<sup>b</sup>*School of Chemistry, Southampton University, Southampton, SO17 1BG, UK*  
*chp81d@bangor.ac.uk, m.a.beckett@bangor.ac.uk*



### ABSTRACT

We are interested in potential micronutrient and/or biostimulant properties of borates and silicate salts and have are developing aspects of the chemistry of salts with non-metal cations.<sup>[1]</sup> This work is in parallel with synthetic studies involving sterically hindering larger cations, such as short chain cationic surfactants (particularly bis-imidazolium salts) and highly alkylated bis(ammonium) salts. It was anticipated that their structure-directing properties would give rise to novel self-assembled hydroxyoxidopolyborate anions.<sup>[2]</sup>

Several polyborate salts have been prepared from aqueous solution by a self-templated reaction. By varying the stoichiometry of reagents, it was possible to obtain tetraborate(2-) and pentaborate(1-) salts from the *N,N,N,N',N',N'*-hexamethylethanediammonium non-metal cation. Initial attempts to obtain *N,N,N,N',N',N'*-hexamethyl-1,3-propandiammonium bis(pentaborate) from the templating cation yielded an unexpected analytically pure *N,N,N*-trimethylallylmmonium pentaborate due to a Hofmann elimination under relatively harsh work-up conditions. Keeping the reaction mixture at room temperature yielded the expected product. The crystalline compounds have been characterized by NMR, FTIR, elemental analysis and XRD analysis. Results of this synthetic work and some related chemistry, including crystal structures of the products, will be presented.

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## Photocleavage of N-Si bonds in Disilylated 9-Amino-9-Borafluorene

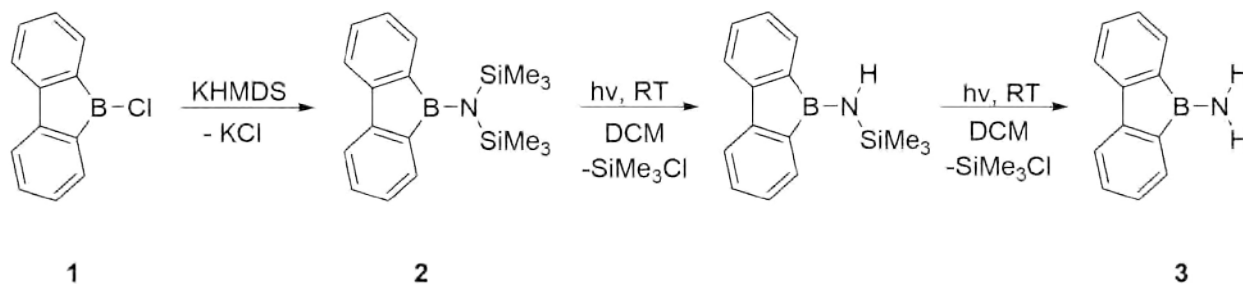
Constanze Keck<sup>a</sup>, Holger F. Bettinger<sup>a\*</sup>

<sup>a</sup>Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18  
72076 Tübingen, Germany  
constanze-ulrike.keck@student.uni-tuebingen.de, holger.bettinger@uni-tuebingen.de

### ABSTRACT

The properties and chemical transformations of boroles and dibenzoboroles, also known as 9-borafluorenes, are currently receiving significant attention.<sup>[1]</sup> In analogy to the monocyclic aminoborole derivative,<sup>[2]</sup> the novel disilylated aminodibenzoborole **2** is readily obtained from the reaction of **1** with KHMDS. The photochemistry of disilylated aminoboroles such as **2** has never been investigated, although a number of reaction pathways are conceivable.

Irradiation at  $\lambda = 254$  nm in dichloromethane leads to sequential loss of the TMS groups yielding **3** as the isolated product of photolysis, while compound **2** is inert in cyclohexane and under cryogenic inert gas matrix isolation conditions. The transformation of **2** to **3** constitutes a photochemical reduction that is without precedence in the chemistry of aminoboranes. The photolysis is suggested to proceed via a single electron transfer mechanism involving dichloromethane as electron acceptor.<sup>[3]</sup>



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## Mechanistic Studies of Formal Thioboration Reactions of Alkynes

Adena Issaian<sup>a</sup>, Darius J. Faizi<sup>a</sup>, Johnathan O. Bailey<sup>b</sup>, Peter Mayer<sup>c</sup>, Guillaume Berionni<sup>c</sup>,  
Daniel A. Singleton<sup>b</sup>, Suzanne A. Blum<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of California, Irvine,  
92617–2025, United States

<sup>b</sup> Department of Chemistry, Texas A&M University, P.O. Box 30012,  
College Station, Texas 77842, United States

<sup>c</sup> Department of Chemistry, Ludwig Maximilian University of Munich,  
Munich, 80539, Germany  
aissaian@uci.edu blums@uci.edu



### ABSTRACT

The catalyst-free formal thioboration reaction of alkynes was investigated to gain mechanistic insight into *B*-chlorocatecholborane (ClBcat) in its new role as an alkynophilic Lewis acid in electrophilic cyclization/dealkylation reactions.<sup>[1]</sup> Kinetic studies showed that the reaction is second-order globally. Carbon kinetic isotope effects supported a rate-determining A<sub>E</sub>3 mechanism wherein alkyne activation by neutral ClBcat is concerted with cyclative attack by nucleophilic sulfur. A Hammett study found a  $\rho^+$  of  $-1.7$ , suggesting cationic charge buildup during the cyclization and supporting rate-determining concerted cyclization. Comparison studies of the ClBcat system with tris(pentafluorophenyl)borane (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>), an activating agent capable of cyclization but not dealkylation,<sup>[2]</sup> and BCl<sub>3</sub>, an activating agent that mediates cyclization but not dealkylation by itself,<sup>[3]</sup> were conducted for comparison.

Overall, the results support a mechanism in which the ClBcat reagent serves a bifunctional role by sequentially activating the alkyne, despite being less electrophilic than other known alkyne-activating boron reagents and then providing chloride for post-rate-determining demethylation/neutralization of the resulting zwitterionic intermediate.

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## A Regioselective Oxyboration Route to Borylated Dihydrofurans and Isochromenes

Kim N. Tu<sup>a</sup>, Chao Gao<sup>a</sup>, Suzanne A. Blum<sup>a,\*</sup>

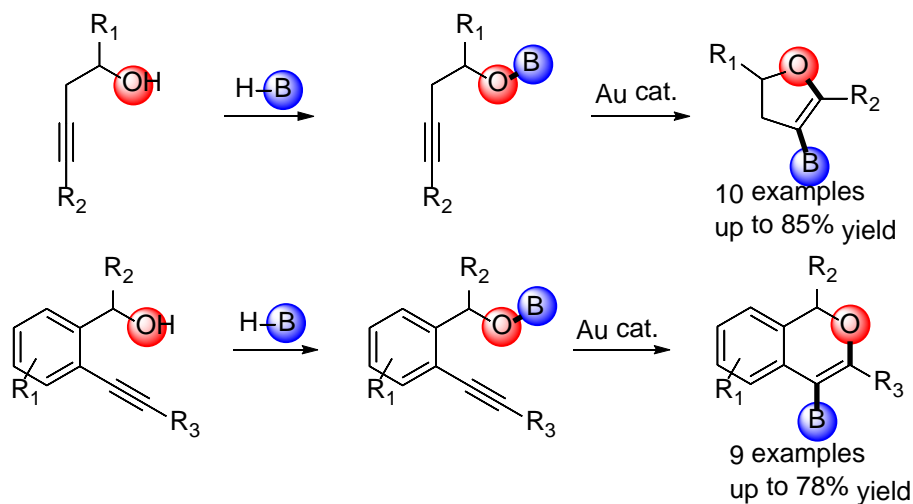
<sup>a</sup> Department of Chemistry, University of California, Irvine, Irvine, California  
92697-2025, United States

[kntu@uci.edu](mailto:kntu@uci.edu)  
\* [blums@uci.edu](mailto:blums@uci.edu)



### ABSTRACT

An oxyboration reaction that employs B–O  $\sigma$  bonds as addition partners to C–C  $\pi$  bonds to form borylated dihydrofurans and isochromenes has been developed. The reaction produces exclusively one regioisomer and is catalyzed by gold. The borylated isochromenes can be accessed from alcohols directly or from a hydroboration–oxyboration sequence starting from the corresponding ketones.



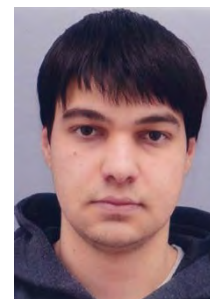


## Determination of Oxidation States in Compounds with Boron-Aluminium Bonds

Alexander Hofmann<sup>a</sup>, Tobias Tröster<sup>a</sup>, Conor Pranckevicius<sup>a</sup>, Holger Braunschweig<sup>a,\*</sup>

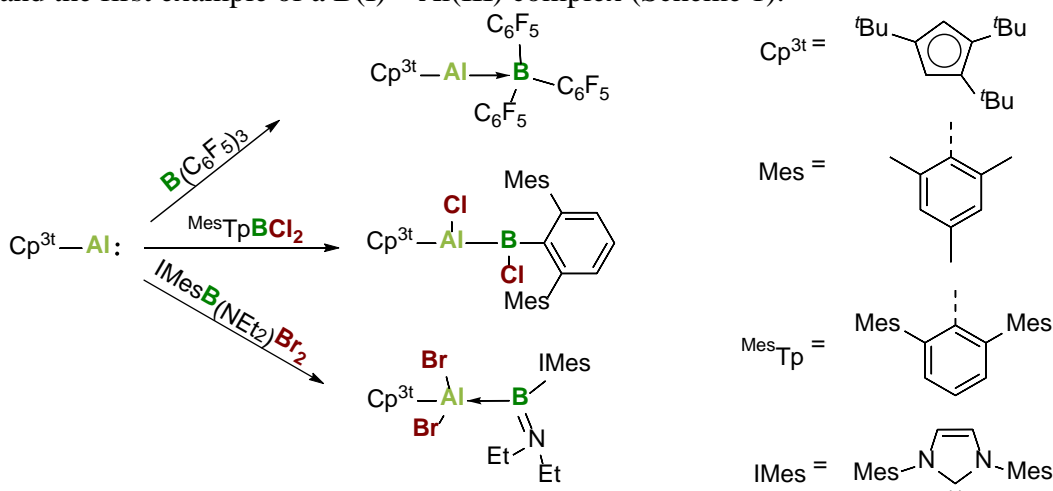
<sup>a</sup>Institute for Inorganic Chemistry and Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

alexander.hofmann@uni-wuerzburg.de; h.braunschweig@uni-wuerzburg.de



### ABSTRACT

After the initial report of the first Al(I)→B(III) Lewis adduct Cp\*Al→B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (Cp\* = pentamethylcyclopentadienide) by Cowey *et al.*,<sup>[1]</sup> low-valent complexes of mixed Group XIII elements have attracted growing attention in recent years.<sup>[2]</sup> While complexes of the form B(I)→Ga(III), have been reported,<sup>[3]</sup> known Al-B donor-acceptor complexes have been limited to Al(I)→B(III). We herein report a new synthetic approach to a monomeric, room-temperature-stable cyclopentadienide-Al(I) species, and its reactivity towards B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and dihaloboranes. Depending on the steric and electronic environment at the boron center, we have observed the formation of different types of Al-B interactions, which include Al(I)→B(III), Al-B covalent bonds, and the first example of a B(I)→Al(III) complex (Scheme 1).



**Scheme 1:** Different types of boron-aluminium bonds constructed in this work.

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## Reactivity of *cis*-1,2-Dihydrodiborane(4) towards Lewis Bases

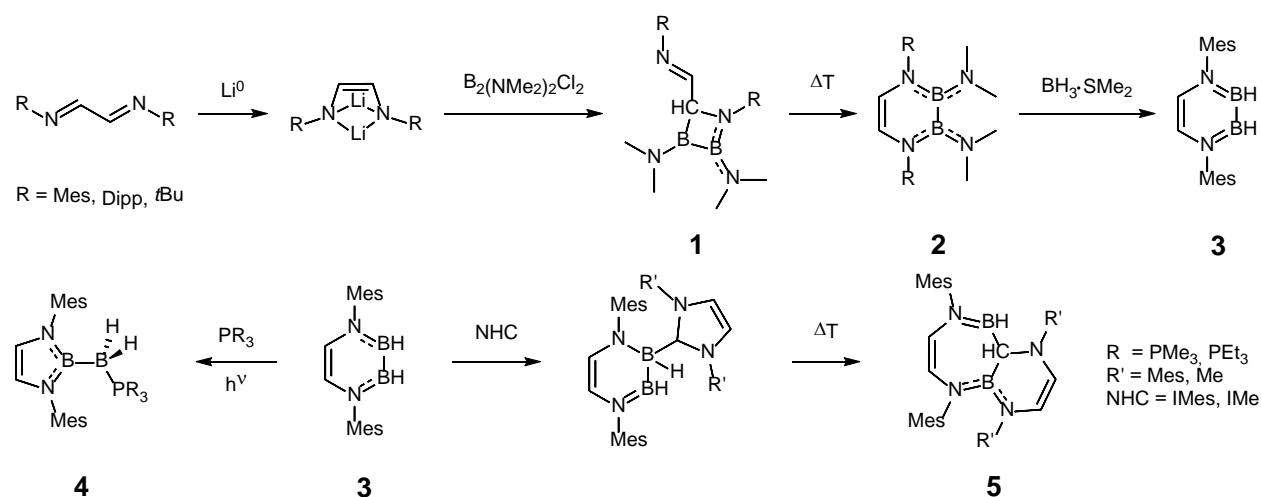
Torsten Thiess<sup>a</sup>, Merle Arrowsmith<sup>a</sup>, Holger Braunschweig<sup>a,\*</sup>

<sup>a</sup>Institute for Inorganic Chemistry and Institute for Sustainable Chemistry & Catalysis with Boron (ICB), Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany  
torsten-thiess@uni-wuerzburg.de  
h.braunschweig@uni-wuerzburg.de



### ABSTRACT

Since the first synthesis of 1,4-diaza-2,3-diborinines in 1963 by Nöth, in the form of a range of benzannulated derivatives,<sup>[1]</sup> there have only been few further examples reported in the literature.<sup>[2]</sup> Only recently an easily applicable method has been reported for the synthesis of monomeric monocyclic 1,4-diaza-2,3-diborinines. Dilithiation of 1,4-diazabutadienes and reaction with B<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> leads to the formation of B<sub>2</sub>-containing compounds with six-membered rings (**2**) *via* four-membered ring intermediates (**1**). The resulting 2,3-bis(dimethylamino)diazadiborinines give access to a range of further-functionalized derivatives. For example the reaction of **2** with BH<sub>3</sub>·SMe<sub>2</sub> leads to the *cis*-1,2-dihydrodiborane(4) (**3**).<sup>[4]</sup> **3** undergoes either ring-contraction (**4**) or ring-expansion (**5**) reactions depending on the nature of the added Lewis base and the reaction conditions.



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## Enantioselective Suzuki-Miyaura Coupling of Alkyl Halides and Unactivated Boronic Esters

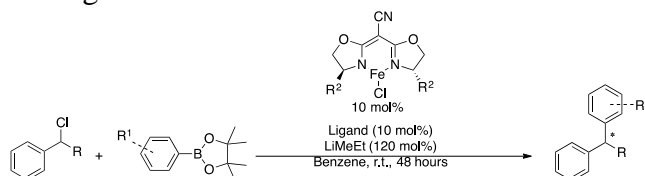
Chet C. Tyrol<sup>a</sup>, Michael. P. Crockett<sup>a</sup>, Jeffrey A. Byers<sup>a,\*</sup>

<sup>a</sup>Eugene F. Merkert Chemistry Center, Department of Chemistry, Boston College, 2609 Beacon Street, Chestnut Hill, Massachusetts 02467, United States  
tyrolc@bc.edu, Jeffery.byers@bc.edu



### ABSTRACT

Iron-catalyzed cross-couplings maintain a high profile due to their low-toxicity, natural abundance and fast reaction kinetics. Despite this, enantioselective iron-catalyzed cross-couplings continue to be a challenging task with only one known example in the literature.<sup>1</sup> Our group has recently developed an efficient and general iron-catalyzed Suzuki-Miyaura system for coupling alkyl halides and unactivated aryl-boronic esters using lithium amide bases which has been further modified to provide enantioenriched products. Using a C<sub>2</sub>-symmetric, chiral cyanobisoxazoline ligand, we are able to couple a variety of benzylic chlorides with various aryl-boronic esters to furnish diarylalkanes with good yields and enantioselectivities. Further investigation has shown the alkyl halide remained racemic after the reaction, suggesting that the reaction is enantioconvergent rather than a kinetic resolution reaction. This finding is important because it suggests that reaction optimization can be achieved to obtain 100% yield of enantioenriched product. To improve enantioselectivity, chiral cyanobisoxazoline ligand variants with phenyl substitution will be synthesized and tested alongside surveying a range of activated and unactivated secondary alkyl halides.



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## UV-light mediated borocyclopropanation of styrenes using continuous flow technology

Morgane Sayes<sup>a</sup>, Guillaume Benoit<sup>a</sup>, André B. Charette<sup>a,\*</sup>

<sup>a</sup>Université de Montréal,  
2900 Boulevard Edouard-Montpetit, Montréal, QC H3T 1J4  
Email of corresponding author: [andre.charette@umontreal.ca](mailto:andre.charette@umontreal.ca)  
Email of presenting author: [morgane.sayes@umontreal.ca](mailto:morgane.sayes@umontreal.ca)

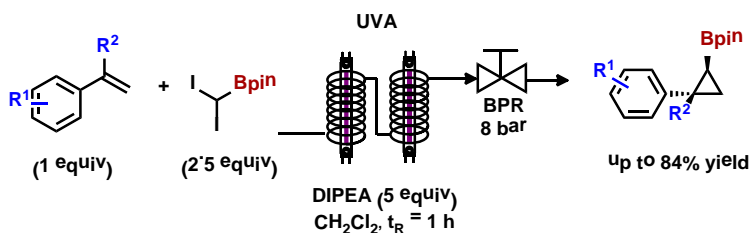


### ABSTRACT

The cyclopropane moiety proved to be essential in biologically active compounds due to its tridimensional architecture which ranked it as the 10<sup>th</sup> most used carbocycle in medicinal chemistry. Developing building blocks to easily introduce a cyclopropane motif in a more complex molecule is therefore of high interest. Boronic acids are a nice handle to do so. Indeed, they are really versatile compounds that allow the formation of C-C bonds (Suzuki-Miyaura cross-couplings), C-O bonds (hydroxydeboronation reactions or Chan Lam couplings) and C-N bonds (Chan Lam couplings).

Previous syntheses of borocyclopropanes either require the use of a metal, which can be pyrophoric such as diethylzinc, or toxic such as chromium, and cryogenic conditions. Furthermore, most of the time, prior synthesis of a borylated olefin is needed.

Herein, we present a user friendly UV-light mediated borocyclopropanation of styrenes using continuous flow technology. A broad range of styrenes can be obtained in good yields with 1 h residence time. The obtained borocyclopropanes can then be engaged in post-functionalization reactions.



Photochemical reactions are really sensitive to irradiation. When using batch chemistry, in a flask, the light only penetrates a few centimeters in, thus only irradiating a small percentage of the reaction mixture. A really good mixing is needed in order to assure homogeneous irradiation of the reaction. Furthermore, when using high wavelengths, special glassware is required. Continuous flow technology overcome all the problems mentioned above: the thin FEP tubing, permeable to light, provide homogeneous and optimal irradiation. On top of that, this technology enables an easy scale-up, which is not the case in batch chemistry, here again due to irradiation issue when using a big flask.

## Boron stereogenic center controlled by a diastereoselective radical reaction

Clara Aupic,<sup>a</sup> Carlotta Figliola,<sup>a</sup> Amel Abdou,<sup>a</sup> Béatrice Tuccio-Lauricella,<sup>b</sup>  
Paola Nava,<sup>a</sup> Gaëlle Chouraqui,<sup>a</sup> Jean-Luc Parrain,<sup>a</sup> Olivier Chuzel<sup>a\*</sup>

<sup>a</sup> *iSm2, Aix-Marseille Université, CNRS, Centrale Marseille, France*

<sup>b</sup> *ICR, Aix-Marseille Université, CNRS, France*

[clara.aupic@etu.univ-amu.fr](mailto:clara.aupic@etu.univ-amu.fr)

[olivier.chuzel@univ-amu.fr](mailto:olivier.chuzel@univ-amu.fr)

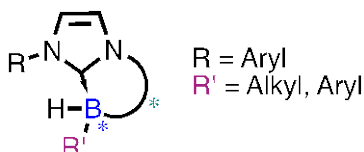


### ABSTRACT

In the last decade, the synthesis and the use of N-Heterocyclic Carbene-Boranes have emerged thanks to their easy access and interesting reactivity profile.<sup>[1]</sup> Those main-group complexes have shown to be very efficient when used as reagent or catalyst, especially for double bond reduction. Nevertheless, only few examples report the use of these compounds in enantioselective reactions, probably due to the challenging access to chiral NHC-Boranes.

Hence, we propose the formation of a new class of boron stereogenic-containing reagents through a radical pathway. Starting from enantioenriched cyclic NHC-Borane scaffolds developed in our team,<sup>[2]</sup> we have been able to functionalize the boron center in a diastereoselective manner.<sup>[3]</sup>

Strategies, synthesis of precursors, scope and limits of the reaction and mechanistic studies will be described and discussed.



*New class of stereogenic NHC-Boranes*

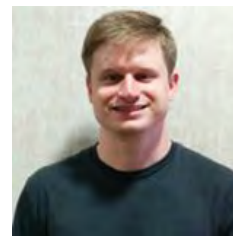
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[3] Manuscript under preparation

## 1-Butyl-3-methylimidazol-2-ylidene borane: A readily available, liquid N-heterocyclic carbene borane reagent

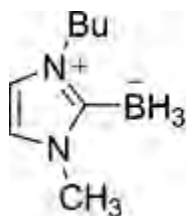
Daniel A. Bolt<sup>a</sup>, Dennis P. Curran<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260  
DAB187@pitt.edu, curran@pitt.edu



### ABSTRACT

1-Butyl-3-methylimidazol-2-ylidene borane has been synthesized directly from two inexpensive commercial reagents: 1-butyl-3-methylimidazolium bromide and sodium borohydride. This NHC-borane reagent is a stable, free-flowing liquid that shows promise for use in radical, ionic, and metal-catalyzed reactions.<sup>1</sup>



- readily available from inexpensive reagents
- air-, water-stable; free-flowing liquid
- undergoes typical radical and ionic reactions

### REFERENCES

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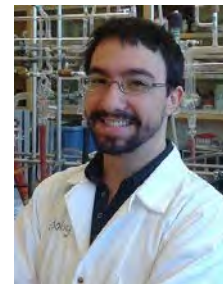


## Metal-Free Borylation of Heteroarenes Using Ambiphilic Aminoboranes

Julien L egar  Lavergne, Arumugam Jayaraman, Luis C. Misal Castro,  
 tienne Rochette and Fr d ric-Georges Fontaine\*

D partement de Chimie, Universit  Laval, 1045 Avenue de la M decine,  
Qu bec City, Qu bec G1V 0A6, Canada.

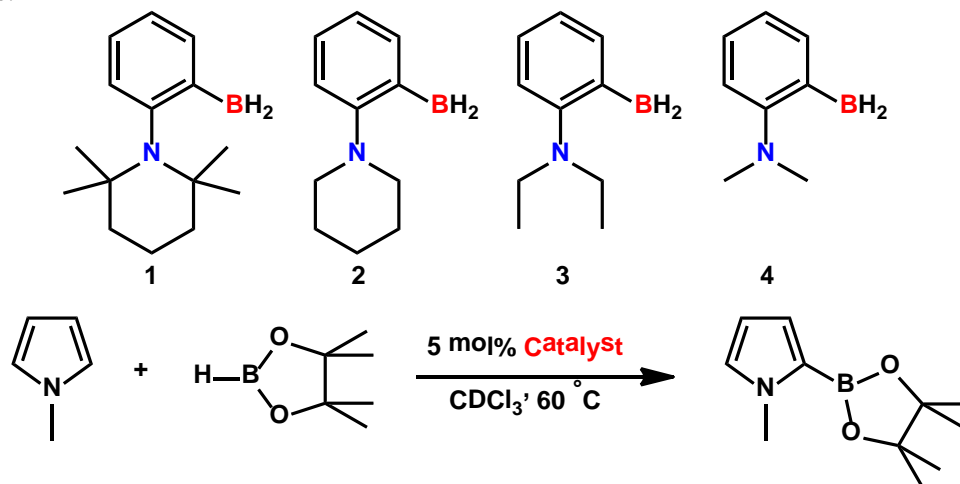
Julien.Legare-Lavergne.1@ulaval.ca, Frederic.Fontaine@chm.ulaval.ca\*



### ABSTRACT

In 2015, we reported the use of ambiphilic aminoborane **1** as catalyst for the borylation of heteroarenes.<sup>[1]</sup> This compound composed of a sterically encumbered amine and an hydroborane in *ortho* positions on a phenylene framework operates using the concept of frustrated Lewis pair (FLP) chemistry.<sup>[1]</sup> Since then, we synthesized new aminoboranes (**2**, **3** and **4**) with smaller amines to study the effect of the steric hindrance on the FLP reactivity.<sup>[2]</sup> Indeed, crystallographic and spectroscopic evidences show that these species are not FLPs in the strict sense of the term since they exist as stable dimeric species.

We investigated the catalytic C-H borylation reaction using NMR kinetics and DFT modelization. The size of the amine has a very important impact on the C-H activation step and the dissociation of the dimeric species. Contrarily to what is expected from FLP chemistry, species **2** and **3**, with a smaller amine improve the efficiency of the catalytic transformation. We also demonstrate that it is also possible to generate air and water stable trifluoroborate precatalysts of these derivatives.<sup>[3]</sup>



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## The Reactivity of the diborane [NMe<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-BH]<sub>2</sub>

Etienne Rochette<sup>a</sup>, Frédéric-Georges Fontaine<sup>a,\*</sup>

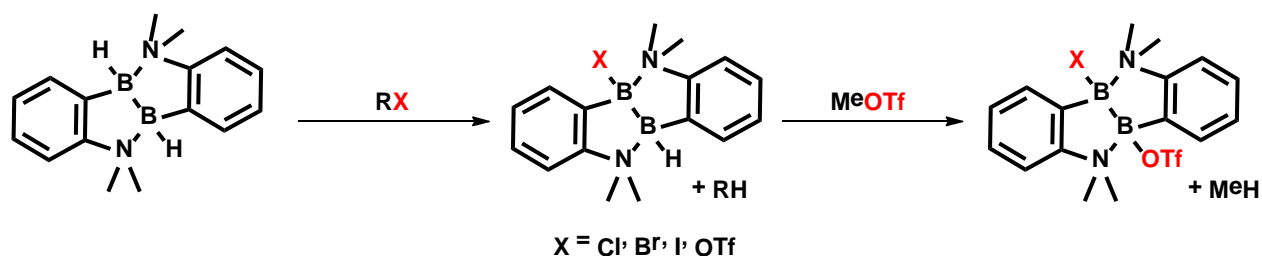
<sup>a</sup> Département de chimie and Centre de recherche en Catalyse et Chimie Verte  
 Université Laval  
 Québec, QC, G1V 0A6, Canada  
 etienne.rochette.2@ulaval.ca  
 frederic.fontaine@chm.ulaval.ca



### ABSTRACT

In 2016, while studying the reactivity of amino hydroborane 1-NMe<sub>2</sub>-2-BH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, we discovered an FLP induced rearrangement leading to the spontaneous formation of a B-B bond.<sup>[1]</sup> Since then, we studied the reactivity of this unique diborane and compared it to other similar systems reported in the literature, notably the guanidinate-bridged dihydrido-diborane, extensively studied by Himmel and coworker.<sup>[2]</sup>

The synthesis and characterization (multinuclear NMR and crystallographic data) of several new species are being reported. We were notably able to isolate unsymmetrical diboranes where one of the hydrides is being substituted by an halogen atom. The experimental and computational investigation of their reactivity will also be presented.



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## Dinuclear Group 6 Metal Complexes comprising Diborane(4) and Diborene(2)

Ranjit Bag<sup>a</sup>, Bijan Mondal<sup>a</sup>, Eluvathingal D. Jemmis<sup>b</sup> and Sundargopal Ghosh<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Madras  
Chennai 600 036, India

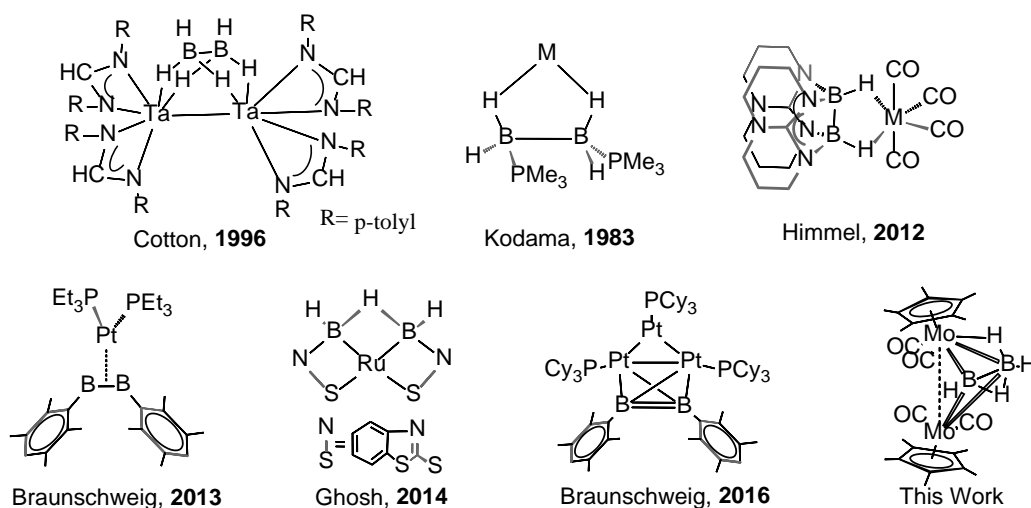
<sup>b</sup>IPC Department, IISc, Bangalore 560 012 India

Email: [mail2ranjitbag@gmail.com](mailto:mail2ranjitbag@gmail.com), [sghosh@iitm.ac.in](mailto:sghosh@iitm.ac.in)



### ABSTRACT

One of the noteworthy developments in the area of transition metals boron chemistry is the structure and bonding of diborane(6), diborane(4) and diborene(2) complexes. Amongst these, diboration reaction stands out as “the most-used organometallic reaction in organic synthesis of diborane(4)” as it offers a valued synthetic route for the introduction of boryl group across the unsaturated organic species.<sup>[1]</sup> Based on the progress of the structures of hydrogen-substituted diborane compounds, shown below, it appears rather surprising that the search for the simple bimetallic transition metal diborane(4) species met with very little success that encouraged us to synthesis of bimetallic diborane(4) compounds.<sup>[2]</sup> Treatment of  $[(Cp^*Mo)_2(\mu-Cl)_2B_2H_6]$  with CO led to the formation of highly fluxional species  $[(Cp^*Mo(CO)_2)_2\{\mu-\eta^2:\eta^2-B_2H_4\}]$ , that represents a rare class of bimetallic-diborane(4). Further in an attempt to replace two hydrogen atoms of the diborane(4) with 2e  $[W(CO)_4]$  fragment,  $[(Cp^*Mo(CO)_2)_2B_2H_2W(CO)_4]$  was isolated when treated with  $[W(CO)_5.thf]$  that shows the presence of  $[B_2H_2]$  with a short B-B length. The key results of this work will be presented.



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## Chemistry of Triple-Decker Sandwich Complexes Containing Four-Membered Open B<sub>2</sub>E<sub>2</sub> Ring (E = S or Se)

Benson Joseph, Rongala Ramalakshmi, Sundargopal Ghosh\*

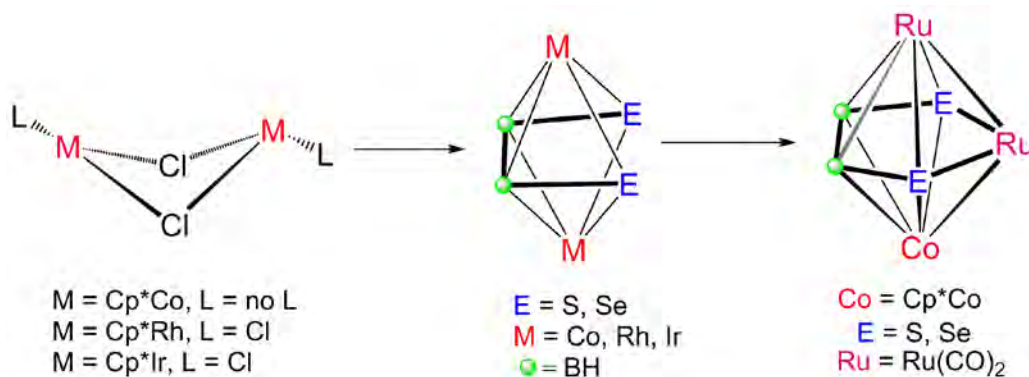
Department of Chemistry, Indian Institute of Technology Madras, Chennai  
600036, India

Email: [bensonjoseph203@gmail.com](mailto:bensonjoseph203@gmail.com), [sghosh@iitm.ac.in](mailto:sghosh@iitm.ac.in)



### ABSTRACT

The chemistry of metallaheteroboranes traditionally achieved by the reaction of polyhedral heteroborane anions with metal fragments or the incorporation of heteroatom into metallaborane clusters.<sup>[1]</sup> The development towards the large number of metallaheteroboranes have gained pronounced deal of interest owing to their utility in the preparation of high-nuclearity clusters.<sup>[2]</sup> Among them, group 9 metallaheteroboranes have received significant attention due to their applications in catalysis.<sup>[3]</sup> Although, metallaheteroboranes comprised of thia and aza-ligands have been explored, compounds that contain heavier heteroatoms such as selenolato and telluroolato ligands are relatively scarce. In the past several years, we have been actively involved in the synthesis of group 5-8 metallaheteroboranes containing heavier chalcogen atoms through the activation of diorganoyldichalcogenide ligands or chalcogen powders. Inspired by the synthesis of [(CpCo)<sub>2</sub>B<sub>2</sub>H<sub>2</sub>S<sub>2</sub>] by Sneddon<sup>[4a]</sup> and our previous studies on [(Cp\*Co)<sub>2</sub>B<sub>2</sub>H<sub>2</sub>E<sub>2</sub>]<sup>[4b]</sup> (1: E = S; 2: E: Se), we explored the chemistry of heavier group 9 metals that yielded group 9 triple decker sandwich metallaheteroboranes containing four-membered open B<sub>2</sub>E<sub>2</sub> central ring (E = S or Se). The key results of this work will be presented.



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## Ruthenium Bis(agostic) Complexes: Utilization of Ruthenium Agostic Complex for Hydroamination and Hydrothiolation of Terminal Alkynes

Mohammad Zafar, Rongala Ramalakshmi, Sundargopal Ghosh\*

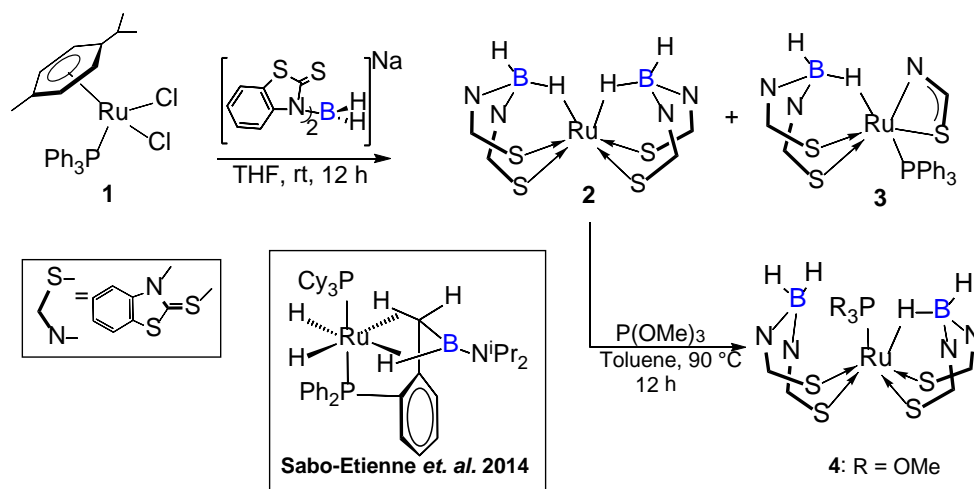
Department of Chemistry, Indian Institute of Technology Madras  
Chennai 600036, India

Email: [jafarnaqvi110@gmail.com](mailto:jafarnaqvi110@gmail.com) and [sghosh@iitm.ac.in](mailto:sghosh@iitm.ac.in)



### ABSTRACT

Transition metal complexes having a  $[M] \cdots H-B$  interaction, sigma or agostic played an important role in various metal-catalyzed B-H activation and hydroboration processes.<sup>[1-2]</sup> In this, two types of  $[M] \cdots H-B$  bonding motifs have been recognized, one is base-stabilized<sup>[2]</sup> and other is base free  $[M] \cdots H-B$  bonding.<sup>[3]</sup> In general, these interactions are mostly stimulated by ligand design, such as, bis and tris(pyrazolyl)borate ligands. As a result, complex  $[(p\text{-cymene})RuPPh_3Cl_2]$  was found to be very appropriate to generate bis(agostic) complexes. Treatment of  $[(p\text{-cymene})RuPPh_3Cl_2]$  with dihydrobis(2-mercapto-benzo thiazolyl)borate, ( $L_1 \equiv [H_2B(mbz)_2]^-$ ) yielded octahedral bis(agostic) (**2**) and agostic complex (**3**). Both the complexes display distorted octahedral geometry around the metal center, surrounded by a tridentate  $[H_2B(mbz)_2]^-$  moiety, in ( $\kappa^3\text{-H,S,S}$ ) coordination mode. The key results of this work will be described.



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## Investigations Into the Mechanism of a Palladium-catalyzed Enantioselective Borylative Migration Reaction

Helen A. Clement,<sup>a</sup> Claude Y. Legault<sup>b</sup>, Dennis G. Hall<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Centennial Centre for Interdisciplinary Science,  
University of Alberta, Edmonton, Alberta T6G 2G2, Canada

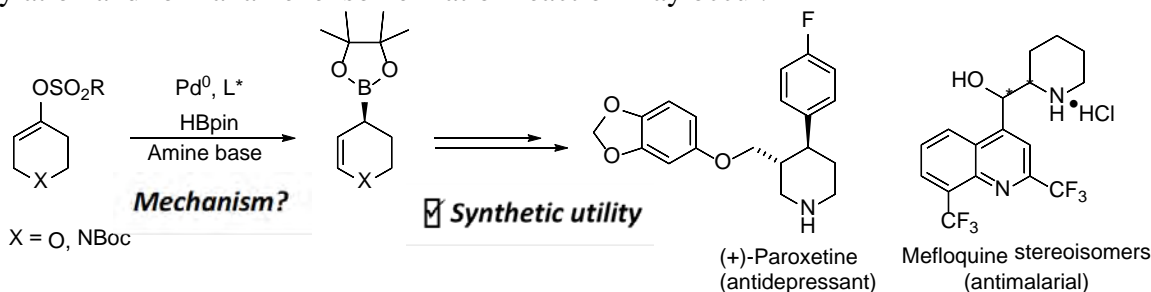
<sup>b</sup> Department of Chemistry, Centre in Green Chemistry and Catalysis,  
University of Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada  
hclement@ualberta.ca; dennis.hall@ualberta.ca



### ABSTRACT

Allylic chiral boronates have been shown to be useful building blocks in organic chemistry.<sup>[1]</sup> In this respect, the Hall Group has developed a palladium catalyzed enantioselective borylative migration reaction, which leads to the synthesis of unique 6-membered tetrahydropyridinyl and dihydropyranyl allylic chiral boronates.<sup>[2]</sup> These enantio-enriched intermediates have been shown to be applicable towards both carbonyl allylboration and Suzuki-Miyaura cross-coupling methodologies. In this regard, the applicability of this chemistry has been displayed towards the total and formal syntheses of numerous biologically active molecules such as mefloquine, paroxetine and anabasin.<sup>[3]</sup>

Considering the vast synthetic utility this reaction may have if it were to become more general, our group is interested in expanding this borylation methodology to other useful substrates. However, first a better mechanistic understanding of this reaction is desirable. Some key questions to be addressed include the nature of the Miyaura-type borylation with pinacolborane, the precise role(s) of the amine base and determining which factors control the preference for the alkene isomerization step. This task has been undertaken by combining both computational and experimental evidence to draw upon the most conceivable pathway whereby this overall Miyaura borylation and formal alkene isomerization reaction may occur.



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## Synthesis of BN-embedded Corannulene via Electrophilic C–H Borylation

Soichiro Nakatsuka, Takuji Hatakeyama\*

Graduate School of Science and Technology, Kwansei Gakuin University,  
2-1 Sanda-city Gakuen, Hyogo 669-1337 Japan  
s.nakatsuka@kwansei.ac.jp and hatake@kwansei.ac.jp



### ABSTRACT

Corannulene<sup>[1,2]</sup> derivatives are an important class of materials for liquid crystals,<sup>[3]</sup> molecular tweezers,<sup>[4]</sup> single-chirality carbon nanotubes (CNTs).<sup>[5]</sup> However, corannulene analogues having heteroatoms incorporated into corannulene skeletons have not yet been studied in detail, even though doping of heteroatoms in PAHs is highly important in order to realize new functions by modulating the physical properties and molecular structures of these species.<sup>[6]</sup> Very recently, corannulene analogues having one nitrogen atom have synthesized, and their bowl-shaped structure and C<sub>60</sub> binding behavior have been revealed.<sup>[7]</sup> Herein, we report the scalable synthesis of the first BN-embedded corannulene via a electrophilic arene borylation reaction.<sup>[8]</sup> The synthetic details, crystal structures, and physical properties of these compounds will be reported in this presentation.

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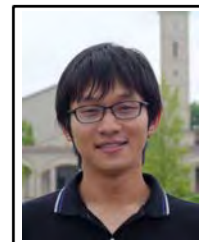
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## One-Shot Multiple Borylation toward BN-Doped Nanographenes

Susumu Oda, Kohei Matsui, Kazuki Yoshiura, Takuji Hatakeyama\*

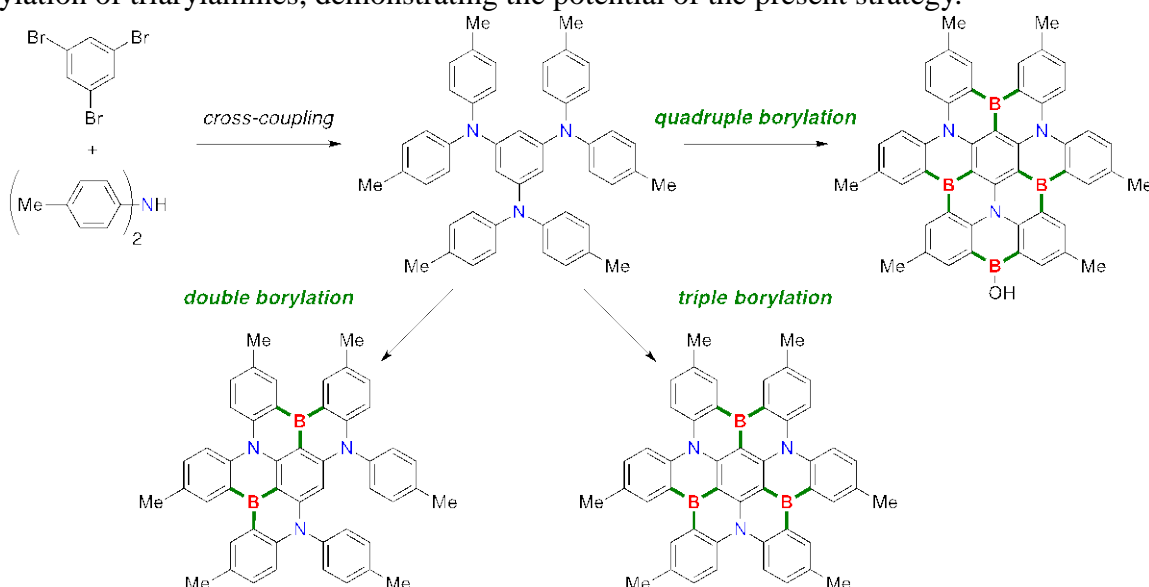
Department of Chemistry, School of Science and Technology,  
Kwansei Gakuin University, 2-1 Gakuen, Sanda, Hyogo 669-1337, Japan

soda@kwansei.ac.jp, hatake@kwansei.ac.jp



### ABSTRACT

Recently, heteroatom-doped nanographenes<sup>[1]</sup> have attracted significant attention not only as starting units for bottom-up syntheses, but also as well-defined substructures for heteroatom-doped graphenes. There have been reported some powerful synthetic methods including dehydrogenative C–C coupling (Scholl reaction) and Friedel-Crafts-type carbon–heteroatom bond forming reaction.<sup>[2]</sup> However, conventional approaches to doped nanographenes require multistep syntheses from commercially available sources, and are not suitable to further extension of their  $\pi$ -conjugated frameworks, or to large-scale production for practical applications. Herein, we report the two-step synthesis of a B<sub>4</sub>N<sub>3</sub>-doped nanographene.<sup>[3]</sup> The key to success is the quadruple borylation of triaryl amines *via* intra- and intermolecular bora-Friedel-Crafts-type reactions, which converts eleven C–H bonds into C–B bonds in one shot. Moreover, we have succeeded in the development of the selective double and triple borylation of triaryl amines, demonstrating the potential of the present strategy.



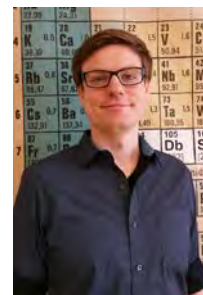
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## 12-Vertex Zwitterionic Bis-phosphonium-*nido*-carborates via Ring-opening Reaction of 1,2-Diphosphetanes

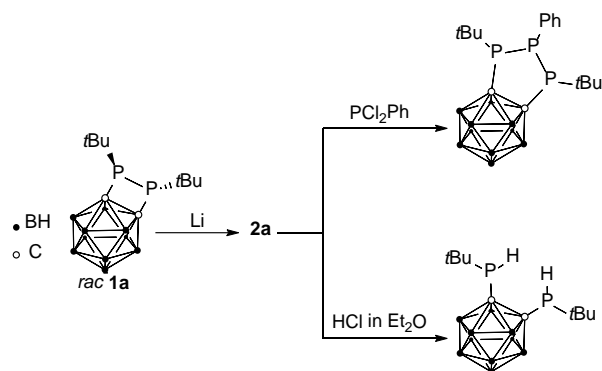
Jan Schulz, Anika Kreienbrink, Evamarie Hey-Hawkins\*

Leipzig University, Faculty of Chemistry and Mineralogy, Institute of Inorganic Chemistry, Johannisallee 29, D-04103 Leipzig  
schulz.jan@web.de; hey@uni-leipzig.de

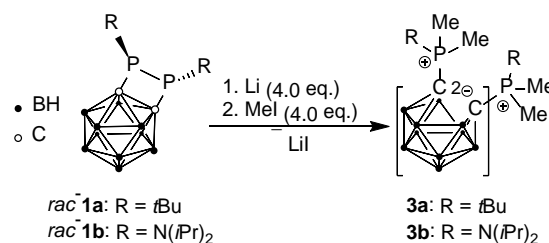


### ABSTRACT

We have previously reported several syntheses incorporating the cleavage of the P–P bond in 1,2-diphosphetanes (**1**) by reaction with lithium, followed by addition of HCl<sup>[1]</sup> or dichlorophosphines<sup>[2]</sup> to give access to open-chain or cyclic derivatives. In case of **1a**, the lithiated intermediate,  $[\{1\text{-}i\text{PrBuLi(THF)}\text{-}6\text{-}i\text{PrBu}\text{-}4,1,6\text{-}closo\text{-Li(THF)}\text{C}_2\text{B}_{10}\text{H}_{10}\}\{\text{Li(THF)}_3\}]_2 \cdot 2\text{THF}$  (**2a**) could be isolated and structurally characterised (Scheme 1). The compound is dimeric, C<sub>2</sub>-symmetric and contains six lithium and four phosphorus atoms. Two lithium ions are capping the six-membered C<sub>2</sub>B<sub>4</sub> faces resulting in two 13-vertex *closo* clusters (according to Wade's rules) with dicosahedral geometry.<sup>[3]</sup> Addition of MeI gave the zwitterionic bis-phosphonium-*nido*-carborates, 7,10-bis(*tert*-butyl-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (**3a**). Additionally, 7,10-bis(*N,N*-diisopropylamino-dimethylphosphonium)-dodecahydro-7,10-dicarba-*nido*-dodecaborate(2–) (**3b**) was obtained in a similar fashion, when **3b** was used as a starting material. **3a** and **3b** exhibit short C<sub>cluster</sub>–P bonds and large C<sub>cluster</sub>⋯C<sub>cluster</sub> distances in the solid state.<sup>[3]</sup>



**Scheme 1.** Synthetic routes incorporating the cleavage of the P–P bond in **1a** with elemental lithium with formation of the lithiated intermediate **2a**.<sup>[1,2]</sup>



**Scheme 2.** Synthesis of zwitterionic 12-vertex bis-phosphonium-*nido*-carborates **3a,b** via ring-opening reaction and methylation of carborane-based 1,2-diphosphetanes **1a,b**.<sup>[3]</sup>

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## Catalytic B–C Coupling by Si/B Exchange: A Versatile Route to $\pi$ -Conjugated Organoborane Molecules, Oligomers, and Polymers

Lars Fritze<sup>a</sup>, Artur Lik<sup>a</sup>, Nicolas A. Riensch<sup>a</sup>, Holger Helten<sup>a,\*</sup>

<sup>a</sup>Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1,  
52056 Aachen/D

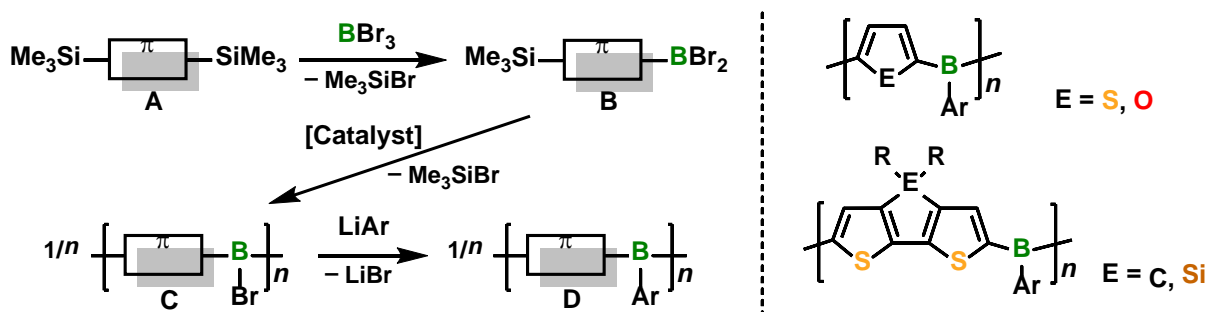
[lars.fritze@ac.rwth-aachen.de](mailto:lars.fritze@ac.rwth-aachen.de); [holger.helten@ac.rwth-aachen.de](mailto:holger.helten@ac.rwth-aachen.de)



### ABSTRACT

$\pi$ -Conjugated oligomers and polymers with tricoordinate boron centers incorporated into the main chain have attracted considerable attention as the interaction of the vacant p orbital on boron with an adjacent  $\pi$  system of the chain leads to extended conjugated materials with intriguing optical and electronic properties. This has enabled applications in organic electronics and optoelectronics (OLEDs, OFETs, photovoltaics) or as sensory materials.<sup>[1]</sup>

We have developed a highly efficient, environmentally benign, and broadly applicable method for the controlled synthesis of a wide range of  $\pi$ -conjugated organoborane molecules, oligomers, and polymers via a novel catalytic Si/B exchange reaction for B–C bond formation.<sup>[2,3]</sup> Our approach has significant advantages over previous protocols in that it uses relatively cost-effective reactants of low toxicity. Moreover, it may be employed in AB type polycondensation processes, using a monomer (**B**) that has both complementary functional groups incorporated required for polymer formation.



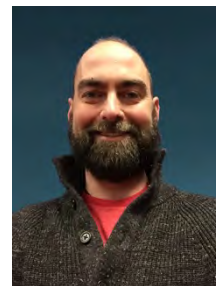
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## Difunctionalization of vinyl arenes with boron and CO<sub>2</sub>

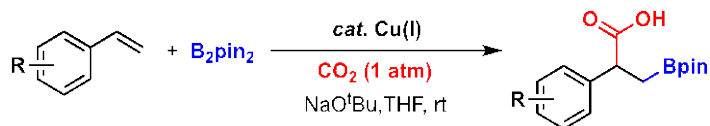
Brian V. Popp<sup>\*a</sup>

<sup>a</sup> C. Eugene Bennett Department of Chemistry, West Virginia University,  
PO Box 6045, Morgantown, West Virginia 26506, United States  
Brian.Popp@mail.wvu.edu



### ABSTRACT

The hetero(element)carboxylation of unsaturated organic substrates is useful due to the installation of a carboxylic acid as well as a synthetically versatile hetero(element)-carbon bond. We reported the first method to achieve boron-carboxylation of an olefinic substrate (vinyl arene).<sup>1</sup> The mild method uses redox-neutral copper catalysis and a single atmosphere of CO<sub>2</sub> to obtain boron-functionalized  $\alpha$ -aryl carboxylic acids, including novel functionalized-NSAIDs such as bora-ibuprofen and bora-naproxen. Recent progress toward the preparation of new bora-olefin compounds, subsequent synthetic elaboration of the carbon-boron bond, and complimentary experimental/computational studies to improve our mechanistic understanding will be presented.



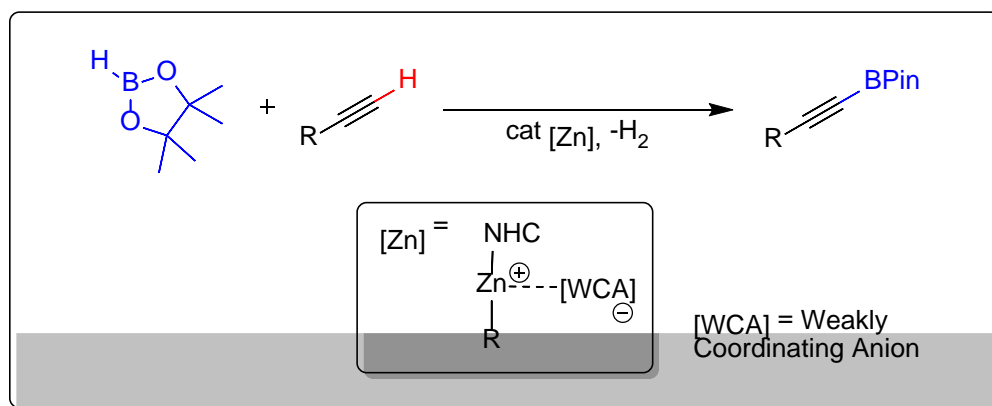
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## Dehydrogenative Borylation of alkynes catalyzed by a cationic zinc species

Richard J Procter<sup>a</sup>, Michael J Ingleson<sup>a,\*</sup><sup>a</sup>School of Chemistry, University of Manchester, Manchester, M13 9PL, UK[richard.procter@postgrad.manchester.ac.uk](mailto:richard.procter@postgrad.manchester.ac.uk), [michael.ingleson@manchester.ac.uk](mailto:michael.ingleson@manchester.ac.uk)

## ABSTRACT



Direct borylation of C-H bonds with H-BPin offers a powerful methodology for the synthesis of boron functionalized compounds with H<sub>2</sub> gas as the only waste byproduct. While aromatic C-H borylation is well developed, particularly using iridium catalysts, examples of dehydrogenative borylation of sp hybridized C-H bonds are less common, often suffering from low selectivity vs. competitive hydroboration.<sup>1,2</sup> The first example of dehydrogenative borylation of terminal alkynes (DHBTA) was reported in 2013 by Ozerov, utilizing an iridium catalyst.<sup>3</sup>

Development of catalysts using first row transition metals or main group elements offers significant potential economic and environmental advantages when compared with heavier transition metals. To this end Horio showed in 2014 the use of Zn(OTf)<sub>2</sub>/pyridine as a catalyst system for DHBTA but required use of HB(DAN) as HBPIn was unproductive under the reaction conditions.<sup>4</sup> Recently Bertrand showed the use of a CAAC-Cu(OTf) complex which enabled the reaction under mild conditions.<sup>5</sup> Here, we demonstrate the capability of a cationic zinc species to catalyse DHBTA with HBPIn, *via* a deprotonation-borylation mechanism.

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## Selective 3,4-Hydroboration of $\alpha,\beta$ -Unsaturated Esters Using NHC-boranes

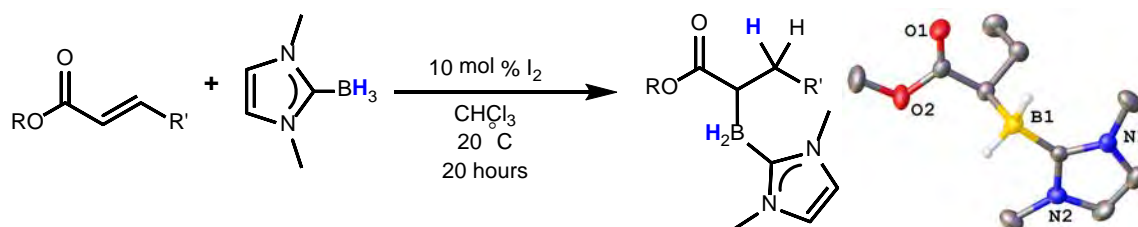
James E. Radcliffe<sup>a</sup>, Michael J. Ingleson<sup>a\*</sup>

<sup>a</sup> School of Chemistry, University of Manchester, Manchester, M13 9PL,  
United Kingdom

james.radcliffe@manchester.ac.uk, Michael.ingleson@manchester.ac.uk

### ABSTRACT

The formation of C-B bonds is of great importance to modern synthetic chemistry. Traditional approaches currently struggle with the borylation of a range of substrates, with the  $\alpha$ -borylation of  $\alpha,\beta$ -unsaturated esters being one such example. So far only reports 1,4-hydroboration of unsaturated esters have been published in the literature, making the 3,4-hydroboration of these substrates a target of interest to our group.<sup>[1]</sup>



Recent work in the Ingleson group has demonstrated the C2-borylation of indoles using NHC-boranes as a source of electrophilic boron upon activation with I<sub>2</sub>.<sup>[2]</sup> It was suggested that these NHC-boryl iodides may be capable of 3,4-hydroborylation with  $\alpha,\beta$ -unsaturated esters, based upon a recent report from Chang et al. concerning the  $\alpha$ -functionalisation of  $\alpha,\beta$ -unsaturated carbonyls via reductive silylation reactions catalysed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>[3]</sup>

Upon computational investigation it has been found that  $\alpha,\beta$ -unsaturated esters thermodynamically favour 3,4-hydroboration using NHC-boranes compared to 1,4-hydroboration. Encouraged by this result a series of screening reactions have been carried out, successfully proving that NHC-boranes undergo the unprecedented 3,4-hydroboration of  $\alpha,\beta$ -unsaturated esters upon activation with iodine. This poster will give the details of this investigation, along with the results of further reactions using our novel  $\alpha$ -borylated ester products.

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## Copper(I)-Catalyzed Enantioselective $\gamma$ -Boryl Substitution of Trifluoromethyl Alkenes via $\beta$ -Fluoroelimination

Sota Akiyama<sup>a</sup>, Ryoto Kojima<sup>a</sup>, and Hajime Ito<sup>a\*</sup>

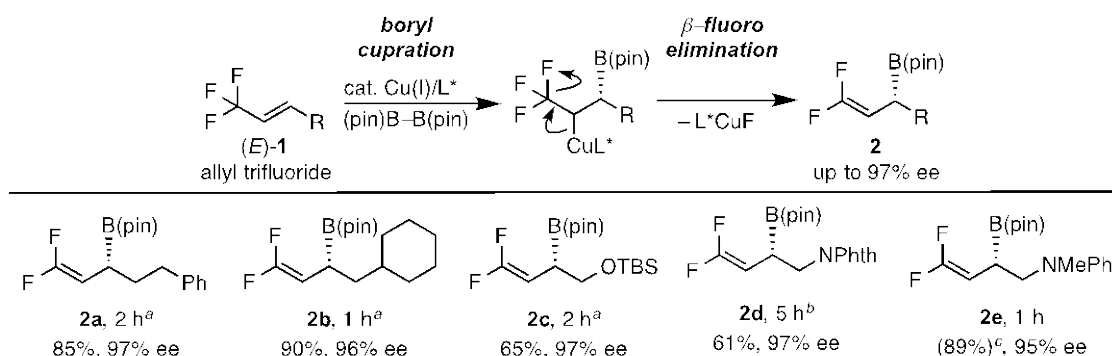
<sup>a</sup>Division of Applied Chemistry, Graduate School of Engineering,  
Hokkaido University, Sapporo, 060-8628

f-m-sckibp\_0311@eis.hokudai.ac.jp; hajito@eng.hokudai.ac.jp



### ABSTRACT

Enantio-enriched organofluorine compounds are known to be of great importance in medicinal chemistry due to the multitude effects that can arise from the introduction of fluorine atoms in small molecules.<sup>[1]</sup> Therefore, the development of efficient routes for their preparation is highly desirable. Optically active organoboron compounds are recognized as a useful chiral building block in synthetic chemistry because they can be readily applied to the stereospecific functionalization using the stereogenic C–B bonds. Allylic boronic acids and their esters stand out as a uniquely versatile class of reagents because allylboron species participate in a range of reactions. Previously, we reported the catalytic asymmetric reaction of allyl acetals via enantioselective copper(I)-catalyzed  $\gamma$ -boryl substitution.<sup>[2]</sup> In this reaction, optically active ( $\gamma$ -alkoxyallyl)boronates were afforded thorough  $\beta$ -alkoxy elimination. Guided by these successes,<sup>[3]</sup> we proceeded to investigate the development of copper(I)-catalyzed asymmetric synthesis of ( $\gamma,\gamma$ -gem-difluoroallyl)boronates via the enantioselective  $\gamma$ -boryl substitution of allyl trifluoride through  $\beta$ -fluoro elimination. The products represent promising chiral intermediates for the preparation of various organofluorine compounds.



<sup>a</sup>Reaction conditions: CuCl (0.025 mmol), ligand (0.025 mmol), (*E*)-1 (0.5 mmol), bis(pinacolato)diboron (0.75 mmol), and NaOMe (0.75 mmol) in THF (1.0 mL) at 30 °C. <sup>b</sup>0.625 mmol of bis(pinacolato)diboron was used. <sup>c</sup>NMR yield.

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# Iterative Development of Chiral Bisphosphine Ligand with Computational and Experimental Analysis for Enantioselective Markovnikov Hydroboration of Aliphatic Terminal Alkenes

Hiroaki Iwamoto<sup>a</sup>, Tsuneo Imamoto<sup>b,c</sup>, Hajime Ito<sup>a\*</sup>

<sup>a</sup> Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan.

<sup>b</sup> Organic R&D Department, Nippon Chemical Industrial Co., Ltd., Kameido, Koto-ku, Tokyo, 136-8515, Japan.

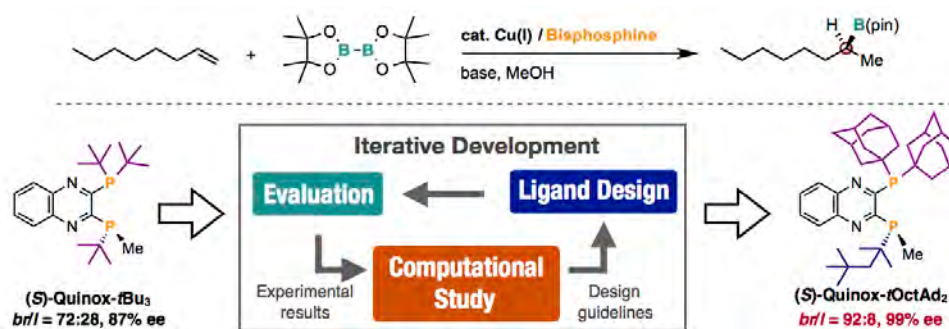
<sup>c</sup> Department of Chemistry, Graduate School of Science, Chiba University, Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan.  
g-iwamoto@eis.hokudai.ac.jp, hajito@eng.hokudai.ac.jp



## ABSTRACT

Efficient and rational development of asymmetric catalysts has been recognized as one of the most challenging issue in organic chemistry because the usual development method often requires numerous experiments for trial-and-error. The recent development of DFT calculation have achieved the prediction of enantioselectivity of asymmetric organic reactions.<sup>[1]</sup> However, there is a scarce example of rational design of asymmetric catalysts using computational study.

Hydroboration of terminal alkenes generally proceeds with *anti*-Markovnikov regioselectivity. Our group previously reported the first example of Markovnikov hydroboration of aliphatic terminal alkenes with the achiral copper(I)-catalyst. Then, two examples of the enantioselective version were recently reported.<sup>[2]–[4]</sup> However, there is still room for improvement on the enantio- and regioselectivities. In this work, we describe the novel design method of the asymmetric catalyst with iterative cycle including experimental and computational study for the enantioselective Markovnikov hydroboration of aliphatic terminal alkenes. After this iterative development, we finally found the high-performance chiral ligand (up to 99% ee).



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## Direct Introduction of Dimesitylboryl Group into Benzofurans via Iridium-Catalyzed C–H Activation

Ryosuke Shishido<sup>a</sup>, Ikuo Sasaki<sup>b</sup>, Tomohiro Seki<sup>a</sup>,  
Tatsuo Ishiyama<sup>a</sup>, Hajime Ito<sup>a\*</sup>

<sup>a</sup>Faculty of Engineering, Frontier Chemistry Center, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

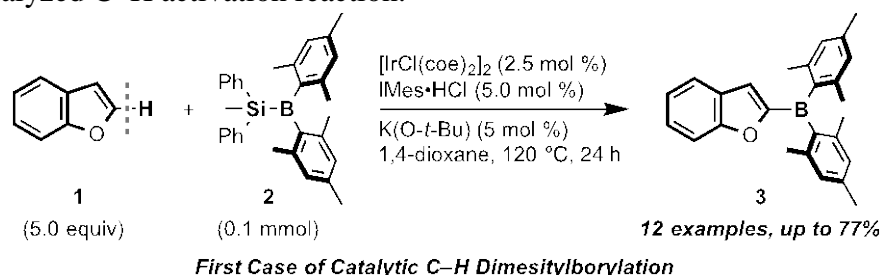
<sup>b</sup>Department of Chemistry and Biological Science, Aoyama Gakuin University, Sagamihara, Kanagawa 252-5258, Japan

shishido-ryosuke@eis.hokudai.ac.jp  
hajito@eng.hokudai.ac.jp



### ABSTRACT

Boron-containing  $\pi$ -conjugated compounds such as triarylboranes have received a great deal of attention as important organic materials due to their unique optical and electronic properties<sup>1</sup>. A dimesitylboryl (BMe<sub>2</sub>) group has usually been used as an important moiety in these compounds due to its strong  $\pi$ -electron acceptability and reasonable air stability. However, the practical introduction methods of a BMe<sub>2</sub> group to aromatic  $\pi$ -conjugated compounds are still limited. The most popular methods for the synthesis of aryl dimesitylboranes include the reactions of dimesitylboryl electrophiles with nucleophilic organometallic reagents. Recently, our group reported a novel method for the direct introduction of a BMe<sub>2</sub> group via the BBS method (Base-mediated Borylation with Silylborane)<sup>2</sup>. However, the stoichiometric amount of organometallic reagents or bases were needed in both of methods. Here, we describe the first example of the direct introduction reaction of the BMe<sub>2</sub> group into aromatic compounds through an iridium-catalyzed C–H activation reaction.



By this catalysis, the corresponding borylated products were obtained in high yield with excellent regioselectivity in one step. Furthermore, several borylated products exhibited a significant luminescent solvatochromism due to the donor-( $\pi$ -spacer)-acceptor structure. This result represents the utility of this direct introduction of BMe<sub>2</sub> group through C–H activation.

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## Borane-Functionalization of Polystyrene for Catalysis and Materials Applications

Huina Lin, Frieder Jäkle\*

Department of Chemistry, Rutgers University – Newark, 73 Warren Street,  
Newark, NJ 07102, USA

Email: [huina.lin@rutgers.edu](mailto:huina.lin@rutgers.edu), [fjaekle@rutgers.edu](mailto:fjaekle@rutgers.edu) Fax: +1 973 353 1264



### ABSTRACT

The incorporation of boron moieties into polystyrene-type polymers has attracted considerable interest due to wide applications in material science, nanotechnology and catalysis.<sup>[1]</sup> I have been pursuing two specific classes of organoborane-functionalized polyolefins:

1. B-N Containing Polymers: The replacement of a C=C unit with an isosteric BN unit in benzene significantly affects the aromaticity and photophysical properties. Thus, we anticipate the incorporation of azaborinine moieties into polymeric materials to expand the diversity and functionality of polystyrenes. 1-Hydro-2-vinyl-1,2-azaborinine and 1-hydro-2-styryl-1,2-azaborinine were polymerized, the polymers exhibit dramatically different solubility, thermal characteristics and photophysical properties compared with all-carbon polystyrene analogues.<sup>[2]</sup> Recently, we extended our studies to a series of new azaborinine-substituted polymers with the BN groups in different positions and investigated the effect of the substitution pattern on the physical properties.

2. Triarylborane Polymers: Lewis acids and so-called “frustrated Lewis pairs” (FLPs) are highly promising as catalysts for hydrogenation and hydrosilylation of organic substrates, as activators for olefin polymerization, and for small molecule activation. The incorporation of boron moieties into polyolefin-type polymers offers access to polymer-supported Lewis acids that may be used in catalysis. In earlier work, our group has succeeded in the synthesis of the highly Lewis acidic polystyrene-BR<sub>2</sub>.<sup>[3]</sup> This type of polymeric Lewis acids is promising to combine with Lewis bases to form FLPs for catalysis. To achieve air-stable yet highly active polymer-supported Lewis acids, we recently prepared new monomers that are sterically hindered to stabilize the boron center. The synthesis and properties of the corresponding polymers will be discussed.

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## Exploiting the Tunability of Lewis Acid/Lewis Base Interactions in the Design of Smart Transient Polymer Networks

Fernando Vidal<sup>a</sup>, Frieder Jäkle<sup>a,\*</sup>

<sup>a</sup>Rutgers University – Newark, 73 Warren Street, Newark, NJ 07102, USA  
fer.vidal@rutgers.edu, fjaekle@newark.rutgers.edu



### ABSTRACT

Supramolecular materials constituted of transient networks are receiving great attention for their unique features, including easy reprocessability, stimuli-responsiveness, and self-healing of macroscopic defects.<sup>[1]</sup> However, formulations based on a combination of gelators and solvents (hydrogels or organogels), while of great synthetic versatility, typically lack the appropriate mechanical strength required for performance materials. Thus, there has been an increased interest in developing polymeric networks that combine the thermal reversibility of the transient bonds with the desirable characteristics of polymer dynamics. In this context, the use of Lewis Acid (LA) and Lewis Base (LB) interactions is surprisingly scarce, and only few examples of using such a strategy are available.<sup>[2]</sup> We have previously introduced a facile approach to the borane Lewis acid functionalization of polystyrene and demonstrated the propensity of these materials to form reversible complexes with molecular Lewis bases.<sup>[3]</sup> In this presentation, we reveal the formation of thermo-responsive and reprocessable polymer networks with self-healing characteristics from polydimethylsiloxane/polystyrene (PDMS/PS) blends that feature complementary binding sites, i.e. one carrying the LA and the other carrying the LB.<sup>[4]</sup> The miscibility of the PDMS/PS domains achieved by the LA/LB interactions provides viscoelastic properties that can be fine-tuned by selecting the strength of the LA/LB pair.

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## Carboranes for nanostructured silicon surfaces and interfaces in electronic applications

Roman Keder<sup>a</sup>, Tomáš Jelínek<sup>a</sup>, Aliaksei Vetushka,<sup>b</sup> Antonín Fejfar,<sup>b</sup> and Tomáš Baše<sup>c</sup>

<sup>a</sup>*Katchem Ltd., El. Krásnohorské 6, Prague 1, 110 00, Czech Republic*

<sup>b</sup>*Institute of Physics, The Czech Academy of Sciences, Cukrovarnická 10, 162 00 Prague 6, Czech Republic*

<sup>c</sup>*Institute of Inorganic Chemistry, The Czech Academy of Sciences, 250 68 Husinec-Řež, č.p. 1001, Czech Republic*

[keder@katchem.cz](mailto:keder@katchem.cz), [tbase@iic.cas.cz](mailto:tbase@iic.cas.cz)



### ABSTRACT

Carboranes have been recognized as an important class of molecules for self-assemblies.<sup>[1]</sup> Their rigid molecular structures and rich isomeric forms enable to investigate particular physical properties of their 2-D assemblies while keeping the surface pattern either identical or very similar.<sup>[2]</sup> The respective self-organized monolayers exhibit fewer types and lower total number of surface defects compared to many of their organic counterparts, partly as a consequence of the low conformational freedom of carboranes.<sup>[3]</sup>

In our laboratories we have focused on several key aspects of this research that might help this area grow and find applications in various fields such as semiconductor industry. In addition to developing new synthetic procedures and optimizing the existing ones we have focused on testing our molecules towards silicon-based electronic devices.

This contribution will show selected results of the interaction between various functionalized carboranes and silicon surfaces. Our research has aimed at two main tasks: first, finding stable anchoring groups for carboranes that exhibit potential to alter the work function of silicon substrates via the orientation and magnitude of molecular dipoles (and thus to adjust the electronic interface of silicon-based electronic devices according to requirement), and second, to simply immobilize carborane cluster molecules as boron-rich carriers for further experimenting with the implantation of boron into the silicon substrate as an alternative way for shallow doping.

The support from the Czech Technology Agency (Project No. TH02020628) is highly appreciated.

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**Stereoselective Homocrotylation of Aldehydes:  
Synthesis of  $\alpha$ -Branched *Z/E* alkenes  
and highly selective flow photocycloaddition reactions**

Leiming Tian<sup>a</sup>, Isaac J. Krauss<sup>a\*</sup>

<sup>a</sup> *Department of Chemistry, Brandeis University, Waltham, Massachusetts 02454-9110, United States*

*lmtian@brandeis.edu*

*kraussi@brandeis.edu*

### ABSTRACT

We have previously shown that cyclopropanated allyl- and crotylboron reagents can be used for homoallylation of aldehydes, and the stereoselectivity can be predicted by Zimmerman-Traxler models.<sup>[1]</sup> Nucleophilic attack occurs from the unsubstituted cyclopropane carbon when one methyl substituent is present on the cyclopropane ring.<sup>[2-4]</sup> Thus only products with a 1,3-relationship between the methyl and the hydroxyl group have been observed.

In this study, we investigated boron reagents with  $\alpha$ -Me-substituents, which may reinforce or conflict with the preference for 1,3-substituted products. For reagents with trans-substituted cyclopropanes, the preference for 1,3-substitution dominates, forcing the formation of 1,3-substituted *Z*- alkenes, which are difficult to synthesize via other methods. However, reagents with cis-substituted cyclopropanes react to give mixtures of products. Natural-product-like scaffolds could be synthesized from our products by intramolecular photocycloaddition reactions, where flow conditions were applied to optimize the regioselectivity and yield.

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## Homoallylboration of Aldehydes: Investigation of Substituent Effect on Cyclopropane Ring

Bokai Xu<sup>a</sup>, Isaac J. Krauss<sup>a,\*</sup>

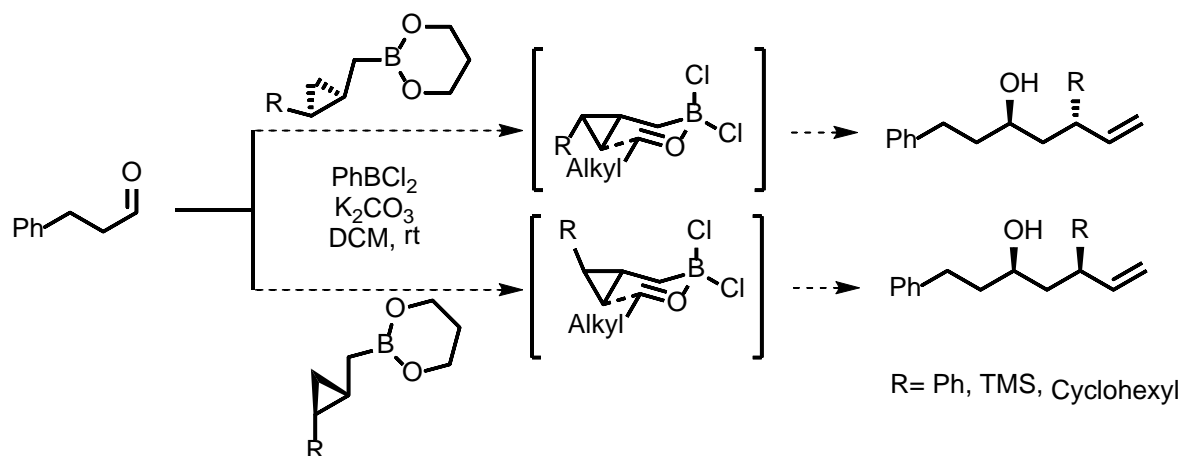
<sup>a</sup> Department of Chemistry, Brandeis University, Waltham, Massachusetts 02454-9110, United States

bokaixu@brandeis.edu

kraussi@brandeis.edu

### ABSTRACT

Enantio- and diastereoselective methods have been developed for allylation and crotylation of aldehydes and ketones. The influence of Zimmerman-Traxler transition states between aldehydes and allylboron or crotylboron reagents are critical in control the enantio- and diastereoselectivity. [1] Based on this idea, our group reported methods for addition of cyclopropanated allylboration reagents to aldehydes in the presence of PhBCl<sub>2</sub> to give high yields of bishomoallylic alcohols. [2-5] To broaden the utility of this method, we are currently testing the effects of various substituents on the cyclopropane ring.



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## The Synthesis, Characterization, and Application of an Unnatural Boron and Nitrogen-containing Tryptophan Analogue

Katherine Boknevitza and Shih-Yuan Liu<sup>a,\*</sup>

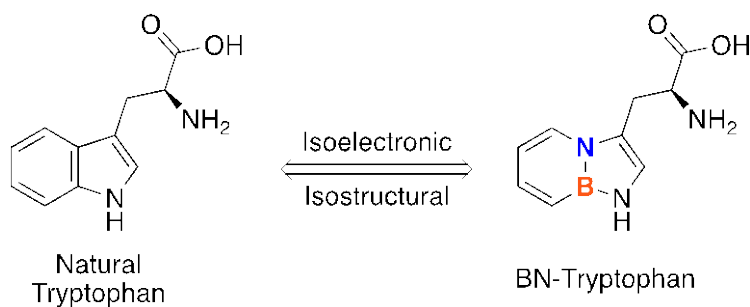
<sup>a</sup> Department of Chemistry, Boston College, Boston, Massachusetts 02467,  
United States

*Katherine.boknevitza@bc.edu, Shihyuan.liu@bc.edu*



### ABSTRACT

Boron and nitrogen (BN) containing heterocycles, such as 1,2-azaborines, have an isosteric and isoelectronic relationship with their carbonaceous counterparts. Arenes are ubiquitous in natural products and biologically active compounds and if we take advantage of the isosteric relationship between arenes and BN-arenes, we can expand the chemical space of arene containing molecules. The essential amino acid tryptophan is a desirable target for BN/CC isosterism studies due to its role in protein stability, structure, and function, as well as its use as a fluorescent marker in proteins. Incorporation of a BN bond into tryptophan through a late stage functionalization of the internal BN-indole offers a new analogue of this amino acid. This presentation will discuss the synthesis of BN-tryptophan, its properties in comparison with natural tryptophan, and its application as an unnatural amino acid.



## Synthesis of COSAN-Based Polyelectrolyte with Polynorbornene Backbone

Jianwei Li<sup>a,\*</sup>, Pavel Matějček<sup>a</sup>

<sup>a</sup>Department of Physical and Macromolecular Chemistry, Faculty of Science,  
Charles University, Hlavova 2030, 128 40 Prague 2, Czechia  
lijia@natur.cuni.cz



### ABSTRACT

Cobalt bis(1,2-dicarbollide), COSAN, is intrinsically amphiphilic metallocarborane cluster.<sup>[1]</sup> It bears one negative charge that is fully delocalized over the cluster. Due to the presence of hydridic B-H vertices, COSAN can form so-called dihydrogen bonds. These make COSAN suitable molecule for designing of macromolecular and supramolecular systems for nanochemistry.<sup>[1,2]</sup>

We used Ring-Opening Metathesis Polymerization, ROMP,<sup>[3]</sup> for synthesis of novel COSAN-containing polyelectrolyte: polynorbornene-COSAN (schematically described in Figure 1). First, we prepared monomer by a reaction of norbornene-methanol with COSAN-dioxanate.<sup>[4]</sup> Then, polynorbornene-COSAN was prepared, where molecular weight was controlled by reaction time (addition of quencher). Since COSAN interacts with the stationary phase of GPC column, the combination of MALDI-TOF, NMR and SAXS was used instead of standard GPC to determine molecular weight and dispersity.

Presence of anionic COSAN in each unit of polynorbornene-COSAN leads to unique polyelectrolyte with hydrophobic backbone and amphiphilic (surface active) charged pendant groups. The chain conformation is thus influenced by COSAN self-assembly and also by nature of counterions. Polynorbornene-COSAN polymer interacts with polycations and PEO-containing polymers leading to hierarchically organized nanostructures as observed by scattering and microscopy techniques.

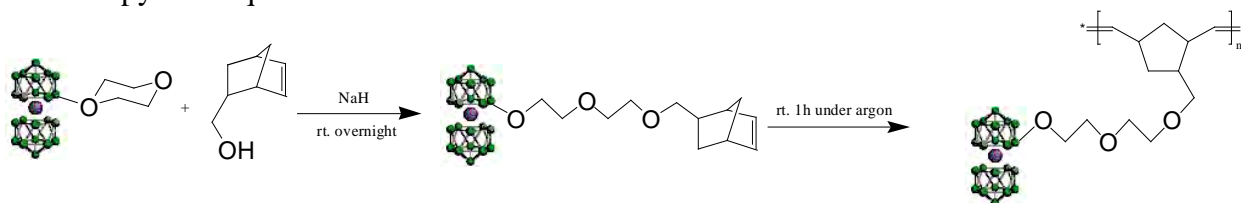


Figure 1. Synthesis of polynorbornene-COSAN by ROMP<sup>[3]</sup> with Grubbs second-generation catalyst of exo-5-norbornene-2-methanol with attached COSAN by COSAN-dioxanate.<sup>[4]</sup>

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## Advances in Conjunctive Cross-Coupling Reactions

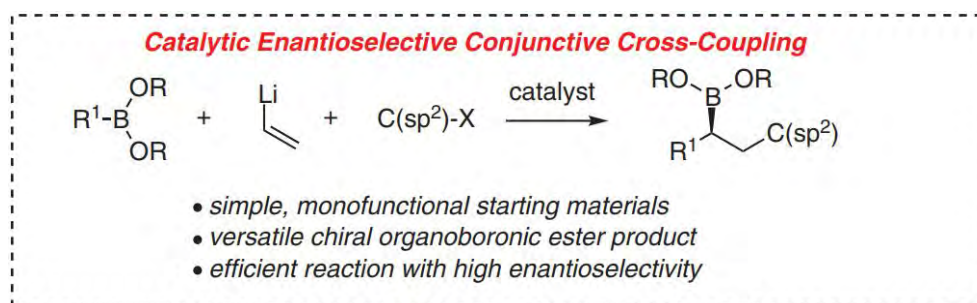
Gabriel J. Lovinger<sup>a</sup>, Liang Zhang, Emma K. Edelstein, Adam A. Szymaniak,  
Matteo P. Chierchia, Mark D. Aparece, Jesse Myhill, James P. Morken\*

Boston College  
Department of Chemistry  
Chestnut Hill, Massachusetts 02467  
<sup>a</sup>Email: [lovingeg@bc.edu](mailto:lovingeg@bc.edu)  
\*Email: [morken@bc.edu](mailto:morken@bc.edu)

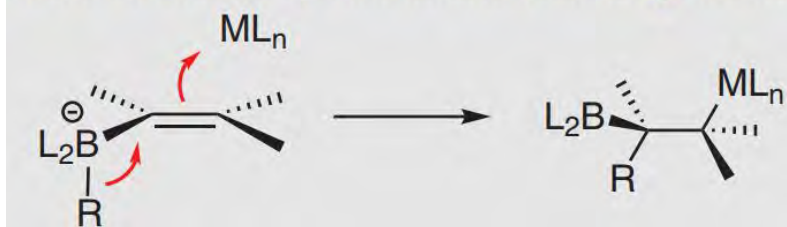


### ABSTRACT

Enantioenriched organoboron compounds are of high value in organic synthesis due to their ideal balance of stability and reactivity, as well as their capacity to undergo enantiospecific conversion into functional groups ranging from alcohols and amines, to carbonyls and organohalides.<sup>[1]</sup> This talk will discuss recent advances in conjunctive cross-coupling, a convergent and modular approach for the synthesis of enantioenriched alkyl boronic esters. Recent advances in the development of an enantioselective nickel-catalyzed conjunctive cross-coupling of alkyl electrophiles will also be presented.



### metal-induced 1,2-metallate rearrangement



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## Ni-Catalyzed Conjunctive Cross-Coupling of 9-BBN Borates with Acyl Electrophiles

Yan Meng<sup>a</sup>, Marshall C. Law<sup>a</sup>, Seung Moh Koo<sup>a</sup>, James P. Morcken<sup>a,\*</sup>

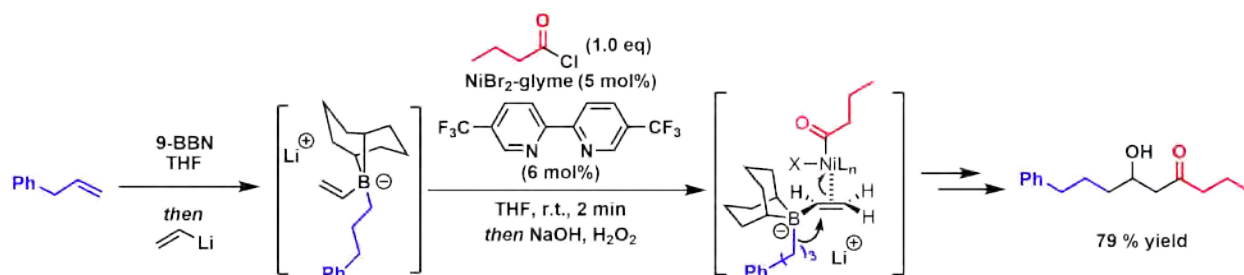
<sup>a</sup> Department of Chemistry, Merkert Chemistry Center,  
Boston College, Chestnut Hill, Massachusetts 02467, United States

[yangms@bc.edu](mailto:yangms@bc.edu) and [morken@bc.edu](mailto:morken@bc.edu)



### ABSTRACT

$\beta$ -keto alcohol is an important motif that widely exists in natural products<sup>[1]</sup>. Lots of efforts are being made on synthesizing it<sup>[1][2]</sup>. Besides directly delivering hydroxyl group,  $\beta$ -keto boron species could not only serve as masked alcohols but also have the potential to convert into other functional groups like amine, alkene, etc., which opens up a new direction toward synthesizing the motif<sup>[3]</sup>. Herein, a Ni-Catalyzed Conjunctive Cross-Coupling of 9-BBN borates with acyl electrophiles to furnish  $\beta$ -keto borane are reported. The ultra-fast reactions of 9-BBN “ate” complex with acyl chloride or anhydride are investigated with high efficiency through stereospecific trans-coplanar 1,2-metallate rearrangement. The product shows interesting properties in terms of borane transformations due to the unique electronic and steric features of 9-BBN borane. To our knowledge, this methodology represents the first example of  $\beta$ -keto borane synthesis.



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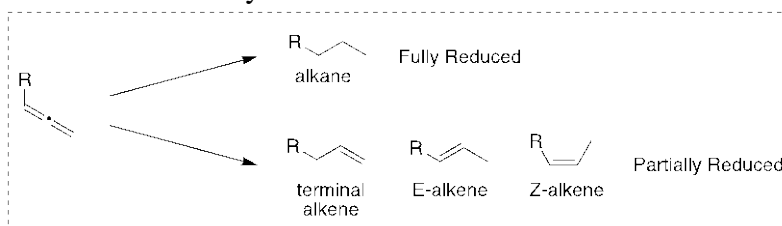
## Semi-Reduction of Allenes to Alkenes via Transfer Hydrogenation Facilitated by Diboron Reagents

Ashley Gates, Webster Santos<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Virginia Tech, 900 West. Campus Dr., Blacksburg, VA 24060  
[agates15@vt.edu](mailto:agates15@vt.edu), [santosw@vt.edu](mailto:santosw@vt.edu)

### ABSTRACT

Achieving regioselectivity and chemoselectivity in the reduction of allenes has historically been difficult. Reduction of both  $\pi$ -bonds will yield an alkane, but reduction of only one  $\pi$ -bond can yield a variety of alkene isomers (Figure 1). Additionally, increasing substitution around the allene provides additional challenges in attaining regioselectivity, chemoselectivity, and stereoselectivity. Most work on partial reduction of allenes has selectively reduced the terminal double bond to produce *Z*-alkenes,<sup>1,2</sup> while semi-reduction to produce the *E*-alkene with high selectivity has been achieved, but was substrate specific as it required chelation between indene and a benzyl functional group on the substrate. Other recent work has sought to reduce the internal double bond stereoselectively.<sup>3</sup>



**Figure 1.** A variety of products can be formed in the reduction of an allene.

In 2016, Stokes and co-workers investigated the use of tetrahydroxydiboron in the reduction of alkenes and alkynes to alkanes via palladium-catalyzed transfer hydrogenation.<sup>4</sup> This work investigates the regioselectivity and chemoselectivity of this process for use in semi-reduction of allenes. Preliminary reactions have shown good *E/Z* selectivity (80:20) and in good yield (72%).

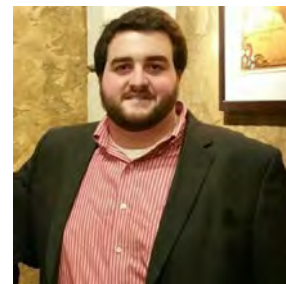
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## Facile Synthesis of Air-Stable Organodifluoroborates.

Eric Medici<sup>a</sup>, Connor Szwetkowski<sup>a</sup>, Laura Wonilowicz<sup>a</sup>, Russell Fritzscheier<sup>a</sup>, Webster Santos<sup>a,\*</sup>

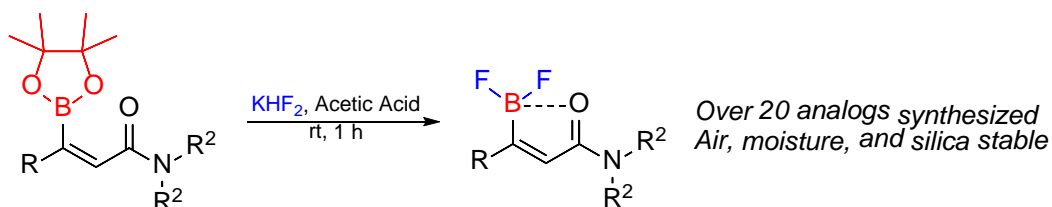
<sup>a</sup>Department of Chemistry, Virginia Tech, 900 West Campus Drive,  
Blacksburg, VA 24061.  
ermedici@vt.edu and santosw@vt.edu



### ABSTRACT

Organoborate salts are useful intermediates in many synthetic transformations.<sup>[1]</sup> While the synthesis and utility of trifluoroborate salts is well-documented, examples of the synthesis and transformation of neutral sp<sup>2</sup> hybridized difluoroborate derivatives are limited.<sup>[2,3]</sup>

We report the synthesis and transformation of air-stable organodifluoroborates. Surprisingly, the reaction of (*E*)- $\beta$ -borylacrylamides and KHF<sub>2</sub> results in pinacol deprotection and formation of difluoroborate product, in contrast to formation of the trifluoroborate salt.<sup>[4]</sup> The corresponding organodifluoroborates are air, moisture, as well as silica gel stable. Substrate scope and limitations are presented as well as transformations demonstrating the unique reactivity of these substrates.



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## Facile Synthesis of Highly Lewis Acidic Chloroboranes

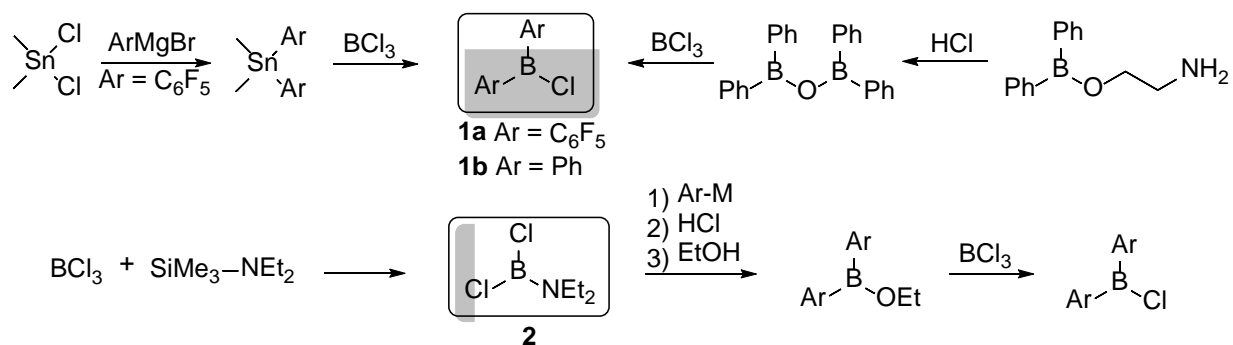
D. H. A. Boom<sup>a</sup>, F. Holtrop<sup>a</sup>, B. de Oude,<sup>a</sup> J. C. Slootweg<sup>a,\*</sup>

<sup>a</sup> Van 't Hoff Institute for Molecular Sciences University of Amsterdam, Science Park 904 PO Box 94157, 1090 GD Amsterdam (The Netherlands)  
d.h.a.boom@uva.nl, j.c.slootweg@uva.nl



### ABSTRACT

Diarylchloroboranes are widely used as boron building blocks in main-group chemistry, especially in the emerging field of frustrated Lewis pair (FLP) chemistry.<sup>[1]</sup> Typically, direct functionalization of BCl<sub>3</sub> with Grignard or organolithium reagents is unselective towards bis-addition and complex reaction mixtures are obtained.<sup>[2]</sup> To overcome this selectivity issue, a synthetic route starting from dimethyltin dichloride was developed by Chivers<sup>[3]</sup> and Piers,<sup>[4]</sup> which resulted in **1a** after tedious workups, such as repeated sublimation and distillation (Figure, top left).



In our group, we optimized the synthesis of diphenylchloroborane **1b** from commercially available materials based on two separate reaction steps that were known in literature (Figure, top right), but never combined for the synthesis of chloroboranes. This finding inspired us to design a selective and straightforward synthesis of a variety of commonly used highly Lewis acidic chloroboranes, which is the topic of our BORAM contribution. We discovered, for example, a protection–deprotection strategy using (diethylamino)dichloroborane **2** as starting material, which can be easily functionalized using the appropriate Grignard or organolithium reagents and converted into the corresponding chloroborane in a few simple, high yielding steps with easy work-up protocols (see Figure, bottom). Based on our findings, we are currently also developing a facile route to new and known perfluorinated triarylboranes.

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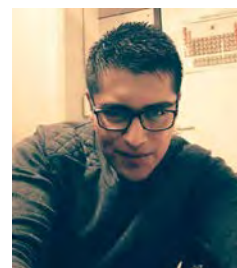
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## Identification by *in silico* assays and synthesis of a L-DOPA boroxazolidone as a potent agonist on D2 dopamine receptor

Abad García Antonio<sup>a,b\*</sup>, Ocampo-Néstor Ana L.<sup>a,b</sup>, Trujillo-Ferrara José G.<sup>b</sup>, Soriano Ursúa Marvin A.<sup>a</sup>

Departments of <sup>a</sup>Physiology and <sup>b</sup>Biochemisty. Sección de Estudios de Posgrado e Investigación. Escuela Superior de Medicina del Instituto Politécnico Nacional, Plan de San Luis y Diaz Mirón s/n, Col. Casco de Santo Tomás, Del. Miguel Hidalgo, Mexico City, México.

Email: [antonioabadgarcia@hotmail.com](mailto:antonioabadgarcia@hotmail.com)



### ABSTRACT

The adrenergic and dopamine receptors in the Central Nervous System (CNS) activate complex signaling cascades subsequently to interaction with endogen or exogen ligands.<sup>[1,2]</sup> Parkinson disease is a malady with a parallel depletion of dopamine and dopaminergic cells causing a decrease in the coordinated movements. Albeit the etiology is unclear, nowadays, the pharmacological “gold standard” of treatment is the exogenous restitution by levodopa administration. However, adverse effects induced by this drug lead us to design new molecules targeting the mentioned receptors, which are key in this pathology<sup>[2,3]</sup>

On the other hand, boron atom in a molecule can form a triplane state which is considered being the most naturally stable. But also, boron atom surrounded symmetrically by some atoms, can form four B-X bonds which are arranged tetrahedrally around the boron atom and all of them lying approximately in the same plane, this is considered the most stable conformation in boroxazolidones. These compounds are synthesized from alpha- amino acids; in these compounds the B-O bond ranges 1.28 Armstrongs, nearly to the B-N bond (1.44Armstrongs).<sup>[4,5]</sup> The resulting system seems attractive to interaction with sidechains of key residues in dopamine receptor binding and activation.

In this work, we tested ability of boroxazolidones for interacting as potential agonist of D2R in comparison with the dopamine, levodopa and other well-known agonists. We evaluated interactions on a recently reported structure of the targeted receptor (January 2018)<sup>[6]</sup> yielding the identification of a potential agonist which have been synthesized for future *in vitro* and *in vivo* evaluation.

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## Effects on lymphocyte clusters by boronic acids administration in mice

Romero-Aguilar Karla S.<sup>a</sup>, Soriano-Ursúa Marvin A.<sup>a</sup>, Arciniega-Martínez Ivonne M.<sup>a</sup>, Rodríguez-Rodríguez Edgar J.<sup>a</sup>, Vega-Valdez Ivan R.<sup>a</sup>, Barrón-González Mónica<sup>a</sup>, Reséndiz-Albor Aldo<sup>a\*</sup>



<sup>a</sup>Sección de Estudios de Posgrado e Investigación. Escuela Superior de Medicina del Instituto Politécnico Nacional, Plan de San Luis y Díaz Mirón s/n, Col. Casco de Santo Tomás, Del. Miguel Hidalgo, Mexico City, México.

E-mails: [ghostydana@hotmail.com](mailto:ghostydana@hotmail.com) and [alrealdoyahoo.com.mx](mailto:alrealdoyahoo.com.mx)

### ABSTRACT

Boron compounds has been recently explored because its multiple functions in animal and plants.<sup>[1]</sup> Among the reported effects, boric acid administration induced modulation of induced immune response in murine models.<sup>[2,3]</sup>

The knowledge regarding effects of boron-containing compounds modulating immune response could to generate strategies to modulate the host-response to damage or infection. This could be key to applications in multiple diseases, or biomedical topics such as the bacterial resistance against antibiotics.<sup>[4]</sup>

In this work, we tested the immunomodulatory response in Balb/C mice. These animals were orally administered with five different boron-containing acids solved in water for 10 consecutive days. Specifically, we tested 4-hidroxymethyl phenylboronic acid (Group A), methylboronic acid (Group B), 3-furanylboronic acid (Group C), 4-methanesulfonyl phenylboronic acid (Group D) and boric acid (Group E). All these were compared with a control group administered just with water. Four lymphocyte clusters from spleen, Peyer's patches and peripheral blood samples were measured. Each compound induced different changes, notably, compounds B and D induced an increase in several cell populations. Our results suggest a structure-activity relationship for boronic acids modulating immune response. However, additional compounds should be tested to establish such relationship.

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## ***In silico* test of Boron-containing genistein and 17- $\beta$ Estradiol analogues on human estrogenic receptors (ER $\alpha$ & ER $\beta$ )**

Vega-Valdez, Ivan Ricardo<sup>a</sup>, Soriano-Ursúa Marvin A.<sup>a</sup> García-Vázquez Benjamín<sup>a</sup>, Velazco-Silveyra Luz<sup>a</sup>, Martínez-Archundia Marleth T.<sup>a\*</sup>,

<sup>a</sup>*Departments of Physiology and Molecular Modelling. Sección de Estudios de Posgrado e Investigación. Escuela Superior de Medicina del Instituto Politécnico Nacional, Plan de San Luis y Diaz Mirón s/n, Col. Casco de Santo Tomás, Del. Miguel Hidalgo, Mexico City, México*  
 Email: [marletm8@gmail.com](mailto:marletm8@gmail.com)



### **ABSTRACT**

Breast cancer is a critical health problem around the world. In instance, it has become the second most common cause of death in Mexico among women aged 30 to 54 years and the third most frequent among the group of 30 to 59 years, after diabetes and heart disease<sup>[1]</sup>. It is known that ER $\alpha$  and ER $\beta$  estrogen nuclear receptors have a fundamental role in this pathology<sup>[2]</sup>. Moreover, there are drugs used in hormone therapy for breast cancer<sup>[3]</sup> such as tamoxifen and fulvestran, which target estrogen receptors ER $\alpha$ , ER $\beta$  and GPR304<sup>[4]</sup>. However, it has been reported many adverse effects related to their lack of selectivity on estrogen receptors<sup>[5]</sup>. Then, it is necessary to generate new ligands that target estrogen receptors with fewer side effects compared to drugs currently used in hormonal treatment.

In our work, we designed borated analogues of genistein<sup>[6]</sup> and 17- $\beta$  estradiol<sup>[7]</sup>, which are natural ligands of estrogen receptors. We perform addition or substitution with boron-containing moieties, strategically, to improve ability of precursors for interactions on the receptor binding sites. We tested by docking procedure the interaction of our compounds on the 3D model of targeted structures. Then, we analyzed the results in order to identify compounds with optimal affinity on targets as well as the key interactions on receptors. We identified compounds with high affinity on orthosteric site, but also boron-containing moieties which can be key for being added to known pharmacophores for increasing affinity and blockage action on estrogenic receptors. These studies will allow us to design new boron-containing molecules for modulating the activity of the receptors involved in breast cancer.<sup>[8]</sup>

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## Reversible Silver Electrodeposition from Boron Cluster Ionic Liquid (BCIL) Electrolytes

Mary A. Waddington,<sup>a</sup> Rafal M. Dziedzic,<sup>a</sup> Sara A. Lee,<sup>b</sup> Jack Kleinsasser,<sup>b</sup>  
John B. Plumley,<sup>c,d</sup>  
Beth D. Bosley,<sup>e</sup> Vincent Lavallo,<sup>b,\*</sup> Thomas L. Peng,<sup>c,\*</sup> Alexander M  
Spokoiny.<sup>a,f,\*</sup>



<sup>a</sup>Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E. Young Drive East, Los Angeles, CA 90095, United States

<sup>b</sup>Department of Chemistry and Biochemistry, University of California, Riverside, 501 Big Springs Rd., Riverside, CA 92521, United States

<sup>c</sup>Air Force Research Laboratory, Kirtland AFB, New Mexico, United States

<sup>d</sup>Department of Chemistry and Chemical Biology, University of New Mexico, 300 Terrace St. NE, Albuquerque, NM 87131, United States

<sup>e</sup>Boron Specialties LLC, 2301 Duss Avenue, Building 9, Ambridge, PA 15003, United States

<sup>f</sup>California NanoSystems Institute (CNSI), University of California, Los Angeles, 570 Westwood Plaza, Los Angeles, CA 90095, United States

### ABSTRACT

Metallic electrodeposition is essential to a variety of technologies including microchips, batteries and display systems.<sup>1</sup> As these applications develop, the ability to electrodeposit metals reversibly is becoming especially attractive as restructuring *in situ* allows for adaptability and the potential for prolonging device lifetimes. Unfortunately, many electrolytes for reversible metal deposition are comprised of organic and aqueous solvent systems, prohibiting applications wherein large thermal ranges or vacuum must be employed. In these instances, ionic liquids (solid salts with melting points <100 °C) can be used to shuttle ions without worry of electrolyte volatility.<sup>2</sup> However, it is known that many anionic components of ionic liquids are susceptible to hydrolysis (BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, etc.), among other degradation pathways, limiting lifetime of these electrolytes.<sup>3,4</sup> Herein, we present a series of monocarborane derived anions as electrolyte components for the reversible electrodeposition of silver. We show devices made with this boron cluster ionic liquid (BCIL) are stable to both prolonged exposure to 98% humidity and repeated electrochemical cycling, suggesting their utility in reversible electrodeposition. Further, infrared imaging provides proof-of-concept for tunable heat emission that could be applied in spacecraft and satellite technologies.

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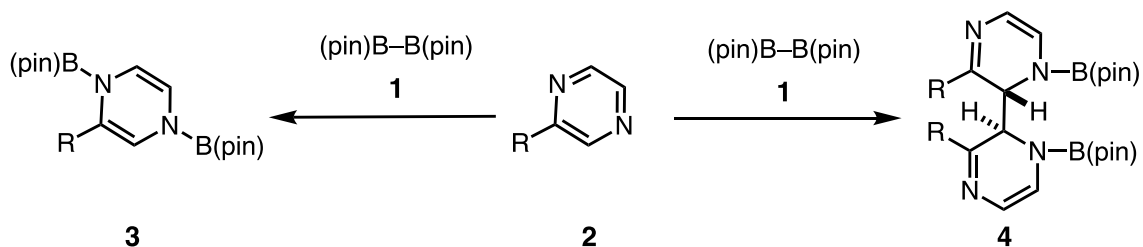
## Dearomatizing Conversions of Substituted Pyrazines in the Transition-metal-Free Reaction with Bis(pinacolato)diboron: Diboration and Diborative Dimerization

Kosuke Kabasawa, Toshimichi Ohmura,\* Michinori Suginome\*

*Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering,  
Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan  
ohmura@sbchem.kyoto-u.ac.jp; suginome@sbchem.kyoto-u.ac.jp*

### ABSTRACT

Addition of boron reagents across nitrogen-containing aromatic compounds is one of the attractive routes to dearomatized unsaturated cyclic amines. Transition-metal-catalyzed methods, including palladium-catalyzed silaboration and rhodium-catalyzed hydroboration of pyrazines,<sup>[1][2]</sup> have been developed. Recently, transition-metal-free reaction of bis(pinacolato)diboron (**1**) with nitrogen-containing aromatic compounds have received much attention. We have reported diboration of pyrazines and 4,4'-bipyridines to give *N,N'*-diboryldihydropyrazines and *N,N'*-diborylbipyridinylidenes.<sup>[3][4]</sup> Tang and coworkers have reported diborative dimerization of isoquinolines.<sup>[5]</sup> Herein, we describe reactions of **1** with pyrazines (**2**) bearing an electron-donating substituent such as alkoxy group. We found that the reaction gave either **3** through diboration or **4** through diborative dimerization depending on the reaction conditions.



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## Fluorophenylboronic acid modified triblock terpolymers and formation of multicompartment micelles

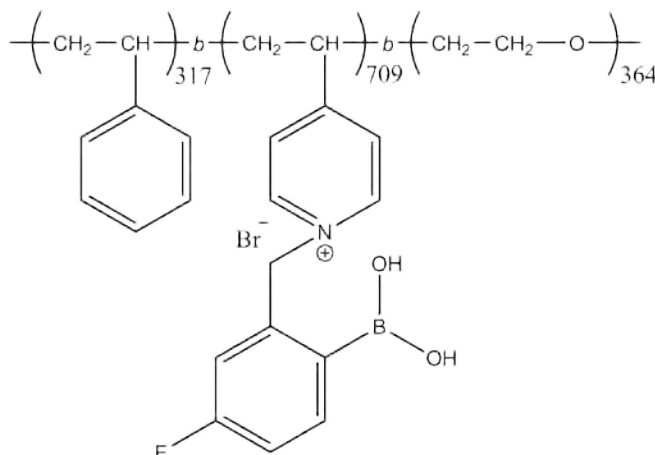
Vladimir Dordovic<sup>a\*</sup>, David Vrbata<sup>a</sup>, Mariusz Uchman<sup>a</sup>

<sup>a</sup>Department of Physical and Macromolecular Chemistry, Faculty of Science,  
Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic,  
vladimir.dordovic@natur.cuni.cz



### ABSTRACT

Phenylboronic acids have been extensively studied for their specific bonding to saccharides and their potential applications to diabetes treatments. In this study, we used 2-bromomethyl-4-fluorophenylboronic acid, PBA, to modify triblock terpolymer poly(styrene-*b*-4-vinyl pyridine-*b*-ethylene oxide), PS-PVP-PEO, by quaternization of pyridine groups of PVP (see figure below). We prepared three types of modified polymers: 100%, 50% and 25% quaternized PVP blocks. These polymers were all insoluble in water; however, dialysis against water to remove DMF induced self-assembly, which led to the formation of multicompartment micelles in aqueous solutions. The hydrophobic PS block cores were stabilized by the hydrophilic PEO blocks. The interaction between the middle block PVP and the solvent depended on pyridine protonation and boronic acid hydroxylation. Furthermore, the micelle structure provides possibilities of dual drug loading. The first type of drug can bind to boronic acid, and the second type of drug can be solubilized in micelle hydrophobic regions. To characterize the solution behavior of these polymers, we used both dynamic and static light scattering, <sup>1</sup>H, <sup>11</sup>B and <sup>19</sup>F nuclear magnetic resonance, fluorescence and cryogenic transmission electron microscopy. The resulting particles show different properties depending on the degree of quaternization, preparation protocol, pH and type of bonded diol compound. Therefore, these polymers may be used for saccharide sensing under specific conditions.



## Incorporation of metallacarborane groups in polymer backbone for as single Lithium-Ion conductors.

Roberto Fernandez-Alvarez<sup>a,\*</sup>, Mariusz Uchman<sup>a</sup>, Pavel Matejicek<sup>a</sup>

<sup>a</sup> Department of Physical and Macromolecular Chemistry., Faculty of Science,  
Charles University., Hlavova 2030, 128 43 Prague 2, Czechia  
[fernandr@natur.cuni.cz](mailto:fernandr@natur.cuni.cz)



### ABSTRACT

Solid polymer electrolytes have great potential as new technologies for solvent free Li rechargeable batteries. At present there is a strong demand for better and safer technologies to substitute the current Li batteries in the market. Already the use of highly delocalized anions has proved useful to increase the mobility of Li ions.<sup>[1]</sup> Metallacarboranes are large anions with a delocalized negative charge which makes them the perfect candidate for such applications.

The polymers/oligomers were synthesized by step-wise polymerization via formation of metallacarboranes with various metals (Ni, Fe, Co). The overall performance of the new polymers was tested both alone and in the presence of poly(ethylene oxide). The identity of linkers between metallacarboranes was changed in order to optimize the polymer characteristics for Li ion mobility. Traits such as distance between metallacarborane units and flexibility of linkers were studied (Figure 1).

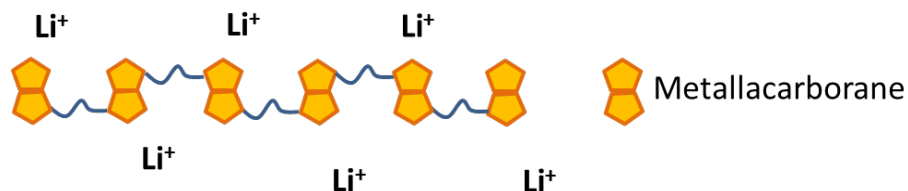


Figure 1. Schematic representation of metallacarborane-containing polymer.

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## Molecular Confinement of Metallocarborane-Polymer Complexes Leading to Lamellar Nanostructures

Pavel Matějčiček<sup>a,\*</sup>, David Vrbata<sup>a</sup>, Vladimír Ďord'ovič<sup>a</sup>, Mariusz Uchman<sup>a</sup>,  
Janne Ruokolainen<sup>b</sup>

<sup>a</sup> Department of Physical and Macromolecular Chemistry, Faculty of Science,  
Charles University, Hlavova 2030, 128 40 Prague 2, Czechia

<sup>b</sup> Department of Applied Physics Nanotalo, Aalto University, Puumiehenkuja 2,  
FI-02150 Espoo, Finland  
*pavel.matejicek@natur.cuni.cz*



### ABSTRACT

Anionic metallocarboranes such as cobalt bis(1,2-dicarbollide), COSAN, are intrinsically amphiphilic clusters that can be used as building blocks for a design of novel nanomaterials.<sup>[1]</sup> Recently, a nanocomposite forming by spontaneous precipitation from COSAN and poly(ethylene oxide), PEO, solutions has been described.<sup>[2]</sup> PEO/COSAN exhibits unique degree of inner ordering, where COSAN clusters and sodium counterions are evenly dispersed in amorphous PEO matrix. It was shown that COSAN can rotate alongside the longitudinal axis within the nanocomposite resembling nanorotors.<sup>[3]</sup>

In this communication, we describe nanostructures formed by telechelic PEO with attached glucose molecules: PEO-glc and glc-PEO-glc. Since COSAN does not interact with glucose end-groups, these behave like molecular confinement agents. It leads to lamellar nanostructures as clearly seen in cryoTEM micrographs. The regular thickness of the lamella is indicative for hydrogen bonding between glucose end-groups leading to compact structures. The shape of resulting membrane is given by number of attached glc (single or both chain ends modified). While PEO-glc/COSAN creates nanosheets, multilayer nanotubes or whisker-like nanostructures, glc-PEO-glc/COSAN nanostructures resemble vesicles.

The PEO/glc/COSAN nanostructures were stained by two fluorescence probes: (i) GB179 – fluorescein moiety with attached two COSAN clusters, which is dispersed within PEO/COSAN membrane, and (ii) RhBB – rhodamine B moiety with attached benzoxaborole, which can attach to glucose end groups. The nanostructures were studied by fluorescence microscopy both in buffer and also in cell cultures.

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## Novel polycaprolacton-based amphiphilic triblock terpolymers with pendant Wulff-type boronic acids for combined smart drug delivery

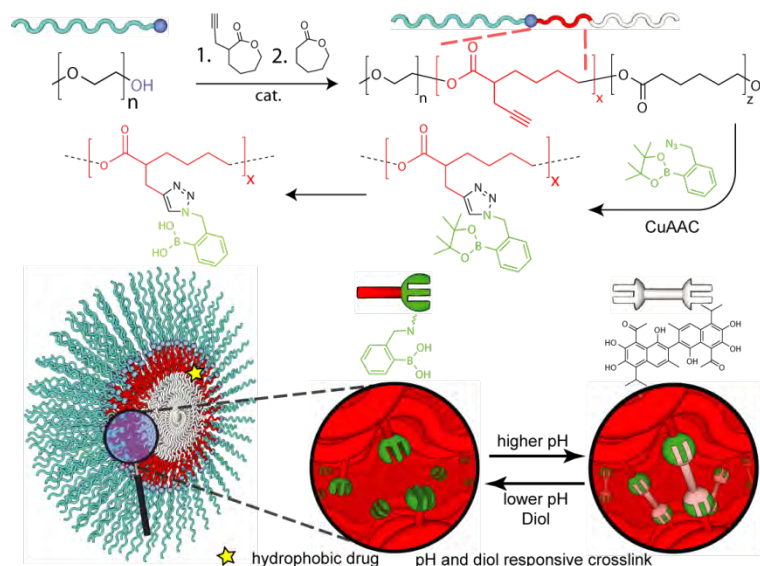
David Vrbata<sup>a</sup>, Dorota Dudičová<sup>a</sup>, Mariusz Uchman<sup>a,\*</sup>



<sup>a</sup>Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic  
vrbata@natur.cuni.cz, uchman@natur.cuni.cz

### ABSTRACT

Self-assembling amphiphilic block copolymers are effective vehicles for hydrophobic drugs delivery. Recently much effort has been put to design vehicles to release the drug in response to acidic cytosolic or endosomal conditions in tumour cells. Accordingly, in this study, such responsiveness is facilitated by pendant boronic acids which are known for their pH dependent ionization, reversible esterification with various diols and pH dependent hydrolysis of their esters. We synthesized biocompatible and biodegradable ABC and ACB triblock terpolymer in which A stands for poly(ethylene oxide), water-soluble and nanoparticles stabilizing block, B for boronic acid modified polycaprolactone forming responsive linkage with hydrophilic drugs and C for poly(caprolactone), vessel for hydrophobic drugs solubilization. The polymerizations were initiated with commercially available poly(ethylene oxide) of two different lengths (2k and 5k) and catalyzed by 1,4,7-Triazobicyclo[4.4.0]dec-5-ene using oxepan-2-one and 3/7-(prop-2-yn-1-yl)oxepan-2-one as monomers. These terpolymers were further modified by the CuAAC click reaction with 2-(azidomethyl)phenylboronic acid pinacol ester, and pinacol protecting groups were removed under acidic conditions. All polymers were characterized by GPC, MALDI-TOF and NMR spectroscopy. Multi-compartment micelle structures formed in water from ABC and ACB triblock terpolymers were assessed by SLS, DLS and Cryo-TEM to resolve their morphology and solution behavior. Resulting micellar solutions were subjected to different environments to evaluate their potential in field of drug delivery applications.



## Diverse Photochemical Transformations of Unsymmetric N,C-Chelate Organoboron Compounds

Cally Li<sup>a</sup>, Soren Mellerup<sup>a</sup>, Suning Wang<sup>a\*</sup>

<sup>a</sup>Queen's University, Department of Chemistry, 90 Bader Lane, Kingston, ON, CA, K7L 3N6  
[12cl88@queensu.ca](mailto:12cl88@queensu.ca), [suning.wang@chem.queensu.ca](mailto:suning.wang@chem.queensu.ca)

### ABSTRACT

Four-coordinated organoboron compounds have gained much interest for their applications in optoelectronic devices, such as organic light-emitting diodes (OLEDs) and molecular switches. One example is the unique class of N,C-chelate organoboron complexes previously discovered by our group, which have been known to undergo unprecedented photochemical/thermal colour switching at the boron core.<sup>[1]</sup> With ample attention directed towards studying the effect of substitution on the chelating ligand, much less is known about the impact of the aryl groups on the boron atom. Recently, we have shown that substitution of the boron centre with two differing aryl groups reveals unprecedented two-stage photochemical and thermal reactivity.<sup>[2]</sup> In an effort to capture the full scope of this family of molecules, we set out to investigate the effects of modifying their electronic structure to manipulate the mechanistic pathways. This work presents the full characterization of a new class of unsymmetric N,C-organoboron chelates, as well as their unique photochemical transformations.

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## Radical Borylation/Cyclization Cascade of 1,6-Enynes and 1,6-Dienes

Feng-Lian Zhang, Shi-Chao Ren, Jing Qi, Yi-Feng Wang\*

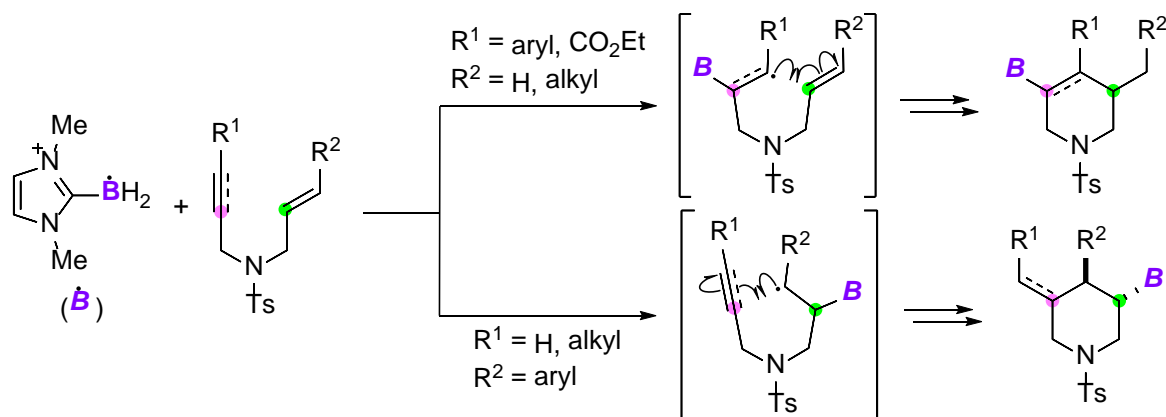
School of Chemistry and Material Science, University of Science and  
Technology of China, 96 Jinzhai Road, Hefei, Anhui, 230026

Email: [zfl9@ustc.edu.cn](mailto:zfl9@ustc.edu.cn); [yfwangzj@ustc.edu.cn](mailto:yfwangzj@ustc.edu.cn)



### ABSTRACT

Organoboron compounds have found widespread applications in modern synthetic chemistry.<sup>1</sup> Despite many borylation methods have been developed,<sup>2</sup> exploration of conceptually distinct approaches for the synthesis of complex organoboron compounds with predictable stereo- and regio-control remains challenging. Herein, we present an *N*-heterocyclic carbene (NHC)–boryl radical-induced borylation/cyclization cascade of 1,6-enynes<sup>3</sup> and 1,6-dienes<sup>4</sup> for the construction of boron substituted cyclic skeletons. The reaction was initiated by the chemo- and regio-controlled addition of an NHC–boryl radical to C–C unsaturated bonds where a functional group could stabilize the newly formed radical species, followed by ring closure to afford alkyl or alkenyl boron-handled cyclic molecules. Furthermore, various transformations of the boron-handled cyclic products to make diverse Paroxetine derivatives were demonstrated.



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- [4] Unpublished results.

## Enantioselective Cooperative Catalysis using Frustrated Acid/Base Complexes

Min Cao, Masayuki Wasa\*

Department of Chemistry, Boston College, Chestnut Hill, MA 02467

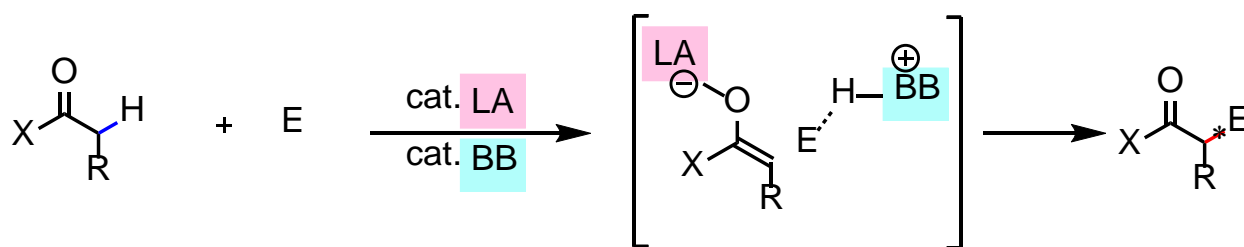
[caomd@bc.edu](mailto:caomd@bc.edu)

[wasa@bc.edu](mailto:wasa@bc.edu)



### ABSTRACT

Methods for enantioselective direct  $\alpha$ -amination reaction and Mannich-type reaction catalyzed by a sterically “frustrated” acid/base complex are disclosed. Cooperative functioning of the acid and base complex gives rise to in situ enolate generation from monocarbonyl compounds. Subsequent reaction with hydrogen-bond activated electrophile delivers desired product in high enantiomeric purity.<sup>[1-3]</sup>



E = Electrophile, LA = Lewis Acid, BB = Brønsted Base

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## Enantioselective $\alpha$ -Amino C–H Functionalization by Cooperative Functions of a Chiral and an Achiral Lewis Acid Catalyst

Jessica Chan<sup>a</sup> and Masayuki Wasa<sup>a,\*</sup>

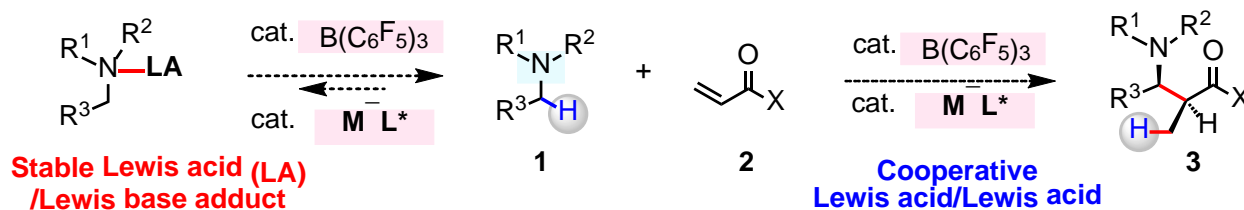
<sup>a</sup> Department of Chemistry, Merkert Chemistry Center, Boston College,  
Chestnut Hill, Massachusetts 02467, United States

chanop@bc.edu and wasa@bc.edu



### ABSTRACT

Catalytic enantioselective transformations of  $\alpha$ -amino C–H bonds furnish valuable chiral  $\alpha$ -substituted amines that are prevalent in pharmaceuticals and bioactive natural products. We present an efficient Lewis acid-catalyzed preparation of chiral  $\alpha$ -substituted amines. The use of a sterically encumbered *N*-alkylamine and hindered Lewis acid circumvents the formation of a “classic” Lewis adduct. Instead,  $B(C_6F_5)_3$  catalyzes the abstraction of a hydride from *N*-alkylamine to generate an ionic pair comprised of iminium ion and borohydride; subsequent borohydride reduction of a Lewis acid-activated  $\alpha,\beta$ -unsaturated compound affords a chiral enolate. Subsequent stereoselective C–C bond forming event between the *in situ*-generated nucleophilic and electrophilic species affords  $\beta$ -amino carbonyl compounds with complete atom economy.



## $\beta$ -C–H Functionalization of Amines through Lewis Acid and Brønsted Base Catalyzed Enamine Formation

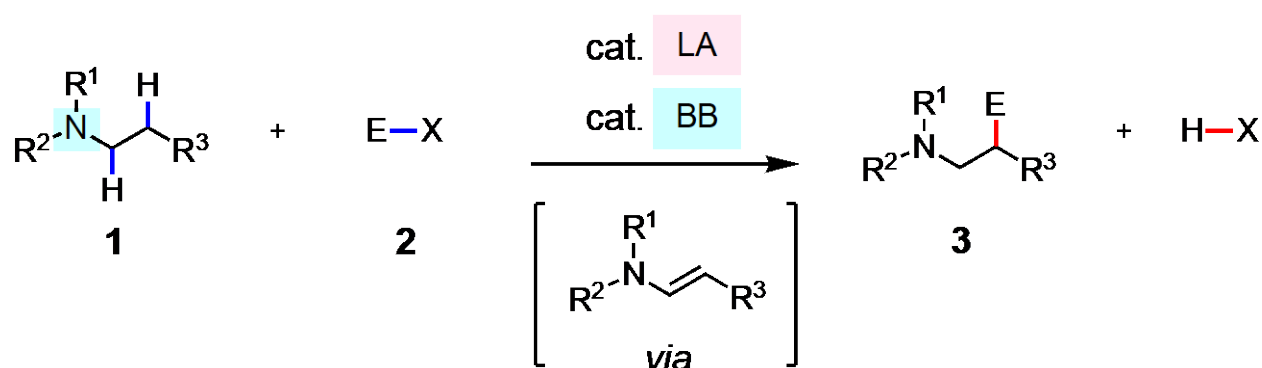
Yejin Chang<sup>a</sup>, Masayuki Wasa<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Boston College, 2609 Beacon Street, Chestnut Hill, Massachusetts 02467, USA

[changfn@bc.edu](mailto:changfn@bc.edu), [wasa@bc.edu](mailto:wasa@bc.edu)



### ABSTRACT



A strategy for functionalization of  $\beta$ -amino C–H bonds via enamine intermediate, which is formed through Lewis acid and Brønsted base cooperative catalysis, is disclosed. The use of a sterically hindered *N*-alkylamine and encumbered Lewis acid catalyst circumvents the formation of a “classic” Lewis adduct. The Lewis acid catalyzes the abstraction of a hydride from amines to yield an iminium ion intermediate. The iminium ion is then deprotonated by Brønsted base to generate a nucleophilic enamine intermediate, which can react with various electrophiles to afford  $\beta$ -substituted amines.



## Photoarylation of Iodocarboranes with Unactivated (Hetero)Arenes: Facile Synthesis of Aryl-*o*-Carboranes and *o*-Carborane-Fused Cyclics

Hangcheng Ni, and Zuowei Xie\*

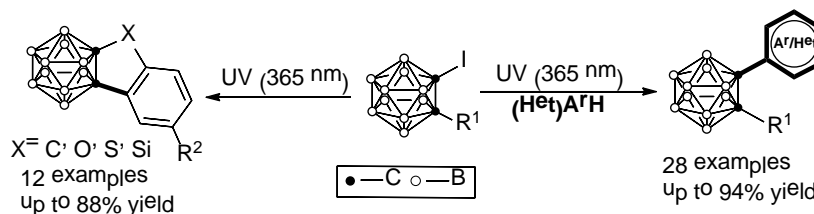
Department of Chemistry and State Key Laboratory of Synthetic Chemistry,  
The Chinese University of Hong Kong Shatin, N.T., Hong Kong (China).

E-mail: zxie@cuhk.edu.hk; nihc@hotmail.com



### ABSTRACT

Carborane is a cluster composed of carbon, boron and hydrogen atoms. It has been received a great attention for its applications in organometallic/coordination chemistry,<sup>[1]</sup> drug design<sup>[2]</sup> and versatile materials.<sup>[3]</sup> In this connection, a variety of methodologies have been developed for the synthesis of functionalized carboranes. Recently, our group reported a nickel-catalyzed arylation of carboranes with the assistance of Grignard agents.<sup>[4]</sup> In this presentation, we described an efficient strategy for the synthesis of aryl-*o*-carboranes and *o*-carborane-fused cyclics through light-induced C<sub>cage</sub>-C<sub>sp2</sub> coupling. This work represents a clean, efficient, transition-metal-free and cheap synthesis of functionalized carboranes, which has significant advantages over the known methods.<sup>[5]</sup>



**Scheme 1.** Cross coupling of iodocarborane with arenes.

This work was supported by a grant from the Research Grants Council of HKSAR.

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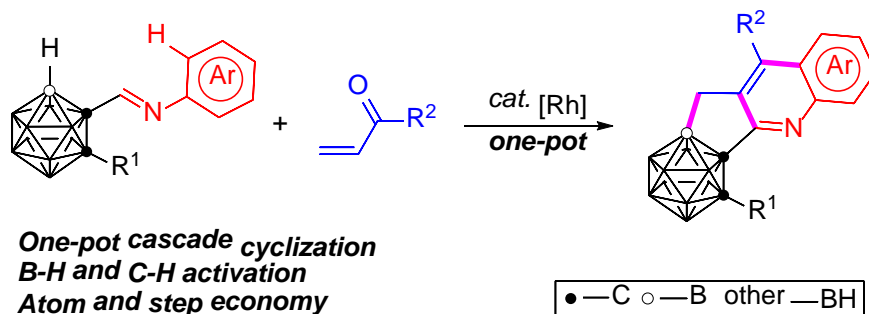
## Rhodium Catalyzed Cascade Cyclization Featuring B-H and C-H Activation: One-Step Construction of Carborane-fused *N*-Polyheterocycles

Hairong Lyu and Zuowei Xie\*

Department of Chemistry and State Key Laboratory of Synthetic Chemistry,  
The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China  
E-mail: zxie@cuhk.edu.hk

### ABSTRACT

Incorporating carborane moiety into  $\pi$ -conjugated molecules or replacing (hetero)aromatic ring in known drugs by carborane unit has provided a series of novel optoelectronic materials and potent drug molecules.<sup>[1]</sup> However, despite of the growing research interest in carborane chemistry, straightforward or one-step construction of carborane-fused polycycles is still rather limited. In view of the recent advances in C-H activation and based on our recent achievements in transition metal catalyzed B-H functionalization of carboranes,<sup>[2]</sup> we herein developed a novel one-pot strategy for efficient and facile synthesis of C,B-substituted carborane-fused *N*-polyheterocycles, which cannot be prepared by other means. Rhodium catalyzed cascade cyclization of carboranyl *N*-arylimines and vinyl ketones enables this effective construction, featuring regioselective cage B-H and  $sp^2$  C-H activation. The resultant previously unavailable C,B-substituted carborane-fused cyclopenta[b]quinoline derivatives may find valuable applications in pharmaceuticals and materials.



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## Reaction of *o*-Carboryne with Styrene and Its Derivatives

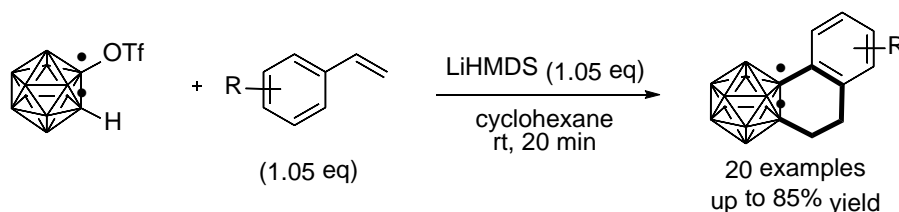
Jie Zhang and Zuwei Xie\*

Department of Chemistry, The Chinese University of Hong Kong, Shatin,  
New Territories, Hong Kong, China  
E-mail for J.Z.: zhjie1989@126.com  
E-mail for Z.X.: zxie@cuhk.edu.hk



### ABSTRACT

1,2-Dehydro-*o*-carborane (*o*-carboryne) is a very reactive intermediate that can be viewed as a three-dimensional relative of benzyne.<sup>1</sup> Styrene and its derivatives are commonly known to participate in [2+1], [2+2] or [4+2] cycloaddition reactions. In addition, the extra-annular [4+2] cycloaddition reaction, in which the exocyclic double bond and one of the neighboring aromatic double bonds in styrenes consist of the diene component, can also take place.<sup>2</sup> We previously reported the reaction of carboryne generated from 1-I-2-Li-1,2-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub> with styrene and its derivatives.<sup>3</sup> In addition to [2+2] cycloaddition reaction and/or ene reaction, an extra-annular [4+2] cycloaddition reaction is also observed, depending upon the substituents on the vinyl unit. More recently, a new *o*-carboryne precursor 1-Li-2-OTf-*o*-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> has been developed in our laboratory.<sup>4</sup> In this work, a more efficient extra-annular [4+2] cycloaddition of *o*-carboryne with styrene and its derivatives under mild reaction conditions will be described.



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## Bora-fluoresceins: A New Family of Fluorescein Analogs with its Absorption and Fluorescence in the Near Infrared Region

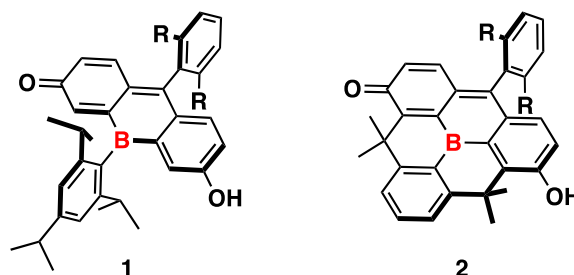
Naoki Ando,<sup>a</sup> Hiroki Soutome,<sup>a</sup> Shigehiro Yamaguchi<sup>b\*</sup>

<sup>a</sup>Graduate School of Science, and <sup>b</sup>Institute of Transformative Bio-Molecules,  
Nagoya University, Furo, Chikusa, Nagoya, 464-8602, Japan

Email : [andou.naoki@c.mbox.nagoya-u.ac.jp](mailto:andou.naoki@c.mbox.nagoya-u.ac.jp)  
[yamaguchi@chem.nagoya-u.ac.jp](mailto:yamaguchi@chem.nagoya-u.ac.jp)



Xanthene is a key skeleton of organic fluorescence dyes, such as fluoresceins and rhodamins. These dyes typically exhibit their absorption and fluorescence in the visible region, which is sometimes not sufficient for their application to fluorescent probes for bio-imaging. Thus, various structural modifications of the xanthene skeleton to impart the red-shifted absorption and fluorescence properties have been intensively studied. One effective strategy to this end is the replacement of the oxygen atom at the 10-position with main group elements. On the basis of this strategy, a series of xanthene dyes containing various main group elements at the 10-position have been synthesized. Nevertheless, the studies of boron-containing xanthene dyes have been limited to tetracoordinate boron derivatives.<sup>1</sup> Herein, we report the synthesis of bora-fluorescein **1** and **2** as a new family of fluorescein analogs with a tricoordinate boron atom. These dyes exhibited strong absorption bands in the near infrared region under basic conditions. This presentation will discuss the impact of a tricoordinate boron atom on the fundamental properties of the fluorescein dyes including photophysical properties and Lewis acidity.



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## Reactivity of Tetraaryldiborane(4) Dianion

Seiji Akiyama, Makoto Yamashita\*

Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

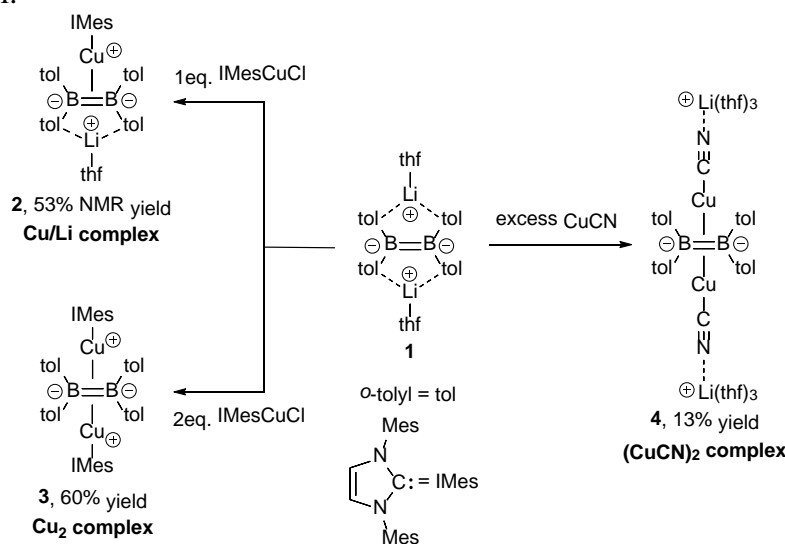
makoto@oec.chembio.nagoya-u.ac.jp



### ABSTRACT

We recently reported that tetraaryldiborane(4),  $(o\text{-tol})_2\text{B}-\text{B}(o\text{-tol})_2$ , has two vacant p-orbitals on boron atoms as LUMO.<sup>1</sup> Therefore, one can expect that its dianion via two-electron reduction of  $(o\text{-tol})_2\text{B}-\text{B}(o\text{-tol})_2$  would have a highly reactive  $\pi$ -electrons as HOMO. Although, only two examples of tetraaryldiborane dianion have been reported with their structures,<sup>2,3</sup> their reactivity have not been disclosed so far. In this research, we investigated the reactivity of diborane(4) dianion derived from  $(o\text{-tol})_2\text{B}-\text{B}(o\text{-tol})_2$ .

Dianion **1**, generated by reduction of  $(o\text{-tol})_2\text{B}-\text{B}(o\text{-tol})_2$  with elemental Li, was treated with 1 equivalent of copper-NHC complex (IMesCuCl) gave the corresponding diborane dianion complex **2** possessing Cu/Li counter cations via transmetalation.<sup>4</sup> While diborane dianion complexes  $\text{Cu}_2$  complex **3** and  $(\text{CuCN})_2$  complex **4** were obtained by a reaction with 2 equivalent of IMesCuCl or excess CuCN. In the presentation, properties of these complexes will be discussed in detail.



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## Catalytic Hydroalkoxylations of Alkenes using Tris(pentafluorophenyl)borane

Jordan N. Bentley,<sup>a</sup> and Christopher B. Caputo<sup>a\*</sup>

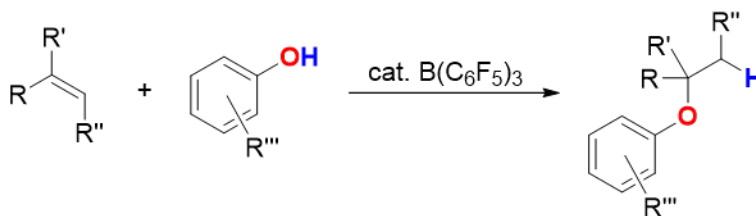
<sup>a</sup>York University, 4700 Keele Street, Toronto ON, Canada, M3J1P3  
caputo@yorku.ca



### ABSTRACT

The development of sustainable methodologies for the formation of carbon-heteroatom bonds is of significant importance. One promising route to achieve this is the use of main-group catalysts, which will eliminate stoichiometric reagents and/or the use of precious metals. The Lewis acid  $B(C_6F_5)_3$  has found extensive applications as a metal-free catalyst and is particularly used as a component in Frustrated Lewis Pair chemistry.<sup>[1]</sup> In addition, it is independently an effective catalyst for the hydrofunctionalization of unsaturated substrates, specifically hydrosilylation,<sup>[2]</sup> hydroamination,<sup>[3]</sup> and hydrothiolation reactions,<sup>[4]</sup> to name a few. However, one overlooked heteroatom for these addition reactions is oxygen.

The hydroalkoxylation of olefins is an atom-economical way of generating ethers from alcohols and olefins, with no by-products. Studies have shown the effectiveness of various transition metal catalysts for this transformation, however main-group alternatives are sparse.<sup>[5]</sup> Our research has shown that  $B(C_6F_5)_3$  is an effective metal-free catalyst for this transformation, promoting this reaction under mild-conditions with low catalyst loadings. Our results will be described in this presentation.



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## Towards the Total Synthesis of Bahamaolide A

Joseph M. Bateman<sup>a</sup>, Teerawut Bootwicha<sup>a</sup>, Alexander Fawcett<sup>a</sup>, Eddie L. Myers<sup>b</sup> and Varinder K. Aggarwal<sup>a,\*</sup>

<sup>a</sup> School of Chemistry, University of Bristol, Bristol, UK

<sup>b</sup> School of Chemistry, NUI Galway, Galway, Ireland

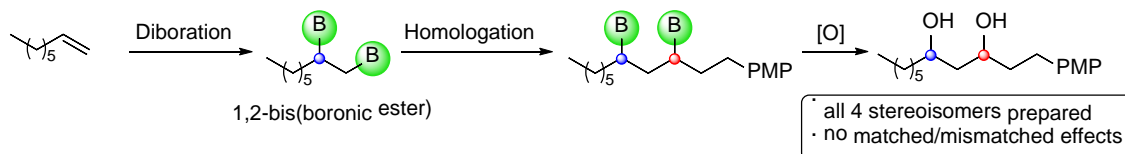
[joe.bateman@bristol.ac.uk](mailto:joe.bateman@bristol.ac.uk), [V.Aggarwal@bristol.ac.uk](mailto:V.Aggarwal@bristol.ac.uk)



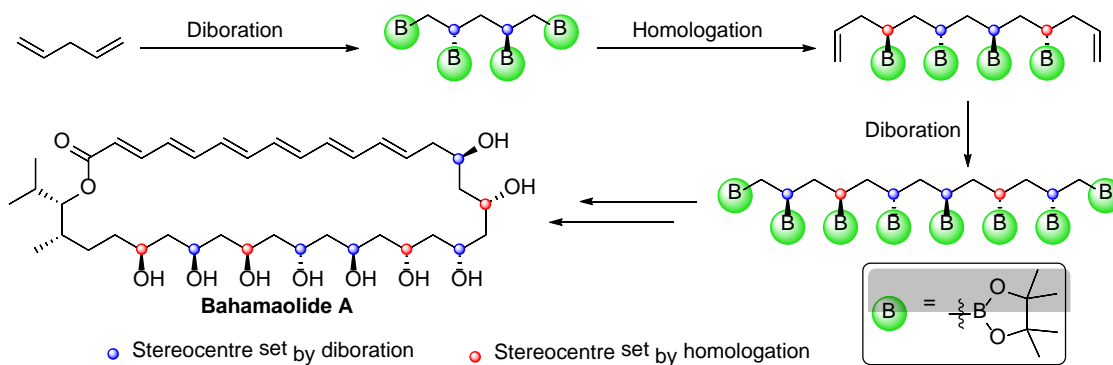
## ABSTRACT

Recently, the Aggarwal group has shown that 1,2-bis(boronic esters) can be homologated selectively at the less hindered terminal boronic ester to afford, after oxidation, 1,3-diols.<sup>1</sup> We sought to extend and apply this methodology to the synthesis of Bahamaolide A, a newly isolated member of the polyene macrolide class of compounds that shows potent antifungal activity.<sup>2</sup> Retrosynthetic disconnections lead to an unprecedented  $C_2$  symmetric *poly*-organoboron fragment, containing eight boronic acid pinacol esters. This ‘*octa*-boronic ester’ is a bench stable solid that can be achieved in three steps by an iterative, two-directional diboration/homologation sequence starting from 1,4-pentadiene.

**Previous work:** selective homologation of 1,2-bis(boronic esters)



**This work:** studies towards the total synthesis of Bahamaolide A



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## Helical Hydrocarbons: Synthesis and Control of Screw-Sense

Johan A. Pradeilles<sup>a</sup>, Siying Zhong<sup>a</sup>, Craig P. Butts<sup>a</sup>, Eddie L. Myers<sup>b</sup>,  
Varinder K. Aggarwal<sup>a,\*</sup>

<sup>a</sup>*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United-Kingdom*

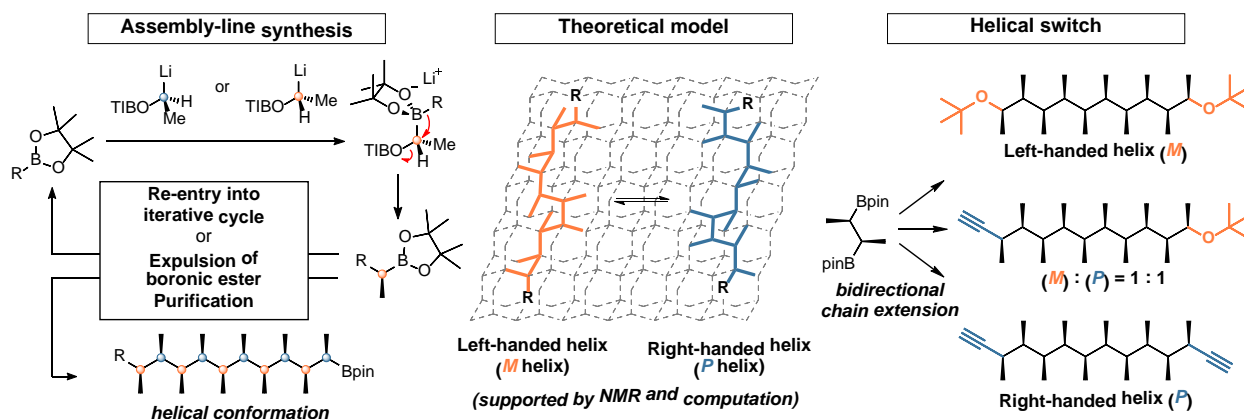
<sup>b</sup>*School of Chemistry, NUI Galway, University Road, Galway, Ireland*  
johan.pradeilles@bristol.ac.uk, v.aggarwal@bristol.ac.uk



### ABSTRACT

Recently, our group has shown that all-*syn* methyl-substituted hydrocarbons can be prepared as single enantiomers by using iterative lithiation–borylation and that they heavily populate a helical conformation<sup>[1]</sup>. These compounds fold into a helix because it is the only conformation where *syn*-pentane interactions are avoided<sup>[2]</sup>. The sense of helicity observed depends upon the environment and the nature of the end-groups. Herein, we report a model that rationalizes this dependence and allows us to predict the screw-sense of our molecules. Extensive conformational analysis employing both computation and NMR spectroscopy has been used to support our model<sup>[3]</sup>.

The molecules were synthesized by using a bidirectional iterative homologation<sup>[4]</sup> of a C<sub>2</sub>-symmetric bis(boronic ester) to install the ‘backbone’ (10 contiguous stereocentres), followed by divergent end-group functionalisations. We applied our new knowledge to design a helical hydrocarbon that undergoes screw-sense interconversion upon sequential chemical modification of end-groups.



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## N-B bifunctionalized polystyrene resins as recyclable pre-catalysts for the metal-free borylation of heteroarenes

Nicolas Bouchard<sup>a</sup>, Frédéric-Georges Fontaine<sup>a\*</sup>

<sup>a</sup> *Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec City, Québec G1V 0A6, Canada.*

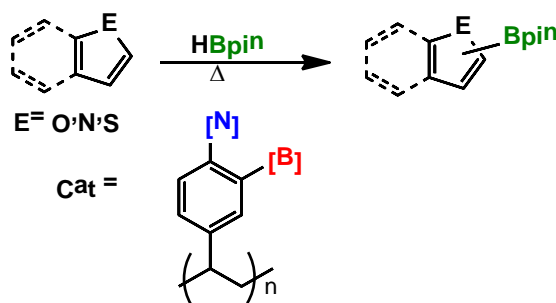
[Nicolas.bouchard.15@ulaval.ca](mailto:Nicolas.bouchard.15@ulaval.ca), [Frederic.fontaine@chm.ulaval.ca](mailto:Frederic.fontaine@chm.ulaval.ca)



### ABSTRACT

In 2015, our group<sup>1</sup> reported the catalytic metal-free borylation of heteroarenes using ambiphilic 1-TMP-2-BH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub> (TMP= 2,2,6,6-tetramethylpiperidine). Since then, we reported air stable<sup>2</sup> (trifluoroborate salts) and more active catalysts bearing smaller amines<sup>3</sup>. The ease of synthesis of these air-stable compounds prepared from commercially available precursors paves the way to the synthesis of polymeric versions of borylation precatalysts.

We wish to report the synthesis of styrenic ambiphilic “Frustrated Lewis Pair” based on the *ansa*-aminoborate motif and the polymerization studies. These materials act as tunable and recyclable resins, making their implementation in flow chemistry systems easier. We will report the reactivity of these materials both in batch and flow chemistry.



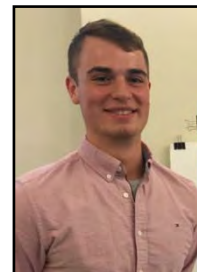
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## Exploring an Enantiospecific Suzuki Coupling: Self-Alkylation of 1,2-Azaborines

John Hoskin, Shih-Yuan Liu\*

Boston College, Merkert Chemistry Center, Chestnut Hill, MA 02467-3860, USA  
 hoskinj@bc.edu, liusd@bc.edu



### ABSTRACT

The Suzuki-Miyaura cross-coupling reaction<sup>1</sup> has emerged as one of the most important synthetic methods for forming carbon-carbon bonds. Most commonly utilized to form  $sp^2$ - $sp^2$  linkages, enantiospecific  $sp^3$  Suzuki couplings are still a challenge with only limited examples.<sup>2</sup> Known enantiospecific couplings are limited by the need for an activating group incorporated into the substrate, due to the significantly lower reactivity of the secondary *B*-alkyl bond than the primary *B*-alkyl bond resulting in problematic transmetalation. Adjacent  $\pi$ -systems, particularly benzylic<sup>3</sup> and allylic<sup>4</sup> groups, have been shown to facilitate the reaction due to their weakening of the B-C bond. Inspired by Molander's report of self-arylation of 2,1-borazaronaphthalenes,<sup>5</sup> this project aims to remove this restriction of substrate by incorporating the  $\pi$ -system into the organoboron coupling partner, using *B*-alkyl 1,2-azaborines. In addition, we hypothesize that due to rearomatization of the azaborine system from the  $sp^3$  boron "ate" complex that transmetalation will be particularly facile. The current state of this project and future applications to a chiral alkylation methodology will be discussed here.

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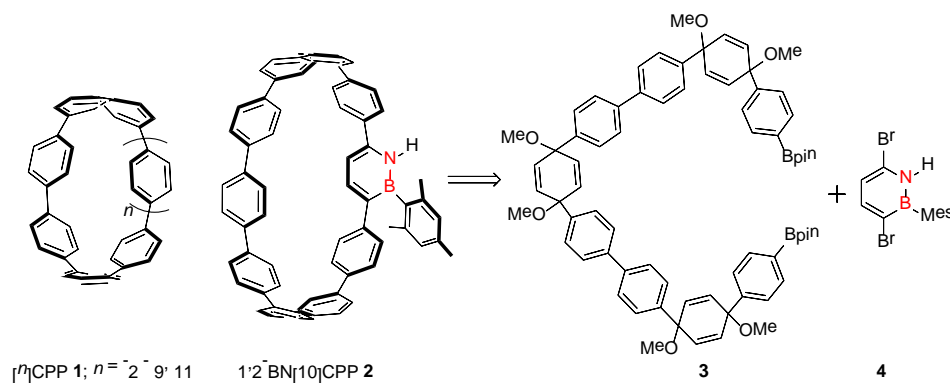
## Synthesis and Functionalization of a 1,2- Azaborine Containing Cycloparaphenylene

Mario Sokolic, Kiran Sagar Unikela, Min Chen, Shih-Yuan Liu\*

Boston College, Merkert Chemistry Center, Chestnut Hill, MA 02467-3860, USA  
[sokolicm@bc.edu](mailto:sokolicm@bc.edu), [ksu367@mun.ca](mailto:ksu367@mun.ca), [min.chen@bc.edu](mailto:min.chen@bc.edu), [liusd@bc.edu](mailto:liusd@bc.edu)

### ABSTRACT

In 2009, the Liu group synthesized the first parent 1,2-dihydro-1,2-azaborine system, which is both isoelectronic and isostructural to its all carbon partner.<sup>1</sup> The insertion of a B-N bond into an arene ring alters its electronic character and thus increases chemical diversity.<sup>2</sup> Cycloparaphenylene (CPP)s are the thinnest slices of carbon nanotubes (CNT) and are now available in various sizes and diameters.<sup>3</sup> Various research groups are trying to explore these CPPs as seeds or precursors for the bottom-up synthesis of CNTs. CPPs themselves may possess interesting properties owing to their unique structure and central cavity. Having access to 3,6-dibrominated-1,2-azaborine **4** in hand, our group is interested in the exploration of azaborine-containing CPPs. In this regard, the successful synthesis of a 1,2-BN-[10]CPP **2** will be discussed, as well as the ongoing efforts to functionalize the final CPP.



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## BORAM XVI ATTENDEES

Antonio Abad-Garcia	Instituto Politecnico Nacional	abadantonio19315@hotmail.com
Eric Adillon	Boston College	adillon@bc.edu
Seiji Akiyama	Nagoya Univeristy	seiji.akiyama@oec.chembio.nagoya-u.ac.jp
Sota Akiyama	Hokkaido University	f-m-sckibp_0311@eis.hokudai.ac.jp
Naoki Ando	Nagoya Univeristy	andou.naoki@c.mbox.nagoya-u.ac.jp
Mark Aparece	Boston College	aparecem@bc.edu
Jeremy Armand	Boston College	armandj@bc.edu
Clara Aupic	iSm2 Institut des Sciences Moléculaires de Marseille	clara.aupic@etu.univ-amu.fr
Tom Autrey	Pacific Northwest National Laboratory	tom.autrey@pnnl.gov
Ranjit Bag	Indian Institute of Technology Madras	mail2ranjitbag@gmail.com
Al Barney	Strem Chemicals	al@strem.com
Joe Bateman	University of Bristol	jb15089@bristol.ac.uk
Michael Beckett	Bangor University	m.a.beckett@bangor.ac.uk
Holger Bettinger	Tübingen University	holger.bettinger@uni-tuebingen.de
Suzanne Blum	University of California, Irvine	SuzB@aol.com
Katherine Boknevit	Boston College	boknevit@bc.edu
Daniel Bolt	University of Pittsburgh	dab187@pitt.edu
Devin Boom	University of Amsterdam	d.h.a.boom@uva.nl
Beth Bosley	Boron Specialties	beth@boron.com
Thomas Bossé-Demers	Université Laval	thomas.bosse-demers.1@ulaval.ca
Nicolas Bouchard	Université Laval	nicolas.bouchard.15@ulaval.ca
Johnathan Bowen	Virginia Tech	jbowen9@vt.edu
Jeffery Byers	Boston College	byersja@bc.edu
Shiang Cai	Strem Chemicals	cai@strem.com
Samantha Cambray	Boston College	cambray@bc.edu
Min Cao	Boston College	caomd@bc.edu
Christopher Caputo	York University	caputo@yorku.ca
Jessica Chan	Boston College	chanop@bc.edu
Yejin Chang	Boston College	changfn@bc.edu
Min Chen	Boston College	chenbqu@bc.edu
Xuenian Chen	Henan Normal University	xnchen@htu.edu.cn
Pin-Shu Chien	PharmaEssentia	ben_chien@pharmaessentia
Matteo Chierchia	Boston College	chierchi@bc.edu
Tak Chio	SUNY Binghamton	tchio1@binghamton.edu
Ching-Wen Chiu	National Taiwan University	cwchiu@ntu.edu.tw
Anna Chrostowska	Université de Pau et des Pays de l'Adour	anna.chrostowska@univ-pau.fr
Helen Clement	University of Alberta	hclement@ualberta.ca
Michael Crockett	Boston College	crockemi@bc.edu
Cathleen Crudden	Queen's University	cruddenc@chem.queensu.ca
Chunming Cui	Nankai University	cmcui@nankai.edu.cn
Mary Sue Daoud	MDPI	daoud@mdpi.com
Jonathan Deegan	Boston College	deeganj@bc.edu
Vjekoslav Dekaris	Chem, Cell Press	vdekaris@cell.com
Vladimir Dordovic	Charles University	vladimir.dordovic@natur.cuni.cz



Simon Duttwyler	Zhejiang University	duttwyler@zju.edu.cn
Gerhard Erker	Westfälische Wilhelms-Universität Münster	erker@uni-muenster.de
Bill Ewing	Boron Specialties	martina@boron.com
Diana Fager	Boston College	fager@BC.EDU
Roberto Fernandez Alvarez	Charles University	rfernandez.99a@gmail.com
Lars Fritze	RWTH Aachen University	lars.fritze@ac.rwth-aachen.de
Russell Fritze	Virginia Tech	rgf004@vt.edu
François Gabbai	Texas A & M University	francois@tamu.edu
Jianmin Gao	Boston College	jianmin.gao@bc.edu
Ashley Gates	Virginia Tech	agates15@vt.edu
Sundargopal Ghosh	Indian Institute of Technology Madras	sghosh@iitm.ac.in
Angelina Gigante	University of Geneva	angelina.gigante@pnnl.gov
Joe Gilroy	University of Western Ontario	joe.gilroy@uwo.ca
Zachary Giustra	Boston College	giustra@bc.edu
Pedro Gois	Lisbon University	pedrogois@ff.ulisboa.pt
Dennis Hall	University of Alberta	dennis.hall@ualberta.ca
Evamarie Hey-Hawkins	Universität Leipzig	hey@uni-leipzig.de
Sunny Ho	Boston College	hond@bc.edu
Alexander Hofmann	Universität Würzburg	alexander.hofmann@uni-wuerzburg.de
John Hoskin	Boston College	hoskinj@bc.edu
Narayan Hosmane	Northern Illinois University	hosmane@niu.edu
Rajeev Hotchandani	Sciligence	rhotchandani@sciligence.com
Jack Hwang	PharmaEssentia	jack_hwang@pharmaessentia.com
Michael Ingleson	University of Manchester	michael.ingleson@manchester.ac.uk
Adena Issaian	University of California, Irvine	aissaian@uci.edu
Hajime Ito	Hokkaido University	hajito@eng.hokudai.ac.jp
Hiroaki Iwamoto	Hokkaido University	g-iwamoto@eis.hokudai.ac.jp
Frieder Jaekle	Rutgers University	fjaekle@rutgers.edu
Paul Jelliss	Saint Louis University	paul.jelliss@slu.edu
Benson Joseph	Indian Institute of Technology Madras	benjonjoseph203@gmail.com
Kosuke Kabasawa	Kyoto University	kabasawa.kousuke.53u@st.kyoto-u.ac.jp
Sang Ook Kang	Korea University	sangok@korea.ac.kr
Piotr Kaszynski	Polish Academy of Sciences	piotrk@cbmm.lodz.pl
Jing Ke	Boston College	keji@bc.edu
Constanze Keck	University of Tübingen	constanze-ulrike.keck@student.uni-tuebingen.de
Roman Keder	Katchem Ltd.	keder@katchem.cz
R. Bruce King	University of Georgia	rbking@chem.uga.edu
Rei Kinjo	Nanyang Technological University	rkinjo@ntu.edu.sg
Marvin Kischkewitz	Westfälische Wilhelms-Universität Münster	m_kisc02@www.de
Seung Koo	Boston College	koosb@bc.edu
Isaac Krauss	Brandeis University	kraussi@brandeis.edu
Raymond Lansing	Strem Chemicals	rlansing@strem.com
Vincent Lavallo	University of California, Riverside	vincentl@ucr.edu
Julien Légaré Lavergne	Université Laval	julien.legare-lavergne.1@ulaval.ca
Weider Lee	PharmaEssentia	weider_lee@pharmaessentia.com
Cally Li	Queen's University	12cl88@queensu.ca
Jianwei Li	Charles University	lijia@natur.cuni.cz

Patrick Lima	Boston College	limapa@bc.edu
Huina Lin	Rutgers University	h1519@scarletmail.rutgers.edu
Chunliang Liu	Boragen, Inc.	cliu@boragenbio.com
Kanglei Liu	Rutgers University	kanglei.liu@rutgers.edu
Qibin Liu	Ally Chem	qliu@allychem.com
Shih-Yuan Liu	Boston College	liusd@bc.edu
Siyuan Liu	Universität Würzburg	wispu64@gmail.com
Xuguang Liu	Tianjin University of Technology	xuguangliu@yahoo.com
Xun Liu	Incyte Pharmaceuticals	xuliu@incyte.com
Yao Liu	Boston College	liukk@bc.edu
Andreas Lorbach	University of Konstanz	andreas.lorbach@uni-konstanz.de
Katherine Lounsbury	Boston College	lounsbu@bc.edu
Gabriel Lovinger	Boston College	gjlovinger@gmail.com
Hairong Lyu	Chinese University of Hong Kong	1155051743@link.cuhk.edu.hk
Matthew Maddess	Merck	matthew_maddess@merck.com
Caleb Martin	Baylor University	caleb_d_martin@baylor.edu
Pavel Matejcek	Charles University	pavel.matejcek@natur.cuni.cz
Cameron McConnell	Boston College	mcconncc@bc.edu
Thomas McTeague	AstraZeneca	thomas.mcteague@astrazeneca.com
Eric Medici	Virginia Tech	ermedici@vt.edu
Rebecca Melen	University of Cardiff	MelenR@cardiff.ac.uk
Soren Mellerup	Queen's University	smelleru@lakeheadu.ca
Yan Meng	Boston College	yangms@bc.edu
Josef Michl	University of Colorado Boulder	michlj@colorado.edu
Malte Mikus	Boston College	mikusmb@bc.edu
James Morken	Boston College	morken@bc.edu
Ryan Morrison	Boston College	morrisrz@bc.edu
Jesse Myhill	Boston College	myhill@bc.edu
Soichiro Nakatsuka	Kwansei Gakuin University	s.nakatsuka@kwansei.ac.jp
Sheila Namirembe	Boston College	namiremb@bc.edu
Kim Ngan Tu	University of California, Irvine	kntu@uci.edu
Hangcheng Ni	Chinese University of Hong Kong	nihc@hotmail.com
Hubert Nienaber	Strem Chemicals	hubert@strem.com
Susumu Oda	Kwansei Gakuin University	susumuoda@kwansei.ac.jp
George O'Doherty	Northeastern University	g.odoherty@neu.edu
Imre Pápai	Hungarian Academy of Sciences	papai.imre@ttk.mta.hu
Silvina Pellegrinet	Instituto de Quimica Rosario	pellegrinet@iquir-conicet.gov.ar
Matthew Perry	Pfizer	matthew.perry@pfizer.com
Dmitry Peryshkov	University of South Carolina	peryskov@sc.edu
Daniel Polyak	Brandeis University	dpolyak@brandeis.edu
Brian Popp	West Virginia University	Brian.Popp@mail.wvu.edu
Johan Pradeilles	University of Bristol	johan.pradeilles@gmail.com
Richard Procter	University of Manchester	richard.procter@postgrad.manchester.ac.uk
Zaozao Qiu	Shanghai Institute of Organic Chemistry	qiuzz@sioc.ac.cn
Yangjian Quan	Chinese University of Hong Kong	yjquan@cuhk.edu.hk
James Radcliffe	University of Manchester	james.radcliffe@manchester.ac.uk
Xavier Riart Ferrer	Boston College	riartfer@bc.edu

Stephen Ritter	American Chemical Society	s_ritter@acs.org
Thomas Rixon	Bangor University	chp81d@bangor.ac.uk
Étienne Rochette	Université Laval	etienne.rochette.2@ulaval.ca
Karla Selene Romero-Aguilar	Instituto Politecnico Nacional	ghostydana@hotmail.com
Théo Rongère	Université Laval	theo.rongere.1@ulaval.ca
Webster Santos	Virginia Tech	santosw@vt.edu
Morgane Sayes	Université de Montréal	morgane.sayes@gmail.com
Thomas Rudolf Schäfer	Idemitsu OLED Materials Europe AG	thomas.schaefer01@idemitsu.com
Jan Schulz	Universität Leipzig	schulz.jan@web.de
Christopher Schuster	Merck	christopher.schuster@merck.com
John Shirley	Labnetwork	john.shirley@labnetwork.com
Ryosuke Shishido	Hokkaido University	shishido-ryosuke@eis.hokudai.ac.jp
Bakthan Singaram	University of California, Santa Cruz	singaram@ucsc.edu
Mitch Smith	Michigan State University	smithmil@msu.edu
Marc Snapper	Boston College	snapper@bc.edu
John Soderquist	University of Puerto Rico	jasoderquist@yahoo.com
Mario Sokolic	Boston College	sokolicm@bc.edu
Marvin A. Soriano-Ursúa	Instituto Politecnico Nacional	soum13mx@gmail.com
Alexander Speed	Dalhousie University	aspeed@dal.ca
Alexander Spokoyny	University of California, Los Angeles	spokoyny@chem.ucla.edu
Thomas Stennett	Universität Würzburg	thomas.stennett@uni-wuerzburg.de
Doug Stephan	University of Toronto	dstephan@chem.utoronto.ca
Michinori Suginome	Kyoto University	suginome@sbchem.kyoto-u.ac.jp
Fuyuan Sun	Ally Chem	fuyuan.sun@allychem.com
Yu Sun	Boston College	suncx@bc.edu
Connor Szwetkowski	Virginia Tech	cszwet@vt.edu
Mark S. Taylor	University of Toronto	mtaylor@chem.utoronto.ca
Torsten Thiess	Universität Würzburg	torsten.thiess@uni-wuerzburg.de
Leiming Tian	Brandeis University	lmtian@brandeis.edu
Sebastian Torker	Boston College	torker@bc.edu
Chet Tyrol	Boston College	tyrolc@bc.edu
Mariusz Uchman	Charles University	uchman@natur.cuni.cz
Ivan Ricardo Vega Valdez	Instituto Politecnico Nacional	psiko.rapper@hotmail.com
Alex Vendola	Boston College	vendolaa@bc.edu
Fernando Vidal	Rutgers University	fer.vidal@rutgers.edu
David Vrbata	Charles University	vrбата@natur.cuni.cz
Mary Waddington	University of California, Los Angeles	Mwadding@chem.ucla.edu
Matthias Wagner	Goethe Universität Frankfurt	matthias.wagner@chemie.uni-frankfurt.de
Jingyi Wang	Boston College	wangasa@bc.edu
Johnny Wang	Boston College	wangbix@bc.edu
Lai-Sheng Wang	Brown University	lai-sheng_wang@brown.edu
Suning Wang	Queen's University	sw17@queensu.ca
Xiaoxu Wang	Boston College	wangapo@bc.edu
Yuansen Wang	United Boron	info@unitedboron.cn
Yong Wang	Boston College	wangasb@bc.edu
Ziyong Wang	Boston College	wangbkc@bc.edu
Masayuki Wasa	Boston College	wasab@bc.edu

Hermann Wegner	Justus-Liebig Universität Giessen	hermann.a.wegner@org.chemie.uni-giessen.de
Andrew Weller	Oxford University	andrew.weller@chem.ox.ac.uk
Xin Wen	Boston College	wenxc@bc.edu
Christopher Wilhelmsen	Boston College	wilhelca@bc.edu
Jingjing Xie	Boston College	xiejd@bc.edu
Zuwei Xie	Chinese University of Hong Kong	zxie@cuhk.edu.hk
Wen Xiu	Boston College	xiuw@bc.edu
Bokai Xu	Brandeis University	bokaixu@brandeis.edu
Chaofan Xu	Boston College	xuci@bc.edu
Pan Xu	Boston College	xuve@bc.edu
Senmiao Xu	Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences	senmiaoxu@licp.cas.cn
Shigehiro Yamaguchi	Nagoya Univeristy	yamaguchi@chem.nagoya-u.ac.jp
Makoto Yamashita	Nagoya Univeristy	makoto@oec.chembio.nagoya-u.ac.jp
Lu Yan	Boston College	yanlu@bc.edu
Xinyu Yang	Boston College	yangpx@bc.edu
Ahmet Yescilimen	Boston College	yesilcim@bc.edu
Andrei Yudin	University of Toronto	ayudin@chem.utoronto.ca
Mohammad Zafar	Indian Institute of Technology Madras	jafarnaqvi110@gmail.com
Chenlong Zhang	Boston College	zhangamg@bc.edu
Congzhe Zhang	Boston College	zhanggf@bc.edu
Fenglian Zhang	University of Science and Technology	zfl9@ustc.edu.cn
Jie Zhang	Chinese University of Hong Kong	zhjie1989@126.com
Shaochen Zhang	Boston College	zhangsv@bc.edu
Yong-Kang Zhang	Boragen, Inc.	yzhang@boragenbio.com
Yuanzhe Zhang	Boston College	zhangiw@bc.edu
Peng Zheng	Ally Chem	pzheng@allychem.com
Yuebiao Zhou	Boston College	zhoufg@bc.edu