



Uniwersytet
ŁÓDZKI



University of Łódź
Faculty of Chemistry
Department of Organic & Applied Chemistry



Polish Chemical Society

Vth International Mini-Symposium

***Boron Containing Compounds in
Organic and Bioorganic Chemistry***

May 24th 2012

Acknowledgement

The City of Łódź Office for financial support

Program & Abstracts

Conference venue:

University of Łódź, Faculty of Chemistry, Tamka-Str. 12,
The Faculty Council Room, #1-020

Organizing committee:

Chairman: Prof. dr. hab. Grzegorz Młostoń

Secretary: Dr. hab. Jarosław Romański, Prof. UŁ

Vth International Mini-Symposium
Boron Containing Compounds in Organic and Bioorganic Chemistry

Program

13:25 *Invitation and opening*

Session 1: *Chairman: Prof. Stefan Jankowski (TU Łódź)*

13:30 – 14:00 **Piotr Kaszyński**

L-1 Vanderbilt University/University of Łódź, USA/Poland

The [closo-1-CB₉H₁₀] cluster as the centerpiece of new classes of liquid crystals

14:00 – 14:30 **Marek Zaidlewicz**

L-2 Nicolaus Copernicus University in Toruń, Poland

Syntheses via Boranes. 5-Lipoxygenase Inhibitors, Compounds of anti-Alzheimer Activity, and New Boron Carriers for BNCT

14:30 – 15:00 **Sergiusz Luliński**

L-3 Technical University of Warsaw, Poland

Formation and Synthetic Applications of Lithiated Aryl Boronates

15:00 – 15:30 *Coffee break*

Session 2 *Chairman: Prof. Piotr Kielbasiński (PAS Łódź)*

15:30 – 16:00 **Anna Chrostowska**

L-4 University of Pau, France

Boron-Nitrogen-Containing Heteroaromatic Compounds. Electronic Structure Studies

16:00 – 16:30 **Tomasz Ruman**

L-5 Rzeszów University of Technology, Poland

Catalytic hydrogenation and hydroboration of model cycloalkene

16:30 – 17:00 **Marek Krzemiński**

L-6 Nicolaus Copernicus University in Toruń, Poland

Asymmetric Reduction of Ketones and their Derivatives Catalyzed with Terpenyl Organoboranes

17:00 – 17:30 **Lothar Weber**

L-7 University of Bielefeld, Germany

Modern Aspects of Molecular Boron Chemistry

17:45 – 19:30 *Garden Grill Party*

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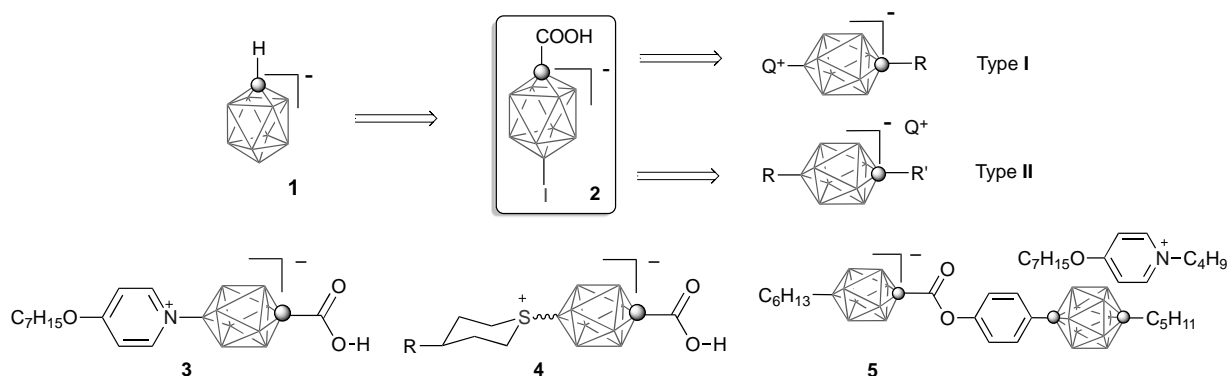
The [closo-1-CB₉H₁₀]⁻ Cluster as the Centerpiece of New Classes of Liquid Crystals

Piotr Kaszyński

*Organic Materials Research Group, Department of Chemistry, Vanderbilt University
Nashville, TN 37235, USA;
Faculty of Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland*

Unusual steric and electronic properties of the inorganic boron cluster [closo-1-CB₉H₁₀]⁻ (**1**) provide opportunities for the preparation of new materials for applications in electrooptics and energy storage, and also for the study of fundamental factors imparting liquid crystalline behavior. The cluster is larger than typical organic rings, has high rotational symmetry axes, is σ -aromatic and has fully delocalized negative charge. This unique combination of properties allows for engineering of rod-like compounds with variable polarity, controlled photophysical properties, and ionic character, exhibiting liquid crystalline properties.

The key precursor to these new materials is iodo acid [closo-1-CB₉H₈-1-COOH-10-I]⁻ (**2**) prepared from B₁₀H₁₄ in 5 steps [1]. Functional group transformations in **2** gave access to polar zwitterionic compounds of type **I** and ion pairs of type **II**. To the former class of compounds belong esters derived from acids **3** and **4** that exhibit nematic behavior. They are characterized by a substantial longitudinal molecular electric dipole moment, >8 D, and therefore have been investigated as high dielectric anisotropy ($\Delta\epsilon$) additives to nematic materials [1,2]. Ion pairs of type **II** containing a total of 4 rings, such **5**, exhibit smectic and rarely nematic properties and constitute first examples of anion-driven ionic mesogens [3].



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L-2

Syntheses via Boranes. 5-Lipoxygenase Inhibitors, Compounds of anti-Alzheimer Activity, and New Boron Carriers for BNCT

Marek Zaidlewicz

Faculty of Chemistry, Nicolaus Copernicus University, 7 Gagarin Street, 87-100 Toruń, Poland

Oxazaborolidines generated from nonracemic β -amino alcohols, derived from monoterpenes and α -amino acids, were used for the enantioselective reduction of oxime ethers with borane. The reaction was a key transformation in the asymmetric synthesis of benzofuranyl and benzothiophenyl N-hydroxyureas which are 5-lipoxygenase inhibitors of anti-asthmatic activity.

The reduction of oxime ethers with borane/oxazaborolidines was also used for the asymmetric synthesis of (*S*)-rivastigmine, exhibiting an anti-Alzheimer activity. Achiral fluorinated benzofuranyl amino ketones, potential β -amyloid aggregation inhibitors, were prepared employing the Suzuki-Miyaura cross-coupling reaction.

Analogues of boronated phenylalanine, containing a quaternary center, which are new boron carriers for the BNCT therapy, were prepared.

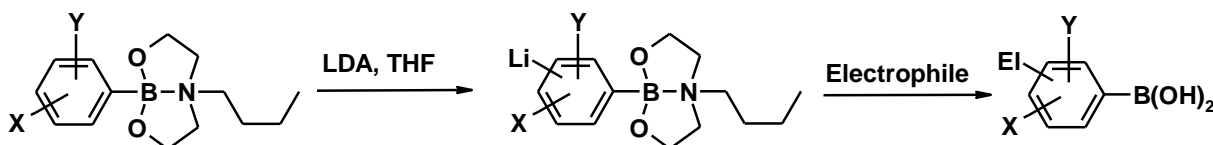
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Formation and Synthetic Applications of Lithiated Aryl Boronates

Sergiusz Luliński

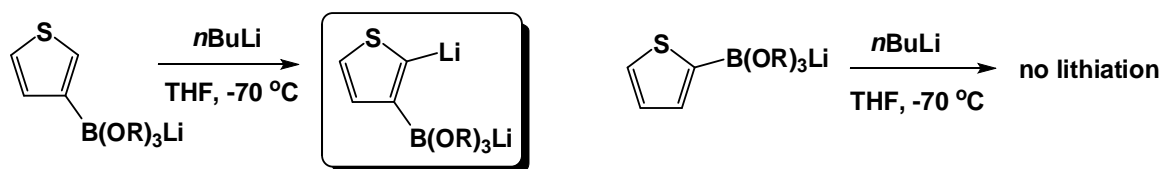
*Warsaw University of Technology, Physical Chemistry Department,
Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland*

Recently, arylboronic acids and esters have become very popular as versatile building blocks in organic synthesis; they have also found applications in other fields [1]. Hence, the development of new simple general synthetic routes to arylboronic acids is an important task. Bimetallic aromatic boron-lithium systems are valuable reagents which can be converted to highly functionalized aryl boronates. Their generation relies on the protection of the boron-atom followed by the lithiation of the aromatic core. The presentation will be devoted to two general approaches to lithiated arylboronates. The first one involves the lithiation of *B*-protected *N*-alkyldiethanolamine arylboronic and heteroarylboronic esters via H/Li or Br/Li exchange [2,3]. Alternatively, the simple one-pot approach to synthetically useful anionic phenyltrialkoxymborates as well as diphenyldialkoxymborates bearing lithium at the phenyl ring has been developed starting with selected dihalobenzenes (Hal = Br, I) [4,5]. The synthesis of functionalized arylboronic and diarylboronic derivatives obtained upon electrophilic quench of bimetallic boron-lithium intermediates will be demonstrated.



X, Y = F, Cl, Br, CF₃

This will be complemented by the discussion of the *ortho*-directing ability of boronate group in the aromatic lithiation. Recent results indicate for the first time that this is the case for the lithiation of some boronated thiophenes [6]. Theoretical calculations provided detailed information about plausible mechanism of the lithiation process.



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**Boron-Nitrogen-Containing Heteroaromatic Compounds.
Electronic Structure Studies.**

Anna Chrostowska^a, Audrey Mazière^a, Alain Dargelos^a, Alain Graciaa^b, Shih-Yuan Liu^c

^a*Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR CNRS 5254, Université de Pau et des Pays de l'Adour, Av. de l'Université, 64 000 Pau, France.*

^b*Laboratoire des Fluides Complexes, UMR CNRS – TOTAL 5150, Université de Pau et des Pays de l'Adour, Av. de l'Université, 64 000 Pau, France.*

^c*Department of Chemistry, University of Oregon, Eugene, Oregon 97403, USA.*

Boron(B)-nitrogen(N)-containing heteroaromatic compounds are a family of aromatic heterocycles that are isoelectronic and isostructural to the versatile family of classic organic counterparts as benzene, or mono-nitrogen containing heterocycles as pyrrole. Their development significantly expands the structural diversity and potential utility of aromatic compounds, but the properties and reactivity of such BN-aromatic heterocycles have not been fully explored due to the lack of available synthetic methods for their preparation. To improve our understanding of the electronic structure of the heterocyclic core of aromatic BN heterocycles, we have been focusing on the investigation of *monocyclic* BN five and six member's heterocycles. In this presentation, we provide a comprehensive electronic structure analysis of BN heterocycles as 1,2-dihydro-1,2-azaborine and 1,3,2-diazaboroline in direct comparison with their carbonaceous derivatives using a combined UV-photoelectron spectroscopy (UV-PES) / computational chemistry approach.

benzene 1,2-dihydro-1,2-azaborine

pyrrole 2,3-dihydro-1*H*-1,3,2-diazaborole

L-5

Catalytic Hydrogenation and Hydroboration of Model Cycloalkene

Joanna Nizioł and Tomasz Ruman

Rzeszów University of Technology, Faculty of Chemistry, 6 Powstańców Warszawy Ave. 35-959 Rzeszów, Poland

The olefin hydrogenation is important chemical modification used in organic synthesis both on the small and industrial scale. The most of the hydrogenation processes utilize catalytic systems based on transition metal complexes and gaseous hydrogen at moderate to high pressures and often also high temperatures [1]. There are only few reports on the hydrogenation processes conducted in mild conditions (atmospheric pressure, room temperature) that use various boranes as hydrogen sources [2-9].

The present work describes unusual activity found in applied catalytic system that is similar to the one reported by Miyaura group [10]. Our experimental data suggest that the main reaction in applied catalytic systems is hydrogenation of cycloalkene to cycloalkane (Figure 1).

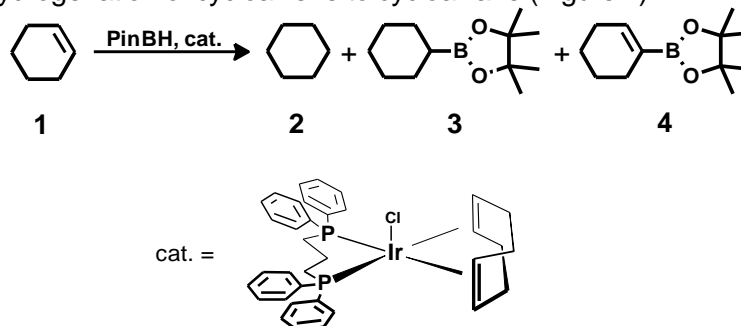


Figure 1. The hydrogenation (2), hydroboration (3) and dehydrogenative borylation (4) of cyclohexene catalyzed by iridium(I) complex.

The experiment that was conducted in benzene-*d*₆ with 3% molar ratio of catalyst and 2 eq. of pinacolborane in the sealed NMR tube gave surprisingly clear ¹H NMR spectrum. The NMR-controlled experiment clearly showed the diminishing of cyclohexene (1) resonances down to ca. 82.0% after 50 min and to 9.6% of their initial areas after 3120 minutes. Moreover, the disappearance of 1 resonances was accompanied with growing singlet resonance at 1.40 ppm. The region of NMR spectrum typical for CH₃ resonances of pinacol-related moieties also has changed. The substrate singlet resonance at 0.99 ppm disappeared during the reaction course while another singlet has risen at 1.01 ppm. What is more, after 3120 min of the reaction also the BH resonance has completely disappeared. The various NMR data and MS experiments confirmed the identity of newly formed product to be cyclohexane. The ¹¹B NMR spectrum of the reaction mixture after 7 min has shown doublet resonance from pinacolborane, disappearing wide singlet at 23.0 ppm, rising wide singlet resonance at 21.9 ppm and very small resonance at 31.3 ppm the last three being most probably the PinBOH, PinB₂O and 3 respectively [10].

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L-6

Asymmetric Reduction of Ketones and their Derivatives Catalyzed with Terpenyl Organoboranes

Marek P. Krzemiński

*Department of Chemistry, Nicolaus Copernicus University
mkrzem@chem.umk.pl*

Terpenyl organoboranes are successfully utilized in a number of asymmetric transformations, e.g. reductions, allylborations, homologations, and ring opening of epoxides.¹ Among these transformations, stoichiometric reduction of prochiral ketones with chiral α -pinene derived organoboranes is an important and well known method.² On the other hand, enantioselective reductions catalyzed with 1,3,2-oxazaborolidines³ are key reactions in asymmetric synthesis of many biologically active compounds.⁴ Oxazaborolidine catalysts are usually derived from amino acids, and there are only a few examples of camphor and α -pinene derived oxazaborolidines.

In the course of our studies on the synthesis of chiral 1,3,2-oxazaborolidines and spiroborate esters, we synthesized several boron catalysts based on bicyclic monoterpene skeletons, and we applied them as catalysts in enantioselective reductions of ketones and their derivatives.

The synthesis of selected *cis*- β -amino alcohols obtained from natural bicyclic monoterpenes will be presented. These compounds were fully characterized by spectroscopic methods. Terpene *cis*- β -amino alcohols were converted into *B*-alkyl and *B*-alkoxy oxazaborolidines and spiroborate esters, and were successfully used as catalysts for the asymmetric reduction of prochiral ketones with borane. Various factors can affect the enantioselectivity in these reactions, and some of them will be discussed in the course of the lecture.

¹ M. Zaidlewicz, H. C. Brown, *Organic Syntheses via Boranes* Vol. 2, Aldrich Chemical Company, 2001.

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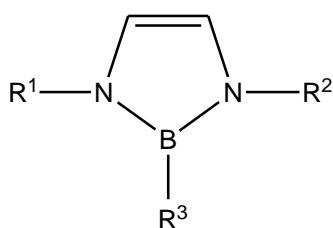
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Modern Aspects of Molecular Boron Chemistry

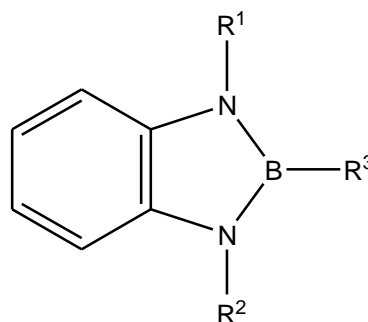
Lothar Weber

Fakultät für Chemie, Universität Bielefeld

The molecular chemistry of boron has experienced an amazing revival within the last few decades. Here transition-metal-catalyzed cross-couplings, hydroborations and heteroelement borations have been highlighted, all of which involve metal boron complexes of various kinds. Another area of current interest is focused on boron-containing π -electron systems as potential building blocks in electro- optical devices. Our research area is circled around the chemistry of 1,3,2-diazaboroles (I) and its fused benzo analogues (II)



I



II

Syntheses of the key compounds with $R^3 =$ halogen and their reactivity towards nucleophiles and alkalimetals are discussed. Extended conjugated π -electron systems which are functionalized by the benzodiazaborolyl unit give rise to intense blue/green luminescence when irradiated by UV-light. They are of potential use as electron transmitters and emitters in Organic Light Emitting Diodes (OLEDs).

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