# 7<sup>th</sup> European Conference on Boron Chemistry



# **Book of Abstracts**



# Organizers

Federal Agency for Scientific Organisations

Russian Academy of Sciences

A.N. Nesmeyanov Institute of Organoelement Compounds

N.S. Kurnakov Institute of General and Inorganic Chemistry

A.A. Baikov Institute of Metallurgy and Materials Science

N.D. Zelinsky Institute of Organic Chemistry

State Scientific Research Institute of Chemistry and Technology of Organoelement Compounds

The conference is financially supported by Russian Foundation for Basic Research (16-03-20203)

# **TECHNICAL PARTNER**



Conference Technical Partner Professional Congress Organizer

www.unifest.ru Tel.: +7 495 234 65 55

## **International Advisory Committee**

Michael Beckett (United Kingdom) Holger Braunschweig (Germany) Vladimir Bregadze (Russia) <u>Igor Chizhevsky (Russia)</u> Maria Elena Fernandez (Spain) Detlef Gabel (Germany) Bohumir Grüner (Czech Republic) Alexander Kudinov (Russia) Zbigniew Leśnikowski (Poland) Todd Marder (Germany) Philippe Miele (France) Andrzej Sporzyński (Poland) Francesc Teixidor (Spain) Lars Wesemann (Germany) Alan Welch (United Kingdom) Andrew Weller (United Kingdom) Andrew Whiting (United Kingdom)

## **Local Organizing Committee**

Vladimir Bregadze (Conference Chair) Yuri Bubnov (Honorary Chair) <u>Igor Chizhevsky (Co-Chair)</u> Elena Shubina (Vice-Chair) Dmitry Loginov (Secretary) Sergey Baranin Natalia Belkova Oleg Filippov Mikhail Gerasimov Valery Kalinin Nikolay Kuznetsov Aziz Muzafarov Andrey Semioshkin Igor Sivaev Konstantin Solntsev Pavel Storozhenko Evgeny Zheludov Konstantin Zhizhin

## Contacts

#### **Conference** secretariat

**UniFest Congress** 

Dmitry Loginov e-mail: <u>euroboron7@ineos.ac.ru</u> 28 Vavilova str., Moscow, 119991, Russia <u>www.euroboron7.ru</u> Project manager - Ekaterina Kashutina e-mail: <u>euroboron7@unifest.ru</u> Tel.: +7 (495) 234-65-55 ext. 348 Fax: +7 (495) 234-65-56 SPONSORS





#### INFORMATIONAL PARTNERS









Химико фармацевтический журнал









# WWW.ETIMADEN.GOV.TR WWW.ETIMADEN.RU

**Eti Maden I. G. M.** is the Turkish state mining company - the world's largest producer of boron compounds and minerals. Turkey has the largest borate reserve of the world, which equates to 74,8% of the total world reserves, and puts it in first place in this respect. Eti Maden I. G. M. supplies 51% of the world boron demand and exports products to over 100 countries. Today, the company has owned more than 15 plants for production and processing of boron-containing products, where products are packaged in high-quality packaging and sent to consumers by various means of transport. The quality of production and the finished products is confirmed by international quality standards. Trade all over the world is carried out through a developed network of representative offices and agencies.

"Etiproducts" Ltd. is the exclusive supplier of Eti Maden in Russia, countries of the Customs Union and the CIS. The presence of an adequate supply of goods in the depot in Russia, flexible pricing and the ability to deliver high quality products timely made "Etiproducts" Ltd. a reliable supplier. "Etiproducts" Ltd. is proud that more than 100 companies in Russia and CIS use boron-containing products of company Eti Maden in their production technologies.

ETIMADEN I. G. M. info@etimaden.gov.tr

#### ETIMADEN-Etiproducts Ltd. (for Russia and CIS countries) info@etimaden.ru Tel: +7 (499) 995 23 83

# **OUR PRODUCTS:**

- Boric Acid H<sub>3</sub>BO<sub>3</sub>
- Boron Oxide B<sub>2</sub>O<sub>3</sub>
- Borax Decahydrate Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10 H<sub>2</sub>O
- Borax Pentahydrate Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.5 H<sub>2</sub>O
- Anhydrous Borax Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>

- Etidot 67 Na<sub>2</sub>B<sub>8</sub>O<sub>13</sub>.4H<sub>2</sub>O
- Ground Colemanite 2CaO.3B<sub>2</sub>O<sub>3</sub>.5H<sub>2</sub>O
- Ground Ulexite Na<sub>2</sub>0.2Ca0.5B<sub>2</sub>O<sub>3</sub>.16H<sub>2</sub>O
- Eticol Ceramic 2CaO.3B2O3.5H2O

**BORON CONSUMING INDUSTRIES:** 



WWW.ETIMADEN.GOV.TR WWW.ETIMADEN.RU

# **Previous EUROBORON meetings**

# EuroBoron1

1997 Platja d'Aro, Spain; Chair – Francesc Teixidor

# **EuroBoron2**

2001 Dinard, France; Chair – Michel Vaultier

# **EuroBoron3**

2004 Pruhonice, Czech Republic; Chair – Bohumil Štíbr

# **EuroBoron4**

2007 Bremen, Germany; Chair –Detlef Gabel

# **EuroBoron5**

2010 Edinburgh, UK; Chair – Alan Welch

# **EuroBoron6**

2013 Radziejowice, Poland; Chair – Andrzej Sporzyński



We at Advanced Chemistry Development. Inc. (ACD/Labs) are honored to be invited as Sponsors to the EUROBORON 2016! For over 20 years, we have been supporting small chemistry R&D, internationally, with our specialized software products. Today, ACD/Labs is a cheminformatics company that develops and commercializes a broad range of applications and ACD/Labs solutions in support of chemistry research. Our software

is used in many industries including pharma/biotech, chemicals, consumer goods, agrochemicals, petrochemicals, food and beverage, academia, and government organizations. Our network of worldwide offices provides sales and support to our customers across Europe, North America, Asia Pacific, and Japan. We are also known for our software contributions to the scientific community, such as broadly used drawing package ACD/ChemSketch, that has been downloadable as freeware since 1998. For more information. please visit www.acdlabs.com.

At EUROBORON 2016, we are pleased to offer the following software packages as prizes:

#### **Oral Presentations Contest**

- 1<sup>st</sup> place
  - Year-long subscription to ACD/NMR Workbook OR ACD/ChemAnalytical Workbook (includes both ACD/Optical Workbook and ACD/Curve Workbook) - winner's choice
- 2<sup>nd</sup> place
  - Year-long subscription to ACD/Optical Workbook OR ACD/Curve Workbook (winner's choice)

#### Posters Contest

1<sup>st</sup> place

- Year-long subscription to ACD/Optical Workbook OR ACD/Curve Workbook (winner's choice)
- Three 2<sup>nd</sup> places
  - Year-long subscription to ACD/Spectrus Processor

We wish you a productive week in Russia, and success in your future research!

Daria Thorp, President and CEO, ACD/Labs

## Sunday (4 September)

15:00	Registration
19:30-22.30	Welcome mixture

## Monday (5 September)

08:00	Registration				
08:45	Opening Ceremony				
09:00-10:30	Session 1	Chair: Vladimir Bregadze			
09:00	I1	Andrzej Sporzyński "Benzoxaboroles - small molecules of exceptional properties and applications"			
09:30	01	Michael A. Beckett "Polyborates templated by cationic transition-metal complexes"			
09:50	02	Jorge J. Carbó "Quantitative Structure-Activity Relationships in Trivalent Boron Compounds: A Computational Tool for Evaluation and Design of Nucleophilic Boryl Species" Boris V. Spitsyn "Synthesis of boron carbonitride films by thermal decomposition of B-triallylborazol"			
10:10	O3	<b>Boris V. Spitsyn</b> "Synthesis of boron carbonitride films by thermal decomposition of B-triallylborazol"			
10:30	COFFEE BREAK	COFFEE BREAK			
11:00-13:15	Session 2	Session to the Memory of Igor Chizhevsky Chair: Francesc Teixidor			
11:05	12	<b>Bohumír Grüner</b> "Metallacarborane Chemistry: site- directed substitutions designed for specific inhibition activity towards CA-IX"			
11:35	04	Alan J. Welch "The Enhanced Structural Carborane Effect"			
11:55	05	<b>Ivan D. Grishin</b> "Reduction of paramagnetic ruthenacarboranes using aliphatic amines in connection with Atom Transfer Radical Polymerization"			
12:15	06	Alasdair P. M. Robertson "Developing Systematic Routes to 'non-Wadian' Metallacarboranes: The Tale of $(Cp*Ru)_2C_2B_{10}H_{12}$ "			
12:35	07	Hiroyuki Nakamura "Maleimide-Functionalized closo-Dodecaborate Albumin Conjugate: Unique Ligation at Cysteine and Lysine Residues Enables Efficient Boron Delivery to Tumor for Neutron Capture Therapy"			
12:55	08	Sergey Taskaev "Investigation of Boron Compounds for Boron Neutron Capture Therapy using accelerator based neutron source"			
13:15	LUNCH				

15:10-16:40	Session 3	Chair: Andrzej Sporzyński			
15:10	13	<b>Yurii N. Bubnov</b> "Diallylboration reactions in the construction of N-heterocycles"			
15:40	09	<b>Cristina Prandi</b> "Heck Functionalization of Asymmetric Aza-Bodipy Core: Synthesis of Far-Red Infrared Probes for Bioimaging Applications"			
16:00	O10	Alexey Yu. Sukhorukov "New B,O,N-containing Adamantanes: Synthesis and Application"			
16:20	011	<b>Ana B. Cuenca</b> "Straightforward access to gem- polymetalloid substituted carbons through metal-free insertion of diazo synthons into Bpin-X bonds"			
16:40	COFFEE BREAK				
17:10-18.55	Session 4	<i>Young Scientists Session</i> Chair: Alan Welch			
17:10	YO1	Antony P. Y. Chan "Catalytically-Active Ruthenium Complexes of the Bis(o-carborane) Chelate"			
17:25	YO2	<b>Benedikt Schwarze</b> "Coordination Chemistry of Half- sandwich Transition Metal Carborate Complexes"			
17:40	Y03	<b>Ines Bennour</b> "Synthesis of new polybranched carborane macromolecules aiming to medicine and biomaterials applications"			
17:55	YO4	<b>Laura E. Riley</b> "Large, Weakly-Basic Phosphines Derived from 1,1'-Bis(o-carborane)"			
18:10	Y05	Arpita Saha "Meta Carboranyl Phosphinates with CdSe Quantum Dots: Physical Fluorescence Intermittency"			
18:25	YO6	Marta Gozzi "Mixed-Sandwich Metallacarborane Complexes: Synthetic Methods and Applications"			
18:40	Sponsor Lecture 1	Sigma-Aldrich			

# Tuesday (6 September)

09:00-10:50	Session 5	Chair: Bohumír Grüner		
09:00	I4	<b>Clara Viñas</b> "On the verge of Bioinorganic and Inorganic Chemistry: Metallacarboranes in Nanomedicine"		
09:30	012	Andrey Semioshkin "Oxonium Ring Cleavage vs Sonogashira reaction. Different Boron Clusters Require Different Approaches towards Conjugates with 5- Ethynyl-2'-deoxyuridine"		
09:50	013	Valentina A. Ol'shevskaya "Carborane-substituted nitrogen heterocycles: synthesis, properties and applications"		
10:10	014	Alexander Shtil "Boronation, What Is Next? Polyfluorinated Carboranylchlorin, a Potent Antitumor Photoradiosensitizer with Advantageous Synthesis and Pharmacological Properties"		
10:30	015	Annamaria Deagostino "Sulfamido Carboranes as MRI-BNCT Multivalent Antitumoral Agents Inhibitors of Carbonic Anhydrase (CA IX)"		
10:50	COFFEE BREAK			
11:20-13:10	Session 6	Chair: Elena Shubina		
11:20	15	Mark A. Fox "Geometries of nido-carboranes"		
11:50	O16	Francesc Teixidor "Hückel's Rule of Aromaticity Applies to closo Boron Hydride Clusters"		
12:10	017	Josep M. Oliva "Mathematics, Physics, Chemistry and Boron"		
12:30	O18	<b>Ivan V. Dudenkov</b> "Theoretical investigation of possible perfluoroboranes, per-BF2-boranes and cluster compounds with bonds of boron to inert gases"		
12:50	019	<b>Valentin K. Kochnev</b> "Theoretical study of protonation of the $B_{10}H_{10}^{2^{2}}$ anion and subsequent hydrogen removal due to the substitution reaction in acidic medium"		
13:10	LUNCH			
15:00-18.00	Excursion			

# Wednesday (7 September)

09:00-10:50	Session 7	Chair: Philippe Miele			
09:00	16	<b>Umit B. Demirci</b> "From ammonia borane to hydrazine bisborane, via hydrazine borane: boron- and nitrogen-based materials for chemical hydrogen storage"			
09:30	O20	Andrea Rossin "Ammonia-borane dehydrogenation mediated by transition metal complexes for H2 storage and production"			
09:50	021	<b>Pascal G. Yot</b> "Low temperature thermal behaviour of boranes: an in-situ X-ray synchrotron thermodiffraction study"			
10:10	022	<b>Vladimir Shayapov</b> "STA-MS analysis of evaporation and thermal decomposition of Triethylamine Borane Complex"			
10:30	Sponsor Lecture 2	INTERTECH			
10:50	COFFEE BREAK				
11:20-13:10	Session 8	Chair: Clara Viñas			
11:20	023	<b>Detlef Gabel</b> "Supramolecular properties of dodecaborates"			
11:40	024	<b>Daoud Naoufal</b> "Functionalization of closo- decahydrodecaborate anion $[B_{10}H_{10}]^{2}$ using click chemistry reagents"			
12:00	025	Rosario Núñez "Boron clusters based hybrid materials"			
12:20	O26	Alexander M. Spokoyny "Visible-Light Induced Olefin Activation using 3D Aromatic Organomimetic Boron-Rich Cluster Photooxidants"			
12:40	F1-F5	Flash presentations			
13:10	LUNCH				
15:00-17:10	Session 9	Chair: Detlef Gabel			
15:00	17	<b>Eduard Bernhardt</b> "The Chemistry of closo- $[B_{21}H_{18}]^{-1}$ "			
15:30	027	<b>Tomasz M. Goszczyński</b> "Conjugates of boron clusters with antineoplastic agents: synthesis and biological evaluation"			
15:50	028	<b>Igor B. Sivaev</b> "Substituent-stabilized rotamers of transition metal bis(dicarbollides)"			
16:10	029	Lukáš Fojt "Electrochemistry of different boron cluster compounds in aqueous media"			
16:30	030	<b>Pakkirisamy Thilagar</b> "Structure-Property Correlations and Functional Opportunities of Aggregation-induced Emissive Organic/Organometallic Materials"			
16:50-19:00	Poster Session				

# Thursday (8 September)

09:00-10:50	Session 10	Chair: Michael Beckett			
00.00	18	Elena Fernández "Unforeseeable synthesis of			
09.00	18	organoboron compounds"			
	~~~	Christian Kleeberg "Unsymmetrical Diborane(4)			
09:30	031	Derivatives (pinB–B((NR) $_2C_6H_4$ )) as Versatile			
09:50	032	Sergey A. Tikhonov "Ultraviolet photoelectron spectra and electronic structure of boron complexes"			
		Anna Chrostowska "A Theoretical and Experimental			
10:10	033	Approach for Electronic Structure Characterization of BN Isosteres of Anthracene"			
		Dmitry V. Muratov "Boron-containing triple-decker			
10:30	O34	complexes as catalysts for oxidative coupling of			
		benzoic acid with alkynes"			
10:50	COFFEE BREAK				
11:20-13:10	Session 11	Chair: Elena Fernández			
11:20	O35	<b>Igor E. Golub</b> "Dehydrogenation of Amine-Boranes by Conner Tetrahydroborates via Dihydrogen Bonds"			
		<b>Ekaterina Titova</b> "Mechanistic insights in amine-			
11:40	O36	borane dehydrogenation by iridium pincer complex			
		Ir(PCP)HCl"			
12:00	O37	Jindrich Fanfrlik "Sigma-Hole Interactions of Boron Clusters"			
12:20	038	Radim Kučera "The chiral separability of anionic			
12.20	038	boron cluster compounds by liquid chromatography"			
12:40	039	Mecit Aksu "Synthesis of NdB <sub>6</sub> , SmB <sub>6</sub> , GdB <sub>6</sub> and			
		TbB <sub>4</sub> with Magnesiothermic Reduction"			
13:00	Sponsor Lecture 3	ETI Products			
13:20	LUNCH				
15:00-17:15	Session 12	Young Scientists Session			
	~	Chair: Igor Sivaev			
15:00	YO7	<b>Núria Miralles</b> "Unexampled transition metal-free borylation of allylic and propargylic alcohols"			
15:15	YO8	Elena Osipova "Catalytic activity of new iridium(III)			
	100	pincer hydride complex"			
15:30	YO9	Enrico La Cascia "Synthesis of 1,1-(Bpin)(SiMe <sub>3</sub> )-			
	- *	aikenes via (diboryimethyi)trimethyisilane"			
15:45	YO10	Isabel Fuentes "Bioelectronic Materials based on Cobaltabisdicarbollide"			
		Marc G. Civit "Modular synthesis of main-group (Si.			
16:00	YO11	B, S) multisubstituted carbons and subsequent			
		alkylation assisted by Bpin moieties"			
16:15	YO12	Yulia V. Vatutina "Localization and structure of B			

**EUROBORON 7** 

		compounds in alumina support of hydrotreating CoMo- catalysts of diesel fuels"	
16:30	YO13	Veronica Sulyaeva "BCxNy film synthesis using organoboron precursors"	
16:45	Y014	Ivan S. Merenkov "SiBCN films obtained by LPCVD and PECVD from novel single-source organoboron- silicon precursor"	
17.00	Y015	<b>Elena Oleshkevich</b> "A new class of purely inorganic ligands: Carboranylphosphinic acids. Aiming towards future multifunctional materials"	
19:30	Closing ceremony and Conference Dinner		

# INVITED LECTURES

# **INTERTECH** Corporation



# **Thermo**

# Научное и аналитическое оборудование для лабораторий



• ПОСТАВКА ОБОРУДОВАНИЯ • МЕТОДИЧЕСКАЯ ПОДДЕРЖКА • СЕРВИСНОЕ ОБСЛУЖИВАНИЕ

Россия:	г. Москва	(495) 232-4225	Украина:	г. Киев	(044) 230-2373
	г. Екатеринбург	(343) 217-9739		г. Донецк	(050) 347-8910
	г. Новосибирск	(383) 335-9635	Беларусь:	г. Минск	(29) 650-5657
	г. Красноярск	(391) 258-0923	Центральная Азия:	г. Астана	(7172) 53-9235, 53-9296
	г. Хабаровск	(4212) 50-1885		г. Алматы	(727) 255-8626, 255-8649
			Азербайджан:	г. Баку	(994 12) 489-5079

# info@intertech-corp.ru

# www.intertech-corp.ru

# Benzoxaboroles - small molecules of exceptional properties and applications

Agnieszka Adamczyk-Woźniak, Andrzej Sporzyński

Faculty of Chemistry, Warsaw University of Technology E-mail: <u>spor@ch.pw.edu.pl;</u> webpage: <u>http://obc.ch.pw.edu.pl</u>

Benzoxaboroles (I), known since 1957,<sup>1</sup> only recently became the object of extensive studies. The rising interest in these compounds can be illustrated by the number of compounds described in two review papers: 66 known compounds in 2009,<sup>2</sup> compared with about 550 compounds described later till 2015.<sup>3</sup>

In 2006 their exceptional property, i.e. sugar-binding at physiological conditions, was



described.<sup>4</sup> The next milestone in their history was the discovery of a very high antifungal activity of 5fluoro-substituted benzoxaborole (**II**), approved later by the FDA for treatment of onychomycosis as KERYDIN.<sup>5</sup> Investigation of the compounds with structural modifications based on rational design lead to numerous biologically active compounds.<sup>6</sup>

Recently, increased interest is paid to their use in materials chemistry and the hybrid formulations of benzoxaborole drugs.<sup>7</sup>

In recent years, our research group developed several novel benzoxaboroles substituted both in oxaborole and phenyl ring ( $R_1$  and  $R_2$  in I). The compounds were fully characterized in crystal state and in solutions.<sup>8-11</sup> For selected compounds antifungal and antibacterial activity have been investigated.<sup>10,11</sup> The results of this research, focused on the influence of substituents on the structures and properties of benzoxaboroles, will be presented. Benzoxaboroles will be compared with their boronic analogues and the differences will be discussed.

#### References

1. K. Torssell, Ark. Kemi 1957, 10, 507.

2. A. Adamczyk-Woźniak, M.K. Cyrański, A. Żubrowska, A. Sporzyński, J. Organomet. Chem. 2009, 694, 3533.

3. A. Adamczyk-Woźniak, K.M. Borys, A. Sporzyński, Chem. Rev. 2015, 115, 5224.

4. M. Dowlut, D.G. Hall, J. Am. Chem. Soc. 2006, 128, 4226.

5. Anacor Pharmaceuticals, http://investor.anacor.com/.

6. E. Seiradake, W. Mao, V. Hernandez, S.J. Baker, J.J. Plattner, M.R.K. Alley, S.J. Cusack, *Mol. Biol.* **2009**, 390, 196.

7. S. Sene, S. Bégu, C. Gervais, G. Renaudin, A. Mesbah, M.E. Smith, P.H. Mutin, A. van der Lee, J.-M. Nedelec, C. Bonhomme, D. Laurencin, *Chem. Mater.* **2015**, *27*, 1242.

8. A. Adamczyk-Woźniak, K.M. Borys, I.D. Madura, A. Pawełko, E. Tomecka, K. Żukowski, *New J. Chem.* **2013**, *37*, 188.

9. A. Adamczyk-Woźniak, K.M. Borys, I.D. Madura, S. Michałek, A. Pawełko, *Tetrahedron* 2013, 69, 8936.

10. D. Wieczorek, J. Lipok, K. M. Borys, A. Adamczyk-Woźniak, A. Sporzyński, Appl. Organometal. Chem. 2014, 28, 347.

11. A. Adamczyk-Woźniak, M. K. Cabaj, P. M. Dominiak, P. Gajowiec, B. Gierczyk, J. Lipok, G. Schroeder, E. Tomecka, P. Urbański, D. Wieczorek, A. Sporzyński, *Bioorg. Chem.* **2015**, *60*, 130.

## Metallacarborane chemistry: Site-directed substitutions designed for specific inhibition activity towards CA-IX

Bohumír Grüner,<sup>a</sup> Josef Holub,<sup>a</sup> Václav Šícha,<sup>a</sup> Jan Nekvinda,<sup>a</sup> Jana Štěpánková,<sup>b</sup> Marián Hajdúch,<sup>b</sup> Pavlína Řezáčová<sup>c,d</sup>, and Jiří Brynda<sup>d</sup>

<sup>a</sup>Institute of Inorganic Chemistry, AS ČR, Hlavní 1001, 250 68 Řež, Czech Rep.; <u>gruner@iic.cas.cz</u> <sup>b</sup>Institute of Molecular and Translational Medicine, Hněvotínská 5, 779 00 Olomouc, Czech Rep. <sup>c</sup>Institute of Org. Chem. and Biochemistry AS ČR, Flemingovo nám. 2, 160 00 Prague 6, Czech Rep. <sup>d</sup>Institute of Molecular Genetics, AS ČR, K vědeckým ústavům 1083/1,142 00, Prague 4, Czech Rep.

Previously we have identified neutral and ionic carboranes to be a promising class of specific inhibitors of the cancer associated Carbonic Anhydrase IX isoenzyme.<sup>1</sup> Subsequent considerations about possible improvements in the inhibitor's structure re-directed our attention to metallacarboranes as the other type of newly emerging pharmacophores.

Indeed, particularly the introduction of the cobalt bis(dicarbollide) ion into molecular design led to a significant increase of *in vitro* activity (with Ki values far below the nanomolar range) along with high selectivity for CA-IX isoform. Here we report mainly on new advances in the synthesis of active inhibitors of CA IX, which were triggered by recent progress in chemical methods of direct substitutions at cobalt bis(dicarbollide). This opened up an easy access to a large variety of carbon substituted building blocks with terminal hydroxy, methylsulfonic, toluenesulfonic, carboxy, amino, rhodano, sulfamide and other groups.<sup>2</sup> Additionally, inhibitors prepared by an alternative "classical" approach that starts from known boron substituted blocks or modified carboranes are presented for comparison. The structure-activity relationship (SAR) for various substitutions at cobalt bis(dicarbollide) ion is outlined. These results are complemented by molecular structures of inhibitor-enzyme complexes and a short overview of pharmacologically relevant factors such as plasma protein binding, cell membrane penetration, and some results from pharmacokinetic studies (mouse model) observed for these families of inhibitors.



Figure 1. Top view on the 1,1'-dietlylsulfamido substituted cobalt bis(dicarbollide) in the active site of the enzyme in the synchrotron structure of the CA-29 mimic- inhibitor complex.

#### Acknowledgements

Supported by Grant Agency of CR, Project No.15-05677S.

#### References

J. Brynda, P. Mader, V. Šícha, M. Fábry, K. Poncová, M. Bakardiev, B. Grüner, P. Cígler, P. Řezáčová, *Angew. Chem., Intl. Ed. Eng.* **2013**, *52*, 13760.
 J. Nekvinda, J. Švehla, I. Císařová and B. Grűner, *J. Organomet. Chem.*, **2015**, *798*, 112, and the refs. therein.

#### Diallylboration reactions in the construction of N-heterocycles

Yury Bubnov,<sup>a,b</sup> Nikolai Kuznetsov<sup>a</sup>

<sup>a</sup> A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences <sup>b</sup> N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences <u>bubnov@ineos.ac.ru</u>; <u>nkuznff@ineos.ac.ru</u>

Diallylated compounds **1**, **2**, **4**, and **5** available via the reactions of triallyl- or trimethallylborane with nitriles, lactams and aromatic nitrogen heterocycles present convenient starting materials for the preparation of diverse N-heterocycles.<sup>1</sup> Intramolecular amination, various cyclization reactions including ring-closing metathesis were successfully applied for the creaction of the final heterocycles.<sup>2,3</sup> From bicyclic boranes **3**, the corresponding chiral N,- S,- and Se-heterocycles were prepared.



Syntheses of alkaloids  $(\pm)$ -Hippocasine<sup>4</sup> and  $(\pm)$ -Cephalotaxine<sup>5</sup> will be also presented.



#### Acknowledgements

The authors thank the RSF (№15-13-00109) and RFBR (№ 15-29-05870-ofi-m) for financial support.

#### References

- 1. Yu.N. Bubnov, et al. J. Organomet. Chem. 2009, 694, 1754.
- 2. N.Yu. Kuznetsov, Yu.N. Bubnov, Russ. Chem. Rev. 2015, 84, 758.
- 3. N.Yu. Kuznetsov, et al., Org. Biomol. Chem. 2016, 14, 4283.
- 4. N.Yu. Kuznetsov, Yu.N. Bubnov et al. Russ. Chem. Bull. 2014, 63, 529.
- 5. N.Yu. Kuznetsov, et al. Eur. J. Org. Chem. 2008, 5647.

## On the verge of bioinorganic and inorganic chemistry: Metallacarboranes in nanomedicine

#### Clara Viñas

#### Institut de Ciència de Materials de Barcelona (CSIC), Campus U.A.B. Spain. clara@icmab.es

Relative to carbon, very little is currently known about boron in therapeutics. The aim of this presentation is to show the ability of boron clusters in producing new molecules for desired application in nanomaterials and nanomedicine. In this regard, a new type of gold NPs, which is hydrophobic and completely insoluble in water when uncharged, but, when offered electrons by a suitable reducing agent, transfers readily to an aqueous.<sup>1</sup> The design of water-soluble boron rich particles or macromolecules is of significance for medicine and for drug delivery.

In addition,  $[3,3'-Co(1,2-C_2B_9H_{11})_2]$  has also been shown to form small monolayer nanovesicles and micelles in water depending on the concentration<sup>2a</sup> while,  $[3,3'-Co(8-I-1,2-C_2B_9H_{10})_2]$  has been found to self-assemble into a lyotropic lamellar phase.<sup>2b</sup> Both boron-rich metallacarboranes have shown to cross through synthetic lipid membranes and to accumulate within living cells, where they can be detected by vB-H Raman Microspectroscopy.<sup>3</sup>

We investigated the interaction of this inorganic membrane system with living cells.<sup>4</sup> [3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] elicits a range of cell biological effects, including altered cell morphology, inhibition of cell growth and in some cases apoptosis. These results reveal unexpected properties at the interface of biological and synthetic membranes<sup>5</sup> and demonstrate an alternative method for cell labelling and detection as well as *"in vivo*" imaging.<sup>6</sup>

In the presentation also a wide view of the recent results on paramagnetic [3,3]-Fe(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>T</sup> from synthesis, characterization and applications will be covered.



Acknowledgements: To projects (CTQ2013-44670-R) and (2014 SGR 149).

#### References

1. A.M. Cioran, A.D. Musteti, F. Teixidor, Z. Krpetic, I.A. Prior, Q. He, C.J. Kiely, M. Brust, C. Viñas, J. Am. Chem. Soc. **2012**, 134, 212.

2. a) P. Bauduin, S. Prevost, P. Farràs, F. Teixidor, O. Diat, T. Zemb, *Angew. Chem., Int. Ed. Engl.* **2011**, *50*, 5298; b) D. Brusselle, P. Bauduin, L. Girard, A. Zaulet, C. Viñas, F. Teixidor, I. Ly, O. Diat, *Angew. Chem., Int. Ed.* **2013**, *52*, 12114.

M. Tarrés, E. Canetta, C. Viñas, F. Teixidor, A.J. Harwood, *Chem. Commun.* **2014**, *50*, 3370.
 M. Tarrés, E. Canetta, E. Paul, J. Forbes, K. Azzouni, C. Viñas, F. Teixidor, A.J. Harwood, *Sci. Rep.* **2016**, *5*, 7804.

5. C. Verdiá-Báguena, A. Alcaraz, V. M. Aguilella, A.M. Cioran, S. Tachikawa, H. Nakamura, F. Teixidor, C. Viñas, *Chem. Commun.* **2014**, *50*, 6700.

6. K.B. Gona, A. Zaulet, V. Gómez-Vallejo, F. Teixidor, J. Llop, C. Viñas, Chem. Commun. 2014, 50, 11415.

#### Geometries of nido-carboranes

#### Mark A. Fox

#### Chemistry Department, University of Durham, m.a.fox@durham.ac.uk

There are many known *nido*-carboranes but not all their geometries have been confirmed or correct. Here we show some examples of *nido*-carborane geometries that are not what they are reported as in the literature. The re-identifications of these *nido*-carborane geometries are demonstrated by comparison with other known *nido*-carboranes and supported by computations.

One difficulty with determining the structures of carboranes by X-ray crystallography correctly is distinguishing between the boron and carbon atoms. One way to resolve this is looking at the C-B and B-B bond lengths where C-B bonds are generally shorter. However, we have shown elsewhere<sup>1</sup> that in the sterically congested assembly **1** the carbon atom is incorrectly located in the original study.

This talk focusses on *nido*-carborane geometries where boron and carbon atoms are incorrectly located in X-ray studies. For example, the X-ray geometries of our reported<sup>2</sup> *closo-nido* carborane anion **2** are re-identified here. The geometries of *nido*-carboranes which have not been structurally characterised are also discussed.<sup>3</sup>



Figure 1. X-ray geometries with corrected locations of boron and carbon atoms.

#### Acknowledgements

MAF appreciates the excellent efforts by many research workers involved in carborane chemistry at Durham, Leeds (C.E. Willans) and Bielefeld (L. Weber) and also thanks EPSRC for funding.

#### References

1. R.A. Harder, J.A.H. MacBride, G.P. Rivers, D.S. Yufit, A.E. Goeta, J.A.K. Howard, K. Wade, M.A. Fox, *Tetrahedron* **2014**, *70*, 5182.

2. C.E. Willans, C.A. Kilner, M.A. Fox, Chem. Eur. J. 2010, 16, 10644.

3. J. Kahlert, L. Böhling, A. Brockhinke, H.-G. Stammler, B. Neumann, L.M. Rendina, P.J. Low, L. Weber, M.A.Fox, *Dalton Trans.* **2015**, *44*, 9766.

# From ammonia borane to hydrazine bisborane, via hydrazine borane: boron- and nitrogen-based materials for chemical hydrogen storage

Romain Moury,<sup>a</sup> Georges Moussa,<sup>a</sup> Jean-Fabien Petit,<sup>a</sup> Sergii Pylypko,<sup>a</sup> Salem Ould-Amara,<sup>a</sup> Pascal G. Yot,<sup>b</sup> Philippe Miele,<sup>a</sup> Umit B. Demirci<sup>a</sup>

 <sup>a</sup> IEM (Institut Europeen des Membranes), UMR5635 (CNRS, ENSCM, UM), Universite de Montpellier, Place Eugene Bataillon, CC047, F-34095, Montpellier, France, <u>umit.demirci@umontpellier.fr</u>
 <sup>b</sup> Institut Charles Gerhardt Montpellier, UMR 5253 (UM-CNRS-ENSCM), Université de Montpellier, Place Eugène Bataillon, 34095 Montpellier cedex 05, France

Among the solid- and liquid-state chemical hydrogen storage materials, boron- and nitrogen-based compounds have attracted much attention owing to high theoretical gravimetric hydrogen densities (15-20 wt%) and "low" dehydrogenation temperatures (<200°C, owing to the presence of both protic and hydridic hydrogens). Despite irreversibility of storage, this kind of materials has some prospects thanks to existing recycling and regenerations schemes.<sup>1</sup>

Ammonia borane H<sub>3</sub>N-BH<sub>3</sub> is a typical example. It has been much investigated, particularly through the development of strategies to improve its dehydrogenation properties.<sup>2</sup> One of the strategies is chemical modification (towards derivatives),<sup>3</sup> and hydrazine borane H<sub>2</sub>N-(H<sub>2</sub>)N-BH<sub>3</sub>, another example of boron- and nitrogen-based compound, can be seen as a derivative also, where the NH<sub>3</sub> moiety in ammonia borane has been substituted by a N<sub>2</sub>H<sub>4</sub> group.<sup>4</sup>

Hydrazine borane in pristine state is not suitable for solid-state chemical hydrogen storage. Like for AB, derivatives have been then considered. First examples of derivatives are alkaline hydrazinidoboranes  $H_2N$ -(HM)N-BH<sub>3</sub>, obtained by reaction (exothermic) of HB and an alkaline hydride MH (M = Li, Na, K).<sup>5</sup> Another example of derivative of hydrazine borane is hydrazine *bis*borane  $H_3B$ -( $H_2$ )N-( $H_2$ )N-BH<sub>3</sub>, where the  $H_2N$ -( $H_2N$ )-BH<sub>3</sub> entity is complexed with an additional BH<sub>3</sub> group.<sup>6</sup> However, the suitability of hydrazine *bis*borane for chemical hydrogen storage has shown to be controversial, especially for the thermolytic approach.

The EUROBORON 2016 conference will be an opportunity to present in details the aforementioned boron- and nitrogen-based materials. They will be described in terms of synthesis, characterizations (e.g. <sup>11</sup>B MAS NMR and *in-situ* thermodiffraction), thermal decompositions and safety issues. And, these aspects are sometimes challenging and surprising...

#### Acknowledgements

The authors acknowledge the CNRS, DGA, Safran Herakles, LabEx CheMISyst (ANR Program IA, ref. ANR-10-LABX-05-01) and the Région Languedoc-Roussillon (Project "Chercheurs d'Avenir" 2013) for funding.

#### References

1. O.T. Summerscales, J.C. Gordon, Dalton Trans. 2013, 42, 10075.

2. C.W. Hamilton, R.T. Baker, A. Staubitz, I. Manners, Chem. Soc. Rev. 2009, 38, 279.

3. Y.S. Chua, P. Chen, G. Wu, Z. Xiong, Chem. Commun. 2011, 47, 5116.

4. R. Moury, G. Moussa, U.B. Demirci, J. Hannauer, S. Bernard, E. Petit, A. van der Lee, P. Miele, *Phys. Chem. Chem. Phys.* **2012**, *14*, 1768.

5. R. Moury, U.B. Demirci, *Energies* 2015, *8*, 3118.

6. S. Pylypko, E. Petit, P.G. Yot, F. Salles, M. Cretin, P. Miele, U.B. Demirci, *Inorg. Chem.* 2015, *54*, 4574.

# The chemistry of closo-[B<sub>21</sub>H<sub>18</sub>]<sup>-</sup>

#### E. Bernhardt

#### FB C-Anorganische Chemie, Bergische Universitaet Wuppertal, Gaussstrasse 20, D-42097 Wuppertal, Germany, <u>edbern@uni-wuppertal.de</u>

Recently we discovered the new *closo*- $[B_{21}H_{18}]^{-}$  and *nido*- $[B_{20}H_{18}]^{2-1}$  species. These were synthesized in good yields by a three-step procedure starting from commercially available salts of  $[B_{10}H_{10}]^{2-1}$ .

 $\textit{closo-}[B_{10}H_{10}]^{2-} \xrightarrow[]{\text{coupling}} \textit{trans-}[B_{20}H_{18}]^{2-} \longrightarrow \textit{fac-}[B_{20}H_{18}]^{2-} \longrightarrow \textit{closo-}[B_{21}H_{18}]^{-}$ 

Now their chemistry was studied in more detail and compared to that of *closo*- $[B_{12}H_{12}]^{2-}$  and *nido*- $[B_{11}H_{14}]^{-}$ . Several chemical reactions of *closo*- $[B_{21}H_{18}]^{-}$  and *nido*- $[B_{20}H_{18}]^{2-}$  are presented. The chemical behavior of *closo*- $[B_{21}H_{18}]^{-}$  and *nido*- $[B_{12}H_{12}]^{2-}$  and *nido*- $[B_{12}H_{12}]^{2-}$  and *nido*- $[B_{11}H_{14}]^{-}$ . The reduction, oxidation and reactions with acids, bases and metal salts will be presented and discussed.<sup>1-4</sup>

#### References

1. E. Bernhardt, D.J. Brauer, M. Finze, H. Willner, Angew. Chem, Int. Ed. Engl. 2007, 46, 2927.

2. F. Schlüter, E. Bernhardt, Z. Anorg. Allg. Chem. 2012, 638, 594.

3. F. Schlüter, The chemistry of closo-borates  $[B_nH_n]^{2-}$  (n = 6-9, 11) and  $[B_{21}H_{18}]^{-}$ , Dissertation,

University of Wuppertal, Wuppertal, **2012**.

4. E. Bernhardt, F. Teixidor, A. Zaulet, unpublished.

## Unforeseeable synthesis of organoboron compounds

#### Elena Fernández

#### Dept. Química Física I Inorg'anica, University Rovira i Virgili, Tarragona, Spain . <u>mariaelena.fernandez@urv.cat</u>

Boron-containing molecules provide enabling platforms for chemical synthesis. The direct generation of  $C(sp^3)$ -B bonds, has been historically regarded to the metal-transition catalysed hydroboration, diboration, allylic borylation or conjugate boron addition to olefins. However, nowadays, all these transformations can be carried out in absence of transition metals, with high control of chemo-, regio- and stereoselectivity.

1) The direct activation of diboron reagents via alkoxide bases, can enhance the nucleophilic character of boryl units and promote borylation reactions towards  $C(sp^3)$ -B and  $C(sp^2)$ -B bonds, extending the reactivity to B-N reagents.[1,2]

2) The direct activation of B-B and B-X (X= P, Se, S, Si) by the substrate itself becomes a concerted reactivity that can be performed even in neat conditions.[2]

3) The  $\alpha$ -boron compounds are reactive species by treatment with bases, via deborylation or deprotonation, to generate "active" carbanions.<sup>2</sup>



#### Acknowledgements

Research supported by the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2013-43395

#### References

1. a) J. Cid, J.J. Carbó, E. Fernández, *Chem. Eur. J.* **2012**, *18*, 12794; b) J. Cid, H. Gulyás, J.J. Carbó, E. Fernández, *Chem. Soc. Rev.* **2012**, *41*, 3558.

2. a) R.D. Dewhurst, E.C. Neeve, H. Braunschweig, T.B. Marder, *Chem. Commun.* **2015**, *51*, 9594; b) S. Pietsch, E.C. Neeve, D.C. Apperley, R. Bertermann, F. Mo, D. Qiu, M.S. Cheung, L. Dang, J. Wang,

U. Radius, Z. Lin, C. Kleeberg, T.B. Marder, Chem. Eur. J. 2015, 21, 7082.

# ORAL PRESENTATIONS

# Let Your Data Live On

# Exploit the Power of Live Data with ACD/Spectrus

# **Unify and Structure Analytical Information**

Collect disparate analytical data from different techniques and instruments into one 'live' environment.

# Generate Knowledge from Information for Faster Decision-Making

Deliver dynamic visualization tools and advanced algorithms that provide decision support.

# **Capture Chemical Context and Retain Analytical Intelligence**

Store interpreted analytical data with associated chemical structures/fragments/recipes and other relevant chemical information to aid future decision making.

# **Make Information Accessible**

Create and share a searchable repository of live instantly re-usable analytical knowledge (searchable by spectral parameters, structure/substructure, meta data, text).

# Integrate with Existing LIMS, ELNs, and Other Informatics Systems



Learn More: www.acdlabs.com/LetYourDataLiveOn

#### Polyborates templated by cationic transition-metal complexes

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

<sup>a</sup> School of Chemistry, Bangor University, Bangor, Gwynedd, LL57 2UW, UK <sup>b</sup> School of Chemistry, Southampton University, Southampton, SO17 1BG, UK

Polyborate anions are readily categorized as 'isolated' (discrete anionic moieties) or 'condensed' (2D or 3D polymeric chains, sheets or networks). Isolated polyborate anions are easily synthesized by the addition of  $B(OH)_3$  to a basic aqueous solution containing templating cations, or by solvothermic methods. Boric acid dissolved in basic aqueous solution exists as a dynamic combinatorial library of various polyborate anions, from which templated salts crystallize. Most commonly, pentaborate(1-) salts (containing the  $[B_5O_6(OH)_4]^-$  anion) are formed, and this is because these salts have a strong H-bonded anionic lattice, which is sufficiently flexible to accommodate many medium sized cations.<sup>1,2</sup> Salts containing polyborate anions other than pentaborate(1-) are relatively rare.

We are interested in the synthesis of structurally novel polyborate anions and have adopted a strategy of templating such species by the use of sterically demanding and/or highly charged cations. We report the synthesis of several salts containing isolated polyborate anions partnered with transition metal cations and describe the synthesis and structures of novel polyborate species such as heptaborate(3-) and octaborate(2-) anions.<sup>3,4</sup> These anions contain numerous fused B-O rings and cages. Other new structures will also be discussed.

#### References

1. M.A. Beckett, S.J. Coles, R.A. Davies, P.N. Horton, C.L. Jones, Dalton Trans. 2015, 44, 7032.

- 2. M.A. Beckett, P.N. Horton, M.B. Hursthouse, D.A. Knox, J.L. Timmis, Dalton Trans. 2010, 39, 3944.
- 3. M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, Inorg. Chem. Commun. 2015, 59, 95.
- 4. M.A. Altahan, M.A. Beckett, S.J. Coles, P.N. Horton, Inorg. Chem. 2015, 54, 412.

# Quantitative structure-activity relationships in trivalent boron compounds: A computational tool for evaluation and design of nucleophilic boryl species

Jorge J. Carbó, Elena Fernández, Diego García-López, Jessica Cid

Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain; <u>i.carbo@urv.cat</u>

Most trivalent boron compounds are electrophiles due to the lack of two electrons to fill the outer orbital of boron atom. However, these compounds can change their reactivity from an electrophilic character to a nucleophilic behavior by changing the nature of the substituents on the boron atom. This tunable reactivity is specially remarked when the boron atom is bonded to different transition metals. Metal-free nucleophilic boryl species can be also generated via formation of a Lewis base adducts of diboron compounds. The base quaternizes one boron tuning the nucleophilic character of the non-quaternized boron.

We had defined computational descriptors to build a tendency map that classifies the boryl fragments according to their nucleophilic character.<sup>1</sup> In a step forward, here, we introduce a steric descriptor<sup>2</sup> and present two Quantitative Structure-Activity Relationship (QSAR) models between the stereoelectronic properties of boryl compounds and their nucleophilic reactivity. The first QSAR model focuses on the substituents of the boron atom, covering a full range of boryl fragments that are bonded to main-group metals and coordinated to transition-metals. The second QSAR models focuses of the different Lewis bases which activate diboron species. To define a quantitative dependent variable that measures the nucleophilic activity, we made use of the computed free-energy barrier for the boryl addition to formaldehyde. Using multivariate regression techniques, we were able to generate mathematical models which correlate well with computed reactivity and which show predictive ability. Additionally, we provide some mechanistic details of these reactions by characterizing their potential energy surfaces.<sup>3</sup>

#### References

1. J. Cid, J.J. Carbó, E. Fernández, Chem. Eur. J. 2012, 18, 12794.

2. S. Aguado-Ullate, M. Urbano-Cuadrado, I. Villalba, E. Pires, J.I. García, C. Bo, J.J. Carbó, Chem. Eur. J. 2012, 18, 14026.

3. N. Miralles, J. Cid, A.B. Cuenca, J.J. Carbó, E. Fernández, Chem. Commun. 2015, 51, 1693.

# Synthesis of boron carbonitride films by thermal decomposition of B-triallylborazole

B. V. Spitsyn,<sup>a</sup> A. E. Alexenko,<sup>a</sup> T. B. Galushko,<sup>a</sup> G. A. Sokolina,<sup>a</sup> Yu. N. Bubnov<sup>b</sup>

<sup>a</sup> Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, Russia, <u>bspitsyn@yahoo.com</u> <sup>b</sup> Institute of Organoelement Compounds Russian Academy of Sciences, Moscow, Russia,

<u>bubnov@ineos.ac.ru</u>

Considerable number of theoretical and experimental works are devoted to boron carbonitride of the general formula  $(BN)_xC_y$ , because of a possibility of practical realization of properties, intermediate, on the one hand, between graphite and hexagonal boron nitride and, also, between diamond and cubic boron nitride - with another. The majority of attempts to obtain such new "hybrid" material between the two isoelectronic analogs - carbon and boron nitride, were carried out in the conditions of high pressures and temperatures. It seemed interesting to us to carry out a deposition of films  $(BN)_xC_y$  by means of high-temperature thermal decomposition of vapors of a monoprecursor at atmospheric pressure. As initial compound the B-triallylborazole  $(C_3H_5)_3B_3(NH)_3$  firstly synthesized in INEOS of Russian Academy of Sciences was used.

$$(C_3H_5)_3B_3(NH)_3 \rightarrow B_xC_yN_z + H_2$$

The films have specific electric resistance from  $10^{-3}$  to  $10^{3}$  Ohm•cm, depending on BN/C ratio.

#### Acknowledgements

Authors are grateful to S. K. Sigalaev for carrying out the element analysis of the boron carbonitride films.

Work is performed under partial support of the Presidium RAS Program I.17.I "Scientific bases of new functional materials synthesis", the subprogram "Synthesis from a vapor phase of the nanodimensional and nanostructured boron nitride and boron carbonitride with controlled phase and chemical composition".

## The enhanced structural carborane effect

Alan J. Welch, Samuel L. Powley, Georgina M. Rosair

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK; a.j.welch@hw.ac.uk

The question of the degree of aromaticity in the exopolyhedral  $C_6$  ring of the wellknown species benzocarborane (1) is an old one, and most authors conclude that there is little, if any, aromatic character present.<sup>1,2</sup>

In this presentation we describe detailed comparisons of the structures of benzocarborane, dihydrobenzocarborane (2) and their transition-metal derivatives (e.g. 3 and 4) which provide evidence for an *enhanced structural carborane effect* (ESCE).<sup>3</sup> The ESCE is related to the difference in the ways in which cyclopentadienyl and indenyl ligands bind to transition metals. Moreover, the presence of an ESCE provides clear evidence for a degree of aromaticity in the C<sub>6</sub> ring of benzocarborane, albeit small. In the course of our studies we have also unexpectedly discovered that compound 4 can be interconverted with an  $\eta$ -(C<sub>4</sub>H<sub>6</sub>)(CO)<sub>2</sub> species and we have explored substitution of the ene of the latter with various 2e donor ligands.<sup>4</sup>



Figure 1. Compounds 1 - 4.

#### Acknowledgements

We thank the EPSRC for a DTP Studentship supporting SLP.

#### References

- 1. D. S. Matteson, N. K. Hota, J. Am. Chem. Soc. 1971, 93, 2893.
- 2. R. C. B. Copley, M. A. Fox, W. R. Gill, J. A. K. Howard, J. A. H. MacBride, R. J. Peace, G. P. Rivers,
- K. Wade, Chem. Commun. 1996, 862.
- 3. S. L. Powley, W. Y. Man, G. M. Rosair, A. J. Welch, J. Organomet. Chem. 2015, 792, 51.
- 4. S. L. Powley, G. M. Rosair, A. J. Welch, *Dalton Trans.* in preparation.

# Reduction of paramagnetic ruthenacarboranes using aliphatic amines in connection with Atom Transfer Radical Polymerization

Ivan D. Grishin<sup>a</sup>, Ksenia S. Agafonova<sup>a</sup>, Fedor M. Dolgushin<sup>b</sup>, Alexander Yu. Kostukovich<sup>b</sup>, Dmitry I. D'yachihin<sup>b</sup>, Dmitry F. Grishin<sup>a</sup>, Igor T. Chizhevsky<sup>b</sup>

<sup>a</sup> N. I. Lobachevsky State University of Nizhny Novgorod, <u>grishin\_i@ichem.unn.ru</u>
<sup>b</sup> A. N. Nesmeyanov Institute of Organoelement compounds, Russian Academy of Sciences, <u>chizbor@ineos.ac.ru</u>

Paramagnetic carborane complexes of Ru(III) with  $\{C_2B_9\}$ -type ligands showed high catalytic activity in polymerization of methacrylic monomers via Atom Transfer Radical Polymerization (ATRP) mechanism [1-2]. This catalytic process based on reversible halogen transfer between polymer chain and transition metal complex and accompanied by changing its oxidation state.

Investigation of mechanism of ruthenacarborane catalysis of ATRP and its activation by aliphatic amines allowed us to isolate novel complexes of Ru(II) bearing three phosphorous atoms coordinated on the ruthenium center. The divalent state of ruthenium in these complexes was confirmed by NMR and X-ray diffraction study.



Thus we believe that amines act as reductants in these reactions transforming Ru(III) to a lower oxidation state. Further experiments show that diamagnetic ruthenium complex can be easily oxidized by carbon tetrachloride to give initial complex of Ru(III). The stability of the Ru(II) derivatives formed decreases either with the increasing of the length of methylene chain in diphosphine ligand or via introduction of methyl substituents to the carborane cage ligand.

The performed experiments allowed us to explain the activating influence of amines on polymerization catalyzed by ruthenacarboranes and to enhance activity of earlier developed systems. Amine additives acting as reducing agents regenerate ruthenium catalyst into a lower oxidation state thus turning polymerization in accordance with AGET ATRP mechanism. The developed catalytic systems based on ruthenacarborane and amines were successfully applied to polymerization of various monomers and to synthesis of functional monomers.

#### Acknowledgements

The work was supported by Russian Foundation for Basic Researches (proj. 15-33-20640\_mol\_a).

#### References

I.D. Grishin, D.I. D'yachihin, A.V. Piskunov, F.M. Dolgushin, A.F. Smol'yakov, M.M. Il'in, V.A. Davankov, I.T. Chizhevsky, D.F. Grishin, *Inorg. Chem.* **2011**, *50*, 7574.
 I.D. Grishin, E.S. Turmina, D.I. D'yachihin, I.T. Chizhevsky, D.F. Grishin, *Polymer Sci., Ser. B.* **2014**, *56*, 1.

EUROBORON 7

# Developing systematic routes to 'non-Wadian' metallacarboranes: The tale of $(Cp^*Ru)_2C_2B_{10}H_{12}$

Alasdair P. M. Robertson, Nicholas A. Beattie, Stuart A. Macgregor, Alan J. Welch

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

Since its inception in the mid-20<sup>th</sup> century, the field of carboranes and their metallated derivatives has produced an ever increasing array of fascinating new main-group cluster compounds.<sup>1</sup> To date, however, almost all of these clusters have fallen within the three major classes enshrined in Wade's rules: n vertices and n+1 skeletal electron pairs (SEPs) [*closo*], n vertices and n+2 SEPs [*nido*] and n vertices and n+3 SEPs [*arachno*].<sup>2</sup> Examples of compounds with sub-Wadian skeletal electron counts *i.e.* n vertices and n (or fewer) SEPs, usually termed *hypercloso*, are particularly scant,<sup>3</sup> and to date no general route to this class of compound, nor systematic studies have yet been reported. The remarkable novel geometries and spectroscopic properties of these preliminary examples, nonetheless, encourage further investigation of this class of compounds.

The small library of known *hypercloso* metallacarboranes share an important common feature, specifically that in all cases a metal occupies at least one highly connected, often degree-six, vertex. With this observation in mind we have recently explored the synthesis of various supraicosahedral *hypercloso* metallacarboranes, an area of potentially rich non-Wadian chemistry due to the necessity for highly connected vertices in supraicosahedral clusters. The results of our recent investigations will be described, with a focus on the unprecedented 14v, 14 SEP cluster (Cp\*Ru)<sub>2</sub>C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, including discussion of synthetic routes to this species (**Figure 1**), characterization of multiple isomers by spectroscopic, crystallographic and computational methods, and preliminary derivatisation studies.



Figure 1. General route to 14 vertex *hypercloso* metallacarboranes via reduction and subsequent metalation of  $C_2B_{10}H_{12}$ .

#### References

1. R. N. Grimes, Carboranes, 2nd Ed, Academic Press (Elsevier), Amsterdam, 2011.

2. K. Wade, J. Chem. Soc. D, 1971, 792.

3. For representative examples see: A. R. Kudinov *et al.*, *Angew. Chem. Int. Ed.*, **2002**, *41*, 4112; M. F. Hawthorne *et al.*, *J. Am. Chem. Soc.*, **1975**, *97*, 296.

# Maleimide-functionalized *closo*-dodecaborate albumin conjugate: Unique ligation at cysteine and lysine residues enables efficient boron delivery to tumor for neutron capture therapy

Hiroyuki Nakamura,<sup>a</sup> Shunsuke Kikuchi,<sup>a</sup> Daisuke Kanoh,<sup>b</sup> Shinichi Sato,<sup>a</sup> Yoshinori Sakurai,<sup>c</sup> Minoru Suzuki<sup>c</sup>

<sup>a</sup> Laboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan, <u>hiro@res.titech.ac.jp</u>
<sup>b</sup> Department of Chemistry, Faculty of Science, Gakushuin University, Tokyo, 171-8578, Japan

 $^{\circ}$  Department of Chemistry, Faculty of Science, Gakushuin University, Tokyo, 171-8578, Japar.  $^{\circ}$  Kvoto University Research Reactor Institute, Osaka, 590-0494, Japan

Albumin, a major plasma protein constituent, is composed approximately 55% of the human plasma protein. Albumin has been extensively investigated as a versatile carrier for therapeutic and diagnostic agents, including diabetes, cancer, rheumatoid arthritis and infectious diseases. For example, Abraxane®, an albumin-paclitaxel nanoparticle, is the most advanced drug delivery product first approved by FDA in 2005 for the treatment of metastatic breast cancer. Furthermore, albumin microspheres have been investigated in controlled release systems as vehicles for delivery of therapeutic agents to local sites.

We focused on bovine serum albumin (BSA) as a boron carrier and studied conjugation of *closo*-dodecaborates to BSA. We chose a maleimide as a functional group to conjugate with BSA and designed a maleimide-conjugating *closo*-dodecaborate (MID). It is known that a maleimide readily reacts with free sulfhydryl groups to form a covalent, thus it has been widely used for protein modification with small molecules at the cysteine residue. In this paper, we report design and synthesis of MID and the preparation of MID-albumin conjugate as a new boron delivery vehicle for boron neutron capture therapy.

MID sodium form synthesized by the nucleophilic ring-opening reaction of *closo*dodecaborate-1,4-dioxane complex with tetrabutylammonium (TBA) azide was found to conjugate to free SH of cysteine and lysine residues in BSA under physiological conditions, forming highly boronated BSA that showed high and selective accumulation in tumor and significant tumor growth inhibition in colon 26 tumorbearing mice subjected to thermal neutron irradiation.<sup>1</sup>



Figure 1. Structure, Western blotting analysis, and BNCT antitumor effect of MID-albumin conjugate.

#### References

1. S. Kikuchi, D. Kanoh, S. Sato, Y. Sakurai, M. Suzuki, H. Nakamura, submitted.

# Investigation of boron compounds for Boron Neutron Capture Therapy using accelerator based neutron source

Sergey Taskaev<sup>a,b</sup>, Yulya Gavrilova<sup>c</sup>, Vladimir Kanygin<sup>d,e</sup>, Dmitrii Kasatov<sup>a</sup>, Alexander Kichigin<sup>a</sup>, Yaroslav Kolesnikov<sup>b</sup>, Alexei Koshkarev<sup>b</sup>, Alexander Makarov<sup>a</sup>, Ludmila Mechetina<sup>f</sup>, Kei Nakai<sup>g</sup>, Rinat Muhamadiyarov<sup>h</sup>, Yuri Ostreinov<sup>a</sup>, Eisuke Sato<sup>g</sup>, Ivan Shchudlo<sup>a</sup>, Evgeniya Sokolova<sup>b</sup>, Igor Sorokin<sup>a</sup>, Olga Volkova<sup>f</sup>, Anna Yarullina<sup>i</sup>, Alexander Zaboronok<sup>g</sup>

<sup>a</sup> Budker Institute of Nuclear Physics, Novosibirsk, Russia, <u>taskaev@inp.nsk.su</u>

<sup>b</sup> Novosibirsk State University, Russia

<sup>c</sup> Institute of Clinical and Experimental Lymphology, Novosibirsk, Russia

<sup>d</sup> Novosibirsk State Medical University Russia

<sup>e</sup> Novosibirsk Neurosurgery Center, Russia

<sup>f</sup> Institute of Molecular and Cell Biology, Novosibirsk, Russia

<sup>g</sup> University of Tsukuba, Tsukuba, Japan

<sup>h</sup> Institute of Complex Problems of Cardiovascular Diseases, Kemerovo, Russia

<sup>i</sup> Irkutsk State Medical University, Russia

A source of epithermal neutrons based on a tandem accelerator with vacuum insulation and lithium target is created in BINP for development of boron neutron capture therapy of malignant tumors [1, 2]. The neutron beam with the average energy of 10 keV is obtained in prolonged stable operation which is suitable for *in vitro* and *in vivo* studies for BNCT. The beam provides the absorbed dose rate to 0.5 Gy eq./min at 40 ppm of boron-10. The effect of neutron irradiation on the viability of U251MG, T98G, CHO-K1, and V79 cells incubated in boron medium, was studied and a decrease in their survival was shown at increasing the boron concentration [3]. New drugs for targeted delivery of boron-based nanotubes and liposomes was tested. Immunodeficient mice grafted with human glioblastoma were radiated using *L-p*-boronophenylalanine. The report presents and discusses the results of the research and declares the possibility of using accelerator neutron source for research to develop new drugs for targeted delivery of boron for BNCT.

#### Acknowledgements

The study was supported by the grants from the Russian Science Foundation (Project No.14-32-00006) and the Budker Institute of Nuclear Physics.

#### References

- 1. S. Taskaev, Physics of Particles and Nuclei 2015, 46, 956.
- 2. A. Ivanov et al., Technical Physics Letters 2016, 42, 607.
- 3. O. Volkova et al., Russian J. Radiology 2016, 5.
# Heck functionalization of asymmetric aza-BODIPY core: Synthesis of far-red infrared probes for bioimaging applications

Cristina Prandi, Stefano Parisotto, Roberto Scudu

Department of Chemistry, University of Turin, via P. Giuria 7, 10125 Torino, cristina.prandi@unito.it

As part of our ongoing work on the synthesis of a new class of plant hormones named Strigolactones and their analogues, we became interested in tracing the bioactive molecules with red emitting BODIPY fluorophores in order to unravel signaling and distribution of Strigolactones in plants.<sup>1</sup>

Strigolactones analogues functionalized with green emitting BODIPY have already been synthetized by our group and observed in plants,<sup>2</sup> however the green auto florescence typical of many plants hampers the application of BODIPY-SLs on a wider base. In addition, the plan of using fluorescent labeled Strigolactones in combination with the GFP tagged receptor of Strigolactones prompted us in investigating new synthetic strategies leading to red emitting asymmetric functionalized BODIPY.

To this purpose we chose to use [3-(4-Bromo-phenyl)-5-phenyl-pyrrol-2-ylidene]-(3,5diphenyl-1H-pyrrol-2-yl)-amine (Scheme 1), previously synthesized by O' Shea *et al.*<sup>3</sup> as a substrate to optimize Heck functionalization and thus be able to introduce functionalities suitable to hook small active molecules of interest and map their distribution *in vivo*.



Scheme 1. Heck functionalization of 1,3,5,7-tetraphenyl aza-BODIPY core.

#### References

1. C. Prandi, H. Rosso, B. Lace, E.G. Occhiato, A. Oppedisano, S. Tabasso, G. Alberto, M. Blangetti, *Molecular Plant* **2013**, *6*, 113-127.

2. C. Prandi, G. Ghigo, E.G. Occhiato, D. Scarpi, S. Begliomini, B. Lace, G. Alberto, E. Artuso, M. Blangetti, *Org. Biomol. Chem.* **2014**, *12*, 2960-2968.

3. M.J. Hall, S.O. McDonnell, J. Killoran, D.F. O'Shea, J. Org. Chem. 2005, 70, 5571-5578.

### New B,O,N-containing adamantanes: Synthesis and application

A. Yu. Sukhorukov, I. S. Golovanov, S. L. loffe, V. A. Tartakovsky

N.D. Zelinsky Institute of Organic Chemistry, 119991, Leninsky prospect, 47, sukhorukov@ioc.ac.ru

Adamantane derivatives find numerous applications in medicine, material sciences, as well as in the rational design of functional molecules and nanosystems.<sup>1</sup> Substitution of carbon atoms for heteroatoms provides vast opportunities for tuning adamatane properties and thus creation of substances and materials with predefined characteristics. Thus, incorporation of heteroatoms such as nitrogen, oxygen, or boron in an adamantane cage results in a significant enhancement of pharmacological activity that led to development of highly potent heteroadamantane based antiviral drugs.

Here, a straightforward synthesis of hitherto unknown 2,4,10-trioxa-1,5,7-triaza-3-boroadamantanes and their fused derivatives has been developed by an unprecedented multicomponent condensation of oximes with boronic acids, aryl trifluoroboronates or  $B(OH)_{3}$ .<sup>2</sup> The process involves an unusual cyclotrimerization of oximes to unstable 1,3,5-trihydroxy-1,3,5-triazaadamantanes,<sup>3</sup> which react with boron derivatives to give the desired heteroadamantanes.

Scheme



In the presentation, the mechanism, scope and limitations of the oxime-boronate condensation, as well as aspects dealing with structure, stability and application of these B,O,N-containing adamantanes will be discussed.

#### Acknowledgements

The work was supported by Russian Foundation for Basic Research (grant #14-03-00933a) and President's council for grants (MK-5957.2015.3).

#### References

- 1. H. Schwertfeger, A.A. Fokin, P.R. Schreiner, Angew. Chem., Int. Ed. 2008, 47, 1022.
- 2. I.S. Golovanov, A.Yu. Sukhorukov, Yu.V. Nelyubina, Yu.A. Khomutova, S.L. loffe, V.A. Tartakovsky, J. Org. Chem. 2015, 80, 6728.
- 3. A.N. Semakin, A.Yu. Sukhorukov, Yu.V. Nelyubina, Yu.A. Khomutova, S.L. loffe, V.A. Tartakovsky,
- J. Org. Chem. 2014, 79, 6079.

# Straightforward access to *gem*-polymetalloid substituted carbons through metal-free insertion of diazo synthons into Bpin-X bonds

Ana B. Cuenca, J. Royes, E. Fernández

Dept. Química Física i Inorgànica University Rovira i Virgili, Tarargona, Spain, <u>anabelen.cuenca@urv.cat</u>

*Gem*-diborylated alkanes have recently emerged as versatile reagents for concise synthesis of more complex molecules through multiple C–C (or C-heteroatom) bond formation, functionalization reactions of the C–B bonds, or both.<sup>1-2</sup> Among the possible route to these species, the insertion reaction of *diazo synthons* into boron-containing targets is particularily attractive. In that context, we would like to report here our progress in metal-free insertion of diazo reagents into a B-B sigma bonds.<sup>3,4</sup> Also, we will illustrate how a particular example of this type of reaction, the insertion of the commercially available (trimethylsilyl)diazomethane into the bis(pinacolato)-diboron molecule (B<sub>2</sub>pin<sub>2</sub>), constitutes an attractive entry point to a series of *gem*-polymetalloid substituted carbons ready for downstream functionalizations.



Figure 1. Metal-free insertion of diazo reagents into a B-X sigma bonds.

#### Acknowledgements

Research supported by the Spanish Ministerio de Economía y Competitividad (MINECO) through project CTQ2013-43395.

#### References

- 1. J. Takaya, N. Iwasawa, ACS Catal. 2012, 2, 1993.
- 2. L. Xu, S. Zhang, P. Li, Chem. Soc. Rev. 2015, 44, 8848
- 3. H. Li, X. Shangguan, Z. Zhang, S. Huang, Y. Zhang, J. Wang, Org. Lett. 2014, 16, 448.
- 4. A.B. Cuenca, J. Cid, D. García, J.J. Carbó, E. Fernández, Org. Biomol. Chem. 2015, 13, 9659.

### Oxonium ring cleavage vs Sonogashira reaction. Different boron clusters require different approaches towards conjugates with 5-ethynyl-2'-deoxyuridine\*

A. Semioshkin, A. Druzina, I. Kosenko, A. Kozlova, V. Bregadze

A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 119991 Moscow, Russia, E-mail: <u>semi@ineos.ac.ru</u>

Our continuous interest aims towards design of nucleoside conjugates with different boron clusters. Representative applications of these conjugates include boron carriers for the boron neutron capture therapy (BNCT) of tumors, antiviral agents, RedOx-labels, inhibitors of the blood platelets aggregation, etc<sup>1</sup>. On the other hand, various 5-alkynyl modified 2'-deoxyuridines have received particular attention because this kind of substitution at position 5 of the pyrimidine nucleobase often does not attenuate susceptibility to nucleoside metabolizing enzymes and does not impart any significant conformational changes in oligonucleotides incorporating the modified unit.

Among the numerous boronated nucleosides synthesized so far, 5-ethynyl-2'deoxyuridines modified with boron clusters were barely studied. In this contribution we present synthesis of novel conjugates of 5-ethynyl-2'-deoxyuridine with *closo*dodecaborate, carboranes and cobalt bis(1,2-dicarbollide) boron clusters. Two approaches towards these conjugates will be discussed.





#### Acknowledgements

This work was partially supported by Russian Foundation for Basic Research (Grant 14-03-00042), Foundation for the Development of Small Business in Science (Grant SMARTY 0002237) and stipendium of the President of Russian Federation (Grant SP-1023.2015.4).

\*In memory of Dr. Irina Lobanova.

#### References

1. A.R. Martin, J.-J. Vasseur, M. Smietana. Chem. Soc. Rev. 2013, 42, 5684-5713.

# Carborane-substituted nitrogen heterocycles: synthesis, properties and applications

Valentina A. Ol'shevskaya, Anton V. Makarenkov, Valery N. Kalinin

#### A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str. 28, 119991 Moscow, Russia

Icosahedral carboranes are widely used in material and biomedical sciences due to unique properties such as chemical and thermal stability, enriched boron content and low toxicity. Development of new synthetic methodologies to obtain carborane derivatives with diverse structural units provides a platform to compounds with desired properties and valuable applications. This presentation analyzes our progress towards functionalization of icosahedral carboranes with polynitrogen heterocycles (triazoles, tetrazoles), details about the preparation and some applications (e.g. biology, agrochemistry). The design of synthesis includes the Cu(II)-catalyzed 1.3-dipolar following approaches: (i) cvcloaddition of 1azidomethylcarborane, 1,2- and 1.7-bis(azidomethyl)-carboranes with terminal alkynes, including alkynyl ferrocenes, vielding 1.2,3-triazolyl-substituted carboranes<sup>1</sup> (Fig.1). (ii) Acylation of 5-R-1H-tetrazoles with carborane carboxylic acid chlorides resulting in carborane keto-tetrazoles<sup>2</sup> (Fig. 2). (iii) Acid catalyzed regioselective alkylation of 5-R-1H-tetrazoles with boron-substituted allylcarboranes yielding carborane alkyltetrazoles (Fig.3).



Thus, a series of efficient synthetic routes to a wide range of carborane nitrogen heterocycles from readily available starting materials was developed, and some properties were investigated. These compounds are considered to be promising for wide applications in coordination, supramolecular, and medicinal chemistry as well as in photochemistry, agrochemistry and the design of potential delivery agents for BNCT.

#### Acknowledgements

The work was financially supported by Russian Foundation for Basic Research (grant 15-29-05812).

#### References

1. V. Ol'shevskaya, A. Makarenkov, E. Kononova, P. Petrovskii, E. Verbitskiy, G. Rusinov, V. Charushin, E. Hey-Hawkins, V. Kalinin, *Polyhedron* **2012**, *42*, 302.

2. V.A. Ol'shevskaya, A.V. Makarenkov, E.G. Kononova, P.V. Petrovskii, M.S. Grigoriev, V.N. Kalinin, *Polyhedron* **2013**, *51*, 235.

EUROBORON 7

# Boronation, what is next? Polyfluorinated carboranylchlorin, a potent antitumor photoradiosensitizer with advantageous synthesis and pharmacological properties

Alexander Shtil,<sup>a</sup> Valentina Ol'shevskaya,<sup>b</sup> Andrei Zaitsev,<sup>b</sup> Albina Petrova,<sup>a</sup> Alina Markova,<sup>b</sup> Victor Tatarskiy Jr.,<sup>a</sup> Svetlana Puchnina,<sup>c</sup> Alexander Suldin,<sup>c</sup> Valery Kalinin,<sup>b</sup> Norio Mivoshi<sup>d</sup>

<sup>a</sup> Blokhin Cancer Center, Moscow, Russia, <u>shtilaa@yahoo.com</u>

<sup>b</sup> Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia, olshevsk@ineos.ac.ru

<sup>c</sup> Perm Pharmaceutical Academy, Perm, Russia, <u>puchninasv@yandex.ru</u>

<sup>d</sup> University of Fukui, Fukui, Japan, <u>nmiyoshi@u-fukui.ac.jp</u>

Chemical modifications of tetrapyrrole containing compounds are aimed at improving their characteristics as antitumor photoradiosensitizers. Conjugation of boron cages to the periphery of various tetrapyrrolic macrocycles can substantially increase the photodamaging potency due to a higher affinity to cellular membranes of the boronated chlorin e<sub>6</sub> amide<sup>1</sup>. Based on the hypothesis that an increased amphiphilicity might benefit for therapeutic potential of the photosensitizer, we synthesized the water soluble {5.10.15.20-tetrakis[4-(1-carba-closo-dodecaboran-1vI)tetrafluorophenvII-17.18-dihvdro-porphyrin)}tetrasodium (compound 1) containing 44 enriched <sup>10</sup>B and 16 F atoms. Synthesis of **1** was convenient, highly reproducible. and included fewer steps than the synthesis of carboranylchlorin. Compound 1 showed a significantly bigger accumulation in B16 mouse melanoma and C6 rat glioma cells(peak at 36 h) than unfluorinated carboranylchlorin or fluorinated chlorin boron). The fluorinated carboranylchlorin **1** demonstrated (no favorable pharmacological characteristics such as low acute toxicity in mice (IC<sub>50</sub>=161 mg/kg i.v.), no significant organ toxicity and a prolonged circulation in the blood. Compound 1 was negligibly cytotoxic in the dark; in contrast, rapid photodamage was detectable within the initial 5-10 min of light illumination of wild type and drug resistant tumor cells loaded low micromolar concentrations of 1. Cell death was associated with the entry of propidium iodide into the nuclei, a hallmark of necrosis. Importantly, 1 was more potent than its single element modified derivatives in photodestruction of s.c. transplanted C6 xenografts in Balb/c-nu/nu mice. Finally, 1 sensitized C6 xenografts to thermal neutrons (boron neutron capture therapy). Altogether, the simplified synthesis, good water solubility, favorable pharmacological properties and a high antitumor potency in cell culture and in vivo make the novel fluorinated carboranylchlorin 1 a perspective drug candidate.

#### Acknowledgements

Supported by the Ministry of Industry and Trade of the Russian Federation (State Agreement 14411.2049999.19.077).

#### References

1. M. Moisenovich et al., PLoS One 2010, 5(9), e12717.

# Sulfamido carboranes as MRI-BNCT multivalent antitumoral agents inhibitors of carbonic anhydrase (CA IX)

Annamaria Deagostino,<sup>a</sup> Silvio Aime,<sup>b</sup> Diego Alberti,<sup>b</sup> Saverio Altieri, <sup>c</sup> Paolo Boggio,<sup>a</sup> Silva Bortolussi,<sup>c</sup> Alessia Michelotti,<sup>a</sup> Nicoletta Protti,<sup>c</sup> Simonetta Geninatti-Crich<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Torino, <u>annamaria.deagostino@unito.it</u>.

<sup>b</sup> Department of Molecular Biotechnologies and Life Sciences, University of Torino,

simonetta.geninatti@unito.it

<sup>c</sup> Department of Nuclear and Theoretical Physics, University of Pavia, <u>saverio.altieri@pv.infn.it</u>

BNCT (boron neutron capture therapy) is a binary radiation therapy for the treatment of cancer, based on the capture of thermal neutrons by <sup>10</sup>B nuclei that have been selectively delivered to tumour cells.<sup>1</sup> In recent years our research group has been working on the preparation of dual agents for BNCT/MRI applications.<sup>2</sup> In these systems a carborane cage is linked to a MRI probe and to a lipophilic unit, in order to exploit LDLs or liposomes as biological vectors. With the goal in mind of improving the efficacy as theranostic agents (therapy + diagnostic) and avoiding the tumour recurrence, BNCT can be combined with synergic therapeutic strategies, exploiting the same versatile theranostic platform. Recently sulfamido-carboranes conjugates have been demonstrated to be promising carbonic anhydrase (CA) inhibitors.<sup>3</sup> CA are metalloenzymes which are selectively expressed in a range of hypoxic tumors,

traditional CA inhibitors contain a sulfonamide or sulfamide moiety that coordinates the zinc cation located in the CA catalytic site.<sup>4</sup> Firstly, MCF-7 cells (human breast adenocarcinoma cell line) containing 1-(sulfamido)methyl-1,2-dicarba-*closo*-dodecaborane (Fig. 1) have been irradiated and the synergic effect of enzymatic inhibition and BNCT has been demonstrated. As a consequence of



this promising result the synthesis of a new compound, where a carborane has been functionalised on one side with a Gd-DOTA complex and on the other side with a sulfamido group as inhibitor of carbonic anhydrase (Fig. 2) has been carried out.



Figure 2. Synthesis of new MRI BNCT carborane based agent inhibitor of CA.

#### References

1 A.H. Soloway, W. Tjarks, B.A. Barnum, F.-G. Rong, R.F. Barth, I.M. Codogni, J.G. Wilson, *Chem. Rev.* **1998**, 98, 1515.

(a) A. Toppino, M.E. Bova, S.G. Crich, D. Alberti, E. Diana, A. Barge, S. Aime, P. Venturello, A. Deagostino, *Chem. Eur. J.* 2013, *19*, 720; (b) D. Alberti, N. Protti, A. Toppino, A. Deagostino, S. Lanzardo, S. Bortolussi, S. Altieri, C. Voena, R. Chiarle, S.G. Crich, S. Aime, *Nanomed.* 2015, *11*, 74.
 J. Brynda, P. Mader, V. Sicha, M. Fabry, K. Poncova, M. Bakardiev, B. Gruener, P. Cigler, P. Rezacova, *Angew. Chem., Int. Ed.* 2013, *52*, 13760.

4 D. Sneddon, S.-A. Poulsen, J. Enzyme Inhib. Med. Chem. 2014, 29, 753.

### Hückel's rule of aromaticity applies to closo boron hydride clusters

Francesc Teixidor,<sup>a</sup> Clara Viñas,<sup>a</sup> Jordi Poater,<sup>b</sup> and Miquel Solà<sup>c</sup>

<sup>a</sup> Institut de Ciència de Materials de Barcelona (CSIC), Campus U.A.B. 08193, Catalonia, Spain. <u>teixidor@icmab.es</u>

<sup>b</sup> Universitat de Barcelona & Institució Catalana de Recerca i Estudis Avançats (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Catalonia, Spain.

<sup>c</sup> Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, 17071 Girona, Catalonia, Spain

Recently,<sup>1</sup> we have evidenced that the concept of aromaticity, in terms of planar or tridimensional aromaticity, was not too distant, and that most probably  $\pi$ -aromaticity and 3D aromaticity are based on the same grounds. To reach such conclusion we compared the conventional  $(4n+2)\pi$  planar organic cyclic compounds with *closo* Boron Hydrides. The aromaticity properties of planar organic cyclic compounds had been demonstrated experimentally by their stability, hydrogenation experimental studies, and substitution but not addition reactivity. Aromatic organic compounds are the paradigm of what chemists expect in one aromatic molecule. Therefore  $(4n+2)\pi$  planar organic cyclic compounds have the necessary experimental and theoretical support to be the archetypes of what "aromaticity" may indicate. On the other hand, *closo* Boron Hydrides that geometrically have the shape of deltahedra have been



demonstrated, mostly by the NICS magnetic criteria, to be aromatic. This fact is also sustained by reactivity, mainly substitution vs. addition. stability criteria. and equalization of bond lengths. Closo Boron Hydrides respond to the formula  $[B_nH_n]^2$ , n = 5 to 12 and are electronically interpreted by Wade's counting rule 2n+2 or by Mingos' rule that is 4n+2. We have demonstrated that aromatic closo Boron Hvdride clusters can be categorized into different series according to the n value of the

Hückel  $(4n+2)\pi$  rule. This classification follows from the existence of a link between the two-dimensional Hückel rule followed by aromatic [n]-annulenes and Wade-Mingos' rule of three-dimensional aromaticity applied to the aromatic  $[B_nH_n]^{2^-}$  closo Boron Hydride clusters.

#### Acknowledgements

To projects (CTQ2013-44670-R) and (2014 SGR 149).

#### References

1 a) J. Poater, M. Solà, C. Viñas, F. Teixidor, *Chem. Eur. J.* **2013**, *19*, 4169-4175; b) J. Poater, M. Solà, C. Viñas, F. Teixidor, *Angew. Chem. Int. Ed.* 2014, *53*, 12191-12195; c) J. Poater, M. Solà, C. Viñas, F. Teixidor, *Chem. Eur. J.* **2016**, *22*, 7437-7443.

### Mathematics, Physics, Chemistry and Boron

#### Josep M. Oliva

Physical Chemistry Institute, Spanish National Research Council 28006 Madrid, Spain

The four organic elements, Hydrogen, Carbon, Nitrogen and Oxygen, together with light and water give life on our small world ( $\mu\mu\rho$ , which in Russian has two meanings: world and peace). Hence the element Carbon is the base of life on our planet; the next element is Nitrogen, which does not combine with itself, except for the N<sub>2</sub> molecule and a few unstable nitrides. What happens if we have a look to the previous element from Carbon? We have Boron, which combines with practically all elements from the Periodic Table, forming beautiful and rich architectural constructs with no rival, except for carbon!

In this talk, we will present the results from fifteen years of research from a quantumchemical point of view, including relevant results in Combinatorial Mathematics, Molecular Magnetism in Physics (front cover of the journal *Molecular Physics*), as well as in different research fields of Chemistry (see the book *Boron: The Fifth Element*).





### Theoretical investigation of possible perfluoroborabes, per-BF<sub>2</sub>boranes and cluster compounds with bonds of boron to inert gases

Ivan V. Dudenkov, Konstantin A. Solntsev

#### A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, Russia, 119991, Moscow, Leninskii pr., 49, <u>ivdudenkoff@mail.ru</u>

Various semi-empirical quantum chemical methods tested on all boron sub-fluorides that experimentally studied by now (BF, B<sub>2</sub>F<sub>4</sub>, B<sub>3</sub>F<sub>5</sub>, B<sub>8</sub>F<sub>12</sub> и B<sub>10</sub>F<sub>12</sub>, B<sub>10</sub>F<sub>10</sub><sup>-2</sup>, B<sub>12</sub>F<sub>12</sub><sup>-2</sup>,  $B_{24}F_{22}^{-4}$ ,  $B_{21}F_{18}^{-1}$ ). Entirely adequate turned out to be only PM6 method from MOPAC2009 program, and PM3, AM1, MNDO etc. methods optimization from HyperChem 8.0 program almost always leads to wrong geometries types. PM6 method carried geometric optimization of all possible perfluorosubstituted B<sub>n</sub>F<sub>n + x</sub>-y and per- BF<sub>2</sub>-substituted  $B_n(BF_2)_n + x^{-y}$  boron sub-fluoride, isostructural to previously obtained or calculated borohydride from hypercloso-(x + y = 0) to pileo- (x + y = 10)series. Surprisingly we found out, that perfluoroboranes are isostructural to known boranes, usually correspond to energy minima, even in the presence of bridging fluorine atoms. These minima energy often worse than the isomers based on the smaller deltahedron substituted by BF<sub>2</sub> groups. It is established that due to the strong mesomeric stabilization the deficit (for per-F-boranes) or excess (for per-BF<sub>2</sub>boranes) of two, or even four electrons normally saves energy minimum close to the starting geometry. On the basis of structural features of  $B_8F_{12}$  we predict the new class of fluoroboranes containing alternating cation-like B (+ III) and anion-like B (-V). The simplest representative of this class of boranes is B(BF<sub>2</sub>)<sub>5</sub>. In more sophisticated representatives of this class convex structural fragments extrapolated to boron fullerene – «boron boride»  $(B^{+III})_{20}(B^{-V})_{12} = B_{32}$  with icosahedral symmetry are found. However, a spherical cluster  $B_{32}$  proved to be unstable, regrouping in other structures, i.e. for the coexistence  $B^{+III}$  and  $B^{-V}$  requires fluorine atoms with their strong inductive effect. As a result, there are many fluoroboranes isomers. In this case, unlike the boranes, there are no simple formal criteria to predict the isomers with the best energy. We assume that in an unique work, where unstable even at 0°C  $B_8F_{12}$  and  $B_{10}F_{12}$  were obtained undivided mixture of other products and their decomposition products are mostly the higher per- BF2-boranes which can be chemically separated. Per-BF<sub>2</sub>-boranes are extremely perspective substrates for  $BF_2$ groups replacement on energy-intensive group, up to metal and Xe-substituted closoboranes obtaining. Xe-substituted type of B10Cl<sub>8</sub>Xe2 and HCB9H4F4Xe may be available for a typical chemistry in analogy with stable up to  $100^{\circ}C C_6H_2F_3XeBF_4$ salts. We did not have adequate methods for the calculation of compounds with Xe-B bonds, therefore the conclusions were made by PM6-calculations for Kr- and Aranalogues. Results for Ar-analogues also ab initio confirmed in 6-31G\* basis, taking into account MP2 electron correlation. PM6 calculations and ab initio 6-31G\* MP2 of planar aromatic  $B_3Ar_3^+$  and  $B_4Ar_4^{+2}$  cations of deltahedral  $B_nH_{n-3}Ar_3^{+1}$ ,  $B_nH_{n-4}Ar_4^{+2}$  and many other cation particles with B-Ar, B-Kr bonds confirmed their stability. He and Ne analogues of these particles do not always have bonded minimums. Hypothetical adducts to the anions of  $BF_2^{+1}$  or  $BF^{+2}$  groups are stable. Joints of deltahedra in the groups through the bridging (from  $\mu^2$  up to  $\mu^6$ ) fluorine atoms also lead to sustainable fluoroboranes. Both these fluroborane classes correspond to deep energy minima but the ways to those minimums are not yet clear, except for the possibility of the  $B_{24}F_{23}^{-3}$  synthesis in analogy with  $B_{24}H_{23}^{-3}$ .

# Theoretical study of protonation of the $B_{10}H_{10}^{2-}$ anion and subsequent hydrogen removal due to the substitution reaction in acidic medium

#### Valentin K. Kochnev, Nikolay T. Kuznetsov

#### N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii Prosp., Moscow, 119991, Russia, <u>kochnev@igic.ras.ru</u>

The protonation of  $B_{10}H_{10}^{2-}$  in the presence of acetonitrile molecules has been studied<sup>1</sup> using the Density Functional Theory on the B3LYP/6-31G\* and more flexible B3LYP/6-311++G<sup>\*\*</sup> levels. The  $B_{10}H_{10}^{2-}$  anion was surrounded by twenty acetonitrile molecules CH<sub>3</sub>CN to complete the first sphere of solvation (Fig.1), and H<sup>+</sup> was added to the system. The protonation of  $B_{10}H_{10}^{2}$  is regarded as a proton H\* transfer from a nitrogen atom of protonated acetonitrile CH<sub>3</sub>CN·H<sup>+</sup> to a facet of a boron cluster, accompanied by overcoming a small activation barrier of ca. 4.9 kcal/mol. The proton affinity (PA) of B<sub>10</sub>H<sub>10</sub><sup>2-</sup> in the presence of solvent molecules is ca. 8.7 kcal/mol, which is much lower than that of the "bare"  $B_{10}H_{10}^{2}$ . The effect of a solvent presence upon the isomerism of  $B_{10}H_{11}$  was studied, and it was shown that the local configuration of acetonitrile molecules facilitates the existence of BH2-isomers for B10H11. The removal of H<sub>2</sub> from the formed B<sub>10</sub>H<sub>11</sub>·20CH<sub>3</sub>CN species was also investigated. In contrast to the "bare" B<sub>10</sub>H<sub>11</sub> that features different activation barriers for H<sub>2</sub> removal from vertices with initial coordination number 6 or 5. the solvation facilitates this process only for the coordination number 6, while the other leads to the deprotonation of  $B_{10}H_{11}$  back to  $B_{10}H_{10}^{2^{-}}$ . Estimated energy barrier value for hydrogen removal is ca. 23.6 kcal/mol, which equals to boiling conditions in the case of actual experiment. One of the nearest CH<sub>3</sub>CN molecules substitutes instead of H<sub>2</sub> giving B<sub>10</sub>H<sub>9</sub>(NCCH<sub>3</sub>). This reaction shows an exothermic effect of ca. 16.1 kcal/mol.



Figure 1. First sphere of solvation of  $B_{10}H_{10}^{2-}$ .

#### References

1. V.K. Kochnev, N.T. Kuznetsov, Computational and Theoretical Chemistry 2016, 1075, 77.

**EUROBORON 7** 

# Ammonia-borane dehydrogenation mediated by transition metal complexes for H<sub>2</sub> storage and production

Andrea Rossin,<sup>a</sup> Stefano Todisco,<sup>a</sup> Lapo Luconi,<sup>a</sup> Igor Golub,<sup>b</sup> Giuliano Giambastiani,<sup>a</sup> Natalia Belkova,<sup>b</sup> Evgenii Gutsul,<sup>b</sup> Maurizio Peruzzini,<sup>a</sup> Elena Shubina<sup>b</sup>

 <sup>a</sup> Consiglio Nazionale delle Ricerche – Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), via Madonna del Piano 10, 50019, Sesto Fiorentino (Firenze), Italy; <u>a.rossin@iccom.cnr.it</u>
 <sup>b</sup> A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (INEOS RAS), Vavilov Str. 28, 119991 Moscow, Russia.

Chemical hydrogen storage with small lightweight and hydrogen-rich molecules like ammonia-borane (NH<sub>3</sub>·BH<sub>3</sub>, AB, 19.3 wt.% H<sub>2</sub>) or amino boranes of general formula RNH<sub>2</sub>·BH<sub>3</sub> (R = alifatic chain or cycle) is a topic of great interest, as witnessed by the exponential growth of the number of papers published in the recent literature.<sup>1</sup> Transition metal complexes can catalyze H<sub>2</sub> release from these species under mild conditions and offer great potential as H-storage materials. The reactions of assorted Co(I), Ir(I), Pd(II) and Ru(II) polyphosphine (Figure 1) and *pincer* type complexes with AB and amine boranes have been analyzed experimentally through variable-temperaure multinuclear (<sup>11</sup>B, <sup>31</sup>P, <sup>1</sup>H) NMR spectroscopy, kinetic rate measurements and kinetic isotope effect (KIE) determination with deuterated isotopologues. At the same time, a DFT modeling of the reaction mechanisms has been carried out, starting from the experimental data available. The results will be presented.<sup>2</sup>



Figure 1. Homogeneous AB dehydrogenation with the classical hydride (NP<sub>3</sub>)Ru(H)<sub>2</sub>.

#### Acknowledgements

The authors would like to thank the bilateral Italian-Russian project CNR-RFBR 2015-2017 for funding this research activity.

#### References

A. Staubitz, A.P.M. Robertson, I. Manners, *Chem. Rev.* 2010, *110*, 4079, and references therein.
 (a) A. Rossin, A. Rossi, M. Peruzzini, F. Zanobini, *ChemPlusChem* 2014, *79*, 1316; (b) A. Rossin,
 G. Bottari, A.M. Lozano-Vila, M. Paneque, M. Peruzzini, A. Rossi, F. Zanobini, *Dalton Trans.* 2013, *42*, 3533; (c) A. Rossin, M. Caporali, L. Gonsalvi, A. Guerri, A. Lledós, M. Peruzzini, F. Zanobini, *Eur. J. Inorg. Chem.* 2009, 3055.

## Low temperature thermal behaviour of boranes: an *in-situ* X-ray synchrotron thermodiffraction study

P. G. Yot,<sup>a</sup> Ph. Miele,<sup>b</sup> U. B. Demirci<sup>b,a</sup>

<sup>a</sup> Institut Charles Gerhardt Montpellier, Université de Montpellier, Montpellier, France, <u>pascal vot@umontpellier.fr</u>

<sup>b</sup> Institut Européen des Membranes, Université de Montpellier, Montpellier, France, philippe.miele@umontpellier.fr, umit.demirci@umontpellier.fr

Boranes of low molecular weight are crystalline materials that have been much investigated over the past decade in the field of chemical hydrogen storage.<sup>1</sup> In the same time only few studies have been dedicated to their behaviour upon thermal stimuli.<sup>2</sup> In the present work, six of them have been selected to be studied by *in-situ* synchrotron X-ray thermodiffraction. The selected boranes are ammonia borane NH<sub>3</sub>BH<sub>3</sub> (AB), hydrazine borane N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> (HB), hydrazine *bis*borane N<sub>2</sub>H<sub>4</sub>(BH<sub>3</sub>)<sub>2</sub> (HBB), lithium LiN<sub>2</sub>H<sub>3</sub>BH<sub>3</sub> (LiHB) and sodium NaN<sub>2</sub>H<sub>3</sub>BH<sub>3</sub> (NaHB) hydrazinidoboranes, and sodium triborane NaB<sub>3</sub>H<sub>8</sub> (STB).

These solids were investigated over a wide range of temperature (80-300 K) upon heating, and subsequently compared. Differences in crystal structures, existence of phase transition, evolutions of unit cell parameters and volumes, and variation of coefficients of thermal expansion are observed. They behave differently depending on the molecular size, the conformation and motion (degree of freedom) of the chemical groups  $(NH_3, N_2H_4, BH_3)$ .<sup>3</sup>

Compared to HB and HBB, AB is highly temperature-sensitive and exhibits a *Pmn21*-to-*I4mm* phase transition at 205 K. HB has an orthorhombic structure (S.G. *Pbcn*) over the whole temperature range but the unit cell volume decreases by ~1% in relation with an increase of the tilt angle between the c axis and the B-N bond. HBB with an orthorhombic structure (S.G. *Pbca*) presents a unit cell contraction around 288 K related to a temperature-induced disorder leads to a new reorganization of the four HBB molecules in the unit cell. The alkali boranes LiHB, NaHB and STB have been studied, and the data compared to those of the previous boranes. For all of them, the cell expansion is anisotropic and with no phase transition over the whole temperature range. LiHB and NaHB behave differently from the parent borane HB. Furthermore, the coefficients of thermal expansions are similar for LiHB and NaHB, suggesting similar disorder-related behavior under heating. In addition STB is highly temperature-sensitive and in one respect has a structural evolution between that of AB and that of NaHB.

#### Acknowledgements

Swiss Norvegian Beam Lines (BM01A) at European Synchrotron Radiation Facility (ESRF, Grenoble, France) are greatly acknowledged for the beam time allowed.

#### References

1. L.H. Jepsen, M.B. Ley, Y.S. Lee, Y.W. Cho, M. Dornheim, J.O. Jensen, Y. Filinchuk, J.E. Jørgensen, F. Besenbacher, T.R. Jensen, *Materials Today* **2014**, *17*, 129-135.

2. (a) Y. Filinchuk, A.H. Nevidomskyy, D. Chernyshov, V. Dmitriev, *Physical Review B* **2009**, 79, 214111:1-11; (b) R. Moury, K. Robeyns, Y. Filinchuk, P. Miele, U.B. Demirci, *Journal of Alloys and Compounds* **2016**, 659, 210-216; (c) S. Pylypko, E. Petit, P.G. Yot, S. Salles, M. Cretin, P. Miele, U.B. Demirci, *Inorganic Chemistry* **2015**, *54*, 4574-4583.

3. P.G. Yot, P. Miele, U.B. Demirci, Crystals 2016, 6, 16:1-13.

### STA-MS analysis of evaporation and thermal decomposition of Triethylamine Borane Complex

Vladimir Shayapov, Pavel Plyusnin, Ivan Merenkov, Veronica Sulyaeva

Nikolaev Institute of Inorganic Chemistry, the Siberian Branch of the Russian Academy of Sciences 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia, <u>shayapov@niic.nsc.ru</u>

Triethylamine Borane Complex (TEAB) ( $C_2H_5$ )<sub>3</sub>N:BH<sub>3</sub> has been long used as a precursor for the production of BC<sub>x</sub>N<sub>y</sub> films which are promising protective hard coatings for various applications. The most appropriate method for the synthesis of BC<sub>x</sub>N<sub>y</sub> coatings is a chemical vapor deposition (CVD). It is possible to adjust TEAB concentration in the operating gas mixture by the heating of the precursor source and therefore to regulate the growth rate of the coating. So, the behavior of TEAB at elevated temperatures is an urgent problem in the BC<sub>x</sub>N<sub>y</sub> coatings technology.

In this work, evaporation and thermal decomposition of the liquid TEAB were investigated by a simultaneous thermal analysis – mass spectrometry (STA-MS). The simultaneous thermal analysis (STA) including thermogravimetry (TGA), differential scanning calorimetry (DSC) and mass spectrometric analysis of the evolved gases was carried out using a STA 449F1 Jupiter system, combined with a QMS 403D Aëolos quadrupole mass spectrometer (NETZSCH, Germany). The samples was heated up to 300°C in an  $Al_2O_3$  crucible under the helium flow of 30 ml/min. Heating rate was constant at 10 °C/min. To determine evaporation and decomposition mechanisms the isothermal analysis at different temperatures was carried out.

STA analysis shown endothermic effects in the temperature range of 80-160 °C attributed to the TEAB vaporization and decomposition. It was determined that the TAEB decomposition process starts at above 80°C. The most pronounced endothermic effect was observed at 145-155 °C. Gas phase mainly consist of diborane and triethylamine as well as other gas products formed by the electron excitation. Content and structure of precipitate after full and partial decomposition were investigated by X-ray microanalysis, FTIR and Raman spectroscopy.

Based on the results obtained it was concluded that TEAB evaporation at elevated temperatures is mainly accompanied by the decomposition through the donor-acceptor bond rupture in the TEAB molecule.

#### Acknowledgements

This work was supported by the Russian Federation President Grants MK-7650.2016.8, SP-736.2016.1.

### Supramolecular properties of dodecaborates

Khaleel Assaf, Werner Nau, Detlef Gabel

Jacobs University Bremen, Germany; <u>d.gabel@jacobs-university.de</u>

Dodecaborates have a weak hydration shell, in which the water associates with the cluster through dihydrogen bonds<sup>1</sup>. This is reflected in the chromatographic properties of such cluster derivatives<sup>2,3</sup>. These properties might be useful for a number of applications. Thus, we have shown recently<sup>4</sup> that dodecaborates interact with  $\gamma$ -cyclodextrin, and actually being the first class of compounds discovered which interact strongly with this macrocyclic compound. Construction of non-covalent frameworks with two different pairs of host/guest combinations, orthogonal to each other, will be possible. The power of such combinations could very recently be demonstrated by us for assessing the concentrations of analytes which themselves are non-fluorescent, but which are able to compete with fluorescent dodecaborate derivatives<sup>5</sup>.

#### References

1. K. Karki, G. Gabel, D. Roccatano, Structure and dynamics of dodecaborate clusters in water. *Inorg Chem.* **2012**, *51*, 4894-48962.

2. P. Fan, J. Neumann, S. Stolte, J. Arning, D. Ferreira, K. Edwards, D. Gabel, Interaction of dodecaborate cluster compounds on hydrophilic column materials in water. *J. Chromatogr. A* **2012**, *1256*, 98-1043.

3. P. Fan, S. Stolte, D. Gabel, Interaction of organic compounds and boron clusters with new silica matrices containing the phosphatidylcholine headgroup. *Anal. Methods* **2014**, *6*, 3045-30554.

4. K.I. Assaf, M.S. Ural, F. Pan, T. Georgiev, S. Simova, K. Rissanen, D. Gabel, W.M. Nau, Water structure recovery in chaotropic anion recognition: High-affinity binding of dodecaborate clusters to gamma-cyclodextrin, *Angew. Chem., Int. Ed. Engl.* **2015**, *54*, 6852-68565.

5. K.I. Assaf, O. Suckova, V. von Glasenapp, W.M.Nau, D.Gabel, Dodecaborate-anchor dyes for cyclodextrin-based indicator displacement application. *Org. Lett.* **2016**, *18*, 932-935.

# Functionalization of *closo*-decahydrodecaborate anion [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> using click chemistry reagents

Suzan El Anwar<sup>a,b,c</sup>, Gregory Dudley<sup>c</sup>, Ali Safa<sup>a</sup> and Daoud Naoufal<sup>a,b</sup>

<sup>a</sup> Faculty of Sciences I, Lebanese University, Inorganic and Organometallic chemistry Laboratory LCIO, Lebanon; <u>dnaoufal@ul.edu.lb</u>

<sup>b</sup> Ecole Doctorale des Sciences et Technologie EDST, PRASE, Lebanese University.

<sup>c</sup> Department of Chemistry and Biochemistry, Florida State University, United States;

gdudley@chem.fsu.edu

closo-Decahydrodecaborate anion [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> and its derivatives [B<sub>10</sub>H<sub>10-n</sub>L<sub>n</sub>]<sup>2-</sup> (L=ligand) have several potential applications depending on the nature of the L group; It has been used as extractants of radioactive cations<sup>1</sup>, as medicinal drugs in Boron Neutron Capture Therapy (BNCT) technique, and several other applications<sup>2</sup>. The major challenge in the development of polyhedral decaborate chemistry especially [B<sub>10</sub>H<sub>10</sub>]<sup>2-</sup> refers to its functionalization. The activation of a B-H bond to B-L bond is a challenge. We presented several methods<sup>3</sup> of activation according to the target application of the derivatives of  $[B_{10}H_{10}]^{2-}$  prepared. In this research, our focus is directed towards functionalization of *closo*-decaborate using click chemistry with linear alkynes and strained cycloalkynes which are known to react with azide to form 1,2,3-triazole rings. We tried different approaches to functionalize directly decaborate with azide but these attempts were unsuccessful. An efficient general synthetic approach giving a facile and rapid access to a wide range of novel 1.2.3-triazoles bearing closo-decaborate anion (click closomer) has been developed. The method is on the nucleophilic cleavage of oxonium decaborate based derivative  $[B_{10}H_9O(CH_2)_4]^-$  with sodium azide and subsequent Huisgen 1,3-dipolar cycloaddition ("click" methodology) of the cleavage azide closomer product  $[B_{10}H_9O(CH_2)_4N_3]^{2-}$  and linear alkynes (phenylacetylene, 5-chloro-1-pentyne, 1-heptyne, 1-octyne, N-Bocpropargylamine) or cycloalkynes (cyclononyne) (Figure 1).



#### References

1. D. Naoufal, B. Grüner, P. Selucký, B. Bonnetot, H. Mongeot, J. Radioanal. Nucl. Chem. 2005, 266, 145.

2. I. Sivaev, A. Prikaznov, D. Naoufal, Collect. Czech. Chem. Commun. 2010, 75, 1149.

3. Z. Laila, F. Abi Ghaida, S. Al Anwar, O. Yazbeck, R. Jahjah, R. Aoun, S. Tlais, A. Mehdi, D. Naoufal *Main Group Chem.* 2015, 14, 301.

### Boron clusters based hybrid materials

Rosario Núñez, Justo Cabrera, Clara Viñas, Francesc Teixidor, Gerard Tobias

Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Barcelona, Spain, rosario@icmab.es

In the last decades, the preparation of boron cluster-based compounds has attracted the interest of scientists due to their applications in a wide range of fields such as materials science, nanotechnology and biomedicine.<sup>1</sup> The most used icosahedral boron clusters are the neutral dicarba-closo-carborane, C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, the anionic closododecaborate,  $[B_{12}H_{12}]^{2^{-}}$ , and cobaltabisdicarbollide,  $[3,3]^{-1}$ -Co $(C_{2}B_{9}H_{11})_{2}^{-1}$ , due to their high thermal and chemical stabilities along with their low toxicity in biological systems. Additionally, the  $[3,3]{-}Co(C_2B_9H_{11})_2^{-}$  has exceptional physico-chemical properties in water due to its self-assembling capacity, inducing the assembling to form micelles and monolayer vesicles.<sup>2</sup> The  $[B_{12}H_{12}]^2$  shows high chemical and hydrolytic stability and surfactant behaviour similar to  $SO_4^{2^-}$  in aqueous media. Throughout all this time, different synthetic strategies have been explored to prepare boron-containing materials by functionalization of different platforms with adequate derivatives of these icosahedral boron clusters. One approach is decorating the periphery of dendrimers to control the structure and benefit from the combination of properties of both systems.<sup>1</sup> Another strategy consists on the functionalization of nanomaterials, including nanoparticles,<sup>3</sup> with boron clusters. In this presentation, I will show easy and efficient methods for covalently grafting different icosahedral boron clusters onto octasilsesquioxanes,<sup>4</sup> CNts<sup>5</sup> and graphene oxide<sup>6</sup> surfaces (Figure 1).

The grafting of these boron clusters produces modification in the properties of the new materials, which show exceptional physico-chemical, electrochemical and thermal properties, paving the way for an enhanced processability and further expanding the range of their applications.



Figure 1. Graphene oxide functionalized with the  $[3,3]{-}Co(C_2B_9H_{11})_2$ .

#### Acknowledgements

I would like to acknowledge to A. González-Campo, A. Ferrer-Ugalde, V. Sánchez, B. Ballesteros, L. Cabana, T. Parella and J. Gierschner for their contribution to this work. This work has been supported by MINECO (CTQ2013-44670-R) and Generalitat de Cataluya (2014/SGR/149).

#### References

1. (a) R. N. Grimes, *Carboranes (Second Edition)*; Academic Press: Oxford, 2011; (b) N. S. Hosmane, *Boron Science: New Technologies and Applications*, Taylor & Francis, 2012.

2. D. Brusselle, P. Bauduin, L. Girard, A. Zaulet, C. Viñas, F. Teixidor, I. Ly, O. Diat, Angew. Chem. Int. Ed. 2013, 52, 12114.

3. A.M.Cioran, A.D. Musteti, F. Teixidor, Ž. Krpetić, I.A. Prior, Q. He, C.J. Kiely, M. Brust, C. Viñas, *J. Am. Chem.* Soc. **2012**, *134*, 212.

4. A. Ferrer-Ugalde, E.J. Juárez-Pérez, F. Teixidor, C. Viñas, R. Núñez, Chem. Eur. J. 2013, 19, 17021.

5. L. Cabana, A. González-Campo, X. Ke, G. Van Tendeloo, R. Núñez, G. Tobias, Chem. Eur. J. 2015, 21, 16792.

6. J. Cabrera-González, L. Cabana, B. Ballesteros, G. Tobias, R. Núñez, Chem. Eur. J. 2016, 22, 5096.

### Visible-light induced olefin activation using 3D aromatic organomimetic boron-rich cluster photooxidants

#### Alexander M. Spokoyny

#### Department of Chemistry and Biochemistry, University of California, Los Angeles <u>spokoyny@chem.ucla.edu</u>, web site: <u>http://www.organomimetic.com</u>

Perfunctionalized icosahedral dodecaborate clusters of the type  $B_{12}(OCH_2Ar)_{12}$  can undergo photoexcitation with visible light, leading to a new class of metal-free photooxidants. Excitation in these species occurs as a result of the charge-transfer between low-lying orbitals located on the benzyl substituents and an unoccupied orbital delocalized throughout the boron cluster core. Here we show how these species, photo-excited with a bench-top blue LED, can participate in electron-transfer process with a broad range of styrene derivatives initiating their polymerization through a cationic mechanism. Efficient initiation is observed in cases of both electron-rich and electron-deficient styrene monomers featuring *para, meta* and *ortho*-substituents at cluster loadings as low as 0.05 mol%. Furthermore, photoexcitation of  $B_{12}(OCH_2C_6F_5)_{12}$  in the presence of 1 psi isobutylene results in the production of highly branched poly(isobutylene). This work represents a first example where a metal-free boron-cluster species are used as a photocatalyst for chemical transformations.

# Conjugates of boron clusters with antineoplastic agents: synthesis and biological evaluation

Tomasz M. Goszczyński,<sup>a</sup> Mateusz Psurski,<sup>a</sup> Zbigniew J. Leśnikowski,<sup>b</sup> and Janusz Boratyński<sup>a</sup>

<sup>a</sup> Neolek – Laboratory of Biomedical Chemistry, Department of Experimental Oncology, Institute of Immunology and Experimental Therapy, PAS, 12 Rudolf Weigl St., 53-114 Wrocław, Poland.
<sup>b</sup> Laboratory of Molecular Virology and Biological Chemistry, Institute of Medical Biology, PAS, 106 Lodowa St., 93-232 Łódź, Poland

Icosahedral boron clusters have extraordinary properties such as nearly-spherical geometry, chemical, biological and thermal stability, low toxicity, high, depending upon structure, hydrophilicity, hydrophobicity or amphiphilicity and susceptibility to derivatization<sup>1</sup>. Application of boron clusters as modifying entities for biomolecules is explored since several decades but till recently it was fueled mainly by the quest for better boron carriers for BNCT (Boron Neutron Capture Therapy)<sup>2</sup>. In the last few years there has been renewed interest in using boron clusters in other areas of medicine, especially the use of carboranes as pharmacophores in small bioactive molecules<sup>3</sup>. In addition ionic boron clusters offer new and unusual opportunities in drug design. For example, derivatives of  $[B_{12}H_{12}]^2$  anion can interact with lipid membranes, proteins and show strong binding to the interior cavity of cyclodextrins<sup>4</sup>. These features afford the opportunity to exploit boron clusters in different areas of medicinal chemistry, particularly to modify biological activity of widely known therapeutic substances.

Recently we have investigated a series of carborane-containing pralatrexates (PDX) where the carboxyl groups of PDX were conjugated with *meta*-carborane moieties. Some of these derivatives revealed cytotoxic activity *in vitro* and improved folate receptor – specific cellular uptake.

Our present work focusses on the conjugation of the ionic boron clusters with known anticancer drugs. Herein, we report the synthesis and biological evaluation of boron-containing antifolates, anthracyclines and protein kinase inhibitors. We report biological properties of the conjugates, its cellular uptake, *in vitro* targeting properties and cytotoxic activity against four different human cancer cell lines.

This work is dedicated to study interaction of boronated antineoplastic compound, with a different mechanism of action, with biological environment in order to design new medically promising compounds with boron clusters.

#### Acknowledgements

Project supported by Wroclaw Centre of Biotechnology, programme: The Leading National Research Centre (KNOW) for years 2014-2018.

#### References

- 1. Z.J. Lesnikowski, Collect. Czech. Chem. Commun. 2007, 72, 1646.
- 2. V. Bregadze, A. Semioshkin, I. Sivaev, Appl. Radiat. Isot. 2011, 69, 1774.
- 3. F. Issa, M. Kassiou, L.M. Rendina, Chem. Rev., 2011, 111, 5701.

4. K.I. Assaf, M.S. Ural, et al., Angew. Chem., Int. Ed. 2015, 54, 6852.

### Substituent-stabilized rotamers of transition metal bis(dicarbollides)

Igor B. Sivaev, Sergey A. Anufriev, Vladimir I. Bregadze

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences 28 Vavilov Str., 119991, Moscow, Russia; <u>sivaev@ineos.ac.ru</u>

Development of new carborane-based materials requires directed stabilization of specific rotation isomers (rotamers) of bis(dicarbollide) complexes of transition metals. Stabilization of different rotamers can be achieved by the introduction of substituents on the upper belt of the dicarbollide ligand. Various types of substituent-directed interactions between the carborane ligands which are able to stabilize specific rotamers, including the intramolecular hydrogen bonds CH...XB (X = Br, I, CI), CH<sub>carb</sub>... $\pi$  interactions between the CH groups of one dicarbollide ligand and aromatic ring of another ligand, BH...M...HB interactions, BO(R)...M<sup>+</sup>...HB interactions between the ligands on alkali atom coordination by oligoethylene-glycol substituent and other, will be discussed.

Synthesis of novel transition metal bis(dicarbollide) complexes bearing MeS substituents at various positions of dicarbollide ligands will be reported and effect of substituents on stabilization different rotamers will be considered.



#### Acknowledgements

This work was supported by Russian Scientific Foundation (RSF-16-13-10331).

### Electrochemistry of different boron cluster compounds in aqueous media

Lukáš Fojt,<sup>a</sup> Radim Vespalec,<sup>a</sup> Miroslav Fojta,<sup>a</sup> Bohumír Grüner<sup>b</sup>

<sup>a</sup> Institute of Biophysics, Czech Academy of Sciences, Královopolská 135, 61265 Brno, Czech Republic, <u>fojt@ibp.cz</u>

<sup>b</sup> Institute of Inorganic Chemistry, Czech Academy of Sciences, Husinec-Řež 1001, 25068 Řež, Czech Republic

In our studies<sup>1,2</sup> we have investigated several 3, 10, 11, 12 and 18 vertex boron cluster compounds (BCCs) and in case of 10, 11 and 12 vertex structures some of their *endo*- and *exo*- skeletal derivatives. In addition, we have initiated study on sandwich structures containing central cobalt atom two dicarbollide ligands and various basic *exo*-skeletal substituents.

For our experiments, we have used phosphate buffers in pH range from pH = 2 to 10. Electrochemical experiments were carried out using polished glassy carbon electrode. We have measured electrochemical responses using differential pulse (DPV) and cyclic voltammogramy (CV) techniques.

We were able to detect electrochemical response in phosphate buffers for quite all of the studied BCCs. We found remarkably high dependence of electrochemical signal on cluster geometry and substituents. By varying the number or position of *endo*- or *exo*- skeletal substituents we can tune the potential and intensity of the electrochemical response. Figure 1 displays sample of electrochemical response for  $[8-HO-(1,2-closo-C_2B_9H_{10})-(1',2'-closo-C_2B_9H_{11})-3,3'-Co)]$ .



E / V vs. Ag AgCl 3M KC

Figure 1. DPV of 1 mM [8-HO-(1,2-*closo*-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-(1',2'-*closo*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-3,3'-Co)], pH 8, phosphate buffer. Polished glassy carbon electrode. Nicely developed peak of the BCC oxidation could be identified on the anodic part of the voltammogram. The distortion of this peak at more positive part of the voltammogram is probably caused by the electrolyte-electrode surface reaction. At the cathodic potential is situated peak coming very probably from Co electrochemical reaction. The inset displays structural formula of used BCC.

#### Acknowledgements

This work was supported by the Grant No. P206/12/G151 from Czech Science Foundation.

#### References

1. L. Fojt, M. Fojta, B. Grüner, R. Vespalec, *J. Electroanal. Chem.* 2013, 707, 38. 2. L. Fojt, M. Fojta, B. Grüner, R. Vespalec, *J. Electroanal. Chem.* 2014, 730, 16.

# Structure-property correlations and functional opportunities of aggregation-induced emissive organic/organometallic materials

#### P. Thilagar

Faculty of Department of Inorganic and Physical Chemistry,Indian Institute of Science (IISc), Bangalore, 560012, India, <u>thilagar@ipc.iisc.ernet.in</u>

Applications of organic/organometallic materials in optoelectronic systems demand their compatibilities in solid-state. Thus, solid-state emissive luminescent materials have found significant importance in recent times owing to their potential applications in OLEDs (organic light-emitting diodes), security, sensor systems etc.<sup>1</sup> In general, most fluorescent dyes are found to show negligible fluorescence in their solid-state resulting from close-range intermolecular interactions, self-absorption and energy-transfer processes.<sup>1</sup> Synthetic control over such cumulative behaviour of dyes is a challenging task. Systematic alteration of configuration, conformation and functionalization of molecules can be effectively used to understand structure-property relationships and the regulatory aspects of solid-state luminescent dyes. In our works, we have developed several systematic strategies in order to gain

insights the molecular and cumulative luminescent properties of organic and organometallic dyes. In course of these investigations, we have also investigated the balanced recipes of obtaining AIEE (aggregation-induced emission enhancement), AIES (aggregation-induced emission switching), FONs (fluorescent organic nano-aggregates) and piezochromic luminescent properties in notably small and easily accessible molecular architectures based on BODIPYs (boron-dipyrromethenes), NPIs (1,8-naphthalimides) and TABs (Triarylboranes).<sup>3</sup> In this talk, some quite interesting aspects of AIEE materials would be presented.

#### Acknowledgements

PT thanks the Science and Engineering Research Board, New Delhi, for the financial support.

#### References

1. D. Yan, D.G. Evans, *Mater. Horiz.* **2014**, *1*, 46-57; (b) S. Varughese, *J. Mater. Chem.* C **2014**, *2*, 3499-3516; (c) S. Mukherjee, P. Thilagar, *Dyes Pigm.* **2014**, *110*, 2-27; (d) S. Mukherjee, P. Thilagar, *Chem. Commun.* **2015**, *51*, 10988-11003; (e) S. Mukherjee, P. Thilagar, *J. Mater. Chem.* C **2015**, *4*, 2647-2662.

2. J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer, Singapore, 2006.

(a) C.A. Swamy, S. Mukherjee, S. Sinha, P. Thilagar, *J. Mat. Chem. C* 2013, *1*, 4691-4698; (b) S. Mukherjee, P. Thilagar, *Chem. Commun.* 2013, 49, 7292-7294; (c) S. Mukherjee, P. Thilagar, *Phys. Chem. Chem. Phys.* 2014, *16*, 20866-20877; (d) S. Mukherjee, P. Thilagar, *Chem. Eur. J.* 2014, *20*, 8012-8023; (e) S. Mukherjee, P. Thilagar, *Chem. Eur. J.* 2015, *21*, 8874-8882.

# Unsymmetrical diborane(4) derivatives (pinB–B((NR)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)) as versatile precursors for diaminoboryl ligands

#### Christian Kleeberg, Corinna Borner

#### Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, <u>ch.kleeberg@tu-braunschweig.de</u>

Diaminoboryl ligands are interesting ligands due to their coordination chemical properties (e.g. strong *trans*-influence, potential structural variability) and the isoelectronic relation to the ubiquitous NHC ligands. Surprisingly, while boryl ligands/complexes in general have been extensively studied, synthetic access to diaminoboryl complexes is still limited in terms of the accessible (transition) metal complexes and the substitution patterns at the ligand.<sup>1</sup>

We have shown that unsymmetrical diborane(4) derivatives of the type pinB– B((NR)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (I) provide efficient and versatile access to diaminoboryl complexes *via* B–B bond activation by different reaction pathways (e.g. oxidative addition,  $\sigma$ -bond metathesis). This complements existing synthetic routes to diaminoboryl complexes and makes unprecedented complexes accessible, e.g. sterically little demanding diaminoboryl complexes or unsymmetrical diboryl complexes (Figure 1).<sup>2</sup> In the contribution selected synthetic, structural, electronic and reactivity aspects of unsymmetrical diborane(4) derivatives as well as of diaminoboryl complexes derived thereof will be addressed. In particular the versatility of the novel synthetic route and the unprecedented properties of the obtained diaminoboryl complexes will be emphasised.



Figure 1. Unsymmetrical diborane(4) derivatives as versatile precursors of diaminoboryl complexes.

#### References

1. For reviews see: L. Weber, *Eur. J. Inorg. Chem.* **2012**, 5595; I.A.I. Mkhalid, J.H. Barnard, T.B. Marder, J.M. Murphy, J.F. Hartwig, *Chem. Rev.* **2009**, *110*, 890; J. Cid, J.J. Carbó, E. Fernández, *Chem. Eur. J.* **2012**, *18*, 12794; M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354; H. Braunschweig, R.D. Dewhurst, A. Schneider, *Chem. Rev.* **2010**, *110*, 3924; M. Yamashita, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 983; J.I. van der Vlugt, *Angew. Chem. Int. Ed.* **2010**, *49*, 252.

2. C. Borner, C. Kleeberg, *Eur. J. Inorg. Chem.* 2014, 2486; C. Borner, K. Brandhorst, C. Kleeberg, *Dalton Trans.* 2015, *44*, 8600.

### Ultraviolet photoelectron spectra and electronic structure of boron complexes

#### Sergey A. Tikhonov, Vitaliy I. Vovna

#### Far Eastern Federal University, Vladivostok, Russia; allser@bk.ru

The relevance of studies of chelate complexes of boron is determined by their fluorescent properties. The determination of relationships between the functional characteristics of substances and their electronic structure opens up opportunities for the direct synthesis of new compounds with prescribed properties. The DFT method allows the calculation of the energies of ionized boron complex states with a high accuracy, thus providing a good theoretical basis for the unambiguous interpretation of photoelectron spectra and analysis of valence electron levels of 26 boron complexes.<sup>1-3</sup>

The PE spectra of vapors of 26 compounds were obtained on an ES-3201, converted electronic spectrometer with a He I (hv = 21.2 eV) monochromatic radiation source. The error in the determination of band maximums was within 0.02 eV. The ionization cuvette temperature depended on the vapour sublimation temperature of a particular sample and varied in the range of 180°C to 220°C. All calculations have been performed using Firefly program package. In DFT method a hybrid exchange-correlation functional B3LYP and basis set def2-TZVPP have been used. We used the analogue of Koopmans' theorem to compare the experimental values of vertical ionization energies (IE) with Kohn-Sham orbital energies  $\epsilon_i$ : IE<sub>i</sub> = -  $\epsilon_i$  +  $\delta_i$ , where IE<sub>i</sub> is ionization energy;  $\epsilon_i$  is Kohn-Sham one-electron energy;  $\delta_i$  is density functional approximation (DFA) defect.

In order to determine effects of heteroatom substitution in the chelate ligand, a comparative analysis was carried out for the electronic structure of three model compounds. In a range of model compounds, the HOMO's nature was revealed to be the same. The HOMO-1 orbital of nitrogen containing model compounds is determined by the presence of lone electron pairs of nitrogen. In a range of the complexes under study, the influence of aromatic substituents on the electronic structure was defined. In the imidoylamidinate complexes, in contrast to formazanates and  $\beta$ -diketonates, it was found the absence of any noticeable mixing of  $\pi$ -orbitals of the chelate and benzene rings. It was shown that within energy range to 11 eV, the calculated results reproduce well the energy differencies between the ionized states of complexes.

#### References

1. S.A. Tikhonov, V.I. Vovna, J. Struct. Chem. 2015, 56, 446.

2. I.S. Osmushko, V.I. Vovna, S.A. Tikhonov, Y.V. Chizhov, I.V. Krauklis, Int. J. Quant. Chem. 2016, 116, 325.

3. S. A. Tikhonov, V. I. Vovna, A.V. Borisenko, J. Mol. Struct. 2016, 1115, 1.

## A theoretical and experimental approach for electronic structure characterization of BN isosteres of anthracene

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, France, <u>anna.chrostowska@univ-pau.fr</u>

<sup>b</sup> Université de Pau et des Pays de l'Adour, LFC, UMR CNRS – TOTAL 5150, France

<sup>c</sup> Department of Chemistry, Boston College, Chestnut Hill, Massachusetts, USA, <u>shihyuan.liu@bc.edu</u>

Boron(B)-nitrogen(N)-containing heteroaromatic compounds are a family of heterocycles that are isoelectronic and isostructural to the family of classical organic counterparts as for example benzene, naphthalene or anthracene. 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 aromatic BN heterocycles.<sup>3,4</sup> In this presentation, we provide a comprehensive analysis of the electronic structure of BN-anthracene and bis-BN-anthracene, in comparison with their carbonaceous parent compound – anthracene, using a combined UV-photoelectron spectroscopy (UV-PES) / computational approach.<sup>5</sup>



Figure 1. Anthracene, BN-anthracene and bis-BN-anthracene.

#### References

1. A. Chrostowska, S. Xu, A.N. Lamm, A. Mazière, C.D. Weber, A. Dargelos, P. Baylère, A. Graciaa, S.-Y. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 10279.

2. A. Chrostowska, A. Dargelos, P. Baylère, C. Darrigan, L. Weber, J. Halama, *Eur. J. Inorg. Chem.* **2015**, *31*, 5196.

3. A. Chrostowska, A. Mazière, A. Dargelos, A. Graciaa, C. Darrigan, L. Weber, J. Halama, *Eur. J. Inorg. Chem.* 2013, 2013, 5672.

4. A. Chrostowska, M. Maciejczyk, A. Dargelos, P. Baylère, L. Weber, V. Werner, D. Eickhoff, H.-G. Stammler, B. Neumann, *Organometallics* **2010**, *29*, 5192.

5. J.S.A. Ishibashi, J.L. Marshall, A. Mazière, G.J. Lovinger, B. Li, L.N. Zakharov, A. Dargelos, A. Graciaa, A. Chrostowska, S.-Y. Liu, *J. Am. Chem. Soc.* **2014**, *136*, 15414.

# Boron-containing triple-decker complexes as catalysts for oxidative coupling of benzoic acid with alkynes

Dmitry V. Muratov,<sup>a</sup> Dmitry A. Loginov,<sup>a</sup> Alexander R. Kudinov<sup>a</sup>

#### A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia, <u>muratov@ineos.ac.ru</u>

Triple-decker complexes with boron-containing heterocycles are well known.<sup>1,2</sup> They have unique structure in which two metal atoms are located between three cyclic frames. Commonly, the bonds of the metal atoms with the bridging ring are considerably weaker than those with the terminal ligands. Owing to this structural feature the triple-decker complexes are able to undergo nucleophilic degradation reactions with generation of electronic unsaturated species (ring)M. Rh- and Ir-containing species of this type can act as catalysts of C-H activation of aromatic compounds.<sup>3</sup>

Herein we report synthesis and structural features of series of the triple-decker complexes with the bridging borole ( $C_4H_4BR$ ) and diborole ( $C_3B_2R_5$ ) ligands. See Fig. 1 for example.



Figure 1. Structure of the tetranuclear rhodium complex with borole ligands.

The complexes synthesized proved to be effective catalysts for oxidative coupling of benzoic acid with alkynes. In particular, they selectively give naphthalenes in good yields.



#### Acknowledgements

This work was supported by Russian Foundation for Basic Research (grant # 15-03-04057a).

#### References

- 1. D.A. Loginov, D.V. Muratov, A.R. Kudinov, Russ. Chem. Bull 2008, 57, 1-7.
- 2. D.V. Muratov, A.S. Romanov, D.A. Loginov et al., Eur. J. Inorg. Chem. 2015, 804-816.
- 3. D.A. Loginov, A.R. Kudinov et al., J. Organomet. Chem. 2015, 793, 232-240.

## Dehydrogenation of amine-boranes by copper tetrahydroborates *via* dihydrogen bonds

Igor E. Golub,<sup>a</sup> Vasilisa A. Kulikova,<sup>a</sup> Oleg A. Filippov,<sup>a</sup> Natalia V. Belkova,<sup>a</sup> Andrea Rossin,<sup>b</sup> Maurizio Peruzzini,<sup>b</sup> Elena S. Shubina<sup>a</sup>

<sup>a</sup> A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences <sup>b</sup> Istituto di Chimica dei Composti Organometallici Consiglio Nazionale delle Ricerche (ICCOM CNR)

Transition metal tetrahydroborates (THBs) are widely used as selective reductive agents and catalytic poly-<sup>2</sup>, iso- and oligomerisation processes<sup>3</sup>. Recently there were reports about using Earth abundant transition metals (Cu, Co, Ni) in heterogeneous catalysis of dehydrocoupling and hydrolysis/alcoholysis of amine boranes (Abs)<sup>4.5</sup>, but there are poor data about homogeneous catalysis and the mechanism of ABs dehydrocoupling in the presence of complexes of these metals.

Dihydrogen bonds (DHBs) as a specific intermolecular interaction of boron hydrides with proton donors largely determine the reactivity of boron hydrides in the processes involving the molecular hydrogen evolution<sup>6,7</sup>.

Here we report recent results of variable temperature FTIR and NMR spectroscopic studies on the interaction  $(PPh_3)_2CuBH_4$  (1),  $(triphos)CuBH_4$  (2) and  $(NP_3)CuBH_4$  (3) with proton donors (MeOH, TFE, MFE, HFIP, PNP, PNA and PNAP) in CH<sub>2</sub>Cl<sub>2</sub>. The formation of DHB complexes (Scheme 1) was observed that precedes proton transfer and H<sub>2</sub> evolution.



. Scheme 1.

The catalytic activity of copper THB complexes **1-3** in ABs dehydrogenation was evaluated on the example of  $NH_3BH_3$ ,  $tBuNH_2BH_3$ , and  $Me_2NHBH_3$  in THF at 25°C. The IR monitoring showed the simultaneous decrease of ABs initial NH/BH bands intensity and appearance of new bands of reaction products. Such changes suggest concerted proton and hydride transfer. Monitoring of the reaction kinetics afforded the reaction rates allowing to compare the activity of **1-3**.

#### Acknowledgements

This work was supported by the Russian Foundation for Basic Research (projects № 16-03-00324 and 16-33-01070).

#### References

1. M.J. Bhanushali, N.S. Nandurkar, M.D. Bhor, B.M. Bhanage, *Tetrahedron Lett.* 2007, 48, 1273-1276.

2. J. Kratsch, M. Kuzdrowska, M. Schmid, N. Kazeminejad, C. Kaub, P. On<sup>~</sup>a-Burgos, S.M. Guillaume, P.W. Roesky, *Organometallics* **2013**, *32*, 1230-1238.

3. P.A. Grutsch, C. Kutal, J. Am. Chem. Soc. 1977, 99, 6460-6463.

4. H.C. Johnson, T.N. Hooper, A.S. Weller, In *Synthesis and Application of Organoboron Compounds*, Vol. 49, E. Fernández, A. Whiting, Eds., Springer, **2015**; pp 153-220.

5. A. Rossin, M. Peruzzini, Chem. Rev. 2016, DOI: 10.1021/acs.chemrev.6b00043.

6. O.A. Filippov, N.V. Belkova, L.M. Epstein, E.S. Shubina, J. Organomet. Chem. 2013, 747, 30-42.

### Mechanistic insights in amine-borane dehydrogenation by iridium pincer complex Ir(PCP)HCI

Ekaterina Titova, Elena Osipova, Oleg Filippov, Natalia Belkova, Elena Shubina

A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, 119991, Vavilov str, 28, Moscow, Russia, <u>e.m.kozinets@gmail.com</u>

The metal-catalysed dehydrocoupling of amine-boranes is an area of considerable current interest because of their possible application in chemical hydrogen storage and the production of new inorganic polymers.<sup>1</sup> Transition metal complexes, including those of Ru, Rh, Pd and Ir, have been investigated for the catalytic generation of dihydrogen from ammonia-borane and other amine-boranes (RNH<sub>2</sub>-BH<sub>3</sub>).<sup>2</sup>

The isoelectronic structure of amineboranes and alkanes suggests that iridium pincer complexes, which are known as efficient homogeneous catalysts for alkane dehydrogenation, should catalyze the release of hydrogen chemically stored in ammonia-borane.<sup>3</sup>

Here we present the mechanistic study of the dimethyl amine-borane dehydrogenation by well-known pincer iridium complex (PCP)IrHCl (1). The reaction of iridium hydride 1 with amine-borane was studied under stoichometric conditions by IR and NMR spectroscopy in a wide temperature range (190-300 K) in combination with DFT-calculations. Based on experimental and theoretical results the mechanism of dimethylamine-borane dehydrogenation is proposed consistent with observations for other iridium pincer complexes.<sup>4</sup>



Figure 1. Proposed mechanism of dimethyl amine-borane dehydrogenation by (PCP)IrHCI.

#### Acknowledgements

The work was supported by the Russian Science Foundation (grant № 14-13-00801).

#### References

1. A. Staubitz, A.P. Soto, I. Manners, Angew. Chem. 2008, 120, 6308

2. A. Staubitz, A.P.M. Robertson, I. Manners, Chem. Rev. 2010, 110, 4079.

3. M.C. Denney, V. Pons, T.J. Hebden, D.M. Heinekey, K.I. Goldberg, J. Am. Chem. Soc. 2006, 128, 12048.

4. J. Choi, A.H.R. MacArthur, M. Brookhart, A.S. Goldman, Chem. Rev. 2011, 111, 1761.

### Sigma-Hole Interactions of Boron Clusters

Jindrich Fanfrlik,<sup>a</sup> Drahomir Hnvk,<sup>b</sup> Ales, Ruzicka,<sup>c</sup> Jan Rezac,<sup>a</sup> Pavel Hobza<sup>a</sup>

<sup>a</sup> Institute of Organic Chemistry and Biochemistry (IOCB) and Gilead Sciences and IOCB Research Center, Prague, Czech Republic, fanfrlik@uochb.cas.cz Institute of Inorganic Chemistry, Řež near Prague, Czech Republic

<sup>c</sup> University of Pardubice, Pardubice, Czech Republic

Polyhedral boron clusters (boranes, boron hydrides) have unique properties and unusual noncovalent interactions. It includes 3D aromaticity and an ability to form dihydrogen bonds<sup>1</sup> and sigma-hole interactions<sup>2,3</sup>. Group V, VI and VII elements (P, As, S, Se, Cl, Br) in neutral heteroboranes can form strong sigma-hole interactions.<sup>4</sup> We have observed the S... $\pi$  type sigma-hole interaction of thiaboranes experimentally in the crystal structure of phenyl-substituted thiaborane.<sup>5</sup> Quantum chemical analysis revealed that this interaction is considerably stronger than in their organic counterparts.<sup>5</sup> We have recently calculated properties such as dipole moment, polarizability and the magnitude of the  $\sigma$ -hole for series of halogenated carboranes and compared them with these properties in comparable organic compounds. The results showed that neutral carboranes with halogen-substituted Cvertex have the potential to form stronger halogen bonds than comparable aromatic hvdrocarbons.6



Figure 1. S... $\pi$  type  $\sigma$ -hole bond found in the X-ray structure of phenyl substituted thiaborane. Figure adopted from Ref. [5].

#### Acknowledgements

We acknowledge the financial support of the Czech Science Foundation (P208/12/G016).

#### References

1. J. Fanfrlík, M. Lepšík, D. Horinek, Z. Havlas, P. Hobza, 2006 Chem. Phys. Chem. 7, 1100.

2. H. Wang, W. Wang, W.J. Jin, 2016, Chem. Rev. DOI: 10.1021/acs.chemrev.5b00527.

3. R. Sedlak, J. Fanfrlík, A. Pecina, D. Hobza, M. Lepsik, Boron: The Fifth Element. Springer International Publishing, 2015, 20, 219.

4. A. Pecina, M. Lepsik, D. Hnyk, P. Hobza, J. Fanfrlik, J. Phys. Chem. A 2015, 119, 1388.

5. J. Fanfrlik, A. Prada, Z. Padelkova, A. Pecina, J. Machacek, M. Lepsik, J. Holub, A. Ruzicka, D. Hnvk, P. Hobza, Angew, Chem. Int. Ed. 2014, 58, 10139.

6. R. Lo, M., Lepsik, J. Fanfrlik, P. Hobza, Phys. Chem. Chem. Phys. 2015, 17, 20814

# The chiral separability of anionic boron cluster compounds by liquid chromatography

Radim Kučera,<sup>a</sup> Monika Janetková,<sup>a</sup> Bohumír Grüner,<sup>b</sup> Radim Vespalec<sup>c</sup>

<sup>a</sup> Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Heyrovského 1203, 500 05 Hradec Kralove, Czech Republic

<sup>b</sup> Institute of Inorganic Chemistry, Academy of Science of the Czech Republic, v.v.i., 250 68 Řež near Prague, Czech Republic

<sup>c</sup> Institute of Biophysics, Academy of Science of the Czech Republic, v.v.i., Královopolská 135, 612 65 Brno, Czech Republic

Medical prospects of cluster compounds belong to most promising topics in contemporary boron chemistry. Considering the boron cluster compounds (BCC), the novelty introduced into drug design is associated with unique properties of BCC that cannot be reached with compounds containing only electron exact and electron rich chemical bonds. However, the scope of properties of BBC covers both, favourable (space filling, sterical, hydrophobic) and unfavourable (solubility behaviour and aggregation) properties. The same trends are reflected in analytical properties respectively.

High performance liquid chromatography (HPLC) is the essential separation technique applied in all steps of drug design and development, as well as in many assays around approved drugs. Chirality of drugs became to be considered as an important factor for drug approval. Considering BCC, HPLC proved to be effective in chiral separations of numerous zwitterionic derivatives, but failed in separations of anionic species, if cyclodextrins<sup>1</sup> or polysaccharides<sup>2</sup> were used as chiral selector. Electrophoretic separations of anionic BCCs with dissolved cyclodextrins<sup>1</sup> proved that cyclodextrins can, in principle, discriminate almost any type of substituted BCCs, regardless it is ionic or not.

The aim of our recently started study is to find experimental conditions that enable the chiral discrimination of anionic BCC by HPLC. This search resulted in successful enantioseparations of several racemic anionic BCCs. In current studies we focus on series of experiments that may give explanation about mechanism of enatiomer's discrimination. Results of these studies form main content of our contribution.

#### Acknowledgements

The financial supports by the Charles University, the PRVOUK project, and by the Czech Science Foundation, grant P206/12/G151, are highly acknowledged.

#### References

1. H. Horáková, B. Grüner, R. Vespalec, Chirality 2011, 23, 307.

2. D. Mengelings, Y. Vander Heyden, R. Vespalec, Biomed. Chromatogr. 2014, 28, 694.

# Synthesis of NdB<sub>6</sub>, SmB<sub>6</sub>, GdB<sub>6</sub> and TbB<sub>4</sub> with Magnesiothermic Reduction

### Mecit Aksu, Sefa Durmuş and Aslıhan Dalmaz Duzce University, Faculty of Arts and Sciences, Duzce, 81620, Turkey

Importance of lanthanide borides is increasing due to their interesting properties. NdB<sub>6</sub>, SmB<sub>6</sub>, GdB<sub>6</sub> and TbB<sub>4</sub> were synthesized by magnesiothermic reduction in open air. Stoichiometric amounts of M<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub> and Mg were mixed, where M is a lanthanide metal. Mixture was heated to 700 °C, 800 °C and 900 °C. Optimum reaction temperature was found by X-ray Diffraction analysis and Scannning Electron Microscopy (SEM). By fixing there action temperature, reaction time has changed to obtaion nanocrystals with homogeneous morphology. It was found that optimum reaction temperature and reaction time of NdB<sub>6</sub> is 700 °C and 3 hour, for SmB<sub>6</sub> 680 °C and 1 hour, for GdB<sub>6</sub> 900 °C and 4 hour and for TbB<sub>4</sub> 900 °C and 2 hour.

### YOUNG ORAL PRESENTATIONS



# Supporting leadership in science

- Технический секретариат и on-line регистрация участников.
- Финансовый менеджмент и управление бюджетом мероприятий.
- Подготовка печатных и рекламных материалов.
- Застройка выставки и постерной сессии.
- Туристическая и визовая поддержка.
- Организация питания.
- Работа со спонсорами и СМИ.

**Адрес:** 119021, г. Москва, Комсомольский проспект, д. 16/2, стр. 3-4 **Тел.:** +7 (495) 234-65-55, **Тел./Факс:** +7 (495) 234-65-56

www.unifest.ru ≽

## Catalytically-active ruthenium complexes of the bis(o-carborane) chelate

Antony P. Y. Chan, Laura E. Riley, Rebekah J. Jeans, Alan J. Welch

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK; apyc1@hw.a.uk

Bis(*o*-carborane)<sup>1</sup> has been shown to undergo both similar and novel metalation chemistry in comparison to its single-cage analogue *o*-carborane.<sup>2,3</sup> However, bis(*o*-carborane) has also been shown to act as a  $\kappa^2$  ligand where two units co-ordinate to a central transition metal. More recently, the use of one equivalent of bis(*o*-carborane) as a  $\kappa^2$  ligand has afforded mononuclear chelated metal complexes.<sup>4,5</sup> Herein, we focus on ruthenium derivatives and their use as homogeneous Lewis acid catalysts.

Reaction of the dilithium salt of 1,1'-bis(o-carborane) and  $[Ru(p-cymene)Cl_2]_2$  affords the complex Ru(p-cymene)(bis(o-carborane)) (1) (Figure 1). The bis(carborane) unit displays X<sub>2</sub>(C,C')L binding where "L" is a B-H $\rightarrow$ Ru B-agostic interaction. This interaction can be easily displaced by CO or MeCN to afford the corresponding saturated 18-electron complex. The lability of the B-agostic interaction prompted the potential use of 1 as a homogeneous Lewis acid catalyst where 1,1'-bis(o-carborane) serves as a hemilabile ligand to the ruthenium centre. Thus far 1 has been shown to catalyse the cycloaddition of cyclopentadiene and several simple enones. Subsequent modifications of 1 using phosphines *in lieu* of *p*-cymene have since been investigated as a means of enhancing its catalytic activity.



Figure 1. Molecular structure of compound 1.

#### References

1. J. A. Dupont, M.F. Hawthorne, J. Am. Chem. Soc. 1964, 86, 1643.

2. D. Ellis, G.M. Rosair, A.J. Welch, Chem. Commun. 2010, 46, 7394.

3. D. Ellis, D. McKay, S.A. Macgregor, G.M. Rosair, A.J. Welch, Angew. Chem. Int. Ed. 2010, 49, 4943.

4. Z.-J. Yao, Y.-Y. Zhang, G.-X. Jin, J. Organomet. Chem. 2015, 798, 274.

5. L.E. Riley, A.P.Y. Chan, J. Taylor, W.Y. Man, D. Ellis, G.M. Rosair, A.J. Welch, I.B. Sivaev, *Dalton Trans.* **2016**, *45*, 1127.

## Coordination chemistry of half-sandwich transition metal carborate complexes

#### Benedikt Schwarze, Evamarie Hey-Hawkins

Universität Leipzig, Faculty of Chemistry and Mineralogy, Institute of Inorganic Chemistry, Johannisallee 29, 04103 Leipzig, Germany; <u>che10efr@studserv.uni-leipzig.de</u>, <u>hey@uni-leipzig.de</u>

In the 1960s, intense investigations on icosahedral carborane clusters (closo- $C_2B_{10}H_{12}$ ) in general and the *nido*-carborate clusters ( $[C_2B_0H_{12}]$ ) in particular were started, after Hawthorne et al. reported that one vertex in ortho-carborane can be removed by treatment with a base. The nido-carborate anion can be further deprotonated to give the corresponding dianion  $[C_2B_9H_{11}]^{2-}$ , the so-called dicarbollide, which is isolobal to a cyclopentadienyl anion and can thus be used for coordination of metals, resulting in metallacarboranes. Compared to the cyclopentadienyl ligand, the dicarbollide ligand exhibits markedly different properties, such as an additional negative charge, higher hydrophobicity and hydridic B-H units. Potential applications of the resulting complexes in different fields such as catalysis. materials science or medicine depending on the metal and co-ligands have already been published.<sup>2</sup> Here, we report the development of specific syntheses for halfsandwich nido-carborate complexes of transition metals as suitable precursors for the introduction of a variety of nitrogen-containing chelate ligands (Figure 1).<sup>3</sup> The applied synthetic route for this type of complexes even allows further cluster functionalisation via a two-step reaction in one pot.



Figure 1. Half-sandwich transition metal carborate complexes and molecular structure of one derivative.

#### Acknowledgements

We thank the Fonds der Chemischen Industrie (FCI, doctoral grant for B.S.) and the Graduate School BuildMoNa for financial support.

#### References

1. M.F. Hawthorne, D.C. Young, T.D. Andrews, D.V. Howe, R.L. Pilling, A.D. Pitts, M. Reintjes, L.F. Warren Jr., R.A. Wegner, J. Am. Chem. Soc. **1968**, *90*, 879-896.

 (a) Z.-J. Yao, G.-X. Jin, Coord. Chem. Rev. 2013, 257, 2522-2535; (b) Sh.M. Gao, N.S. Hosmane, Russ. Chem. Bull., Int. Ed. 2014, 63, 788-810; (c) J.F. Valliant, K.J. Guenther, A.S. King, P. Morel, P. Schaffer, O.O. Sogbein, K.A. Stephenson, Coord. Chem. Rev. 2002, 232, 173-230; (d) C.Verdiá-Báguena, A. Alcaraz, V.M. Aguilella, A.M. Cioran, S. Tachikawa, H. Nakamura, F. Teixidor, C. Viñas, Chem. Commun. 2014, 50, 6700-6703; (e) K.B. Gona, A. Zaulet, V. Gómez-Vallejo, F. Teixidor, J. Llop, C. Viñas, Chem. Commun. 2014, 50, 11415—11417.

3. B. Schwarze, Master thesis, Leipzig University, 2015.
## Synthesis of new polybranched carborane macromolecules aiming to medicine and biomaterials applications

Ines Bennour, Clara Viñas, Francesc Teixidor

#### Institut de Ciència de Materials de Barcelona (ICMAB-CSIC); Campus UAB, 08193 Bellaterra, Spain, <u>ibennour@icmab.es</u>

Carboranes are molecules with unique structural features due to their rigid geometry and rich derivative chemistry, which make them of great interest as building blocks for macromolecular or supramolecular entities. *o*-Carborane derivatives with precisely defined patterns of substitution have been prepared from 8,9,10,12-I<sub>4</sub>-1,2-*closo*- $C_2B_{10}H_8^{-1}$  by replacing the iodine atoms, bonded to four adjacent boron vertices in the



cluster. with allvl. and subsequently 3hydroxypropyl, chloro, bromo, tosyl, organic acid and azide groups.<sup>2</sup> These groups allow posterior derivatization demonstrating wide possibilities of the icosahedral carboranes to produce new macromolecules.<sup>3</sup> qlobular polybranched *m*-Carborane is also being studied to perform as core of new globular macromolecules starting from 9,10- $I_2$ -1,7-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>.<sup>4</sup> To meet this objective, precisely defined substitution patterns of terminal

olefin groups on the *m*carborane framework were subjected to hydroboration reaction

leading to hydroxyl terminated arms for posterior derivatization. The resulting highly dense multibranched structures, comprising four and six arms either in ocarborane or *m*-carborane can be envisaged as versatile precursors for dendritic growth. The compounds shall be relevant in facets as diverse as Boron Neutron Capture Therapy (BNCT), Drug Delivery or Neutron sensing.



The aim of this presentation is to show the ability of both *o*- and *m*-carborane cluster derivatives in producing new polybranched macromolecules with high boron content looking to relevant applications in medicine and biomaterials.

## Acknowledgements

We thank the scientific projects (CTQ2013-44670-R) and (2014 SGR 149).

## References

1. A. Vaca, F. Teixidor, R. Kivekäs, R. Sillanpää, C. Viñas, Dalton Trans. 2006, 4884.

2. (a) A.V. Puga, F. Teixidor, R. Kivekäs, R. Sillanpää, C. Viñas, Chem. Commun., 2011, 47, 2252; (b)

F. Teixidor, R. Sillanpää, A. Pepiol, M. Lupu, C. Viñas, *Chem. Eur. J.* **2015**, *21*, 12778; (c) S. Janczak, A. Olejniczak, S. Balabańska, M. K. Chmielewski, M. Lupu, C. Viñas, Z. J. Lesnikowski, *Chem. Eur. J.* **2015**, *21*, 15118.

## Large, weakly-basic phosphines derived from 1,1'-bis(o-carborane)

Laura E. Riley,<sup>a</sup> Alan J. Welch,<sup>a</sup> Igor B. Sivaev<sup>b</sup>

<sup>a</sup> Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK; <u>ler30@hw.ac.uk</u>
<sup>b</sup> A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28
Vavilov Str., 119991 Moscow, Russia

In recent years there have been several examples of a single equivalent of 1.1'-bis(ocarborane) coordinating as a  $\kappa^2$  (or  $\kappa^3$ ) ligand to a transition metal.<sup>1-3</sup> Four bonding modes for 1.1'-bis(o-carborane) have been observed:  $X_2(C,C')$ ,  $X_2(C,C')L$ ,  $X_2(C,B')$ and  $X_2(C,B')L$ . The only main group derivatives known are  $\mu$ -2,2'-E-1,1'-bis(ocarborane), where E = AsMe or PPh, having  $X_2(C,C')$  bonding modes.<sup>4</sup> However, the phosphine has been barely characterised and no subsequent chemistry reported. This work describes comprehensive studies of two phosphine derivatives of 1.1bis(o-carborane) acting in the  $X_2(C,C')$  bonding mode. The compounds  $\mu$ -2.2'-PEt-1.1'-bis(o-carborane) (1) and  $\mu$ -2.2'-PPh-1.1'-bis(o-carborane) (2), together with their AuCI and Se derivatives, have been synthesised and fully characterised by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction (Figure 1). From the crystallographic data the Tolman cone angles and percent buried volumes of 1 and 2 have been calculated. From the  ${}^{1}J_{PSe}$  values of the selenides we have also estimated the basicity of these phosphines. Collectively these data indicate that phosphines derived from 1,1'-bis(o-carborane) are both sterically demanding and weakly basic.



Figure 1. μ-2,2'-PEt-1,1'-bis(o-carborane) (1) and μ-2,2'-PPh-1,1'-bis(o-carborane) (2).

## References

1. M.J. Martin, W.Y. Man, G.M. Rosair, A.J. Welch, J. Organomet. Chem. 2015, 798, 36.

2. Z.-Y. Yao, Y.-Y. Zhang, G.-X. Jin, J. Organomet. Chem. 2015, 798, 274.

3. L.E. Riley, A.P.Y. Chan, J. Taylor, W.Y. Man, D. Ellis, G.M. Rosair, A.J. Welch, I.B. Sivaev, *Dalton Trans.* 2015, 45, 1127.

4. L.I. Zakharkin, N.F. Shemyakin, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.)* **1978**, 27, 1267; A.I. Yanovsky, N.G. Furmanova, Yu.T. Struchkov, N.F. Shemyakin, L.I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim. (Russ.)* **1979**, 1523.

## Meta carboranyl phosphinates with CdSe quantum dots: Physical fluorescence intermittency

Arpita Saha, Elena Oleshkevich, Clara Viñas, Francesc Teixidor

#### Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

Revealing optical properties at reduced dimensionality make Colloidal Quantum dots a brilliant subject of research. They have a great combination of low cost synthetic approach and efficient spectral tunability across the quantum regime. But the notorious problem of concentration quenching plagues these dots and is termed as Aggregation Caused Quenching (ACQ)<sup>1</sup>, because the quenching is a direct effect of the aggregation of the particles. It is a major detrimental property with regard to the practical applications so most work is done towards producing stabilized quantum dots in the solutions using a multitude of passivating ligands to deter the growth of size and accrecate formation. But if the size could be maintained and also the aggregates could be switched back into a dispersive state in the solution with the retention of the fluorescence intensity, it would be the dawn of a whole new dimension for quantum dot fluorescenece properties. Carborane derivatives can act as efficient capping agents as seen in Gold nanoparticles capped with Mercapto Carborane<sup>2</sup> so Meta Carboranyl Phosphinates<sup>3</sup> were used here. The reversal of fluorescence back into its original intensity even after the particles aggregated was detected in Metacarboranyl Phosphinic acid capped CdSe quantum dots and also they provided an efficient capping ability producing smaller dots having dimensions comparable to quantum dots synthesized in organic medium. The most striking

feature was though the glimpse of Physical Fluorescence Intermittency, as the particles even though they aggregated could be returned to their dispersive state in aqueous solution with the exact retention of the fluorescence intensity. Universal blinking<sup>4</sup> has been noted in single quantum dots and nanowires but here the most striking feature about this was the physical form of fluorescence intermittency as this can be controlled with just a little kinetic energy.



Figure 1. Physical Fluorescence Intermittency.

## Acknowledgements

Scientific projects CTQ2013-44670-R and 2014 SGR 149.

## References

1. J. Mei, Y. Hong, J.W.Y. Lam, A. Qin, Y. Tang, B.Z. Tang, Adv. Mater. 2014, 26, 5429-5479.

2. A.M. Cioran, A.D. Musteti, F. Teixidor, Ž. Krpetic, I.A. Prior, Q. He, C.J. Kiely, M. Brust, C. Viñas, J. Am. Chem.Soc. 2012, 134, 212-221.

3. E. Oleshkevich, F. Teixidor, D. Choquesillo-Lazarte, R. Sillanpää, C. Viñas, Chem. Eur. J. 2016, 11, 3665-3670.

4. P. Frantsuzov, M. Kuno, B. Janko, R. Marcus, Nature Phys. 2008, 4, 519-522.

## Mixed-sandwich metallacarborane complexes: Synthetic methods and applications

Marta Gozzi,<sup>a</sup> Evamarie Hey-Hawkins,<sup>a</sup> Dijana Drača,<sup>b</sup> Danijela Maksimović-Ivanić,<sup>b</sup> Sanja Mijatović<sup>b</sup>

<sup>a</sup> Universität Leipzig, Faculty of Chemistry and Mineralogy, Institute of Inorganic Chemistry, Johannisallee 29, 04103 Leipzig, Germany; <u>marta.gozzi@studserv.uni-leipzig.de</u>
<sup>b</sup> University of Belgrade, Institute for Biological Research ``Sinisa Stanković``, Bul. despota Stefana 142, 11060 Belgrade, Serbia

The *nido*-carborate(-2) cluster  $[C_2B_9H_{11}]^{2-}$  and derivatives thereof are very useful synthons for the formation of  $\eta^5$ -coordinated transition metal complexes.<sup>1</sup> Attachment of specific substituents at carbon and/or selected boron vertices allows to fine-tune the physico-chemical properties of the metallacarborane complex, and thus, to tailor the compound for a specific application.<sup>2</sup>

Based on the isolobal analogy between cyclopentadienyl(-1) and *nido*-carborate(-2) ligands,<sup>3</sup> we are currently investigating synthetic methods that give facile access to mixed-sandwich-type complexes, incorporating a *nido*-carborate(-2) ligand and a cyclopentadienyl or arene system.

Here, we present the synthesis and biological activity studies (*in vitro*) on several ruthenium(II)–carborate complexes.



Figure 1. Crystal structure of [*closo*-3-( $\eta^5$ -*p*-cymene)-3,1,2-Ru<sup>II</sup>C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>].

## Acknowledgements

We would like to thank the Saxon Ministry of the Arts and Sciences (*SMWK*, doctoral grant for M.G.), the Graduate School *Leipzig School of Natural Sciences - Building with Molecules and Nano-objects* (BuildMoNa) and Ministry of Education, Science and Technological Development of the Republic of Serbia (project No. 173013) for financial support.

## References

1. (a) R.N. Grimes, *Carboranes* Elsevier Inc. (London UK), 2<sup>nd</sup> Edition **2011**; (b) S.V. Timofeev, I.B. Sivaev, E.A. Prikaznova, V.I. Bregadze, *J. Organomet. Chem.* **2014**, 751, 221.

2. (a) A.S. Louie, L.E. Harrington, J.F. Valliant, *Inorg. Chim. Acta* **2012**, *389*, 159; (b) K.B. Gona, A. Zaulet, V. Gómez-Vallejo, F. Teixidor, J. Llop, C. Viñas, *Chem. Commun.* **2014**, *50*, 11415.

3. (a) M.F. Hawthorne, R.L. Pilling, *J. Am. Chem. Soc.* **1965**, *87*, 3987; (b) D.A. Brown, M.O. Fanning, N.J. Fitzpatrick, *Inorg. Chem.* **1978**, *17*, 1620.

## Unexampled transition metal-free borylation of allylic and propargylic alcohols

Núria Miralles,<sup>a</sup> Rauful Alam,<sup>b</sup> Kálmán J. Szabó,<sup>b</sup> Elena Fernández<sup>a</sup>

<sup>a</sup> Dept. Química Física I Inorgànica, Universitat Rovira i Virgili, Tarragona, Spain, <u>nuria.mirallesp@urv.cat</u>
<sup>b</sup> Dept. Organic Chemistry, Stockholm University, Sweden

The borylation of allylic alcohols has become one of the most suitable methods for preparing the corresponding allyl boronates since allylic alcohols are stable and readly available substrates.<sup>1</sup>

Here we aim to use these substrates in an environmental friendly system by carrying out the catalytic borylation of allylic alcohols only in the presence of the diboron reagent, base and MeOH.<sup>2</sup> With the optimal conditions in hand, we studied the scope of the different alkyl substituents, and propargylic alcohols.

Furthermore, when the reaction was carried out at 90°C, and with an excess of  $B_2pin_2$ , the triborated product was formed as consequence of the *in situ* diboration of the allylic double bond.<sup>3</sup>



Figure 1. Transition metal-free borylation of allylic alcohols followed by concatenated diboration.

## Acknowledgements

The present research was supported by the Spanish Ministerio de Economia y Competitividad (MINECO) through project CTQ2013-43395P.

## References

1. V.J. Olsson, S. Sebelius, N. Selander, K.J. Szabó, J. Am. Chem. Soc. 2006, 128, 4588.

2. J. Cid, H. Gulyás, J.J. Carbó, E. Fernández, Chem. Soc. Rev. 2012, 41, 3558.

3. N. Miralles, R. Alam, K.J. Szabó, E. Fernández, Angew Chem. Int. Ed. 2016, 55, 4303.

## Catalytic activity of new iridium(III) pincer hydride complex

Elena Osipova<sup>a</sup>, Ekaterina Titova<sup>a</sup>, Oleg Filippov<sup>a</sup>, Natalia Belkova<sup>a</sup>, Lina Epstein<sup>a</sup>, Elena Shubina<sup>a</sup>, Giuliano Giambastiani<sup>b</sup>, Lapo Luconi<sup>b</sup>, Andrea Rossin<sup>b</sup>, Maurizio Peruzzini<sup>b</sup>

<sup>a</sup> A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilov Street 28, 119991 Moscow, Russia, <u>aosipova92@gmail.com</u>

<sup>b</sup> Istituto di Chimica dei Composti Organometallici (ICCOM-CNR) via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

The transition-metal complexes supported by pincer-type ligands have been extensively studied over the last decades because of the wide range of their catalytic applications<sup>1</sup>. Such hydride complexes could be used for catalytic generation of dihydrogen from ammonia-borane, which features high hydrogen content and stability in solid state. The ammonia-borane catalytic dehydrogenation was investigated for a quite big number of complexes, however the ideal one has not yet been found<sup>2.3</sup>.

In this contribution we present the results of the study on the catalytic activity of the new (PCN)IrHCl complex (**1**, Scheme 1) in dehydrogenation of different amineboranes (NHMe<sub>2</sub>BH<sub>3</sub>, <sup>tBu</sup>NH<sub>2</sub>BH<sub>3</sub>, NH<sub>3</sub>BH<sub>3</sub>). The activity of **1** was compared to that of well-known (PCP)IrHCl (**2**, Scheme 1). The interaction of complexes **1** and **2** with amine-boranes was investigated by IR and NMR spectroscopy (<sup>1</sup>H, <sup>31</sup>P, <sup>11</sup>B) in a wide temperature range (190-300K) in combination with DFT-calculations. The identity of amine-borane dehydrogenation products was established on the base of spectroscopic data. Kinetics of iridium hydrides reaction with amine-boranes was studied both under the stoichiometric and catalytic conditions. Reaction rates, orders and TOFs were determined. The data acquired allow to discuss the influence of nature of pincer ligand, amine-boranes and solvents on the hydrogen evolution.





## Acknowledgements

The work was supported by the bilateral Italian-Russian project CNR-RFBR (RFBR project number 15-53-78027).

## References

1. J. Choi, A.H.R. MacArthur, M. Brookhart, A.S. Goldman, Chem. Rev. 2011, 111, 1761.

2. H.C. Johnson, T.N. Hooper, A.S. Weller, Top. Organomet. Chem. 2015, 49, 153-220.

3. A. Rossin, M. Peruzzini, Chem. Rev. 2016, DOI: 10.1021/acs.chemrev.6b00043.

## Synthesis of 1,1-(Bpin)(SiMe<sub>3</sub>)-alkenes via (diborylmethyl)trimethylsilane

E. La Cascia,<sup>a</sup> A. Whiting,<sup>b</sup> A. B. Cuenca,<sup>a</sup> E. Fernández<sup>a</sup>

<sup>a</sup> Dept. Química Física i Inorgànica University Rovira i Virgili, Tarragona, Spain <sup>b</sup> Dept. of Chemistry, Durham University, UK <u>enrico.lacascia@urv.cat</u>

The synthesis of tetrasubstituted alkenylboronates has been established via the deprotonation/nucleophilic addition reaction of 1,1-organodiboronates to carbonyl compounds.<sup>1</sup>

Here we describe the insertion of the diazocompound  $Me_3SiCHN_2$  into bis(pinacolato)diboron to form (diborylmethyl)trimethylsilane.<sup>2</sup> The multisubstituted reagent HC(Bpin)<sub>2</sub>(SiMe<sub>3</sub>) is susceptible of deprotonation, to generate a boron stabilised carbanion that easily reacts with carbonylic substrates. The concomitant B-O syn-elimination through a Peterson type olefination pathway takes place to generate the tetrasubstituted alkene.

Substrate scope and mechanistic studies are also studied.



## References

1. K. Endo, M. Hirokami, T. Shibata, J. Org. Chem. 2010, 75, 3469.

2. K. Endo, F. Kurosawa, Y. Ukaji, Chem. Lett. 2013, 42, 1363.

## Bioelectronic materials based on cobaltabisdicarbollide

Isabel Fuentes, Sara Szkudlarek, Clara Viñas, Francesc Teixidor

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC). Campus UAB, 08193 Bellaterra, Barcelona, Spain

One of the mostly used conducting organic polymers (COPs) is the polypyrrole (PPy) due to its properties and practical applications. PPy materials are reasonably stable in air, present high conductivity, good electrochemical properties and thermal stability and are easily generated both chemically and electrochemically. It is well known that PPy needs to be oxidized and doped by a counterion to achieve significant conductivity. Cobaltabisdicarbollide  $[3,3'-Co(1,2-C_2B_9H_{11})_2]^-$  (COSAN) and its iodo derivatives have been used as counterions of the PPy oxidation. All of them provide enhanced properties to PPy, the most striking one is the high overoxidation resistance and when iodinated COSAN is used as doping agent, the cathodic and anodic peaks get closer one to each other.<sup>1</sup>

Instead of using free COSAN as a counterion, it can be linked to pyrrole via a spacer to get a self-doped PPy material, electrochemically producing a polymer or a copolymer with pyrrole. Both materials provide also a high overoxidation resistance.<sup>2</sup> Once prepared the PPy material (self-)doped with COSAN, it can be possible to achieve cationic selectivity by control of the applied potential with alkylammonium and phosphonium salts.<sup>3</sup> With this methodology, we are carrying out studies to prepare bioelectronic materials with biologic macromolecules as for instance proteins. To do so, PPy needs to be electrogenerated in water (Figure 1). In this presentation the PPy generated in water and the influence of the biomolecule will be reported.





## Acknowledgements

This work has been supported by scientific projects FP7-OCEAN-2013 (614168 SEA-on-a-CHIP), (CTQ2013-44670-R) and (2014/SGR/149).

## References

1. A. Pepiol, F. Teixidor, R. Sillampää, M. Lupu, C. Viñas, Angew. Chem. Int. Ed. 2011, 50, 12491.

- 2. C. Masalles, J. Llop, C. Viñas, F. Teixidor, Adv. Materials, 2002, 14, 826.
- 3. C. Masalles, S. Borrós, C. Viñas, F. Teixidor, Adv. Materials, 2002, 14, 449.

## Modular synthesis of Main-Group (Si, B, S) multisubstituted carbons and subsequent alkylation assisted by Bpin moieties

M. G. Civit,<sup>a</sup> J. Royes,<sup>a</sup> Ch. Vogels,<sup>b</sup> A.B. Cuenca,<sup>a</sup> S.A. Westcott,<sup>b</sup> E. Fernández<sup>a</sup>

<sup>a</sup> Dept. Química Física i Inorgànica University Rovira i Virgili, Tarargona, Spain, <u>marc.garcia@urv.cat</u> <sup>b</sup>Dept. of Chemistry and Biochemistry, Mount Allison University, Canada

Among the insertion of diazocompounds into interelement species, the use of borane reagents affords a valuable synthetic strategy towards the preparation of unprecedented organoboranes.

Here we describe the insertion of the diazocompound Me<sub>3</sub>SiCHN<sub>2</sub> into B-S bonds to promote a direct synthesis of main group multisubstituted H-C(sp<sup>3</sup>)-(B)(Si)(S) to further transform them into quaternary centres *via* S<sub>N</sub>2 and S<sub>N</sub>2' base-mediated alkylation.<sup>1,2</sup>

We have conducted deborylative alkylation with a series of primary and secondary alkyl halides in the presence of NaO'Bu (THF, rt, 3h). The reaction exhibited a remarkable tolerance to the presence of multiple bonds, halogens as well as epoxides. Interestingly, when reaction applies to allylic electrophiles, divergent behaviour is found depending of the conditions essayed. Hence, alternative  $S_N2'$  process takes place under the presence of a copper catalyst and the appropriate base while direct  $S_N2$  process occurs in the presence of only NaO'Bu.



Figure 1. pinB-SR insertion and subsequent deborylative alkylation.

## Acknowledgements

The present research was supported by the Spanish Ministerio de Economia y Comptetitividad (MINECO) through project CTQ2013-43395P.

## References

1. K. Hon, X. Liu, J.P. Morken, *J. Am. Chem. Soc.* **2014**, *136*, 10581. 2. J. Kim, S. Park, J. Park, S.H. Cho, *Angew. Chem. Int. Ed.* **2016**, *55*, 11498.

## Localization and structure of B compounds in alumina support of hydrotreating CoMo-catalysts of diesel fuels

Yu. V. Vatutina, O. V. Klimov, K. A. Nadeina, I. G. Danilova, E. Yu. Gerasimov, A. S. Noskov

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, yuliy.vatutina@yandex.ru

Boron was used as modifying agent in hydrotreating CoMo-catalysts of diesel fuel. Supports with 0, 1, 1.5, 2 and 3 wt.% of boron were prepared and denoted as Al-x, where x-boron content in a support. CoMo-catalysts based on these supports with 10 wt.% Mo and 3 wt.% Co were synthesized and denoted as CoMo/Al-x. The method of catalysts preparation is given in previous study<sup>1</sup>. Boron was added in molding paste during preparation of the supports. H<sub>3</sub>BO<sub>3</sub> was used as precursor.

It is noted that boron does not influence textural properties of the supports and catalysts: the exclusion is CoMo/Al-3. The surface areas of the supports and catalysts are equal to 216±5 m<sup>2</sup>/g and 172±4 m<sup>2</sup>/g and pore diameters — 9,8±4 nm, 9,5±2 nm, respectively. The surface area of AI-3 increases to 233 m<sup>2</sup>/g, while the one of CoMo/AI-3 decreases to 156 m<sup>2</sup>/g. Simultaneously, the average diameter of pores decreases to 9.1 nm for AI-3 and increases to 9.9 nm for CoMo/AI-3. It indicates that addition of boron results in formation of micropores in Al-3, which are plugged by active component particles after impregnation. The peaks at v=1040 cm<sup>-1</sup>, 1230 cm<sup>-1</sup>, 1385 cm<sup>-1</sup> and 3695 cm<sup>-1</sup> appear after addition of boron that could be attributed to  $BO_3$  trigonal species<sup>2</sup>, the small one to  $BO_4$  tetrahedral species<sup>2</sup> and B–OH groups<sup>3</sup>. Intensity of the peaks at v=3685 cm<sup>-1</sup> and v=3730 cm<sup>-1</sup> which correspond to weak acidic bringed  $AI^{VI}(OH)AI^{IV}$  and  $AI^{VI}(OH)AI^{VI}$  bands, decreases. Intensity of the peaks at v=3755-3790 cm<sup>-1</sup> which correspond to basic terminal AI-OH bands, changes slightly. Thus, boron interacts with bringed  $AI^{VI}(OH)AI^{V}$  and  $AI^{VI}(OH)AI^{VI}$  bands that results in formation of B-OH monolavers on surface. It results in deacrease of interaction between active component and a support, that is confirmed by the increase of visial amount of layers of active component particles per 1000 nm<sup>2</sup> from 35 to 45 slabs. The higher mentioned changings results in increase of catalytic activity in hydrodesulfurization and hydrodenitrogenation reactions.

## Acknowledgements

The work was supported by Ministry of Education and Science of Russian Federation: Project No. 14.610.21.0008, identification number of the project RFMEFI61015X0008, title 'Development of production technology of import-substituted catalysts for deep hydrotreatment of vacuum gasoil'.

## References

- 1. O.V. Klimov, A.V. Pashigreva, J. Mol. Catal. A. 2010, 322, 80.
- 2. W. Chen, F. Mauge, J. Catal. 2013, 304, 47-62.
- 3. E.C. Decanio, J.G. Weissman, Colloid Surf. A. 1995, 105, 123.

## BC<sub>x</sub>N<sub>y</sub> film synthesis using organoboron precursors

## Veronica Sulyaeva, Marina Kosinova

#### Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3 Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia, <u>veronica@niic.nsc.ru</u>

 $BC_xN_y$  films have attracted great attention of researchers due to their promising functional properties such as high hardness, high transparency, wide optical band gap, low-k values, etc. Variation of composition and structure of  $BC_xN_y$  films allows to the control of their properties. Some of the factors affecting the film properties are type of CVD process, precursor design, deposition temperature and additional gas. In this work, synthesis of boron carbonitride films was carried out by both thermal and plasma-chemical decomposition of N-trimethylborazine (TMB), N-triethylborazine (TEB), trimethylamine borane (TMAB) and triethylamine borane (TEAB) precursors with different atomic ratio B:C:N in the molecule equal to 1:1:1, 1:2:1, 1:3:1 and 1:6:1, respectively. Precursors have been used in mixtures with nitrogen, ammonia, helium or hydrogen. Investigation of surface morphology shown that there are nanoparticles on the surface of high temperature films (500-700 °C), their size is up to 50 nm, while the low temperature films (100-400 °C) had smooth, featureless surfaces. According to transmission electron microscopy and XRD with synchrotron radiation, the film structure can be amorphous or containing nanocrystals in an amorphous matrix. Using FTIR-spectroscopy data it was found that BC<sub>x</sub>N<sub>y</sub> films have two bands v(BN)and  $\overline{\delta}(BNB)$  which correspond to h-BN spectrum or wide band centered at 1240 cm<sup>-1</sup> correspond to ternary compound BC<sub>x</sub>N<sub>y</sub>, depending on the growth conditions. The low temperature films are amorphous hydrogenated BC<sub>x</sub>N<sub>y</sub>.H films, since they contain hydrogen bonded to the boron, carbon and nitrogen. High temperature films contain additional graphite phase as impurity that was determined by Raman spectroscopy. TXRF NEXAFS method detected complicated structure of K-edges and environment of boron by various types of atoms. The measurements also indicated the presence of B-C and C-N bonds in the synthesized films. Nanoindentation study shown that maximal microhardness of boron carbonitride films synthesized from the mixture of TMAB+He was equal to 34 GPa, and from the mixture of TEAB+N<sub>2</sub> - 40 GPa. Study of electrophysical characteristics was carried out using of C-V and C-I measurements. BC<sub>x</sub>N<sub>y</sub> films grown by PECVD from TMAB at low temperatures (200-450 °C) are low-k materials with a relative dielectric constant of 3.8-4.6 and resistivity  $\rho = 5.0 \cdot 10^{12} - 1.3 \cdot 10^{15} \Omega$  cm at investigated grows conditions. The transmittance of the BC<sub>x</sub>N<sub>y</sub>/fused silica structures prepared from TMB and TEB in the temperature range of 100-400 °C and from mixture of TMAB with ammonia in the temperature range of 500-700°C is up to 93% in visible range of spectra (400-800 nm). While using TEAB as the precursor leads to reducing of transmittance to 80% at the same synthesis conditions. Optical band gap energy of deposited material estimated from spectrophotometry data varied in range of 1-5 eV independence of kind of precursor and growth conditions. Thus, it was shown that type of CVD process, the design of the precursor, deposition temperature along with an additional gas ( $N_2$ ,  $NH_3$ , He and  $H_2$ ) defines the chemical composition, structure and functional properties of the deposited BC<sub>x</sub>N<sub>y</sub> films.

## Acknowledgements

This work was partly supported by the RFBR (project 16-33-00448\_мол\_а) and SP-736.2016.1.

## SiBCN films obtained by LPCVD and PECVD from novel singlesource organoboron-silicon precursor

I. S. Merenkov,<sup>a</sup> S. I. Sysoev,<sup>a</sup> B. A. Gostevsky,<sup>b</sup> M. N. Khomyakov,<sup>c</sup> A. V. Lis,<sup>b</sup> M. L. Kosinova<sup>a</sup>

<sup>a</sup> A.V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3 Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia, <u>merenkov@niic.nsc.ru</u>

<sup>b</sup> A.E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of Russian Academy of Sciences, 1 Favorsky St., Irkutsk, 664033, Russia, <u>irk\_inst\_chem@irioch.irk.ru</u>

<sup>c</sup> Institute of Laser Physics, Siberian Branch of Russian Academy of Sciences, 13/3 Acad. Lavrentiev Ave, Novosibirsk, 630090, Russia, <u>mnkhomy@gmail.com</u>

B-C-N system phases based films are promising hard coatings. Unfortunately, they cannot be widely used in industry because of the crystallization started at high temperature. It leads to degradation of the film functional properties (for example, adhesion and Young's modulus). One of the problem solution ways is using four-component Si-B-C-N system based materials that possess the same mechanical characteristics and keep the amorphous state up to 1400°C.

This work is devoted to the synthesis and characterization of new organoboronsilicon compounds, which are potential precursors in film deposition by CVD technique. The most available CVD-precursor was chosen based on the equilibrium vapor pressure study depending on temperature. The SiB<sub>x</sub>C<sub>y</sub>N<sub>z</sub> films were produced by both low pressure and plasma enhanced chemical vapor deposition (LPCVD and PECVD) and their composition and structure depending on growth conditions were investigated.

А new organoboron-silicon compounds such as MeB[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (1).  $HC \equiv CB[N(SiMe_3)_2]_2$  (2) and  $Me_3SiC \equiv CB[N(SiMe_3)_2]_2$  (3) were produced by reaction between FB[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and MeLi, NaC=CH, Me<sub>3</sub>SiC=CLi, respectively. The compound composition and structure were verified by NMR, FTIR, Raman spectroscopies. The equilibrium vapor pressure dependencies on temperature were measured by static tensimetry method with glass-membrane zero manometer using. The enthalpy and entropy of vaporization were calculated from tensimetry data. The collected tensimetry data comparison showed that compound (3) is the most volatile from room temperature to 140°C. Further mixture of this compound and ammonia was used for the SiB<sub>x</sub>C<sub>v</sub>N<sub>z</sub> film deposition by LPCVD and PECVD techniques. The partial vapor pressures of precursor and ammonia were 5.5 10<sup>-3</sup>-1.4 10<sup>-2</sup> and 0-2.2 10<sup>-2</sup> Torr, respectively. The EDS and XPS researches showed that carbon, boron, silicon and nitrogen are main film components. Si-C, Si-N, Si-CH<sub>3</sub>, B-N and B-C bonds were detected in films by FTIR spectroscopy. According to Raman data it was found that there are amorphous carbon inclusions in the films deposited at high temperature and low ammonia pressure. The film surface was investigated by SEM and AFM. The refraction index increases from 2.4 to 2.7 under rising deposition temperature. The film transparency increases and achieves a more than 80% value under ammonia partial vapor pressure rises. The SiB<sub>x</sub>C<sub>v</sub>N<sub>z</sub> coating hardness and Young's modulus values were studied by nanoindentation.

## Acknowledgements

The reported study was funded by RFBR according to the research project No. 16-33-00404 мол\_а.

## A new class of purely inorganic ligands: Carboranylphosphinic acids. Aiming towards future multifunctional materials

<u>Elena Oleshkevich</u>,<sup>a</sup> Francesc Teixidor,<sup>a</sup> Anna Rosell Novel,<sup>b</sup> Anna Morancho Retana,<sup>b</sup> Arpita Saha,<sup>a</sup> Clara Viñas<sup>a</sup>

<sup>a</sup> Institut de Ciència de Materials de Barcelona (ICMAB-CSIC),Campus UAB, 08193 Bellaterra, Spain. <sup>b</sup> Neurovascular Research Laboratory, Institut de Recerca Hospital Vall d'Hebron Barcelona, Spain

Organophosphorous compounds are of remarkable technological interest, e.g. organophosphines are important ligands in catalysis and asymmetric synthesis;<sup>1</sup> phosphonates have found applications as, among others, herbicides<sup>2</sup> and medicine.<sup>3</sup> Phosphinates have also been applied as herbicides.<sup>4</sup> Both phosphonates and phosphinates are good chelating agents of interest as metal extractants.<sup>5</sup> In the organophosphorus compounds the carbon atom linked to the phosphorus is part of an organic functional group. In this work the C is a member of a boron cluster: a carborane.

Recently purely inorganic carboranyl phosphinates were prepared, and the influence of the cluster on the reactivity of phosphinate group was studied.<sup>6</sup> Carboranylphosphinic acids are principally new coordination reagents in boron cluster chemistry. Although, few carboranylphosphinic acids have been previously synthesized,<sup>7</sup> their coordination chemistry, together with their physical and chemical properties, remained still unexplored. Obviously, no examples of

carboranylphosphinic acid complexes have been found; hence no coordination polymers with this motif have been described until now.

Having all this in mind, we produced a few examples of an air-stable fully inorganic coordination polymers of Mn<sup>II</sup> and Cd<sup>II</sup> using the carboranylphosphinate ligand 1-OPH(OH)-1,7-closo-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>. Then, was discovered the ability of carboranylphosphinates to control the size of CdSe Quantum Dots (as a capping agent) and its ability to coordinate on surface of magnetite/maghemite (Fe<sub>3</sub>O<sub>4</sub>/γ-Fe<sub>2</sub>O<sub>3</sub>) nanoparticles.



## Acknowledgements

Scientific projects CTQ2013-44670-R and 2014 SGR 149.

## References

1. J.C. Chadwick, R. Duchateau, Z. Freixa, P.W.N.M. van Leeuwen. Homogeneous Catalysts: Activity - Stability - Deactivation; Wiley-VCH, Weinheim, **2011**.

2. J. Lipok, Ecotox. Environ. Safe. 2009, 72, 1701-1706.

3. K.A. Kennel, M.T. Drake, Mayo Clin. Proc. 2009, 84, 632-638.

4. P. Böger, K. Wakabayashi, K. Hirai. Herbicide Classes in Development: Mode of Action, Targets, Genetic Engineering, Chemistry, Springer/Berlin/ Heidelberg, **2002**.

5. D.G. Kalina, E.P. Horwitz, L. Kaplan, A.C. Muscatello, Separ. Sci. Technol. 1981, 16, 1127-1145.

6. E. Oleshkevich, F. Teixidor, D. Choquesillo-Lazarte, R. Sillanpää, C. Viñas, Chem. Eur. J. 2016, 11, 3665-3670.

7. L.I. Zakharkin, A.V. Kazantsev, M.N. Zhubekova, Russ. Chem. Bull. 1969, 9, 2056-2059.

EUROBORON 7

## POSTER PRESENTATIONS

## КАТРОСА РЕАКТИВ



САТРОБА - официальный представитель одного из крупнейших европейских производителей химических реактивов Panreac-Applichem и поставщик химических реактивов бренда Panreac Applichem на территории России. Выпуск продукции обеспечивают две производственные площадки, расположенные в Испании (Барселона) и Германии (Дармштадт).

Качество продукции **PanReac<sup>®</sup>AppliChem** признано во всем мире. В настоящее время производитель экспортирует реактивы более чем в 80 стран мира. Каталог **PanReac<sup>®</sup>AppliChem** насчитывает около 4000 продуктов для различного применения:





для синтеза;

для анализа (ACS-ISO grade);

• высокочистые растворители для хроматографии и спектросокопии (HPLC, UV, IR, GC, LC-MS);

высокочистые кислоты для анализа следов металлов;

 растворители с низким содержанием воды;

стандартные растворы, рН
 буферные растворы, стандарты для
 атомной абсорбционной спектроскопии
 и спектроскопии с индуктивно
 связанной плазмой (ICP и AAS анализа);



 сырьё и вспомогательные вещества фармакопейного качества, питательные среды для использования в крупномасштабных ферментационных процессах;

• продукты для биохимии, молекулярной биологии, работы с клеточными культурами, микробиологии, гистологии.

Мы поставляем расходные материалы для хроматографии Teknokroma (Испания) и лабораторный пластик.

Для наших покупателей: реактивы только в заводской европейской упаковке, большой склад в Москве, сертификаты анализа на всю продукцию.

www.catrosa.ru www.panreac.es www.teknokroma.es

## New series of electroactive electrolytes for molecular electronics

Ana Begoña Buades, Adnana Zaulet, Clara Viñas, Francesc Teixidor

Institut de Ciència de Materials de Barcelona (CSIC). Campus UAB, 08193 Bellaterra, Spain

The electrophilic halogenation of a metallacarborane, in this case  $[3,3]^{-}Co(C_2B_9H_{11})_2]^{-}$  (COSAN), is a useful way to modify its redox potential with the objective to obtain an electroactive electrolyte for molecular electronics, and in particular for dye sensitized solar cells (DSC). The addition of an extra halo substituent implies a reduction near 0,12V of the redox potential of the parent complex<sup>1</sup>. Then if the redox potential of COSAN is around -1.76V vs. Fc in acetonitrile<sup>2</sup>, chlorination between ten and twelve positions in COSAN imply that the redox potential can be adjusted to the iodide/triiodide redox couple (E°(I<sub>3</sub>-/I<sup>-</sup>)= -0.30 vs Fc in acetonitrile) that is the reference electrolyte in DSC.<sup>3</sup>

The chlorination reaction is carried on the protonated form of the metallacarboranes. Several procedures including temperature, pressure, reaction time, solvent and reagents have been studied to produce the highly chlorinated COSAN in the most pure form. Chlorination up to twelve positions has been obtained. All the products produced have been analysed with different electrochemical and spectroscopy methods.



Figure 1. Schematically display how the introduction of different substituents to the parents  $[3,3] - Co(C_2B_9H_{11})_2]^-$  (M=orange) and  $[3,3] - Fe(C_2B_9H_{11})_2]^-$  (M=brown) allow to tune the  $E_{1/2}(M^{3+/2+})^{4,5-}$ 

## Acknowledgements

Scientific projects: FP7-OCEAN-2013 (614168 SEA-on-a-CHIP); CTQ2013-44670-R; 2014 SGR 149.

## References

1. P. González-Cardoso, A.I Stoica, P. Farràs, A. Pepiol, C. Viñas, F. Teixidor, Chem. Eur. J. 2010, 16, 6660-6665.

2. A. Pepiol, F. Teixidor, R. Sillanpää, M. Lupu, C. Viñas, *Angew. Chem. Int. Ed.* 2011, *50*, 12491-12495.

3. E.A. Gibson, L. Le Pleux, J. Fortage, Y. Pellegrin, E. Blart, F. Odobel, A. Hagfeldt, G. Boschloo, *Langmuir* **2012**, *28*, 6485-6493.

4. M. Lupu, A. Zaulet, F. Teixidor, E. Ruiz, C. Viñas, Chem. Eur. J. 2015, 21, 6888-6897.

5. M. Tarrés, V.S. Arderiu, A. Zaulet, C. Viñas, F. Fabrizi de Biani, F. Teixidor, *Dalton Trans.* 2015, 44, 11690-11695.

## Development and biological evaluation of high boron content hybrid entities for their potential use in brain diseases

Marcos Couto,<sup>a,b</sup> Ignacio Mastandrea,<sup>a</sup> Mauricio Cabrera,<sup>a</sup> Pablo Cabral,<sup>a</sup> Francesc Teixidor,<sup>b</sup> Clara Viñas,<sup>b</sup> Hugo Cerecetto<sup>a</sup>

<sup>a</sup> Facultad de Ciencias, Universidad de la República, Uruguay. <u>mcoutosire@gmail.com</u>

<sup>b</sup> Institut de Ciència de Materials de Barcelona (CSIC), Campus U.A.B. Spain. <u>clara@icmab.es</u>

Glioblastoma multiforme, the most common primary brain tumor is the most aggressive variant within the central nervous system (CNS).

The CNS standard treatment is surgical resection of the tumor followed by a combination of radiation and chemotherapy in order to kill any remaining tumor cells that could stay infiltrated into the brain parenchyma. However, the current therapeutic success of this treatment is limited.<sup>1</sup>

Boron neutron capture therapy (BNCT) is a strategy that involves radiotherapy "*in situ*". It is based on the unusual ability of <sup>10</sup>B (a stable isotope) to capture low energy thermal neutrons to yield alpha particles and recoiling <sup>7</sup>Li nuclei that, destroy cells within about 10  $\mu$ M from the site of the capture reaction.<sup>2</sup>

Furthermore, targeted therapy is another approach currently under investigation in the treatment of cancer. Targeted therapy is technically considered as chemotherapy, but it takes advantages of small differences between normal cells and cancer cells. One of the targeted therapies is specifically based on inhibitors of tyrosine kinase domains.

In this presentation, the synthesis of tyrosine kinase domains inhibitors hybridized with boron cluster pharmacophore (Figure 1) will be described as well as the biological study of these compounds as carriers for potential use in antitumor therapy of glioblastoma multiforme using BCNT.



## Acknowledgements

We thank ANII for scholarship to M Couto and thank CSIC-Universidad de la República (Uruguay), PEDECIBA (Uruguay) and Scientific projects (CTQ2013-44670-R) and (2014 SGR 149) for financial support.

## References

1. C. Adamson, O. Kanu, Al. Mehta, C. Di, N. Lin, AK. Mattox, DD. Bigner. *Expert Opin. Invest. Drugs.* **2009**, 18,1061.

2. R. Barth, M. Vicente, O. Harling, W. Kiger, K. Riley, P. Binns, F. Wagner, M. Suzuki, T. Aihara, I. Kato, S. Kawabata. *Radiat Oncol.* **2012**, 7, 146.

## Conjugates of boron clusters with thymosin β4: physicochemical properties and biological activity

Krzysztof Fink,<sup>a</sup> Tomasz M. Goszczynski,<sup>a</sup> Konrad Kowalski,<sup>a</sup> Monika Kasztura,<sup>b</sup> Zbigniew J. Lesnikowski,<sup>c</sup> Janusz Boratynski<sup>a</sup>

<sup>a</sup> Neolek - Laboratory of Biomedical Chemistry, Department of Experimental Oncology, Institute of Immunology and Experimental Therapy PAS, 12 Rudolf Weigl St., 53-114 Wroclaw, Poland, <u>krzysztof.fink@iitd.pan.wroc.pl</u>

<sup>b</sup> Laboratory for Applied Research on Cardiovascular System, Department of Heart Diseases, Wroclaw Medical University, 5 Rudolf Weigl St., 50-981 Wroclaw, Poland

<sup>c</sup> Laboratory of Molecular Virology and Biological Chemistry, Institute of Medical Biology, PAS, 106 Lodowa St., 93-232 Lodz, Poland

Thymosin  $\beta$ 4 (T $\beta$ 4) is a peptide composed of 43 amino acids with an ubiquitous distribution in human body. T $\beta$ 4 is highly soluble in water (>100 mg/ml). In physiological conditions, T $\beta$ 4 is mostly unstructured, with a tendency towards the formation of an  $\alpha$ -helical conformation between amino acid residues 5 and 16. T $\beta$ 4 prevents further damage of injured tissue and stimulate its regeneration by: 1) promotion of cell migration and tissue integrity, 2) angiogenesis, 3) inhibition of inflammatory response, 4) anti-apoptosis/cell survival processes, 5) anti-microbial activity, 6) wound healing, 7) anti-fibrotic processes, and 8) stem/progenitor cell recruitment and differentiation.<sup>1</sup> Many of T $\beta$ 4 pleiotropic biological activities are defined by its two main active sites: N-terminal tetrapeptide (Ac-SDKP) and the central actin binding domain (17-LKKTET-22).<sup>2</sup> Half-life of T $\beta$ 4 administered intravenously to humans was 1-2 h, depending on dose.<sup>3</sup> That means that T $\beta$ 4 is cleared from the body shortly after administration.

Boron clusters are polyhedral boron hydrides with a non-planar, cage-like structure. In this study, two distinct boron cluster donors were chosen, dioxane adduct of closo-dodecaborate anion and dioxane adduct of cobalt bis(dicarbollide). Dodecaborate anion can interact with lipid membranes, proteins and form strong inclusion complexes with  $\gamma$ -cyclodextrins.<sup>4</sup> This interaction is caused not by hydrophobic forces but by chaotropic effect. The introduction of a cobalt bis(dicarbollide) moiety into a molecule structure usually results in the decrease of water solubility of the molecule and tendency to self-assemble.<sup>5</sup> Metallacarboranes form complexes with human serum albumin (HSA).<sup>6</sup> The attachment of a selected boron cluster to a T $\beta$ 4 can be a good strategy to prolong the half-life of the peptide in the circulation and enhance its therapeutic effect.

The reaction was performed in solid state and high temperature (80°C). The effects of boron cluster attachment to T $\beta$ 4 on its secondary structure, tendency to aggregation and interaction with bovine serum albumin (BSA) will be presented. Furthermore, the comparison of the biological activity of native and modified peptide will be shown, based on the *in vitro* studies on human and rat cardiomyocytes.

## References

1. A.L. Goldstein, E. Hannappel, et al., Expert Opin. Biol. Ther. 2012, 12, 37.

- 2. G. Sosne, P. Qiu, et al., FASEB J. 2010, 24, 2144.
- 3. D. Ruff, D. Crockford, et al., Ann. N.Y. Acad. Sci. 2010, 1194, 223.
- 4. K.I. Assaf, M.S. Ural, et al., Angew. Chem. Int. Ed. Engl. 2015, 54, 6852.
- 5. P. Matejicek, P. Cigler, et al., Langmuir 2008, 24, 2625.
- 6. J. Rak, B. Dejlova, et al., Mol. Pharm. 2013, 10, 1751.

## Piezoelectric properties of the crystals of chiral ortho-carborane derivatives

Dmitry Gruzdev,<sup>a</sup> Alla Nuraeva,<sup>b</sup> Pavel Zelenovskiy,<sup>b</sup> Galina Levit,<sup>a</sup> Valentina Ol'shevskava.<sup>c</sup> Valery Kalinin.<sup>c</sup> Vladimir Shur.<sup>b</sup> Victor Krasnov<sup>a</sup>

<sup>a</sup> Postovsky Institute of Organic Synthesis. RAS (Ural Branch). 22/20 S. Kovalevskava St. /

Akademicheskaya St., Ekaterinburg, 620990 Russia, <u>gruzdev-da@ios.uran.ru</u> <sup>b</sup> Institute of Natural Sciences, Ural Federal University, 51 Lenin Ave., Ekaterinburg, 620000, Russia

<sup>c</sup> Nesmeyanov Institute of Organoelement Compounds, RAS, 28 Vavilov St., Moscow, 119991 Russia

The search for piezo- and ferroelectric organic and organoelement compounds is an urgent task of current chemical physics. Crystals of piezoactive compounds are interesting in the view of designing new biocompatible and environmently friendly devices, such as piezoelectric motors, sensors, actuators, frequency standards etc. The promising piezoelectric properties were found in the crystals of some amino acid derivatives and peptides.<sup>1-3</sup> Recently, for the first time we have demonstrated that the crystals of an organoboron compound can possess piezoelectric properties.<sup>3</sup>

In this work, we measured piezoelectric coefficients of single crystals of (1.2-dicarbacloso-dodecaboran-1-vl)acetic acid (ortho-carboran-1-vl)acetic acid] (1), its planary chiral derivatives rac-2 and 3, and amide (S)-4 bearing 3-amino-ortho-carborane moiety (Figure 1).

It has been found that piezoelectric responses of crystals of amides  $(S, S_P)$ -3 and (S)-4 even exceed that of classical inorganic piezoelectric LiNbO<sub>3</sub>. It has been also shown that the value of piezoelectric response depends on stereo configuration of ortho-carborane fragment. Piezoelectric coefficients for the crystals of amide  $(S, S_P)$ -3 were 10 times higher than for the crystals of diastereomeric amide  $(S, R_P)$ -3, parent acid 2, and structurally related amide (S)-5 lacking a carborane moiety.

Thus, piezoelectrics have been found among chiral ortho-carborane derivatives. It has been shown that the presence of *ortho*-carborane cage can cause piezoelectric properties, the piezoelectric responses depending on stereo configuration.



Figure 1. Piezoelectric coefficients of the compounds studied.

## Acknowledgements

The equipment of the Ural Center for Shared Use "Modern Nanotechnology" UrFU was used. The work was financially supported by the Russian Foundation for Basic Research (grant 16-33-60122).

## References

1. P.S. Zelenovskiy, V.Ya. Shur, A.S. Nuraeva et al., Ferroelectrics 2015, 475, 127.

- 2. S. Vasilev, P. Zelenovskiy, D. Vasileva et al., J. Phys. Chem. Solids 2016, 93, 68.
- 3. A.S. Nuraeva, D.S. Vasileva, S.G. Vasilev et al., Ferroelectrics 2016, 496, 1.

## Development of microsensors for the detection of antibiotics using ion pair complexes of protonated amine groups and metallacarboranes

<u>Abhishek Saini</u>,<sup>a</sup> Isabel Fuentes,<sup>a</sup> Clara Viñas,<sup>a</sup> Nadia Zine,<sup>b</sup> Joan Bausells,<sup>c</sup> Abdelhamid Errachid,<sup>b</sup> Francesc Teixidor<sup>a</sup>

<sup>a</sup> Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain

<sup>b</sup> Universite Claude Bernard Lyon 1, ISA, UMR 5280, Villeurbanne, France

<sup>c</sup> Instituto de Microelectronica de Barcelona, IMB-CNM (CSIC), Campus UAB, 08193 Bellaterra, Spain

Ion pair complexes of various protonated amine group compounds with metallacarboranes have been synthesized for use as ion selective electrodes for the potentiometric detection of the said amine groups, namely, Tetracycline, Sulfanilamide, Sulfapyridine and Irgarol. Potentiometry is a simple and effective technique for the rapid determination of analytes. The protonated amine groups were prepared with  $Cs[Co(C_2B_9H_{11})_2]$  to form ion pair complexes. This ion pair complex acts as an ionophore and in conjunction with a polymer matrix (like PVC) and a suitable plasticizer (like NPOE, DOP etc) can be used for the potentiometric detection of the desired antibiotic (tetracycline,sulfanilamide, sulfapyridine and Irgarol).

Metallacarboranes like  $[Co(C_2B_9H_{11})_2]$  have been known to show very good performances as an lon selective electrode membrane lipophilic anion additive<sup>1</sup>. Also cobaltabis(dicarbollide)  $[3,3'-Co(1,2-C_2B_9H_{11})_2]$  has shown to provide a high stability to the polymer when used as a dopant anion with a conducting polymer like Polypyrrole<sup>2</sup>. The ISEs prepared using cobaltabis(dicarbollide)  $[3,3'-Co(1,2-C_2B_9H_{11})_2]$  also show low charge density and produce  $C_c$ -H···H–B and B–H···H–N

dihydrogen bonds, and  $C_c$ -H···O ( $C_c$ =Carbon cluster) hydrogen bonds which play an important role in the stability of the membrane<sup>3</sup>.These factors have been used to make microelectrodes having a conducting polymer layer of Cobaltabis(dicarbollide) and Polypyrrole while the ion pair complexes of the aforementioned protonated amine groups act as ionophores. These devices have shown good selectivity and sensitivity during the potentiometric detection of these antibiotics.

This is a novel method for the detection of these compounds in sea water and will be useful in finding out the levels of these toxic compounds in sea water and ultimately aiding in its purification.



Figure 1. Miniaturized Sensor

## Acknowledgements

SwScientific projects CTQ2013-44670-R and 2014 SGR 149. Sea on a chip Project (FP7-KBBE) under the reference 614168.

## References

A. Stoica, C. Viñas, F. Teixidor, *Chem. Commun.* 2008, 6492-6494.
 N. Zine, J. Bausells, A. Ivorra, J. Aguiló, M. Zabala, F. Teixidor, C. Masalles, C. Viñas, A. Errachid, *Sensors and Actuators B: Chemical.* 2003, *91*, 76-82.
 A. Stoica, C. Viñas, F. Teixidor, *Chem. Commun.* 2009, 4988-4990.

## Synthesis of new sulfonium derivatives of nido-carborane

Sergey A. Anufriev, Igor B. Sivaev, Vladimir I. Bregadze

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991, Moscow, Russia, <u>trueMan476@mail.ru</u>

Reactions of the protonated *nido*-carborane [7,8-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub>] with dimethylsulfide and dimethylsulfoxide were studied. The reaction with dimethylsulfide gives symmetrically substituted dimethylsulfonium derivative [10-Me<sub>2</sub>S-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>], whereas the reaction with dimethylsulfoxide produces asymmetrically substituted isomer [9-Me<sub>2</sub>S-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]. Demethylation-alkylation reactions of the sulfonium derivatives were studied. Earlier we studied alkylation of [9-SMe-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] with various alkylation agents<sup>1</sup>. In this work a series of new *nido*-carborane-based amines and carboxylic acids were prepared by alkylation of [9-SMe-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] with various  $\omega$ -halogenalkyl N-phthalimides and  $\omega$ -halogenalkyl carboxylic acids. It was found that [9-SMe-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] readily reacts with dichloromethane and its reactions with various alkylation agents were investigated. Reactions of [10-SMe-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] with various of the compounds synthesized will be discussed.



## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (project 16-33-00607).

## References

1. M.V. Zakharova, I.B. Sivaev, S.A. Anufriev, S.V. Timofeev, K.Yu. Suponitsky, I.A. Godovikov, V.I. Bregadze, *Dalton Trans.* **2014**, *43*, 5044.

## New commo-ferracarboranes meso- and dl- [PPh<sub>3</sub>Me][commo-Fe(2,4-closo-C<sub>2</sub>B<sub>8</sub>H<sub>10</sub>)<sub>2</sub>] derived from 5,6-*nido*- dicarbadecaborane(12)

Elena Balagurova, Anastasia Silivonenko, Irina Pisareva, Fedor Dolgushin, Alexander Smol`yakov, Alexander Kostukovich, Igor Chizhevsky

A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street, 119991, Moscow, Russian Federation, <u>chizbor@ineos.ac.ru</u>

As a part of our ongoing studies on the chemistry and reactivity of commometallacarborane clusters derived from the medium-size carborane [5.6-nido- $C_2B_8H_{12}$ , we have developed a convenient synthesis of new paramagnetic ferracarborane complex of the type  $[PPh_3Me][commo-Fe^{III}(2.4-isonido-C_2B_8H_{10})_2]$  (1) which was isolated in two meso (1a) and dl (1b) isomeric forms in ca. 2:1 ratio. respectively. This was based on the room-temperature reaction in THF between anhydrous FeCl<sub>2</sub> and in situ generated [Na]<sup>+</sup> salt of [nido-C<sub>2</sub>B<sub>8</sub>H<sub>11</sub>]<sup>-</sup>. The above mixture of isomers of 1 thus prepared was successfully separated into 1a and 1b via column chromatography on silica gel in 36 and 17 % yields, respectively. The X-ray diffraction studies established very unusual closo geometry of both isomeric complexes 1a and 1b (fig. 1), wherein the cage carbon atoms are in positions 2 and 4, and all M-B and M-C distances involving hexagonal belts of the  $\{C_2B_8\}$ -ligands do not exceed 2.4 Å. Parallel examination of the solution behavior of 1a and 1b showed that these species are chemically quite reactive and some changes were observed in CH<sub>2</sub>Cl<sub>2</sub> solution after several hours at room temperature. Monitoring of these processes by TLC showed the facile transformation of **1a** into **1b** as well as **1b** into **1a** resulting in the formation of equilibrium between these species.



Figure 1. Molecular structures of 1a (meso, left) and 1b (dl, right).

## Acknowledgements

This work has been supported by Grant No 15-03-08415 from the Russian Foundation for Basic Research.

## Boron chelate-assisted synthesis of new pyrazolylidene derivatives from cyanoacetic acid hydrazide and *O*-methyl lactimes

Sergey Baranin, Sergey Ruban, Tamara Potapova, Yuri Bubnov

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Scienses, 47 Leninsky Prosp., 119991 Moscow, Russian Federation. E-mail: <u>svbar@ioc.ac.ru</u>

Cvanoacetic acid hydrazide (1) reacts with O-methylbutyrolactime (2a) at the methylene group of 1 with subsequent cyclization of enamine formed to 3-amino-4-(pyrrolidin-2-ylidene)-4,5-dihydropyrazol-5-one (3a) in 36% yield. Conversely the condensation of O-methylvalero- (2b) or O-methylcaprolactime (2c) with hydrazide 1 proceeds exclusively at amino group, leading in both cases to polymethylene triazoles (4b,c) in high yields<sup>1</sup> (Scheme 1). In order to exclude the condensation of the lactim ethers at the amino group of hydrazide 1. we carried out the reaction of the latter with DMF dimethyl acetal. To activate the methylene group in hydrazide 1, we used an approach where hydrazide 1 is replaced with its diphenylboron chelate 6. which is easily obtained upon treatment of compound 5 with Ph<sub>2</sub>BOBu. Chelate 6 was found to smoothly react with lactim ethers 2a-c upon heating with the formation of chelates 7a-c (Scheme 2). Deboronation of chelates 7a-c takes place upon heating in a butanol solution of HCI and is accompanied by an intramolecular cyclization involving the cyano group, resulting in the formation of 3-aminopyrazol-5one derivatives **3a-c**  $(n = 1-3)^2$ . In conclusion, the synthesis of ylidene derivatives of the type **3** of 3-aminopyrazolon is yet another example of an efficient application of the chelate-assisted synthesis methodology for the design of heterocycles.



Scheme 2.

## References

D.B. Nilov, V.G. Granik, *Russ. Chem. Bull. (Int. Ed.)* 2006, 55, 1636.
 S.V. Ruban, T.V. Potapova, S.V. Baranin, V.A. Dorokhov, *Russ. Chem. Bull. (Int. Ed.)* 2014, 63, 2260.

```
EUROBORON 7
```

September 4-8, 2016

# Sulfamido carboranes equipped with an MRI probe for multimodal cancer treatment: BNCT agents with inhibitor activity for carbonic anhydrases

P. Boggio,<sup>a</sup> A. Michelotti,<sup>a</sup> S. Geninatti-Crich,<sup>b</sup> D. Alberti,<sup>b</sup> S. Aime,<sup>b</sup> T. S. Balaban,<sup>c</sup> A. Deagostino<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Torino, via P. Giuria 7, 10125, Torino, Italy.

<sup>b</sup> Department of Molecular Biotechnology and Health Sciences; University of Torino, via Nizza 52, 10126, Torino, Italy.

<sup>c</sup> Aix Marseille Université, Institut des Sciences Moléculaires de Marseille (iSm2) Chirosciences, Service 442, Avenue Escadrille Normandie-Niemen, F-13397 Marseille CEDEX 20, France

Human carbonic anhydrases (CAs) are zinc metalloenzymes involved in several physiological and pathological processes like obesity, epilepsy, gluconeogenesis and tumorigenicity.<sup>1</sup> The synthesis of inhibitors able to inactivate the enzymatic activity of CAs appears thus a promising strategy to treat these pathologies. CA inhibitors contain a sulfamide moiety exploited to coordinate the zinc cation located in the carbonic anhydrase catalytic site.<sup>2</sup> Recent studies developed by Řezáčová and coworkers<sup>3</sup> have shown that sulfamido carborane derivatives present interesting inhibitor activity towards CAs with high selectivity for cancer-associated form CAIX. Carboranes, icosahedral clusters containing boron, carbon and hydrogen, present high in vivo stability and increase the bioavailability of biologically active molecules. Starting from these results a new synthetic approach to provide sulfamido carborane inhibitors equipped with an organometallic complex active to MRI has been developed (Figure 1). The introduction of an MRI probe and the high selectivity of this class of inhibitors for cancer-associated enzyme CAIX allows the not invasive detection of their in vivo biodistribution and tumor mass localization in patients. This approach leads to the synthesis of sulfamido carborane inhibitors active to MRI and potentially suitable for a therapeutic treatment based on BNCT (Boron Neutron Capture Therapy). <sup>10</sup>B presents a high neutron cross-section that leads to the generation of large amounts of unstable <sup>11</sup>B nuclei after neutron irradiation. The subsequent <sup>11</sup>B nuclei scission induces the formation of particles with high-energy content resulting in biomolecule ionization and cellular death. The high selectivity of carborane-based CA inhibitors for CAIX can be exploited for a selective cancer treatment thanks to the synergic effect due to their inhibition activity (based on the sulfamide mojety) and to the BNCT treatment (based on the carborane cage).



Figure 1. Schematic representation of proposed MRI-active sulfamido carborane CA inhibitors.

## References

C.T. Supuran, *Nat. Rev. Drug Discov.* 2008, 7, 168-181.
 V.M. Krishnamurthy, G.K. Kaufman, A.R. Urbach, I. Gitlin, K.L. Gudiksen, D.B. Weibel, G.M. Whitesides, *Chem. Rev.* 2008, 108, 946-1051.
 J. Brynda, P. Mader, V. Šícha, M. Fábry, K. Poncová, M. Bakardiev, B. Grüner, P. Cígler, P. Řezáčová, *Angew. Chem. Int. Ed.* 2013, 52, 13760-13763.

## Reactivity of germylene stabilized by boraguanidinate ligand with CC and NC unsaturated systems

## Jiri Boserle, Libor Dostal

#### Department of General and Inorganic Chemistry, University of Pardubice, Studentska 573, CZ-53210, Pardubice, jiri.boserle@student.upce.cz

Tetrylenes containing boraguanidinate ligand in their structures represent a relatively unexplored branch of organometallic chemistry.<sup>1, 2</sup> However, high reactivity of these compounds to various substrates is expected due to the presence of free electron pair and vacant *p*-orbital on the central Group 14 atom.<sup>3</sup>

This study is focused on the reactivity of germylene **1** with acetylenes and variously substituted isonitriles RNC (Figure 1). Reactions of germylene **1** with symmetrically or non-symmetrically substituted acetylenes lead to the formation of cyclodigermabutenes. The properties of substituents on carbon atoms in the backbone of acetylenes are not important in these types of reactions. On the other hand, structure of products in the reactions of germylene **1** with variously substituted isonitriles RNC depend on the electronic and steric properties of the substituents R.



Figure 1. Reaction scheme of preparation of germylene 1 derivatives.

## Acknowledgements

The authors thank the Grant agency of the Czech Republic project no. P207/12/0223.

## References

- 1. Ch. Fedorchuk, M. Copsey, T. Chivers, Coord. Chem. Rev. 2007, 251, 897.
- 2. A.M. Corrente, T. Chivers, Inorg. Chem. 2008, 47, 10073.
- 3. J. Boserle, R. Jambor, A. Ruzicka, L. Dostal, RSC Advances 2016, 6, 19377.

## Looking for new anti-trypanosomatid agents from boron-containing compounds

Marcos Couto, Gonzalo Rodríguez, Carlos Osorio, Javier Nargoli, Hugo Cerecetto, Mercedes González

Facultad de Ciencias, Universidad de la República, Uruguay. mcoutosire@gmail.com

At present, the trypanosomatids affections are no-cure diseases due to the low efficacy of the clinic current pharmacology. For that reason, organization like DNDi (Drug for Neglected Diseases initiative) has been developing projects able to find new effective drugs. One of these projects has been based in the benzo[c]oxaborole **1** (Figure 1) that is currently evaluated in pre-clinic as anti-*Trypanosoma brucei* drug.<sup>1</sup> Taking compound **1** as structural template we have biological evaluated, from our chemical-library, a series of boron-containing compounds against *Trypanosoma cruzi* in order to identify new anti-Chagasic pharmacophores. In this sense, different chemotypes have been biologically studied: i) phenylboronic acids and the corresponding esters (chemotype (I), Figure 1), as the non-cyclic derivatives of **1**; ii) 4,4-dialkyl(aryl)oxy-4-bora-3a,4a-diaza-s-indacene (chemotype (II), Figure 1), as derivatives of the previous chemotype; iv) carborane-containing bioactive derivatives (chemotype (IV), Figure 1), as carrier of potential new anti-trypanosomatids pharmacophore (carborane system).



Figure 1. Template compound and chemotypes biologically studied against *T. cruzi*.

## Acknowledgements

We thank ANII, CSIC-Universidad de la República (Uruguay) and PEDECIBA (Uruguay).

## References

1. C. Tony Liu, John W. Tomsho, Stephen J. Benkovic, Bioorg. Med. Chem. 2014, 22, 4462.

## New approach to synthesis of the borosiloxanes via Piers-Rubinsztajn reaction

Fedor Drozdov<sup>a</sup>, Sergey Milenin<sup>a</sup>, Vadim Gorodov<sup>a</sup>, Mihail Buzin<sup>b</sup>, Aziz Muzafarov<sup>a,b</sup>

<sup>a</sup> Institute of Synthetic Polymer Materials, Russian Academy of Sciences, Moscow, Russia
<sup>b</sup> Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

Polysiloxanes are the most common and one of the most important polymers used in different branches of industry. These polymers are known for their useful properties, such as flexibility, permeability to gases, low glass transition temperature, and low surface energy. Nevertheless, polysiloxanes could not be applicable as high performance elastomers without specific modifications. Crosslinking of the polysiloxanes chains – is possible method to improve their physical and mechanical properties. The formation of weak Si-O-B interactions because of introduction boronic derivatives into siloxanes can significantly modify physics and phase behavior of such derivatives. For example, Dow Corning published a patent of bikers' flexible protective suit based on polyboronsiloxane resins.<sup>1</sup>

The aim of this work was to try Piers-Rubinsztajn reaction potential for Si-O-B bond formation by using polydimethylsiloxanes with functional hydrides and alkoxyboron derivatives with different functionality.



Figure 1. Formation of polyboronsiloxanes with different structure via Piers-Rubinstein reaction.

As results, the series of the polyboronsiloxane resins were prepared (Figure 1) and isolated in individual states. Almost all products are stable under atmospheric conditions. Gel permeation chromatography (GPC) data prove that average weights of the products were equally increased compared with initial polysiloxanes. Thermal stability of the products was estimated by thermal gravimetric analysis (TGA). All products show 10% weight losses after 400 °C.

Thus, the series of polyboronsiloxanes were sufficiently synthesized in Piers-Rubinsztajn reaction conditions. All products were characterized by GPC, NMR, TGA analysis.

## References

1. Patent DE 100 10 182 A1; (2000).

**EUROBORON 7** 

## Theoretical prediction of new superdense binary and ternary boron carbides

## Ivan V. Dudenkov, Konstantin A. Solntsev

#### A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, Moscow, Russia, 119991, Moscow, Leninskii pr., 49, <u>ivdudenkoff@mail.ru</u>

On the basis of the conventional for boron carbides and carboranes bond lengths we theoretically predict several binary and ternary (with minor contents of the third element) boron carbides turn out to be superdense related to mixtures B( $\alpha$ -rhomb.) + B<sub>4</sub>C or B<sub>4</sub>C + C(graphite) of the same composition. Crystallographic parameters that identify these carbides were calculated by powder XRD-specters.

First of all, we outline the possible binary carbides containing closo-icosahedra. For a hypothetical rhombohedral carbide  $B_{10}C_4 = (B_{10}C_2)(C_2)$  (R  $\overline{3}m$ ; a = 5.12 Å; z = 3) with ethane analogue intra-icosahedral C2 groups relating to the known  $B_6P$  class expected density is 2.88 g/cm<sup>3</sup>. For the hypothetical cubic carbide  $B_{10}C_5 = (B_{10}C_2)(C)_3$  (Pm  $\overline{3}n$ ; a = 5.77 Å; z = 2) with methane analogue intra-icosahedral C atoms expected density is 2.91 g/cm<sup>3</sup>

Let us turn to triple carbides containing icosahedra. For the CaB<sub>12</sub>C<sub>6</sub> = Ca(B<sub>12</sub>)(C<sub>2</sub>)<sub>3</sub> (Pm  $\overline{3}$ ; a = 5.20 Å; z = 1) carbides with ethane analogue intra-icosahedral C2 groups expected density is 2.85 g/cm<sup>3</sup>. For the MgB<sub>12</sub>C<sub>22</sub> carbide where icosahedra enclosed in an array of tetrahedral-coordinated carbon atoms with voids of Mg size two cubic polymorphs are possible. For  $\alpha$ - MgB<sub>12</sub>C<sub>22</sub> (Fm  $\overline{3}$ ; a = 9.36 Å; z = 4) expected density is 3.38 g/cm<sup>3</sup>. For  $\beta$ -MgB<sub>12</sub>C<sub>22</sub> (F23; a = 9.30 Å) expected density is 3.45 g/cm<sup>3</sup>. For B<sub>10</sub>C<sub>14</sub>Si<sub>3</sub> = (B<sub>10</sub>C<sub>2</sub>)(Si<sup>+1V</sup>)<sub>3</sub>(C<sub>4</sub>)<sub>3</sub> (Pm  $\overline{3}$ n; a = 7.33Å; z = 2) carbide with cyclobutane clusters C<sub>4</sub>, linked through a tetrahedral-coordinated atoms of Si calculated density is 3.04 g/cm<sup>3</sup>

Let us turn to binary boron carbide with incomplete icosahedral clusters. For the carbide (B<sub>6</sub>C<sub>3</sub>), containing only clusters of *arachno*-B<sub>6</sub>C<sub>3</sub>H<sub>12</sub> (R3m; a =8.02 Å; c = 3.05 Å) core, calculated density is 3.04 g/cm<sup>3</sup>. For the B<sub>8</sub>C<sub>14</sub> = (B<sub>4</sub>C<sub>4</sub>)<sub>2</sub>(CC<sub>4</sub>)(C) (thetr.; a = 5.51Å; c = 8.57Å; z = 2) carbide containing clusters of *hypho*-B<sub>4</sub>C<sub>4</sub>H<sub>12</sub> connected through the neo-pentane group CC<sub>4</sub> and the ethane-analogue atoms of C calculated density is 3.25 g/cm<sup>3</sup>. In addition, the B<sub>12</sub>C<sub>14</sub> = (B<sub>6</sub>C<sub>4</sub>)<sub>2</sub>(C<sub>6</sub>) carbide was constructed with paired arachno-B<sub>6</sub>C<sub>3</sub>H<sub>12</sub> clusters connected through cyclohexane cycles C<sub>6</sub>.

On the basis of non-icosahedral carborane  $B_8C_2H_{10}$ , sustainability comparable with icosahedral one yet theoretically constructed the only carbide – tetragonal  $B_8C_3 = (B_8C_2)C$  with density 2.58 g/cm<sup>3</sup> only slightly superior to the normal density.

We admit the possibility of the synthesis of certain predicted compounds under high pressures. Hardness of those compounds may be high enough for practical use, moreover, their semiconductor properties and resistance to radiation could be of interest.

## Unexpected synthesis of cobalt dicarbollides in organic acids

Sergey Dugin, Oleg Alexeyenko, Ella Gurkova, Marianna Kuznetsova, Alexander Kisin, Pavel Storozhenko, Vladimir Pasko

The State Research Center "State Research Institute for Chemistry and Technology of Organoelement Compounds", Russian Federation, Moscow, 38 Entuziasts Road, <u>18-7@eos.su</u>

Metallacarboranes were first synthesized in 1965.<sup>1,2</sup> Cobalt bis(1,2- and 1,7dicarbollides) were the first metallacarboranes synthesized. The classical approach to the synthesis of the cobalt dicarbollide consists in the deprotonation of *nido*-[7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] or *nido*-[7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>] with strong bases to dianions  $[7,8-C_2B_9H_{11}]^2$  or  $[7,9-C_2B_9H_{12}]^2$  followed by the reaction with cobalt (II) chloride (CoCl<sub>2</sub>). Usually the dicarbollide dianion is generated *in situ* by the treatment of *nido*-[7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> or *nido*-[7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> with sodium hydroxide in aqueous solution<sup>3,4</sup>, with sodium hydride in tetrahydrofuran,<sup>2,3</sup> with potassium *tert*-butoxide in 1,2-dimethoxyethane <sup>5</sup> or with *n*butyllithium in tetrahydrofuran.<sup>6</sup>

During the study of *nido*-[7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> and *nido*-[7,9-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> protonation, as well as search for new synthetic routes for dicarbollide transition metals, the atypical formation of cobalt dicarbollide by the interaction of cobalt acetate [Co(OAc)<sub>2</sub>·4H<sub>2</sub>O] with potassium and cesium *nido*-dicarbaundecaborates in the boiling organic acid medium (acetic and propionic) was established in our laboratory. The reaction products [*commo*-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] and [*commo*-2,2'-Co(1,7-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub>] in the form of potassium or cesium salts were formed with high yield (85-95% recrystallized product) under stirring of initial components in boiling acetic or propionic acid for 6 hours, followed by separation. In this case, the reaction proceeds with C-alkyl (aryl) and B-halogen substituted potassium and cesium *nido*-dicarbaundecaborates. The structure of the products was confirmed by the method of NMR spectroscopy (<sup>11</sup>B, <sup>1</sup>H and <sup>13</sup>C).

Thus, in our laboratory a new method for the synthesis of cobalt dicarbollides that allows gaining a new insight into the mechanism of metallacarboranes formation is developed.

## References

1. M.F. Hawthorne, D.C. Young, P.A. Wegner, J. Am. Chem. Soc. 1965, 87, 1818.

2. M.F. Hawthorne, T.D. Andrews, J. Chem. Soc., Chem. Commun. 1965, 443.

3. M.F. Hawthorne, D.C. Young, T.D. Andrews, D.V. Hove, R.L. Pilling, A.D. Pitts, M. Reinjes, L.F. Warren, P.A. Wegner, J. Am. Chem. Soc. **1968**, *90*, 879.

4. J.N. Francis, C.J. Jones, M.F. Hawthorne, J. Am. Chem. Soc. 1972, 94, 4878.

5. C. Viñas, J. Pedrajas, J. Bertran, F. Teixidor, R. Kivekäs, R. Sillanpää, *Inorg. Chem.* **1997**, 36, 2482. 6. T.E. Paxson, M.K. Kaloustian, G.M. Tom, R.J. Wiersema, M.F. Hawthorne, *J. Am. Chem. Soc.* **1972**, *94*, 4882.

## Mechanochemical synthesis of titanium, zirconium, and hafnium borohydrides for the purpose of chemical vapor deposition of ultra high temperature diboride films and composite materials production

Sergey Dugin<sup>a</sup>, Alexander Grebennikov<sup>a</sup>, Oleg Alexeyenko<sup>a</sup>, Ella Gurkova<sup>a</sup>, Marianna Kuznetsova<sup>a</sup>, Alexander Kisin<sup>a</sup>, Pavel Storozhenko<sup>a</sup>, Alexander Drachev<sup>a</sup>, Evgenii Bogachev<sup>b</sup>, Ivan Kolomiitsev<sup>b</sup>

<sup>a</sup> SRC "State Research Institute for Chemistry and Technology of Organoelement Compounds", Russia, 105118, Moscow, 38 Entuziasts Road, <u>18-7@eos.su</u>
<sup>b</sup> JSC "Kompozit", Russia, 141070, Moscow region, Korolev, 4 Pionerskaya Str., <u>info@kompozit-mv.ru</u>

Originally titanium, zirconium, and hafnium borohydrides were synthesized in the middle of the last century (1947-1949).<sup>1</sup> The increased interest in these compounds is due to their ability to form ultra thermostable borides at relatively low temperatures (150-250°C), which allows effective use of these products for the chemical vapor deposition (CVD) and production of composite materials capable for operating under extreme conditions.<sup>2</sup>

A conventional approach to the synthesis of IV-group metal borohydrides is a reaction of metal tetrachloride with aluminum or lithium borohydride.<sup>3,4</sup>

We have developed a method for producing of titanium, zirconium, and hafnium borohydrides by the interaction of titanium, zirconium or hafnium tetrachlorides with sodium borohydride, which proceeds under an inert atmosphere in an inert organic solvent (heptane, isooctane or decalin) in the presence of a catalytic amount of anhydrous lithium chloride. The process consists of the reaction mixture stirring in a planetary mill packed with ceramic (ZrO<sub>2</sub>) grinding balls during 60 minutes (20x3 at 30 min intervals) at 20-90°C followed by the filtration of final product solution. Also, the experiments on chemical vapor deposition of metal diborides directly from corresponding borohydride solutions were carried out.

The structure of synthesized compounds was confirmed by the method of <sup>11</sup>B-NMR spectroscopy. The resulting diboride films were analyzed by the method of scanning electron microscopy.

Thus, a new convenient method for the synthesis of titanium, zirconium, and hafnium borohydrides for the purpose of chemical vapor deposition of ultra thermostable diboride films for use in the aerospace industry is developed in our laboratory.

## References

1. H.R. Hoekstra, J.J. Katz: J. Am. Chem. Soc. 1949, 71, 2488.

2. E.P. Simonenko, D.V. Sevasť vanov, N.P. Simonenko, V.G. Sevasť vanov, N.T. Kuznetsov, Russ. J. Inorg. Chem. 2013, 58, 1669.

3. K. Franz, H. Fusstetter, H Noth. Z. Anorg. Allg. Chem. 1976, 427, 97.

4. A.P. Borisov, V.D. Makhaev, E.B. Lobkovskii, K.N. Semenenko, Zh. Neorg. Khim. 1986, 31, 86.

## Synthesis, structural, spectroscopic and cytotoxic studies of the BODIPY dyes

M. Laine,<sup>a</sup> A. Kochel,<sup>a</sup> B. Osiecka,<sup>b</sup> G. Szewczyk,<sup>c</sup> T. Sarna,<sup>c</sup> P. Ziółkowski,<sup>b</sup> R. Wieczorek,<sup>a</sup> <u>A. Filarowski</u><sup>a,d</sup>

<sup>a</sup> Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50-383 Wrocław, Poland

<sup>b</sup> Department of Pathology, Wroclaw Medical University, Marcinkowskiego 1, 50-368 Wroclaw, Poland

<sup>c</sup> Department of Biophysics, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian

University, 30-387 Cracow, Poland

<sup>d</sup> Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia,

aleksander.filarowski@chem.uni.wroc.pl

Three 4.4-difluoro-4-bora-3a.4a-diaza-s-indacene (BODIPY. Figure 1) dves have been synthesized and investigated by biological, spectroscopic, crystallographic and computational methods. The spectroscopic and structural properties of the dyes have been investigated with UV. steady-state fluorimetry and X-ray methods. The spectral features have been characterized with respect to DFT and TD-DFT calculations. The cvtotoxic and photocvtotoxic studies of the synthesized BODIPY dves on the colon cancer SW480 cells have been performed. 4.4-difluoro-8-[4-(methoxycarbonyl)phenyl]-1,3,5,7-tetramethyl-2-formyl-3a,4a-diaza-4-bora-s-indacene (1) with moderate cytotoxicity has been incubated with the colon cancer SW480 cells and investigated with a confocal spectroscopy. The photocytotoxicity of compound 1 on the colon cancer SW480 cells as function of the light dose and concentration of incubated dye has been studied. The synthesized compounds have been studied in terms of the singlet oxygen production. Detection of superoxide anion formation through Electron Paramagnetic Resonance (EPR) spin-trapping has been accomplished.



compound 1





compound 3

compound **2** Figure 1.

## Acknowledgements

This work was supported by KNOW-9 consortium and the Polish Plenipotentiary in JINR.

## Novel heterocyclic carboranes via direct C-C coupling of carboranyllithium and phthalazine-N-oxide

Lidiya Galliamova,<sup>a</sup> Olga Stepanova,<sup>a</sup> Mikhail Varaksin,<sup>a,b</sup> Oleg Chupakhin,<sup>a,b</sup> Valery Charushin<sup>a,b</sup>

<sup>a</sup> Ural Federal University, 620002, Ekaterinburg, Mira, 19.

<sup>b</sup> Institute of Organic Synthesis, 620990, Ekaterinburg, S. Kovalevskaya, 22, <u>chupakhin@ios.uran.ru</u>

Azaheterocyclic carboranes are of interest among boron-enriched organic compounds. At the same time, substances bearing phthalazine moiety possess a broad biological activities: anti-inflammatory, antibacterial, and anti-tumor properties. In the project, the reactivity of phthalazine-N-oxide and carboranyllithium in the C-H functionalization processes has been studied. As a result, various carborane derivatives **4a-d** have been synthesized.

It has been found that phtalazine-2-oxide **1** smoothly react with carboranyllithium **2**, the coupling products structures are determined by acylating agent used. These uncatalyzed by transition metals coupling reactions result in phthalazinylcarborane **4a** in 42 % yield, when trichloroacetyl chloride used as an acylating agent. In case of using the other halogen anhydrides **3b-d**, dihydrophthalazinyl carboranes **4b-d**, containing an N-oxide group in the heterocyclic fragment, have been obtained in 38-70% yields<sup>1</sup>.



Scheme 1. Synthesis of phtalazin-1-yl carborane 4a and dihydrophtalazinyl carboranes 4b-d.

## Acknowledgements

The study was financially supported by the Russian Science Foundation (Project № 14-13-01177) and the Russian Foundation for Basic Research (Project № 16-03-00958.

## References

1. L. Galliamova, M. Varaksin, O. Chupakhin, P. Slepukhin, V. Charushin, *Organometallics* 2015, 34, 5285-5290.

## Physicochemical studies of compositions based on liquid glass sodium silicates and the $[B_nH_n]^{2-}$ (n = 10, 12) boron cluster anions

Lyudmila Goeva<sup>a</sup>, Vera Skachkova<sup>b</sup>, Elena Malinina<sup>a</sup>, Nikolay Kuznetsov<sup>a</sup>

<sup>a</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,

<sup>b</sup> Semenov Institute of Chemical Physics, Russian Academy of Sciences,

4 Kosygin Str., Moscow, 119991 Russia

The compositions of sodium silicates of liquid glass (LG) and the  $[B_nH_n]^{2^-}$  (n = 10, 12) boron cluster anions were studied by IR spectroscopy, TGA, DSC, and TMA. The composites were prepared by reaction between triethylammonium *closo*-borate (Et<sub>3</sub>NH)<sub>2</sub>[B<sub>n</sub>H<sub>n</sub>] with aqueous LG at the following LG/[B<sub>n</sub>H<sub>n</sub>]<sup>2-</sup> ratios: 85/15 (I), 70/30 (II), 60/40 (III), 50/50 (IV), and 40/60 (V) (wt.%).

Because of the electronic structure of the  $[B_{10}H_{10}]^{2^{-}}$  and  $[B_{12}H_{12}]^{2^{-}}$  anions, they have different reactivity, which affects not only the process of interaction with LG silicates, but also thermal and thermomechanical properties of the reaction products. At  $T = 20-100^{\circ}$ C, the interaction is followed by removal of water, release of trimethylamine, and replacement of the Et<sub>3</sub>NH<sup>+</sup> cation by Na<sup>+</sup>. In the prepared materials,  $[B_{n}H_{n}]^{2^{-}}$  are involved in specific multicenter cation-anion interactions with silicate cations containing silanol groups  $(B-H^{\delta^{-}}....H^{\delta^{+}}-O-Si \ \mu \ B-H^{\delta^{-}}....Na^{\delta^{+}}-O-Si \ )$  and water molecules  $(B-H^{\delta^{-}}....H^{\delta^{+}}-O)$  resulting in uniform supramolecular structure.

In the LG/[B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> systems (I-II), along with the v(BH) band at 2460 cm<sup>-1</sup> there are v(BH)<sub>MHB</sub> bands in the range of 2360-2300 cm<sup>-1</sup> corresponding to 3c2e NaHB bonds. The relative intensity of v(BH)<sub>MHB</sub> bands as compared to v(BH) at 2460 cm<sup>-1</sup> increases with the growth of silicate content in the starting mixture. When t  $\geq$  400°C, the bands in the range of 2360-2320 cm<sup>-1</sup> disappeared indicating the degradation of specific contacts and release of low molecular weight silicates. In systems with a high content of LG (I-II), this reduces the deformation stability (450-500°C). In addition, formation of trace amounts of the [B<sub>12</sub>H<sub>11</sub>NEt<sub>3</sub>]<sup>-</sup> substituted derivative was observed during the triethylamine removing step in the LG/[B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> systems with a high content of the boron cluster (V-III). According to the TMA data, it has a plasticizing effect on the compositions.

Formation of substituted derivatives was not detected in the compositions based on the  $[B_{10}H_{10}]^{2^{\circ}}$  anion; they have deformation resistance up to 600°C.

Compositions based on  $LG/[B_nH_n]^2$  can be used to develop neutron-absorbing materials with high thermal stability.<sup>1</sup>

## Acknowledgements

This work was supported by The Presidium of the Russian Academy of Sciences No. 1 14 P.

## References

1. RU 2550156 07.04.2015, "Boron-containing neutron-absorbing material".

<sup>31</sup> Leninskii Prosp., Moscow, 119991 Russia; <u>lyudmila.goeva@mail.ru</u>

## Acid-base properties and alcoholysis of amine-boranes mediated by dihydrogen bonds

E. S. Gulyaeva<sup>a,b</sup>, I. E. Golub<sup>a</sup>, O. A. Filippov<sup>a</sup>, N. V. Belkova<sup>a</sup>, E. S. Shubina<sup>a</sup>

<sup>a</sup> A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, <u>shu@ineos.ac.ru</u>

<sup>b</sup> Department of Chemistry, M.V. Lomonosov Moscow State University, <u>elenor.kagami@gmail.com</u>

Gaseous hydrogen can be used as a fuel due to the high heat of combustion, low density and excellent chemical activity. Such kind of fuel is cost-effective and environmentally friendly. However, the problems of hydrogen storage and transportation are far from being solved.<sup>1,2</sup>

Nowadays amine-boranes ( $R_x^1$ NH<sub>(3-n)</sub>BH<sub>(3-y)</sub> $R_y^2$ ;  $R^1$ , $R^2$  = Alkyl, Ph) are considered as prospective materials for reversible hydrogen storage due to high H<sub>2</sub> volumetric and gravimetric density of these compounds.<sup>3,4</sup> Amine-boranes as well as other BNH bifunctional compounds containing both an acidic and basic group are capable to hydrogen evolution at heating due to existence of dihydrogen bonds BH<sup>5-...+δ</sup>HN between acidic and basic functional groups.<sup>5,6</sup> The investigation of such compounds can help to solve one of the most pressing problems related to utilization of the lightest element as an energy carrier.

In view of these problems, the interactions of NH<sub>3</sub>BH<sub>3</sub> (AB), (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>BH<sub>3</sub> (TBAB), and (CH<sub>3</sub>)<sub>2</sub>NHBH<sub>3</sub> (DMAB) with a number of proton donors and organic bases were studied in dichloromethane, tetrachloromethane, nitromethane and acetone. Formation of hydrogen-bonded complexes (intermediates of proton transfer reaction) was observed by variable temperature FTIR and NMR spectroscopy (190-300 K). Proton accepting ability of BH ligands and proton donating ability of NH groups were characterized by logansen rule of factors ( $\Delta H = \Delta H_{11} \cdot P_i \cdot E_j$ ). The acidity factor  $P_i$ (NH) is 0.26 (AB) < 0.51 (DMAB)  $\approx$  0.52 (TBAB) The basicity factor  $E_j$ (BH) is 0.60 (DMAB) < 0.80 (t-BuAB) < 0.98 (AB). The reaction products were isolated and characterized by X-ray diffraction. The results obtained were used to rationalize possible mechanisms of amine-boranes alcoholysis.<sup>7</sup>

## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (projects № 16-03-00324 and 16-33-01070).

## References

1. U. Eberle, M. Felderhoff, F. Schueth, Angew. Chem. Int. Ed. 2009, 48, 6608-6630.

2. W.I.F David, Faraday Discuss 2011, 151, 399-414.

3. T.B. Marder, Angew. Chem. Int. Ed. 2007, 46, 8116-8118.

4. J. Zhang; J. Lee, Korean J. Chem. 2012, 29, 421-431.

5. G. Moussa, R. Moury; U.B. Demirci; T. Şener, P. Miele, Int. J. Energ. Res. 2013, 37, 825-842.

6. T. Richardson; S. de Gala; R.H. Crabtree; P.E.M. Siegbahn, J. Am. Chem. Soc. 1995, 117, 12875-12876.

7. I.E. Golub, E.S. Gulyaeva, O.A. Filippov, V.P. Dyadchenko, N.V. Belkova, L.M. Epstein, D.E. Arkhipov, E.S. Shubina, *J. Phys. Chem. A*, 2015, **119**, 3853-3868.

## 1*H*-2,1-Benzazaborolyl radicals and aromatic anions - highly reactive species leading to molecules with exceptional C-C bond

## Martin Hejda, Libor Dostál

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ - 532 10, Pardubice, Czech <u>Republic,martin.hejda@student.upce.cz</u>

Recently, we have describe the synthesis of the first 1*H*-2,1-benzazaborolyl anion in form of its potassium salt, utilizing redox transformation in the backbone of the redoxactive *C*,*N*-chelating ligand of *C*,*N*-chelated chloroborane.<sup>1</sup> Further inspection of this  $6\pi$ -aromatic anion containing a B-N bond revealed the extreme reactivity towards various reactants, but also towards starting *C*,*N*-chelated chloroborane. Now we were able to characterize the respective neutral radical which is the unstable species during formation of the mentioned aromatic anion. Termination of these neutral 1*H*-2,1-benzazaborolyl radicals lead to dimers - molecules which show quite extraordinary behaviour of the C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bond at the junction.



Figure 1. 1*H*-2,1-benzazaborolyl radical (left) and  $6\pi$ -aromatic anion (right).

## Acknowledgements

The authors wish to thank the Grant Agency of the Czech Republic project No. P207/12/0223.

## References

1. M. Hejda, R. Jambor, A. Růžička, A. Lyčka, L. Dostál, Dalton Trans. 2014, 43, 9012-9015.
# Recent progress in the development of halogenated building blocks based on *closo*-decaborate and *closo*-dodecaborate anions

Josef Holub,<sup>a</sup> Mario Bakardjiev,<sup>a</sup> Tomáš Jelínek,<sup>b</sup> Zdeňka Růžičková,<sup>c</sup> Detlef Gabel,<sup>d</sup> Bohumír Grüner<sup>a</sup>

<sup>a</sup> Institute of Inorganic Chemistry, CAS v.v.i., Husinec-Řež 1001, 250 68 Řež, Czech Republic

<sup>b</sup> Katchem Ltd., Elišky Krásnohorské 6, 110 00 Prague 1, Czech Republic

<sup>c</sup> University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic

<sup>d</sup> Jacobs University, Campus Ring 1, 28759 Bremen, Germany

The chemistry of halogenated cluster species has been studied since the first syntheses of polyhedral boron compounds.<sup>1</sup> Currently, it receives particular attention due to the high kinetic stability of cage-B-X (X= F, Cl, Br, I) bonds. Additionally, halogenation of borane cages can be used to tune physicochemical properties (stability, polarity, lipophilicity, pK<sub>a</sub>, solubility, electrochemical, etc.). Due to these properties, the salts of highly halogenated borane compounds are being considered for application as solid electrolytes in lithium and magnesium batteries, low nucleophilic anions,<sup>2</sup> materials and hydrophobic pharmacophores in medicinal chemistry.

In this contribution, we report on procedures that facilitate easy perhalogenation of basic 10- and 12-vertex borate anions. New preparative methods for perhalogenation of the  $[B_{10}H_{10}]^{2-}$  ion that produce  $[B_{10}X_{10}]^{2-}$  species (X= CI, Br, I) have been developed starting from old original procedures.<sup>1</sup> In addition to this series, we have more recently focused on synthetic procedures to derivatives with mixed substitutions - borane anions consisting of at least one sufficiently reactive functional group that further enables the anchoring of the halogenated cage into structures of materials, drugs or biomolecules, or on solid supports. Thus, a series of  $[2-NH_3-B_{10}X_9]^-$ ,  $[1-HO-B_{12}X_{11}]^-$ ,  $[1-NH_3-B_{12}X_{11}]^-$  (X= CI, Br, I) halogenated anions was successfully prepared, along with some polyhalogenated diamines of the latter, icosahedral ion. The spectral, structural and physicochemical properties of these halogenated compounds are outlined along with basic insight into reactivity and substitution chemistry at the reactive sites of these compounds.



Figure 1. Crystal structure of the [1-NH<sub>3</sub>-B<sub>12</sub>I<sub>11</sub>] salt incorporating sodium atoms with an unusual coordination of acetonitrile ligands.

#### Acknowledgements

The support from the Czech Technology Agency (Project No. TH 01020844) is highly appreciated.

#### References

1. W.H. Knoth, H.C. Miller, J.C. Sauer, J.H. Balthis, Y.T. Chia, E.L. Muetterties, *Inorg. Chem.* 1964, 3, 159.

2. S.V. Ivanov, J.J. Rockwell, O.G. Polyakov, Ch.M. Gaudinski, O.P. Anderson, K.A. Solntsev, S.H. Strauss, *J. Am. Chem. Soc.* **1998**, *120*, 4224, and the references therein.

# Boron stuffing increases the strength of carbon and boron nanotubes, an *ab*-initio study

## Naiwrit Karmodak, E. D. Jemmis

#### Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

Carbon nanotubes have become material of choice for admiring strength. The strong near  $sp^2 - sp^2$  C-C bond and the ideal hexagonal graphite structure contribute to the properties of carbon nanotubes.<sup>1</sup> Here we present ways to stuff carbon nanotubes with adjacent element boron which reinforces the properties of carbon. The carbon nanotube is stuffed by incorporation of linear chain of icosahedral C2B10 unit, bounded by extra boron atoms through  $\eta^3$  and  $\eta^2$  connectivity. Even more interestingly, we notice that the stuffed boron nanotube, designed from the B<sub>84</sub> fragment of  $\beta$ -rhombohedral boron has greater strength than the hollow  $\alpha$ -boron tubes.<sup>2</sup> A density functional theory based approach has been implemented to study the electronic and mechanical properties of these stuffed carbon and boron nanotubes. The stuffing changes the symmetry and the bonding pattern of the hollow boron fullerenes.<sup>3</sup> Thus, much changes in the mechanical strength and the electronic properties has also been observed for these nanotubes. Both the stuffed carbon and boron nanotubes show metallic electronic behavior at the Fermi level. In addition, the incorporation of boron core enhances the Young's modulus of the hollow nanotubes by about 1.5 times.<sup>4</sup> Thus, our effort opens up a new direction towards building stronger one-dimensional nanomaterials.



Figure 1. Stuffed boron and carbon nanotubes.

#### References

1. S. lijima, Helical microtubules of graphitic carbon. Nature 1991, 354, 56-58.

2. A.K. Singh, A. Sadrzadeh, B.I. Yakobson, Probing properties of boron  $\alpha$ -tubes by ab initio calculations. *Nano Lett.* **2008**, *8*, 1314-1317.

3. (a) D.L.V.K. Prasad, E.D. Jemmis, Stuffing improves the stability of fullerenelike boron clusters. *Phys. Rev. Lett.* **2008**, *100*, 165504; (b) D.L.V.K. Prasad, E.D. Jemmis, Stuffed fullerenelike boron carbide nanoclusters. *Appl. Phys. Lett.* **2010**, *96*, 023108.

4. A. Krishnan, E. Dujardin, T. Ebbesen, P. Yianilos, M. Treacy, Young's modulus of single-walled nanotubes. *Phys. Rev. B* **1998**, *58*, 14013.

## Chemistry of the decachloro-closo-decaborate anion

Irina Kochneva,<sup>a</sup> Varvara Avdeeva,<sup>a</sup> Eleonora Kravchenko,<sup>a</sup> Anna Vologzhanina,<sup>b</sup> Nikolay Kuznetsov<sup>a</sup>

 <sup>a</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii Prosp., Moscow, 119991, Russia, <u>malinina@igic.ras.ru</u>
 <sup>b</sup> Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences 28 Vavilov Str., Moscow, 119991, Russia

Reactivity of boron cluster anions  $[B_nH_n]^{2-}$  (n = 10, 12) and their substituted derivatives are now relatively well studied in both substituted reactions and complexation. Information on chemistry of the corresponding perhalogenated derivatives  $[B_nH_n]^{2-}$ , which can be found in the literature, is fragmented. Meanwhile, our analysis of some physicochemical characteristics of the anion  $[B_{10}CI_{10}]^{2-}$  such as its size, charges on the terminal chlorine atoms, reducing properties of the anion, softness according Pearson allow us to consider the  $[B_{10}CI_{10}]^{2-}$  anion as a potential ligand.

A number of salts  $Cat_2[B_{10}Cl_{10}]$  with alkali metals, alkyl ammonium or phosphonium cations were synthesized and characterized. Structure, properties, and general rules of formation were determined for a number of mono- and polynuclear metal complexes with the  $[B_{10}Cl_{10}]^{2^{\circ}}$  anion and organic ligands L or solvents.

It has been found that the nature of the complexing metal, the ligand L, and the ratio of components have a pronounced effect on the composition and structure of the complexes formed. For Co(II) and Mn(II), mononuclear [ML<sub>3</sub>][B<sub>10</sub>Cl<sub>10</sub>] or binuclear  $[M_2(\mu-Cl_2)L_4][B_{10}Cl_{10}]$  complexes can be isolated depending on the M:L ratio. Tetranuclear Cu(II) complex  $[Cu_4(Phen)_4(OH)_4][B_{10}CI_{10}]$ and mononuclear  $[Cu(Bipy)_3][B_{10}Cl_{10}], [Fe(Bipy)_3][B_{10}Cl_{10}] and [Cu(Bipy)_2Cl]_2[B_{10}Cl_{10}] were isolated$ depending on reaction conditions. A series of complexes with NH<sub>3</sub>, Ph<sub>3</sub>P, DMF, H<sub>2</sub>O ligands were isolated and studied by X-ray and other diffraction:  $[Cu(NH_3)_4(CH_3CN)_2][B_{10}CI_{10}], [Ag(NH_3)_2]_2[B_{10}CI_{10}],$  $[Aq(Ph_3P)_3(H_2O)]_2[B_{10}CI_{10}],$ [Co(DMF)<sub>6</sub>][B<sub>10</sub>Cl<sub>10</sub>].

Among the synthesized complexes, compounds  $[Ag_2(DMF)_2[B_{10}CI_{10}]]$ ,  $(Et_3NH)_2[B_{10}CI_{10}]$ , and  $(Ph_4P)_2[B_{10}CI_{10}]$  should be noted. The relatively short Ag-Cl bonds and the CI....H-X specific contacts, where X = N, O, C, were revealed by X-ray diffraction. <sup>35</sup>Cl NQR spectroscopy was first applied to identify the nature of the interactions; the <sup>35</sup>Cl NQR measurements were performed at 19 and 77K on a home-built phase coherent pulsed NMR/NQR spectrometer.

From the obtained results, it can be concluded that the  $[B_{10}CI_{10}]^{2-}$  anion can act as both an outer-sphere ligand or a ligand of second coordination sphere due to formation of specific contacts Ag-Cl and/or Cl....H-X.

## Acknowledgements

This work was supported by the Russian Science Foundation, Grant No. 14-13-01115.

# New conjugate of chlorin e<sub>6</sub> with iron bis(dicarbollide)

<u>Yulia S. Korostey</u>, <sup>a,b</sup> Anastasija A. Ignatova, <sup>a,c</sup> Mikhail A. Grin, <sup>b</sup> Andrey F. Mironov, <sup>b</sup> Igor B.Sivaev, <sup>d</sup> Vladimir I. Bregadze, <sup>d</sup> Alexey V. Feofanov<sup>a,c</sup>

<sup>a</sup> Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, 16/17 Miklukho-Maklay Str., 117997, Moscow, Russia

<sup>b</sup> Moscow Technological University, 78 Vernadskii Prosp., 119571, Moscow, Russia

<sup>c</sup>Biological Faculty, Lomonosov Moscow State University, 1 Vorobyevi Gori, 119991, Moscow, Rissia

<sup>d</sup> Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,

28 Vavilov Str., 119334, Moscow, Russia

New conjugate of aminoamide chlorin  $e_6$  with iron bis(dicarbollide) was synthesized (Figure 1), and its biological properties were investigated. Due to the conjugation of high efficiency photosensitizer chlorin  $e_6$  with iron bis(dicarbollide) nanocluster comprising 18 boron atoms, the synthesized conjugate can be considered as a binary agent for photodynamic (PDT) and boron neutron capture therapy (BNCT) of cancer.

Biological properties of the conjugate were studied on a rat glioblastoma C6 cell culture using ethods of laser scanning confocal microscopy and confocal microspectroscopy. It was shown that the conjugate accumulates effectively in rat glioblastoma C6 cells with K = 88 (K is a distribution factor, i.e. the ratio of the average cytoplasmic concentration of a conjugate to its extracellular concentration). It provides intracellular concentration of  $10^9$  boron atoms per cell, which is required for successful BNCT. The conjugate has a high photo-induced cytotoxicity: LD<sub>50</sub> = 35 nM, LD<sub>90</sub> = 80 nM (the concentrations that provide 50% and 90% photoinduced cells death), thus surpassing effective second-generation photosensitizers, which are based on chlorophyll *a* derivatives.Fluorescence in a red region together with high accumulation in cancer cells allows one to consider the new conjugate as a prospective candidate for theranostics.



Figure 1. Conjugate of aminoamide chlorin e6 with iron bis (dicarbollide).

# The synthesis of <sup>10</sup>B and hyaluronic acid polychelates and their biological distribution in mice with melanoma B-16 tumor

Sergey N. Koryakin,<sup>a</sup> Stepan E. Ulyanenko,<sup>a</sup> Evgeny E. Beketov,<sup>a</sup> Sergey A. Uspenskiy,<sup>b</sup> Elena V. Isaeva,<sup>a</sup> Mikhail A. Selyanin<sup>b</sup>

<sup>a</sup> A. Tsyb Medical Radiological Research Centre - Branch of the National Medical Research Radiological Centre of the Ministry of Health of the Russian Federation, Obninsk, Russia <u>korsernic@mail.ru</u>

<sup>b</sup> Martinex Research Centre, Moscow, Russia

The use of neutron radiation and specific preparations providing local dose escalation in a tumor due to secondary radiation improves the efficacy of radiation therapy and reduces the risk of surrounding tissues damages. Basic requirements for agents for neutron capture therapy include: high tumor tropism (concentration gradient is higher than 3), accumulation in the tumor is not lower than 30  $\mu$ g/g and low toxicity (high therapeutic index).

The aim of this work was the synthesis of compounds based on hyaluronic acid and stable isotope <sup>10</sup>B and the study of biological distribution homogeneity in mice with melanoma B-16.

The substances used: hyaluronic acid MM = 1000 kDa, WT = 11 % specific IR spectra and borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>•10H<sub>2</sub>0) synthesized from enriched isotope <sup>10</sup>B. Experiments were carried out on male mice (50 animals) F1(CBAxC<sub>57</sub>Bl<sub>6</sub>), 20-22 g with B-16 melanoma cells in their paw. When tumor volume gained 0.8-1.2 cm<sup>3</sup> the boron compound was introduced to mice intratumorally at the concentration of 300 micrograms per tumor. At various times after the injection (0.25-24 h) mice were decapitated under anesthesia. The tumor samples were collected as well as other tissues and analyzed for boron content. It was shown using Raman and FT-IR spectroscopy that the acid in the tested compound according to the developed technology of hyaluronic acid and sodium decahydroborate solid state modification using Bridgman Anvil device acts as a boron oxide polydentate ligand. The content of <sup>10</sup>B in the synthesized compound was 3.0 ± 0.5 mg/ml.

In 15 min after the intratumoral administration of the tested compound the boron concentration in the tumor was up to 55 mg/g (~ 18 % of injected). The analysis of the dynamics of compound distribution in the tumor showed pronounced two-exponential dependence with tissue half-lives of the compounds for the fast and slow phase of 0.7 and 5.2 hours, respectively. These results indicate that the compound has no tumor tropism properties. The greatest accumulation of boron were observed in the skin (15 min after the administration – 11.7 % of the injected; and in the liver, kidneys and muscles – in the range of 3.9 - 4.3 %; in blood, spleen and lungs – 1.7 - 0.7 % of the injected. Thus in 24 hours after the administration of the boron content (per 1 g) in the skin and muscle is decreased by less than 1 %, in other tissues – it was less than 0.5 % of the injected.

It was concluded that the most favorable time for neutron capture therapy, based on clinical practice and the accumulation of the tested compound is 15-30 min after the administration. The content of <sup>10</sup>B in the tumor was 55-30 mg/g, tumor/blood concentration gradient varied from 11 to 3.

The use of a non-toxic boron compound based on hyaluronic acid for the aims of neutron capture therapy requires the further research connected with enhance of its tumor tropism.

# Reactions of bromine-bridged cobalt bis(1,2-dicarbollide) with arenes and nucleophiles\*

Irina Kosenko, Andrey Semioshkin, Julia Laskova, Ivan Ananyev, Vladimir Bregadze

A.N.Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, <u>kosenko@ineos.ac.ru</u>

Generation of Br-bridged complex of cobalt bis(1,2-dicarbollide) (8,8'- $\mu$ -Br-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>) (1)<sup>1</sup> and its reactions with arenes and some nucleophiles were studied. Complex 1 was generated *in situ* by an action of 8-monobromo derivative of cobalt bis(1,2-dicarbollide) and AlX<sub>3</sub> (X=Cl, Br) in various aromatic solvents. This unstable complex was characterized by <sup>11</sup>B NMR technique for the first time. Its reactions with an appropriate arene led to [8-Br-8'-Ar-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> species even without an addition of activating Lewis base. Reactions of 8,8'- $\mu$ -Br-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> species for the corresponding charge compensated derivatives (8-Br-8'-Y-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>) and [8-Br-8'-Ph-3,3'-Co(1,2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>]<sup>-</sup> species respectively.





#### Acknowledgements

This work was supported by Russian Foundation for Basic Research (16-03-00724, Synthesis) and Russian Science Foundation (14-13-00884, X-Ray study).

#### References

1. J. Plešek, B. Štíbr, S. Heřmánek, Collect. Czech. Chem. Commun. 1984, 49, 1492.

\* In memory of Dr. Irina Lobanova

# Formation and rearrangement of bimetallic rhodium-ruthenium complexes containing $\{C_2B_9\}$ -carborane ligand

Alexander Kostyukovich, Dmitrii D`yachihin, Ivan Godovikov, Fedor Dolgushin, Alexander Smol`yakov, Igor Chizhevsky

A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, 28 Vavilov Street, 119991, Moscow, Russian Federation, chizbor.ineos.ac.ru

As part of our attempts to prepare heterometallic metallacarboranes of platinum metals exo-nido-ruthenacarboranes **1a-1d** were synthesized and further successfully used as precursors, according to the reaction scheme outlined below. Thus, **1a-1d** reacted readily in benzene with 16-e ( $\eta^4$ -NBD)Rh(acac) in the presence of AcOH at ambient temperature to give series of bimetallic Rh<sup>1</sup>-Ru<sup>II</sup> zwitterionic complexes **2a-2c** and **3**, respectively, in 55-85% yields. Both Rh and Ru atoms in these zwitterionic complexes have 18-electron configurations and are coordinated with the carborane cage ligand via {C<sub>2</sub>B<sub>3</sub>}-pentagonal open face, in the case of the RhNBD-moiety, and by three 2e,3c bond (B-H)<sub>3</sub>...M system, in the case of the Ru(PPh<sub>3</sub>Cl) fragment. Spontaneous ``1,2→1,7`` polyhedral rearrangement was observed in the reaction of **1d** with ( $\eta^4$ -NBD)Rh(acac), which eventually yielded isomerized complex [*exo*-{10,11,12-{Ru(PPh<sub>3</sub>)<sub>2</sub>Cl}-10,11,12-( $\mu$ -H)<sub>3</sub>}-2,2-(2,5- $\eta^4$ -C<sub>7</sub>H<sub>8</sub>)-1,8-Ph<sub>2</sub>-2,1,8-*closo*-RhC<sub>2</sub>B<sub>9</sub>H<sub>6</sub>] **3** as the main product. All structures of the synthesized compounds have

 $RhC_2B_9H_{6}$ ] 3 as the main product. All structures of the synthesized compounds have been established on the basis of analytical and multinuclear NMR data and a singlecrystal X-ray diffraction study of 3.



Figure 1. Molecular structure of 3.

## Acknowledgements

This work has been supported by Grant No 15-03-08415 from the Russian Foundation for Basic Research.

```
EUROBORON 7
```

# Physicochemical properties of human insulin conjugated with boron cluster

Konrad Kowalski,<sup>a</sup> Krzysztof Fink,<sup>a</sup> Zbigniew J. Leśnikowski,<sup>b</sup> Janusz Boratyński<sup>a</sup>

<sup>a</sup> Laboratory of Biomedical Chemistry, Institute of Immunology and Experimental Therapy, Polish Academy of Sciences, 12 Rudolf Weigl Street, 53-114 Wrodaw, Poland.
<sup>b</sup> Laboratory of Molecular Virology and Biological Chemistry, Institute of Medical Biology, Polish Academy of Science, 106 Lodowa Street, 93-232 Łódź, Poland

Nowadays, the use of boron clusters as pharmacophores creates new opportunities in innovative biopharmaceutical drug design. Thanks to their remarkable features, like chemical stability, low toxicity, ability to form dihydrogen bonds (proton-hydride bonds) and an amphiphilic character this compounds seems to be ideal for modification of bioactive macromolecules.

Although that synthesis of protein - boron cluster conjugates as boron rich boron donors for BNCT was extensively studied and is well described in literature there is still lack of knowledge about direct influence of boron clusters on carrier molecule. Studies performed previously in our laboratory, on boron clusters conjugates with hen egg lysozyme proved dramatic change in their physiochemical and biochemical properties. Conjugates showed an increased tendency to self-aggregation and most likely also interaction with other proteins and polysaccharides.<sup>1,2</sup>

Long-acting insulin analogues have a huge impact on the quality of life for diabetic patients. Modifying human insulin rate of absorption is nowadays one of the major challenges of diabetes. Protein multimerization being the result of  $Zn^{2+}$  ions coordination and the interaction with serum albumin are two the most widely used strategies for prolongation of insulin half-life.

Performed studies are based on both synthesis of single substituted metallocarborane conjugate on human insulin and detailed analysis of their physiochemical and biochemical properties. The analysis performed using LC-MS, CD and DLS techniques compared metallocarborane insulin analog with others commercially available long-acting insulin analogues.<sup>2</sup>

#### References

K. Kowalski, T.M. Goszczyński, Z.J. Leśnikowski, J. Boratyński, *ChemBioChem* 2015, *16*, 424-431.
 T.M. Goszczyński, K. Kowalski, Z.J. Leśnikowski, J. Boratyński, *Biochim. Biophys. Acta* 2015, *1850*, 411-418.

# Methods of obtaining *closo*-decaborate anion sulfanyl derivative and its reactivity study

A.S. Kubasov,<sup>a</sup> E.Yu. Matveev,<sup>a,b</sup> I.N. Polyakova,<sup>a</sup> K.Yu. Zhizhin,<sup>a,b</sup> N.T. Kuznetsov<sup>a</sup>

<sup>a</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Russia, 31 Leninskii Prosp.,11991, Moscow, Russia, <u>fobosax@mail.ru</u>

<sup>b</sup> Moscow Technological University, 86 Vernadskii Prosp., 119571, Moscow, Russia

Features of neutron capture therapy of malignant tumors (NCT) have been actively studied for more than half a century. At the same time clinical studies generally concern NCT using boron-10 compounds. The major achievements in clinical practice have been currently obtained using derivatives of boron cluster compounds. This is due to the high mass content of boron in the resulting compounds, non-toxicity of *closo*-borate anions and the existence of a variety of modification methods. Sulfur-containing substituted derivatives of *closo*-dodecaborate anion (e.g., sodium sulfanyl-*closo*-dodecaborate) can successfully act as compounds for <sup>10</sup>B-NCT malignancies. The synthesis of such derivatives of other *closo*-borate ions is also relevant, as they provide a useful synthon for further modifications.<sup>1</sup>

In this work we have investigated the reaction of  $[B_{10}H_{11}]$  with thiourea and thioamide. Thus derivatives of the *closo*-decaborate anion equatorial location of exopolyhedral substituents were obtained. The reaction of tetrabutylammonium salt of *closo*-decaborate anion with tetramethylurea (TMTU) and dimethylthioformamide (TDMF) proceeds in the presence of a Bronsted acid (TFA) in dichloromethane and is complicated by the formation of byproducts.<sup>2</sup> Similar reactions with the participation of  $[B_{10}H_{11}]$  do not require the presence of acid, flow faster and lead to a higher yield of the desired products. Obtained substituted derivatives were restored by hydrazine to the sulfanyl derivative  $[B_{10}H_9SH]^2$ . The advantages of the developed synthetic procedures of this compound are selectivity and higher yields compared to previously known. The alkylation reaction and acylation of the obtained sulfanyl derivative by alkyl and aryl halides have been studied. Features and regularities of these reactions



Scheme 1.

## Acknowledgements

This work was supported by the President Grant RF MK-7075.2016.3.

#### References

N.T. Kuznetsov, I.G. Belaya (Makarenko), A.V. Dolganov, G.E. Zelinskii, E.Yu. Matveev, K.Yu. Zhizhin, Ya.Z. Voloshin, Yu.N. Bubnov, *Russ. Chem. Bull.* 2011, 60, 2518.
 A.S. Kubasov, E.Yu. Matveev, I.N. Polyakova, G.A. Razgonyaeva, K.Yu. Zhizhin, N.T. Kuznetsov, *Russ. J. Inorg. Chem.* 2015, 60, 198.

**EUROBORON 7** 

# closo-Dodecaborate containing amines. Synthesis and properties. Conjugates with non-natural nucleosides

<u>Julia Laskova</u>,<sup>a</sup> Andrey Semioshkin,<sup>a</sup> Alexandra Kozlova,<sup>a</sup> Vladimir Bregadze,<sup>a</sup> Zbigniew J. Leśnikowski<sup>b</sup>

<sup>a</sup> A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences <sup>b</sup> Institute for Medical Biology, Polish Academy of Sciences <u>laskova@ineos.ac.ru</u>

We report synthesis and investigation of *closo*-dodecaborate based ammonium salts **1-4** (Scheme 1).



Next we synthesized first bis(*closo*-dodecaborate) species with amino group tethered *via* linkers of different types **5**, **6** (Scheme 2) via alkylation the compounds **2** and **3**.



Scheme 2.

Previously only a few examples of species, containing two or more *closo*-dodecaborate units in one molecule have been reported.<sup>1-2</sup>

Ammonium derivative **1** was also successfully applied for the synthesis of the first conjugates of  $[B_{12}H_{12}]^{2^{-}}$  with non-natural nucleoside 7-deaza-8-aza-2'-deoxyadenosine (Scheme 3).



Biological investigations of the compounds 5-7, will be also communicated.

## Acknowledgements

This work was partially supported by Russian Foundation for Basic Research (Grant 14-03-00042).

#### References

1. A. Semioshkin, O. Tsaryova, O. Zhidkova, V. Bregadze, D. Wöhrle, *J. Porphyrins Phthalocyanines*, **2006**, *10*, 1293-1300.

2. H. Koganei, S. Tachikawa, M.E. El-Zaria, H. Nakamura, New J. Chem., 2015, 39, 6388-6394.

# Iridium halide complexes with C-substituted charge-compensated dicarbollide [2-SMe<sub>2</sub>-2,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup>: Synthesis and reactivity

Alexander P. Molotkov, Dmitry A. Loginov, Alexander R. Kudinov

#### A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russian Federation, <u>dloginov@ineos.ac.ru</u>

Metallacarborane halide complexes [CarbMX<sub>2</sub>]<sub>2</sub> are known to be useful synthons of the [CarbM]<sup>2+</sup> fragments in organometallic synthesis and catalysis. For example, rhodium and iridium complexes with B-substituted charge-compensated dicarbollide [9-SMe<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> proved to be effective catalysts for C-H activation.<sup>1</sup> Recently we shown that reaction of [(cod)IrCl]<sub>2</sub> with C-substituted dicarbollide [7-SMe<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup> is accompanied by polyhedral rearrangement of the carborane ligand giving 1-cod-8-SMe<sub>2</sub>-1,2,8-IrC<sub>2</sub>B<sub>9</sub>H<sub>10</sub> (1).<sup>2</sup>

In this work we found that treatment of **1** by hydrohalogenic acids affords the halide complexes  $[1,1-X_2-8-SMe_2-1,2,8-IrC_2B_9H_{10}]_2$  (X = Br (**2a**), I (**2b**)).



Scheme 1.

Subsequent reaction of **2a** with TI[TI(7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)] leads to the unsymmetrical complex 1,1'-Ir(8-SMe<sub>2</sub>-2,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(2,3-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>) **(3)** containing two different dicarbollides. Noteworthy, similar reaction of **2a** with TICp is accompanied by partial demethylation of the SMe<sub>2</sub> group giving iridacarborane 1-Cp-8-SMe-1,2,8-IrC<sub>2</sub>B<sub>9</sub>H<sub>10</sub> **(4)**. The structures of complexes **3** and **4** were determined by X-ray diffraction.



Figure 1. Structures of iridacarboranes 3 and 4.

## Acknowledgements

This work was supported by Russian Foundation for Basic Research (grant # 15-03-04057a).

## References

1. D.A. Loginov, A.R. Kudinov et al., J. Organomet. Chem. 2015, 793, 232-240.

2. D.A. Loginov, V.I. Bregadze, A.R. Kudinov et al., Inorg. Chem. Commun. 2015, 51, 80-82.

**EUROBORON 7** 

# First polynuclear copper complexes with $[B_{12}H_{12}]^{2^{2}}$ and ligands L (L = *bipy*, *phen*): synthesis, structure and properties

Elena Malinina, Irina Polyakova, Lyudmila Goeva, Nikolay Kuznetsov

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii Prosp., Moscow, 119991, Russia, <u>malinina@igic.ras.ru</u>

Complexes  $[Cu_2(L)_4(\mu-CO_3)][B_{10}H_{10}]$  were isolated from the reaction solutions as a result of redox in systems  $[Cu_2[B_{10}H_{10}]]/(phen)$  in a mixture of CH<sub>3</sub>CN and DMSO or DMF and  $[Ag_2[B_{10}H_{10}]]/Cu^*/bipy$  in a mixture of DMF and DMSO. Amoung the synthesized complexes, phen-containing compounds, namely  $[Cu_2(phen)_4(\mu-CO_3)]B_{10}H_{10}\cdot2.5DMSO\cdot2H_2O$  (I) and  $[Cu_2(phen)_4(\mu-CO_3)]B_{10}H_{10}\cdot4DMF$  (II) have attracted our attention. The cations in I and II have different spatial orientations of the Cu-O bonds: *anti-syn* and *anti-anti*, respectively. Compound I has weak magnetic interactions caused by a short Cu...Cu distance (4.441 Å) in the dimer. No exchange coupling is observed in II.

Bridging µ-CO3 group compounds, binuclear Cu(II) complexes [Cu2(L)4(µ- $CO_3$ ]B<sub>12</sub>H<sub>12</sub> and trinuclear complex {[Cu(*bipy*)<sub>2</sub>]<sub>3</sub>(µ-CO<sub>3</sub>)}B<sub>12</sub>H<sub>12</sub>, were formed in the  $Cu^{+}/[B_{12}H_{12}]^{2}/L/DMF$  system as a result of redox reactions. According to the electron paramagnetic resonance and magnetic susceptibility data, in the dimer complex  $[Cu_2(o-phen)_4(\mu-CO_3)]B_{12}H_{12}$ ·DMF (III), with anti-syn coordination of  $\mu$ -CO<sub>3</sub> group, antiferromagnetic interaction between Cu(II) atoms is observed. Cu...Cu distance is 5.107 Å for the dimer. Exchange interactions for the trimer complex  $\{[Cu(bipy)_2]_3(\mu-$ CO<sub>3</sub>)}(B<sub>12</sub>H<sub>12</sub>)<sub>2</sub>·4DMF (IV) are significantly weaker. The reaction between Cat[Cu[B<sub>12</sub>H<sub>12</sub>]] and phen in CH<sub>3</sub>CN lead to the heterovalent complex {[Cu<sup>ll</sup>(phen)<sub>3</sub>][Cu<sup>l</sup>(phen)<sub>2</sub>]<sub>2</sub>}[B<sub>12</sub>H<sub>12</sub>]<sub>2</sub> (V). Tri- and four-nuclear Cu(II) complexes with  $[B_{12}H_{12}]^{2}$  were isolated in the presence of two complexing metals Ag(I) and Cu(I) from the  $[Aq_2[B_{12}H_{12}]]/Cu^+/bipv$  system in a mixture of DMF and CH<sub>3</sub>CN and from the [CsAa[B<sub>12</sub>H<sub>12</sub>]]/Cu<sup>+</sup>/phen system in DMF: compounds {[Cu(bipy)<sub>2</sub>]<sub>3</sub>(u- $CO_3$ }[B<sub>12</sub>H<sub>12</sub>]<sub>2</sub>·4DMF (IV) and [Cu<sub>4</sub>(phen)<sub>4</sub>(µ-OH)<sub>4</sub>)(DMF)<sub>2</sub>][B<sub>12</sub>H<sub>12</sub>] (VI) were formed, respectively.

The peculiarity of the preparation of complexes Cu (II) in the presence of anions  $[B_nH_n]^{2^-}$  primarily determined by their reducing ability and can be characterized quantitatively by the corresponding electronic chemical potential values (Parr's absolute electronegativity):  $\mu(B_{10}H_{10}^{2^-}) = 6.09 \text{ eV}$  and  $\mu(B_{12}H_{12}^{2^-}) = 5.50 \text{ eV}$  (using DFT at B3LYP/6-31+G\* level).



a)

Figure 1. The structure of complexes I (a) and II (b).

## Acknowledgements

This work was supported by the Russian Science Foundation, Grant No. 14-13-01115.

# *N*-(Fluorophenyl)piperazine derivatives of 2-formylphenylboronic acid

Alicja Matuszewska, Krzysztof M. Borys, Karolina Czerwinska, Agnieszka Adamczyk-Wozniak, Izabela D. Madura, Andrzej Sporzynski

Faculty of Chemistry, Warsaw University of Technology, spor@ch.pw.edu.pl

Piperazine is the second most common scaffold in medicines registered by FDA<sup>1</sup> till 2013. Compounds containing piperazine moiety exhibit high potency as anti-cancer, anti-depressant and anti-bacterial drugs<sup>2,3</sup>. Substituted *N*-(phenyl)piperazines were found to significantly increase inhibition of acetylocholinoesterase<sup>4</sup> and glucose detection<sup>5</sup>. Moreover, substitution on phenyl ring can be used to enhance selectivity of pharmacophores. Phenylboronic acids and benzoxaboroles containing piperazine unit are promising receptors of biologically important analytes, such as sugars or catecholamines<sup>6</sup>. Benzoxaboroles themselves are also very promising anti-fungal agents<sup>7</sup>.

*N*-(Fluorophenyl)piperazine derivatives of 2-formylphenylboronic acid have been obtained and characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>11</sup>B NMR, <sup>19</sup>F NMR.



Figure 1. Crystal structures of *N*-(fluorophenyl)piperazine derivatives of 2-formylphenylboronic acid.

## Acknowledgements

This work has been supported by the EU in the framework of European Social Fund through the Warsaw University of Technology Development Programme, by the scholarship awarded by the Center of Advanced Studies for Alicja Matuszewska.

## References

1. R.D. Taylor, M. MacCoss, A.D.G. Lawson, J. Med. Chem. 2014, 57, 5845.

2. A. Khalaj, N. Adibpour, A.R. Shahverdi, M. Daneshtalab, Eur. J. Med. Chem. 2004, 39, 699.

3. A. Adamczyk-Woźniak, K. Czerwińska, I. D. Madura, A. Matuszewska, A. Sporzyński, A. Żubrowska-Zembrzuska, *New. J. Chem.* **2015**, *39*, 4308.

4. P. Piplani, C.C. Danta, *Bioorg. Chem.* 2015, 60, 64.

5. M.F. Khan, P. Kumar, J. Pandey, A.K. Srivastava, A.K. Tamrakar, R. Maurya, *Bioorg. Med. Chem. Lett.* **2012**, *22*, 4636.

6. A. Adamczyk-Woźniak, K.M. Borys, I.D. Madura, A. Pawełko, E. Tomecka, K. Żukowski, New J. Chem. 2013, 37, 188.

7. A. Adamczyk-Woźniak, K.M. Borys, A. Sporzyński, Chem. Rev. 2015, 115, 5224.

# Synthesis and biological properties of bacteriochlorin based nanoconjugate with cobalt bis(dicarbollide)

<u>S. O. Pasynkova</u>,<sup>a,b</sup> A. A. Ignatova,<sup>b,c</sup> A. F. Mironov,<sup>a</sup> M. A. Grin,<sup>a</sup> I. B. Sivaev,<sup>d</sup> V. I. Bregadze,<sup>d</sup> A. V. Feofanov<sup>b,c</sup>

<sup>a</sup> Moscow Technological University, 78 Vernadskii Prosp.,119571, Moscow, Russia

<sup>b</sup> Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences,

16/10 Miklukho-Maklay Str., 117997, Moscow, Russia

<sup>c</sup> Biological Faculty, Lomonosov Moscow State University, 1 Vorobyevi Gor, 119991, Moscow, Russia <sup>4</sup>A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,

28 Vavilov Str., 119991, Moscow, Russia

Active development of bimodal approaches to cancer treatment occurs during last decade including boron neutron capture therapy (BNCT) and photodynamic therapy (PDT). In this paper we report on a synthesis of a new conjugate suitable for BNCT and PDT, in which cobalt bis(dicarbollide) is attached to natural bacteriochlorin via the combined diethyleneglycol-aminohexamethyleneamide linker. Synthesis was performed using nucleophilic cleavage of the E ring in bacteriopheophorbide *a* methyl ester. It was shown that addition of the linker to boron cluster followed by interaction of the product, aminoalkyl derivative of cobalt bis(dicarbollide), with natural bacteriochlorin is an optimal way for synthesis of this conjugate.

It was found that the conjugate penetrates efficiently and quickly into rat C6 glioblastoma cells, stains cytoplasm diffusely and accumulates in cytoplasmic granular structures. Maximal ratio of an average cytoplasmic concentration of the conjugate to its extracellular concentration is very high and equal to 184±9. Providing delivery of more than 10<sup>9</sup> boron atoms per cell the conjugate meets an essential requirement to a BNCT agent. Conjugate absorbs light in the 760 nm region and possesses photoinduced cytotoxicity at nanomolar concentrations that allow one to classify it as a prospective IR-photosensitizer for enhanced photodynamic treatment of pigmented and deeply located tumors. Additionally, conjugate fluorescence can be used for tumor diagnostics and navigation.



Figure 1. Structure of conjugate of bacteriochlorin with cobalt bis(dicarbollide).

# A study of the permeation of cobalt bis(dicarbollide) and its conjugates with biologically relevant molecules through planar bilayer lipid membranes

Tatyana I. Rokitskaya,<sup>a</sup> Yuri N. Antonenko,<sup>a</sup> Anna A. Druzina,<sup>b</sup> Andrey A. Semioshkin,<sup>b</sup> Igor B. Sivaev,<sup>b</sup> Vladimir I. Bregadze<sup>b</sup>

<sup>a</sup> Belozersky Institute of Physico-Chemical Biology, Lomonosov Moscow State University, Moscow 119991, Russia

<sup>b</sup> Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Str., 119991, Moscow, Russia

In recent years carboranes and their derivatives are increasingly used not only for boron neutron capture therapy of cancer but also for enhancing the permeability of different pharmacologically active compounds through cell membranes (i.e. pharmacophores). In this regard we compared the ability of the most used anionic carboranes - cobalt bis(dicarbollide) (COSAN) and monocarborane - to penetrate through planar bilayer lipid membranes (BLM). The translocation rate constants through the hydrophobic part of the lipid bilayer membranes were estimated by the method of electrical current relaxation. They were 9.4 and 0.05 s<sup>-1</sup> for COSAN and monocarborane, respectively, for membrane formed from diphytanylphosphatidyl-choline. The rate of the penetration of COSAN conjugate with tyrosine and 2'-deoxyuridine was assessed by the electric current value and turned out to be significantly less than for COSAN anion. However, the rate exceeded substantially the permeability of non-conjugated tyrosine and 2'-deoxyuridine.

The ability of the studied compounds to penetrate through the BLM was also explored by measurements of the diffusion potential when creating a concentration gradient across planar bilayer lipid membranes. A 3-fold concentration difference caused potential difference of  $30\pm4$  mV,  $26\pm2$  mV,  $26\pm5$  mV and  $39\pm8$  mV on the BLM for COSAN, monocarborane, COSAN conjugate with tyrosine and COSAN conjugate with 2'-deoxyuridine, respectively. These values are close to the theoretical values according to Nernst equation.

Thus, COSAN can serve as a locomotive for penetration of biologically important hydrophilic molecules through the lipid membranes.

## Acknowledgements

This work was supported in parts by the Russian Science Foundation grants 16-03-00724 and 16-14-10025, the Russian Foundation for Basic Research grant 15-04-01688 and stipendium of the President of Russian Federation (Grant SP-1023.2015.4) (AD).

# Carboranes as protonophores and uncouplers of oxidative phosphorylation in mitochondria

Tatyana I. Rokitskaya,<sup>a</sup> Ljudmila S. Khailova,<sup>a</sup> Anton V. Makarenkov,<sup>b</sup> Valentina A. Ol'shevskaya,<sup>b</sup> Valery N. Kalinin,<sup>b</sup> Yuri N. Antonenko<sup>a</sup>

<sup>a</sup> Belozersky Institute of Physico-Chemical Biology, Lomonosov Moscow State University, Moscow, Russia

<sup>b</sup> Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia

ortho-Carborane (1,2-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, a cluster composed of boron, carbon and hydrogen atoms) was found to be a carrier of protons in lipid membranes and membranes of mitochondria suggesting that it can reversibly release hydrogen ions and diffuse through the membrane in neutral and anionic forms. Similar to classical uncouplers, it stimulated mitochondrial respiration and decreased the membrane potential at concentrations of tenths of micromoles. Pyranine-loaded liposomes and planar lipid bilayers (BLM) were used as a proton transport assay. *Meta*-isomer, 1,7-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>, having two carbons separated in cluster by boron atom lacked protonophoric activity. The activities of 1-methyl-o-carborane and especially 1-benzyl-o-carborane on bilayer

lipid membrane and pyranine-loaded liposomes were found to be more pronounced compared to the pristine molecule. However, 1-benzyl-o-carborane exhibited both protonophoric activity and inhibition of succinate-dehydrogenase on mitochondria and hardly can be regarded as effective uncoupler.

The finding of new class of uncoupling compounds is of substantial interest owing to anti-obesity and anti-diabetic properties of uncouplers.

#### Acknowledgements

This work was supported in part by the Russian Science Foundation grant 16-14-10025 and the Russian Foundation for Basic Research grant 15-04-01688.

# μH-Tautomeric behavior of substituted 7,8-dicarba-*nido*undecaborates and correlations in the <sup>11</sup>B NMR spectra

**Dmitry Rudakov** 

The Institute of Physical Organic Chemistry of the NAS of Belarus, deach@list.ru

 $\mu$ H-tautomeric behavior of mono-substituted carborane anions [9-X-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] is determined by the signal position of atoms B(5) and B(6). More about this is written in the review article of Hermanek.<sup>1</sup>

From the analysis of a large number of <sup>11</sup>B NMR spectra of mono- and polysubstituted compounds of anion [7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub>]<sup>-</sup> synthesized by us and described in literature there was found a correlation that more clearly reflects the position of the terminal  $\mu$ H-atom to the substitutes.



In the graph symbol ( $\Box$ ) marks the compounds with the location of  $\mu$ N-atom in position B(10)- $\mu$ H-B(11), and the symbol ( $\star$ ) - compounds with the location of  $\mu$ N-atom in the position B(9)- $\mu$ H-B(10)). H-tautomeric equilibrium and reaction behavior of the cluster is caused by a set of spatial factors of the substitute and reaction particles and the reagent activity. Donor properties of the substitute at the C-atom may be leveled by its steric properties and direct the attack of the substrate in a remote position from the substitute.

Separately, there were obtained the expected NMR <sup>11</sup>B spectra of the not synthesized hitherto fluorinated compounds: [n-F-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>-</sup> (n = 5, 9), [9,11-F<sub>2</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]<sup>-</sup>. It was found that the literature data of spectra [1,5,6-F<sub>3</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>9</sub>]<sup>-</sup> and [1,5,6,10-F<sub>4</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>]<sup>-</sup> are different from the expected ones. We believe that this is due to a change in acidic properties of  $\mu$ H-atom and fixing by NMR method of dianions such as 8,9,12-F<sub>3</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>]<sup>2-</sup> and [8,9,10,12-F<sub>4</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>7</sub>]<sup>2-</sup>, as we recorded on the example of the anions [8,9,10,12-X<sub>4</sub>-1,2-C<sub>2</sub>B<sub>9</sub>H<sub>7</sub>]<sup>2-</sup> and [1,5,6,10-X<sub>4</sub>-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>8</sub>] (X = CI, Br, I).

#### References

1. S. Hermanek. Chem. Rev. 1992, 92, 325.

**EUROBORON 7** 

# Halogenation of salts $Me_4N^{+}[9-X-7,8-C_2B_9H_{11}]^{-}$ (X = SCN, CI) and structure of $Me_4N^{+}[9-Br-11-CI-7,8-C_2B_9H_{10}]^{-}$

Dmitry Rudakov,<sup>a</sup> Olga Kazheva,<sup>b</sup> Vladimir Potkin<sup>a</sup>

<sup>a</sup> The Institute of Physical Organic Chemistry of the NAS of Belarus, <u>deach@list.ru</u> <sup>b</sup> The Institute of Problems of Chemical Physics of the RAS, <u>koh@icp.ac.ru</u>

We synthesized a number of little-studied asymmetrical B(9) and B(11)-disubstituted 7,8-dicarba-*nido*-undecaborates that are of interest for the purposes of BNCT, and in terms of research of their H-tautomeric behavior.

The action of elementary iodine or bromide iodine on thiocyanate  $Me_4N^+[9-SCN-7,8-C_2B_9H_{11}]^- 1$  resulted in derivative  $Me_4N^+[9-SCN-11-I-7,8-C_2B_9H_{10}]^- 2$  with a yield of 10% and 32% depending on the reagent. Similarly, the action of an excess of elemental iodine on  $Me_4N^+[9-CI-7,8-C_2B_9H_{11}]^- 3$  in methanol at boiling resulted in  $Me_4N^+[9-CI-11-I-7,8-C_2B_9H_{10}]^- 4$  with a yield of 70%. The action of 2.5 equivalents of bromosuccinimide on **3** in acetonitrile at boiling resulted in bromo-chloro derivative  $Me_4N^+[9-CI-11-Br-7,8-C_2B_9H_{10}]^- 5$  with a yield of 41%.



The composition and structure of compounds were confirmed by elemental analysis and IR, <sup>1</sup>H, <sup>11</sup>B, <sup>11</sup>B, <sup>11</sup>B, <sup>11</sup>B COSY NMR spectra.

Structure **5** was confirmed by X-ray spectral analysis. Also the population of position B(10) by a light atom, apparently, a chlorine atom, with a distance of 1.906(8)Å was detected.



## Bond distance, Å

Br1...B11 1.930(8) Cl1...B11 1.880(12) Br2...B9 1.972(7) Cl2...B9 1.736(12) Cl3...B10 1.906(8) C7...C8 1.535(8) C8...B9 1.566(9) B9...B10 1.779(10) B11...B10 1.817(9)

# Synthesis and study of melamine dodecahydro-closo-dodecaborate half-hydrate

Vitaly Saldin, Vasily Sukhovey, Natalia Savchenko, Lidia Ignatieva

Institute of Chemistry, The Far-Eastern Branch, Russian Academy of Sciences, sald@ich.dvo.ru

2,4,6-Triamine-1,3,5-triazine (melamine,  $C_3H_6N_6$ ) is one of the well-known products applied in different industrial fields. Its structure contains 6 donor nitrogen atoms and, as a result, can form salts with acids. Some of them are of interest as starting compounds for obtaining hexagonal boron nitride, nanoporous composites based on graphitic carbon nitride  $C_3N_4^{1,2}$  with important practical applications.

The objective of the present work was to study the interaction of  $C_3H_6N_6$  with dodecahydro-*closo*-dodecaboric acid  $H_2B_{12}H_{12}$  and the products formed in this process.

Interaction of  $C_3H_6N_6$  with an aqueous solution of  $H_2B_{12}H_{12}$  was carried out at components molar ratios 2 : 1÷3 and temperatures 40-50°C under stirring using a magnetic stirrer. Solutions were filtered after cooling until room temperature. The obtained precipitates and filtrates underwent chemical analysis and physical-chemical studies.

The chemical analysis of the precipitate on the content of  $B_{12}H_{12}^{2-}$ -anion suggests the formation of a compound of the following composition ( $C_3H_6N_6H)_2B_{12}H_{12}$ ·0.5H<sub>2</sub>O (I). The X-ray studies of I indicate to formation of a new compound.

The IR spectroscopic studies demonstrate a substantial difference of IR spectra of initial  $C_3H_6N_6$  and I. An emergence of the band in the range 2500-2400 cm<sup>-1</sup> that is characteristic for the stretching vibrations of the B-H bond indicates to inclusion of the  $B_{12}H_{12}^{2^-}$ -anion into the structure of I. Moreover a splitting of  $v_{B-H}$  of the  $B_{12}H_{12}^{2^-}$ -anion, which is clearly expressed (2447, 2516, 2469, 2456 cm<sup>-1</sup>) and a noticeable change in the IR spectrum of the  $C_3H_6N_6$  suggests the presence of significant cation-anion interaction. The bands at 1650 and 1635 cm<sup>-1</sup> ( $\delta NH_2$ ) (in the spectrum of the  $C_3H_6N_6$ ) become shifted to 1666 and 1647 cm<sup>-1</sup> (in the spectrum of I), respectively, which is characteristic of cations protonated on the cycle nitrogen atom<sup>3,4</sup>. The presence of the crystalline water upon in the structure of I is confirmed by the absorption band at 3560 cm<sup>-1</sup>.

The solubility of **I** in water has been determined: it is equal to 0.3 g per 100 g of water at 20°C. The solubility of **I** in ethanol is an order of magnitude lower.

According to the thermogravimetry data of I the crystalline water upon the removal takes place at a temperature of about 190°C. Further weight loss begins in the region of 250°C.

Simplicity of fabrication of  $(C_3H_6N_6H)_2B_{12}H_{12}$  and affordability of melamine enable one to consider the compound as a promising energy-rich component distinguished by improved thermal stability, which requires further studies.

## References

1. Y. Xu, W.De, Eur.J.Inorg. Chem. 2015, 1744.

2. J. Shen, H.Yang, Q.Shen, Y.Feng, Q.Cai, H.Yang, Eur. J. Inorg. Chem. 2015, 2618.

3. Physical methods in chemistry of heterocyclic compounds. Ed. by A.P. Katritsky, Khimia, Moscow-Leningrad. **1966**, 658.

4. A.I. Konovalov, I.S. Ryzhkina, L.I. Murtazina et al., Russ. Chem. Bull. 2008, 57, 1231.

# Direct observation of activation of hypervalent iodanes by BF<sub>3</sub>: structure and reactivity of PhI(OAc)<sub>2</sub>•BF<sub>3</sub>

Susana Izquierdo,<sup>a</sup> Pietro Vidossich,<sup>b</sup> Agustí Lledós,<sup>b</sup> Alexandr Shafir<sup>b</sup>

<sup>a</sup> Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007, Tarragona, Spain, <u>ashafir@iciq.es</u>

<sup>b</sup> Department of Chemistry, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain

Hypervalent organoiodanes are a common class of reagents in organic synthesis and are used in a wide range of transformations.<sup>1</sup> Frequently, the use of Lewis acid, most notably BF<sub>3</sub>·OEt<sub>2</sub>, renders such species more reactive, or may even alter the reactivity of the iodane. In the case of the ubiquitous PhI(OAc)<sub>2</sub>, the coordination of BF<sub>3</sub> to one of the acetate "ligands" is generally assumed to be responsible for this activation effect. However, such putative BF<sub>3</sub> complex has, until now, never been observed.

Our recent work on the oxidative arene-arene coupling<sup>2</sup> using a combination of  $PhI(O_2CCF_3)_2$  and  $BF_3 \cdot Et_2O$  has led us to take a deeper look at this phenomenon. Indeed, while the coupling takes place in 1 h at -78 °C, no reaction takes place in the absence of  $BF_3 \cdot Et_2O$ . Now, for the first time, we provide direct spectroscopic and structural evidence for the  $PhI(OAc)_2 \cdot BF_3$  complex, including its isolation and X-ray structure determination. Implications of the  $BF_3$  binding on iodane reactivity are also discussed. Effects of  $BF_3$  coordination have also been explored by DFT calculations, confirming the increased Lewis-acidity of the resulting iodine center.



Figure 1. Synthesis of the activated hypervalent iodine species PhI(OAc)<sub>2</sub>·BF<sub>3</sub>.

## Acknowledgements

We thank Spain's MINECO (CTQ2013-46705-R, CTQ2014-54071-P) for funding and the Cellex Foundation for postdoctoral contract to S.I.

## References

1. A. Yoshimura, V.V. Zhdankin, Chem. Rev. 2016, 116, 3328-3435.

2. (a) E. Faggi, R.M. Sebastián, R. Pleixats, A. Vallribera, A. Shafir, A. Rodríguez-Gimeno, C. Ramírez de Arellano, *J. Am. Chem. Soc.* **2010**, *132*, 17980-17982; (b) W. Guo, E. Faggi, R.M. Sebastián, A. Vallribera, R. Pleixats, A. Shafir, *J. Org. Chem.* **2013**, *78*, 8169-8175.

# Synthesis of cobalt bis(dicarbollide) derivatives with short spacer between the boron cage and terminal functional group

Akim Shmal'ko,<sup>a,b</sup> Marina Stogniy,<sup>a</sup> Igor Sivaev,<sup>a</sup> Leonid Kovalenko,<sup>b</sup> Vladimir Bregadze<sup>a</sup>

<sup>a</sup> A. N. Nesmevanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Str., 119991, Moscow, Russia
 D. I. Mendeleev Russian Chemical Technological University, 9 Miusskaya Sq., 125047, Moscow,

Russia, akimBend@yandex.ru

The 1.4-dioxane derivative of cobalt bis(dicarbollide) reacts with dialkylsulfides and triphenylphosphine giving the corresponding sulfonium and phosphonium derivatives  $[8-L(CH_2CH_2O)2-3.3'-Co(1.2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})]$  (L = SMe<sub>2</sub>, S(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, PPh<sub>3</sub>). The treatment of the triphenylphosphonium derivative with sodium hydroxide results in contraction of the side chain with formation of [8-HOCH<sub>2</sub>CH<sub>2</sub>O-3,3'-Co(1,2- $C_2B_9H_{10}(1^2,2^2-C_2B_9H_{11})^{-1}$ . The same product was obtained on the treatment of the dimethylsulfonium derivative with poorly nucleophilic base t-BuOK, whereas the stronger nucleophiles induce the sulfur demethylation to give [8-MeS(CH<sub>2</sub>CH<sub>2</sub>O)2- $3.3^{\circ}$ -Co(1.2-C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)(1<sup>{\circ}</sup>.2<sup>{\circ}</sup>-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)]. The alcohol was used for synthesis of a series [8-XOCH<sub>2</sub>CH<sub>2</sub>O-3.3'-Co(1.2of other short-spacer functional derivatives  $C_2B_9H_{10}(1',2'-C_2B_9H_{11})$  (X = SH, N<sub>3</sub> NH<sub>2</sub>).<sup>1</sup>



Scheme 1.

The similar contraction of the disclosed 1,4-dioxane ring via the reactions with SMe<sub>2</sub> and PPh<sub>3</sub> can be used for synthesis of short-spacer functional derivatives of nidocarborane.

## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (16-03-00724).

## References

1. A.V. Shmal'ko, M.Yu. Stogniv, G.S. Kazakov, S.A. Anufriev, I.B. Sivaev, L.V. Kovalenko, V.I. Bregadze, Dalton Trans. 2015, 44, 9860.

**EUROBORON 7** 

# Some reactions of 1,1'-bis(ortho-carborane)

Igor B. Sivaev,<sup>a</sup> Grigorii S. Kazakov,<sup>a</sup> Vladimir I. Bregadze,<sup>a</sup> Alan J. Welch<sup>b</sup>

<sup>a</sup> A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences 28 Vavilov Str., 119991, Moscow, Russia
<sup>b</sup>Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

The hydroxy derivative of bis(*ortho*-carboranyl)fluorene (A) was synthesized by the reaction of dilithium derivative of 1,1'-bis(*ortho*-carborane) with ethyl formate. Both the hydroxy and the CH groups in the compound A were found to demonstrate more acidic character than similar groups in known bis(*ortho*-carboranyl)methanol (B), that can be explained by an increase of electron-withdrawal effect of the carboranyl substituent due to connection with the second carboranyl fragment.



Acidity

The parent 1,1'-bis(*ortho*-carborane) itself can be easily deboronated in the presence of water as nucleophile to give *closo-nido*-bis(carborane). Halogenation of *closo-nido*-bis(carborane) was studied. The chlorination reaction with *N*-chloro-succinimide proceeds highly regioselectively, whereas the reactions with elementary bromine and iodine are regiospecific.



## Acknowledgements

This work was supported by the Russian Foundation for Basic Research (15-03-05822).

# New efficient method for the synthesis of water-soluble derivative of boron cluster anion $1,2-[B_{12}H_{10}(OH)_2]^{2^2}$

Grigoriy Sukhorukov,<sup>a</sup> Aleksandr Ogarkov,<sup>a</sup> Andrey Chernyavskiy,<sup>a</sup> Sergey Sakharov,<sup>a,b</sup> Konstantin Solntsev<sup>a</sup>

<sup>a</sup> Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences <sup>b</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences

The first stage of the development of BNCT preparations based on polyhedral  $[B_{12}H_{12}]^{2-}$  boron anion consists in the introduction of primary substituent (reaction site) in the *closo*-dodecaborate system, which subsequently can be modified. In the present study, efficient method for the synthesis of *closo*-dodecaborate anion derivative in using hydroxyl group as the primary substituent is suggested.

An original method for the synthesis of water-soluble  $1,2-[B_{12}H_{10}(OH)_2]^{2-}$  cluster boron anion derivative via the alkaline hydrolysis of product of the reaction between the bis(tetrabutylammonium) dodecahydro-*closo*-dodecaborate (2-) and benzene-1,2dicarboxylic acid melt at temperatures of 190-195 °C in a dry argon atmosphere is developed. In the reaction under consideration, benzene-1,2-dicarboxylic acid is both reagent and solvent. The synthesis was performed using the tetrabutylammonium salt, which is sufficiently soluble in benzene-1,2-dicarboxylic acid. The nucleophilic attack of benzene-1,2-dicarboxylic acid molecule to boron skeleton was found to be realized almost simultaneously on two sites with the formation of only a dihydroxy derivative. The attack of substrate with more than one benzene-1,2-dicarboxylic acid molecule is limited by the temperature of melting (accompanied by decomposition) of benzene-1,2-dicarboxylic acid. It was shown that the regioselectivity under considered synthesis conditions is determined by the geometry of used reagent, namely, benzene-1,2-dicarboxylic acid. Product was identified by elemental analysis, IR spectroscopy, and <sup>11</sup>B NMR spectroscopy.



Figure 1. Scheme of reaction between the bis(tetrabutylammonium) dodecahydro-*closo*-dodecaborate (2-) and benzene-1,2-dicarboxylic acid melt at temperatures of 190-195 °C in a dry argon atmosphere.

# Orientation effect of substituent during subsequent substitution in $[B_{12}H_{12}]^{2}$ cluster anion

Grigoriy Sukhorukov,<sup>a</sup> Aleksandr Ogarkov,<sup>a</sup> Andrey Chernyavskiy,<sup>a</sup> Sergey Sakharov,<sup>a,b</sup> Konstantin Solntsev<sup>a</sup>

<sup>a</sup> Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences

<sup>b</sup> Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences

Reactions of the following monosubstituted derivatives of dodecahydro-*closo*-dodecaborate (2-) anion were studied:

•Reaction of  $[B_{12}H_{11}]^2$ ,  $[B_{12}H_{11}OH]^2$ ,  $[B_{12}H_{11}OC(O)CH_3]^2$ , and  $[B_{12}H_{11}SCN]^2$  with acetic acid in the presence of oxygen and atmospheric moisture. The single-stage procedure of the hydroxy group introduction into monosubstituted  $[B_{12}H_{12}]^2$  anion derivatives without the formation of acetoxo derivatives is developed.

• Reaction of  $[B_{12}H_{11}I]^2$ ,  $[B_{12}H_{11}OH]^2$ ,  $[B_{12}H_{11}OC(O)CH_3]^2$ , and  $[B_{12}H_{11}SCN]^2$  with formic acid in an inert atmosphere.

• Reaction of  $[B_{12}H_{11}]^{2^{-}}$ ,  $[B_{12}H_{11}OH]^{2^{-}}$ ,  $[B_{12}H_{11}OC(O)CH_{3}]^{2^{-}}$ , and  $[B_{12}H_{11}SCN]^{2^{-}}$  with dimethyl sulfoxide in the presence of acetic anhydride in an inert atmosphere.

• Reaction of  $[B_{12}H_{11}I]^{2^{-}}$ ,  $[B_{12}H_{11}OH]^{2^{-}}$  and  $[B_{12}H_{11}OC(O)CH_{3}]^{2^{-}}$  with  $(SCN)_{2}$  solution in dichloromethane in an inert atmosphere.

It was found for the reactions under consideration that substituents have the electronseeking effect and decrease the reactivity of monosubstituted anions as compared to that of  $[B_{12}H_{12}]^2$ .

The reactions under consideration were shown to have the regioselective character. The I, OH, OC(O)CH<sub>3</sub> and SCN substituents are meta-orientants with respect to the introduced OH, OC(O)H and S(CH<sub>3</sub>)<sub>2</sub> groups and the OH, OC(O)CH<sub>3</sub> substituents are meta-orientants with respect to the introduced SCN group. In the case of the reaction of thiocyanogenation of monoiodosubstituted derivative of  $[B_{12}H_{11}I]^{2-}$ , the 1,12- $[B_{12}H_{10}I(SCN)]^{2-}$  para-isomer is formed.

It was found that the introduction of hydroxyl group into monosubstituted derivatives of  $[B_{12}H_{12}]^{2^{-1}}$  increases substantially their water solubility as compared to that of non-substituted anion.

Data on the synthesis of disubstituted derivatives of cluster  $[B_{12}H_{12}]^{2-}$  boron anion and on the orientation effect of substituents can be used in developing BNCT preparations in the case of two biologically active substituents introduced into the boron skeleton of molecule.

## Chelate synthesis of steroids containing heterocyclic fragments

V. A. Present, I. V. Zavarzin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky Prosp., 119991 Moscow, Russia, <u>zavi@ioc.ac.ru</u>

An approach to the synthesis of earlier unknown steroids containing heterocyclic fragments is proposed. Diphenylboron complex **1** is synthesized for the first time by the action of diphenylboric acid butyl ester on 17-amino-16-acetylfndrost-16-en-3-ol **2**. The acetyl group activated in the boric chelate easily reacts with amide acetals to form the corresponding condensation product **3**, which is the key substance for the construction of a wide series of earlier inaccessible heterocyclic systems.





Scheme 1.

## References

1. V.A. Dorokhov, M.A. Present, V.C. Bogdanov, Russ. Chem. Bull. 1994, 43, 832.

2. V.A. Dorokhov, M.A. Present, Russ. Chem. Bull. 1994, 43, No. 12, 2091.

# A new method of bioinorganic system synthesis based on nucleophilic addition of aminoacids derivatives to [2-B<sub>10</sub>H<sub>0</sub>NCR]<sup>-</sup> (R = Me. Et. <sup>t</sup>Bu. Ph) anion

Andrey P. Zhdanov,<sup>a</sup> Alexey V. Nelvubin,<sup>a,b</sup> Konstantin Yu. Zhizhin,<sup>a</sup> Nikolav T. Kuznetsov<sup>a</sup>

<sup>a</sup> Kurnakov Institute of General and Inorganic Chemistry, Rusian Academy of Sciences, Moscow, Russia, zhizhin@igic.ras.ru

<sup>b</sup> Moscow Technological University, Moscow, Russia

An important aspect of boron compounds application, in particular, of higher boron hydride anions is <sup>10</sup>B-NCT of malignant tumors. Thus such boron drugs should be capable to accumulate selectively in tumor cells: so biologically active compounds and fragments of biomolecules etc. are most selected transport groups.

In this work, the method for preparation of substituted derivatives of *closo*-decaborate anion containing in the structure amino acid fragments was proposed. Thus, the process of nucleophilic addition of amino acids esters to the nitrilium derivatives [2- $B_{10}H_9NCRI$  was investigated (R = Me. Et. <sup>t</sup>Bu. Ph). Reactions occur under mild conditions (MeCN, 80°C, 1 h) and in quantitative vields (on the boron).



R = Me, Et, <sup>t</sup>Bu, Ph R₁ = H, Bn

Furthermore, we proposed and optimized a method of functionalization of free amino acids in water-alcohol solution. N-iminoacylation reaction of certain alighatic and aromatic amino acids proceeds in the presence of acetate buffer (pH = 6.0), and at the ratio of anion  $[2-B_{10}H_9NCR]^2$  / amino acid = 1 / 2.



A significant advantage of this process is the simplicity of the apparatus, high yields and ease of product isolation. The received data allow us to consider the proposed approach as a perspective for the creation of products for <sup>10</sup>B-NCT.

## Acknowledgements

This study was supported by RFBR, research project №/№ 16-33-60182 mol a dk, 16-03-01039 a and by the Council for Grants of the President of the Russian Federation, project MK-4654.2016.3.

# The mechanism of formation, crystal structure and biological activity of 3,5-di(phenyl-o-carboranyl)buterolide

<u>Yerlan Suleimen,</u><sup>a</sup> Alexandr Kazantsev,<sup>b</sup> Kristof Van Hecke,<sup>c</sup> Zharkyn Ibatayev,<sup>a</sup> Zhanar Iskakova,<sup>a</sup> Kydyrmolla Akatan,<sup>d</sup> Sana Kabdrahmanova<sup>d</sup>

<sup>a</sup> The Institute of Applied Chemistry, L.N. Gumilyov Eurasian National University, Astana, Republic of Kazakstan, <u>suleimen\_em@enu.kz</u>
<sup>b</sup> Central Kazakstan Academy, Karagandy, Republic of Kazakstan
<sup>c</sup> XStruct, Department of Inorganic and Physical Chemistry, Ghent University, Ghent, Belgium, <u>Kristof, VanHecke@UGent.be</u>

<sup>d</sup> S. Amanzholov East Kazakstan State University, Ust-Kamenogorsk, Republic of Kazakstan, <u>ahnur.hj@mail.ru</u>

Synthesis was done on the basis of 2-phenyl-*o*-carboranyl lithium **1** according to Scheme **1**. The structure of compound **2** was determined by single-crystal X-ray analysis and NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>13</sup>C Dept, <sup>1</sup>H-<sup>1</sup>H (COSY), <sup>1</sup>H-<sup>13</sup>C (HSQC, HMBC)). It has been found that lactone **2** has high antioxidant activity in comparison with butylhydroxyanisole (DPPH-method).



Figure 2. Molecular structure of 2

## Will borophene outperform graphene?

A. Dudek,<sup>a</sup> N. Gonzalez Szwacki<sup>b</sup>

<sup>a</sup> Centre of New Technologies, University of Warsaw, <u>a.dudek@cent.uw.edu.pl</u>

<sup>b</sup> Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, gonz@fuw.edu.pl

Motivated by a recent experimental evidence that single-atom layer boron sheets with hexagonal vacancies, called borophenes, can be produced on metallic substrates,<sup>1</sup> we conducted a detailed computational analysis involving all the theoretically anticipated and experimentally obtained 2D boron structures.

Using first principles calculations, we established that the key mechanism that accounts for the stabilization of 2D boron structures (over 3D ones) on metallic substrates is the charge transfer from the substrate to the layer. In general, negative charge stabilizes 2D boron structures over 3D geometries, whereas positive charge makes bulk structures energetically more feasible. Moreover, the amount of the negative charge that is transferred may serve as a parameter that controls the type of structure that is formed on the substrate.

The second purpose of this work was to compare the properties of one specific form of borophene denoted as the  $\beta$ -sheet, which is predicted by theory but not yet obtained experimentally, with graphene. In the same way as benzene can be regarded as the origin of graphene, the  $\beta$  boron sheet has an aromatic building block called borozene.<sup>2</sup> From first principles calculations, we determined that the lattice constant of the  $\beta$ -sheet is about twice as large as that of graphene, however its density is more than two-times larger. The  $\beta$ -sheet is much softer (the 2D bulk modulus is 107 N/m) than graphene and therefore should be easier to wrap up into a nanotube. The electronic band structure of the  $\beta$  boron sheet is quite similar to that of graphene with that main difference that the valence and conduction bands, instead of being in contact, overlap each other at the vicinity of the K point of the BZ. This and the newly-created sheets of boron atoms<sup>1</sup> could outperform even graphene as electrically-conductive material. The comparison of the  $\beta$ -sheet with other 2D and quasi 2D materials will be also given.

## Acknowledgements

This work is supported by the Polish National Science Centre under Grant nr. 2011/03/D/ST3/02654

## References

1. A. J. Mannix *et al.*, *Science* **2015**, 350, 1513.

2. N. Gonzalez Szwacki, V. Weber, and C.J. Tymczak, Nanoscale Res. Lett. 2009, 4, 1085.

# X-ray diffraction for the characterization of new borane-amidebased materials/composites

Salem Ould Amara,<sup>a</sup> Pascal G.Yot,<sup>b</sup> Umit B. Demirci<sup>a</sup>

<sup>a</sup> Institut Européen des Membranes, Université de Montpellier, Place E. Bataillon, F- 34095, Montpellier, France, <u>Salem.Ould-Amara@iemm.univ-montp2.fr</u>
<sup>b</sup> Institut Charles Gerhardt Montpellier, Université de Montpellier, Montpellier, France

In the beginning of the 2000s, a big interest has been given to ammonia borane (NH<sub>3</sub>BH<sub>3</sub>), in the field of solid-state hydrogen storage by the fact that it contains three hydridic hydrogens (3H<sup> $\delta$ +</sup>) and three protic hydrogens (3 H<sup> $\delta$ +</sup>). It has then high gravimetric hydrogen of 19.6 wt% H. This feature has attracted a flurry of recent investigations focusing on hydrogen release from this borane.<sup>1</sup>

In this dynamic context, other nitrogen-containing boranes have been considered for the same application. One of these materials is hydrazine borane ( $N_2H_4BH_3$ ), which is prepared from sodium borohydride and hydrazine hemisulfate:

 $NaBH_4 + 0.5(N_2H_4)_2SO_4 \rightarrow N_2H_4BH_3 + 0.5Na_2SO_4 + 0.5H_2$ 

Like ammonia borane, it has a high gravimetric capacity hydrogen, with 15.4 wt%, owing to 4  $H^{\delta^+}$  and 3  $H^{\delta^-,2}$  Under heating, the decomposition of hydrazine borane starts at 60°C, but besides the expected hydrogen high amounts of the unwanted and toxic hydrazine N<sub>2</sub>H<sub>4</sub> are released. Therefore, alternatives have been searched for with the objective to propose a material that produces only hydrogen<sup>3</sup>.

When reacted with an alkali hydride MH (M = Li, Na, K), hydrazine borane transforms to a hydrazinidoborane derivative. <sup>3</sup> Another strategy is to make hydrazine borane react with an alkali amide. We considered both approaches, the latter being the newer. Recently, we used the hydrogen-rich rich lithium amide LiNH<sub>2</sub> (8.7 wt%) to make it react with the borane and get a new material. The synthesis was done by ball milling at different ratios of the borane, and the as-obtained samples were fully characterized. Indeed, our new materials were scrutinized by XRD and a new phase was clearly identified. Tools dedicated to crystallography were intensely used to solve the structure. We used the softwares Fullprof, Fox and Jana. Despite some difficulties, we have been able to identify the crystal phase of the new material.

This meeting will be thus an opportunity to present, for the first time, our results about the aforementioned novel material.

## Acknowledgements

The authors thank the LabEx CheMISyst (ANR Program IA, ref. ANR-10-LABX-05-01) and the Région Languedoc-Roussillon (Project "Chercheurs d'Avenir" 2013) for fundings.

## References

1. (a) P.V. Ramachandran, P.D. Gagare, *Inorg. Chem.* **2007**, *46*, 7810; (b) F.H. Stephens, V. Pons, R.T. Baker. *Dalton Trans.* **2007**, 2613; (c) A. Kantürk Figen. *Int. J. Hydrogen Energy* **2013**, *36*, 16215.

2. R. Moury, G. Moussa , U.B. Demirci, J. Hannauer, S. Bernard, E. Petit, A. van der Lee, P. Miele. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1768.

3. (a) H. Wu, W. Zhou, F.E. Pinkerton, T.J. Udovic, T. Yildirim, J.J. Rush, *Energy Environ. Sci.* **2012**, 5, 7531; (b) R. Moury, U.B. Demirci, V. Ban, Y. Filinchuk, T. Ichikawa, L. Zeng, K. Goshome, P. Miele, *Chem. Mater.* **2014**, *26*, 3249; (c) G. Moussa, R. Moury, U.B. Demirci, T. Sener, P. Miele, *Int. J. Energy Res.* **2013**, *37*, 825; (d) R. Moury, U.B. Demirci, T. Ichikawa, Y. Filinchuk, R. Chiriac, A. Van der Lee, P. Miele, *Chem. Sus. Chem.* **2013**, *6*, 667.

# Reduction of CoO with NaBH<sub>4</sub> in Muffle Furnace

Mecit Aksu<sup>a,b</sup>, Omar Ali Al-Zain<sup>a</sup> and Reem Almasoudi<sup>a</sup>

<sup>a</sup>King Abdulaziz University, Faculty of Science, Department of Chemistry Jeddah Saudi Arabia <sup>b</sup>Duzce University, Faculty of Arts and Sciences, Department of Chemistry, Duzce Turkey

In this work, Co<sub>2</sub>B was synthesized by reduction via NaBH<sub>4</sub> at 450 °C under argon atmosphere. 2 mmol CoO mixed with 2 mmol of NaBH<sub>4</sub> in a porcelain crucible. Heated to 450 °C in an autoclave reactor under argon atmosphere. Reaction mixture kept 4 hour at this temperature. Cooled to room temperature. Reaction mixture was put in a beaker with 100 ml distilled water for 10 minute and filtered. Precipitate was washed two times with distilled water and dried in vacuum oven at 70 °C. Precipitate was analyzed with X-ray diffraction (XRD) and Scanning electron Microscopy (SEM). Results showed that pure Co<sub>2</sub>B was formed.



Figure 1.XRD diagram of Co<sub>2</sub>B

Adamczyk-Woźniak	Agnieszka	19, 121
Agafonova	Ksenia S.	33
Aime	Silvio	43, 97
Akatan	Kydyrmolla	135
Aksu	Mecit	67, 138
Alam	Rauful	77
Alberti	Diego	43, 97
Alexenko	A. E.	31
Alexeyenko	Oleg	102, 103
Almasoudi	Reem	138
Altahan	Mohammed A.	29
Altieri	Saverio	43
Al-Zain	Omar Ali	138
Ananyev	Ivan	114
Antonenko	Yuri N.	123, 124
Anufriev	Sergey A.	56, 94
Assaf	Khaleel	51
Avdeeva	Varvara	111
Bakardjiev	Mario	109
Balaban	S.	97
Balagurova	Elena	95
Baranin	Sergey	96
Bausells	Joan	93
Beattie	Nicholas A.	34
Beckett	Michael A.	29
Begoña Buades	Ana	89
Beketov	Evgeny E.	113
Belkova	Natalia V.	48, 63, 64, 78, 107
Bennour	Ines	73
Bernhardt	Ε.	25
Bogachev	Evgenii	103
Boggio	Paolo	43, 97
Boratyński	Janusz	55, 91, 116
Borner	Corinna	59
Bortolussi	Silva	43
Borys	Krzysztof M.	121
Boserle	Jiri	98
Bregadze	Vladimir I.	40, 56, 94, 112, 114, 118, 122, 123, 129, 130
Brynda	Jiří	20
Bubnov	Yury	21, 31, 96
Buzin	Mihail	100
Cabral	Pablo	90
Cabrera	Justo	53
Cabrera	Mauricio	90
Carbó	Jorge J.	30
Cerecetto	Hugo	90, 99

Chan	Antony P. Y.	71
Charushin	Valery	105
Chernyavskiy	Andrey	131, 132
Chizhevsky	lgor T.	33, 95, 115
Chrostowska	Anna	61
Chupakhin	Oleg	105
Cid	Jessica	30
Civit	M. G.	81
Couto	Marcos	90, 99
Cuenca	Ana B.	39, 79, 81
Czerwinska	Karolina	121
D'yachihin	Dmitry I.	33, 115
Dalmaz	Aslıhan	67
Danilova	I. G.	82
Dargelos	Alain	61
Darrigan	Clovis	61
Deagostino	Annamaria	43, 97
Demirci	Umit B.	24, 49, 137
Dolgushin	Fedor M.	33, 95, 115
Dostál	Libor	98, 108
Drača	Dijana	76
Drachev	Alexander	103
Drozdov	Fedor	100
Druzina	Anna A.	40, 123
Dudek	Α.	136
Dudenkov	Ivan V.	46, 101
Dudley	Gregory	52
Dugin	Sergey	102, 103
Durmuş	Sefa	67
El Anwar	Suzan	52
Epstein	Lina	78
Errachid	Abdelhamid	93
Fanfrlik	Jindrich	65
Feofanov	Alexey V.	112, 122
Fernández	Elena	26, 30, 39, 77, 79, 81
Filarowski	Α.	104
Filippov	Oleg A.	63, 64, 78, 107
Fink	Krzysztof	91, 116
Fojt	Lukáš	57
Fojta	Miroslav	57
Fox	Mark A.	23
Fuentes	Isabel	80, 93
Gabel	Detlef	51, 109
Galliamova	Lidiya	105
Galushko	Т. В.	31
García-López	Diego	30
Gavrilova	Yulya	36

Geninatti-Crich	Simonetta	43, 97
Gerasimov	E. Yu.	82
Giambastiani	Giuliano	48, 78
Godovikov	Ivan	115
Goeva	Lyudmila	106, 120
Golovanov	I. S.	38
Golub	lgor E.	48, 63, 107
González	Mercedes	99
Gonzalez	Szwacki N.	136
Gorodov	Vadim	100
Gostevsky	B. A.	84
Goszczyński	Tomasz M.	55, 91
Gozzi	Marta	76
Graciaa	Alain	61
Grebennikov	Alexander	103
Grin	Mikhail A.	112, 122
Grishin	Dmitry F.	33
Grishin	Ivan D.	33
Grüner	Bohumír	20, 57, 66, 109
Gruzdev	Dmitry	92
Gulyaeva	E. S.	107
Gurkova	Ella	102, 103
Gutsul	Evgenii	48
Hajdúch	Marián	20
Hejda	Martin	108
Hey-Hawkins	Evamarie	72, 76
Hnyk	Drahomir	65
Hobza	Pavel	65
Holub	Josef	20, 109
Horton	Peter N.	29
Ibatayev	Zharkyn	135
Ignatieva	Lidia	127
Ignatova	Anastasija A.	112, 122
loffe	S. L.	38
Isaeva	Elena V.	113
Iskakova	Zhanar	135
Izquierdo	Susana	128
Janetková	Monika	66
Jeans	Rebekah J.	71
Jelínek	Tomáš	109
Jemmis	E. D.	110
Kabdrahmanova	Sana	135
Kalinin	Valery N.	41, 42, 92, 124
Kanoh	Daisuke	35
Kanygin	Vladimir	36
Karmodak	Naiwrit	110
Kasatov	Dmitrii	36

Kasztura	Monika	91
Kazakov	Grigorii S.	130
Kazantsev	Alexandr	135
Kazheva	Olga	126
Khailova	Ljudmila S.	124
Khomyakov	M. N.	84
Kichigin	Alexander	36
Kikuchi	Shunsuke	35
Kisin	Alexander	102, 103
Kleeberg	Christian	59
Klimov	O. V.	82
Kochel	Α.	104
Kochnev	Valentin K.	47
Kochneva	Irina	111
Kolesnikov	Yaroslav	36
Kolomiitsev	Ivan	103
Korostey	Yulia S.	112
Koryakin	Sergey N.	113
Kosenko	Irina	40, 114
Koshkarev	Alexei	36
Kosinova	Marina	83, 84
Kostukovich	Alexander Yu.	33, 95, 115
Kovalenko	Leonid	129
Kowalski	Konrad	91, 116
Kozlova	Alexandra	40, 118
Krasnov	Victor	92
Kravchenko	Eleonora	111
Kubasov	A. S.	117
Kučera	Radim	66
Kudinov	Alexander R.	62, 119
Kulikova	Vasilisa A.	63
Kuznetsov	Nikolai	21
Kuznetsov	Nikolay T.	47, 106, 111, 117, 120, 134
Kuznetsova	Marianna	102, 103
La Cascia	Ε.	79
Laine	М.	104
Laskova	Julia	114, 118
Leśnikowski	Zbigniew J.	55, 91, 116, 118
Levit	Galina	92
Lis	A. V.	84
Liu	Shih-Yuan	61
Lledós	Agustí	128
Loginov	Dmitry A.	62, 119
Luconi	Lapo	48, 78
Macgregor	Stuart A.	34
Madura	Izabela D.	121
Makarenkov	Anton V.	41, 124

Makarov	Alexander	36
Maksimović-Ivanić	Danijela	76
Malinina	Elena	106, 120
Markova	Alina	42
Mastandrea	Ignacio	90
Matuszewska	Alicja	121
Matveev	E. Yu.	117
Mechetina	Ludmila	36
Merenkov	Ivan	50, 84
Michelotti	Alessia	43, 97
Miele	Philippe	24, 49
Mijatović	Sanja	76
Milenin	Sergey	100
Miralles	Núria	77
Mironov	Andrey F.	112, 122
Miyoshi	Norio	42
Molotkov	Alexander P.	119
Morancho Retana	Anna	85
Moury	Romain	24
Moussa	Georges	24
Muhamadiyarov	Rinat	36
Muratov	Dmitry V.	62
Muzafarov	Aziz	100
Nadeina	K. A.	82
Nakai	Kei	36
Nakamura	Hiroyuki	35
Naoufal	Daoud	52
Nargoli	Javier	99
Nau	Werner	51
Nekvinda	Jan	20
Nelyubin	Alexey V.	134
Noskov	A. S.	82
Núñez	Rosario	53
Nuraeva	Alla	92
Ogarkov	Aleksandr	131, 132
Ol'shevskaya	Valentina A.	41, 42, 92, 124
Oleshkevich	Elena	75, 85
Oliva	Josep M.	45
Osiecka	В.	104
Osipova	Elena	64, 78
Osorio	Carlos	99
Ostreinov	Yuri	36
Ould Amara	Salem	24, 137
Parisotto	Stefano	37
Pasko	Vladimir	102
Pasynkova	S. O.	122
Peruzzini	Maurizio	48, 63, 78

Petit	Jean-Fabien	24
Petrova	Albina	42
Pisareva	Irina	95
Plyusnin	Pavel	50
Poater	Jordi	44
Polyakova	Irina	117, 120
Potapova	Tamara	96
Potkin	Vladimir	126
Powley	Samuel L.	32
Prandi	Cristina	37
Present	V. A.	133
Protti	Nicoletta	43
Psurski	Mateusz	55
Puchnina	Svetlana	42
Pylypko	Sergii	24
Rezac	Jan	65
Řezáčová	Pavlína	20
Riley	Laura E.	71, 74
Robertson	Alasdair P. M.	34
Rodríguez	Gonzalo	99
Rokitskaya	Tatyana I.	123, 124
Rosair	Georgina M.	32
Rosell Novel	Anna	85
Rossin	Andrea	48, 63, 78
Royes	J.	39, 81
Ruban	Sergey	96
Rudakov	Dmitry	125, 126
Ruzicka	Ales	65
Růžičková	Zdeňka	109
Safa	Ali	52
Saha	Arpita	75, 85
Saini	Abhishek	93
Sakharov	Sergey	131, 132
Sakurai	Yoshinori	35
Saldin	Vitaly	127
Sarna	т.	104
Sato	Eisuke	36
Sato	Shinichi	35
Savchenko	Natalia	127
Schwarze	Benedikt	72
Scudu	Roberto	37
Selyanin	Mikhail A.	113
Semioshkin	Andrey A.	40, 114, 118, 123
Shafir	Alexandr	128
Shayapov	Vladimir	50
Shchudlo	Ivan	36
Shmal'ko	Akim	129
Shtil	Alexander	42
---------------	---------------	-------------------------------------
Shubina	Elena S.	48, 63, 64, 78, 107
Shur	Vladimir	92
Šícha	Václav	20
Silivonenko	Anastasia	95
Sivaev	lgor B.	56, 74, 94, 112, 122, 123, 129, 130
Skachkova	Vera	106
Smol`yakov	Alexander	95, 115
Sokolina	G. A.	31
Sokolova	Evgeniya	36
Solà	Miquel	44
Solntsev	Konstantin A.	46, 101, 131, 132
Sorokin	lgor	36
Spitsyn	B. V.	31
Spokoyny	Alexander M.	54
Sporzyński	Andrzej	19, 121
Štěpánková	Jana	20
Stepanova	Olga	105
Stogniy	Marina	129
Storozhenko	Pavel	102, 103
Sukhorukov	A. Yu.	38
Sukhorukov	Grigoriy	131, 132
Sukhovey	Vasily	127
Suldin	Alexander	42
Suleimen	Yerlan	135
Sulyaeva	Veronica	50, 83
Suzuki	Minoru	35
Sysoev	S. I.	84
Szabó	Kálmán J.	77
Szewczyk	G.	104
Szkudlarek	Sara	80
Tartakovsky	V. A.	38
Taskaev	Sergey	36
Tatarskiy Jr.	Victor	42
Teixidor	Francesc	44, 53, 73, 75, 80, 85, 89, 90, 93
Thilagar	Ρ.	58
Tikhonov	Sergey A.	60
Titova	Ekaterina	64, 78
Tobias	Gerard	53
Todisco	Stefano	48
Ulyanenko	Stepan E.	113
Uspenskiy	Sergey A.	113
Van Hecke	Kristof	135
Varaksin	Mikhail	105
Vatutina	Yu. V.	82
Vespalec	Radim	57, 66
Vidossich	Pietro	128

EUROBORON 7

September 4-8, 2016

Viñas	Clara	22, 44, 53, 73, 75, 80, 85, 89, 90, 93
Vogels	Ch.	81
Volkova	Olga	36
Vologzhanina	Anna	111
Vovna	Vitaliy I.	60
Welch	Alan J.	32, 34, 71, 74, 130
Westcott	S.A.	81
Whiting	Α.	79
Wieczorek	R.	104
Yarullina	Anna	36
Yot	Pascal G.	24, 49, 137
Zaboronok	Alexander	36
Zaitsev	Andrei	42
Zaulet	Adnana	89
Zavarzin	I. V.	133
Zelenovskiy	Pavel	92
Zhdanov	Andrey P.	134
Zhizhin	Konstantin Yu.	117, 134
Zine	Nadia	93
Ziółkowski	Ρ.	104



## stable element for your laboratory and researches

Andrey I. Chazov ELEMENT company, <u>element@element.utk.ru</u>

ELEMENT company is a general distributor of Japanese Shimadzu Corporation, one of the world-leading manufacturers in the analytical control field. We are ready to offer you a wide range of equipment for variety of technological and research fields: gas and liquid mass-spectrometers and chromatographs; X-ray spectrometers; UV-Vis., FTIR, AA and ICPE-spectrometers; total organic carbon and nitrogen analyzers; balances; MALDI-spectrometers and others. Besides we offer cell cultivation and fermentation systems; nitrogen, hydrogen and pure gas generators; nucleic acids automatic extraction systems and other solutions for laboratories of different types and levels.

ELEMENT company is an official distributor of Spark Holland, manufacturer of innovative systems of automatic sample preparation for analytical systems HPLC-MS/MS, completely compatible with mass spectrometers, most of OEM companies.

Also ELEMENT company is a distributor of Major Science, manufacturer of innovative system of cell cultivation and fermentation.

The specialists we have in Ekaterinburg, Moscow and Novosibirsk offices are ready to assist you in the choice of main and auxiliary equipment, according to your tasks and wishes. The company personnel have all the projects under careful control from your very first application to the last day of equipment operation warranty. After that, we are always glad to give you an opportunity of taking post-warranty service.

There are highly skilled service engineers in the company, who perform installation works, teaching of instruments operators and all the operations with post-warranty service. Every year our personnel attend skills improvement courses provided by Shimadzu Corporation and other company suppliers.

Our Moscow and Ekaterinburg demonstration laboratories show all the advantages and capabilities of our equipment usage to customers. Beside this, every year we hold workshops focused on gas-liquid chromatography, mass spectrometry, X-ray spectrometry, infrared spectroscopy and other modern analysis methods.

Over the years of work in the market of analytical equipment, more than a thousand organizations, big and small, from different regions and fields, have estimated the quality of instruments being delivered and services being provided by our company. The majority of them choose us again as reliable and trusted supplier and partner. Among our loyal Customers there are pharmaceutical and food industry enterprises, higher education institutions and Russian Academy of Sciences, metallurgical plants, machinery plants, departments of Ministry of Home Affairs, petrochemical and gas industry enterprises and others.



AVIABOR

## JSC «AVIABOR»

# Production of Boron Compounds



JSC «AVIABOR» is a unique company in Russia that produces a broad range of boron compounds. The plant is situated in Dzerzhinsk, Nizhny Novgoro region, 400 km away from



Moscow.

JSC «AVIABOR» is unique because production goes together with science here. The company has its own scientific-research and RD departments that make it possible to implement various projects from the research to setting up the production process.

Over the past two decades more than ten technological processes were developed and implemented, that provided manufacturing of new high-quality and competitive products. The main consumers of the JSC «AVIABOR» production are well known international electronic and pharmaceutical companies.

Nowadays JSC «AVIABOR» activity is concentrated on several high-priority directions:

- Production of technical grade boron trichloride;
- Production of high purity boron trichloride (5N) for microelectronics;
- Production of diborane and various borane-based complexes for pharmaceutical industry;

## JSC «AVIABOR»



# Production of Boron Compounds

- Production of amorphous boron for nuclear power industry;
- Manufacture of organoboron compounds for pharmaceutical industry;
- Synthesis of carborane compounds for production of high temperature high strength adhesives, that are effective over a wide temperature range;
- Manufacture of nanopowders by plasma chemical synthesis;
- Synthesis of Realization of various boron-containing compounds on demand.



JSC «AVIABOR» has two production sites of total area 446 600  $\mbox{m}^2$  combined in one technological line.



Sergey Anufriev A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences trueMan476@mail.ru

Mecit Aksu Duzce University,Faculty of Arts and Sciences <u>mecitaksu@gmail.com</u>

Elena Balagurova A.N.Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences balena.ran@mail.ru

Sergey Baranin Zelinsky Institute of Organic Chemistry <u>svbar@ioc.ac.ru</u>

> Michael Beckett Bangor University m.a.beckett@bangor.ac.uk

Natalia Belkova A.N. Nesmeyanov Institute of Organoelement Compounds RAS nataliabelk@ineos.ac.ru

Ines Bennour Institute of sciences of materials of Barcelona ibennour@icmab.es

> Amanda Benton Heriot-Watt University benton.amanda437@gmail.com

Eduard Bernhardt University of Wuppertal edbern@uni-wuppertal.de

Alexey Bilyachenko A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences bilyachenko@ineos.ac.ru

Paolo Boggio University of Torino Department of Chemistry paolo.boggio@edu.unito.it

Jiri

Boserle University of Pardubice, Department of General and Inorganic Chemistry <u>st26855@student.upce.cz</u>

Vladimir Bregadze A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences bre@ineos.ac.ru

> Ana Buades ICMAB/CSIC abuades@icmab.es

Jorge Carbo Universitat Rovira i Virgili j.carbo@urv.cat

Alexander Chamkin A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences sasha8686@gmail.com Antony Chan Heriot-Watt University apyc1@hw.ac.uk

Andrey Chernyavskiy Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences ogarkov\_al@mail.ru

lgor Chizhevsky A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences chizbor@ineos.ac.ru

> Anna Chrostowska University of Pau, France anna.chrostowska@univ-pau.fr

Marcos Couto Universidad de la Republica (Uruguay) / CSIC-Espana <u>mcoutosire@gmail.com</u>

> Ana Belen **Cuenca** University Rovira i Virgili (Tarragona) <u>anabelen.cuenca@urv.cat</u>

> > Clovis Darrigan University of Pau, France clovis.darrigan@univ-pau.fr

Annamaria Deagostino Universita degli Studi di Torino annamaria.deagostino@unito.it Umit Bilge Demirci University of Montpellier umit.demirci@umontpellier.fr

> Fedor Drozdov

fedor.drozdov@gmail.com

Ivan Dudenkov

ivdudenkoff@mail.ru

Sergey Dugin State Research Institute of Chemistry and Technology of Organoelement Compounds carboran@mail.ru

Lina Epstein A.N. Nesmeyanov Institute of Organoelement Compounds RAS epst@ineos.ac.ru

Jindrich **Fanfrlik** Institute of Organic Chemistry and Biochemistry AS CR, v.v.i. <u>fanfrlik@uochb.cas.cz</u>

> Elena Fernandez University Rovira i Virgili mariaelena.fernandez@urv.cat

Aleksander Filarowski Joint Institute of Nuclear Reaserch aleksander.filarowski@chem.uni.wroc.pl Oleg Filippov A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences <u>H-Bond@ineos.ac.ru</u>

Krzysztof Fink Institute of Immunology and Experimental Therapy in Wroclaw krzysztof.fink@iitd.pan.wroc.pl

> Lukas **Fojt** Institute of Biophysics v.v.i., <u>fojt@ibp.cz</u>

Lyudmila Goeva Kurnakov Institute of General and Inorganic Chemestry Russian Academy of Science Iyudmila.goeva@mail.ru

lgor Golub A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences seraph347@gmail.com

Nevill Gonzalez Szwacki Institute of Theoretical Physics, Faculty of Physics, University of Warsaw gonz@fuw.edu.pl

Mark Fox University of Durham m.a.fox@durham.ac.uk

Isabel Fuentes Sempere ICMAB-CSIC ifuentes@icmab.es Goszczynski Ludwik Hirszfeld Institute of Immunology and Experimental Therapy, Polish Academy of Sciences goszczynski@iitd.pan.wroc.pl

Tomasz

Marta Gozzi University of Leipzig marta.gozzi@studserv.uni-leipzig.de

Aleksandr Grebennikov State Research Institute of Chemistry and Technology of Organoelement Compounds carboran@mail.ru

lvan Grishin Lobachevsky State University of Nizhny Novgorod grishin i@ichem.unn.ru

Bohumir Gruner Institute of Inorganic Chemistry AS CR gruner@iic.cas.cz

Gabel Jacobs University d.gabel@jacobs-university.de

Detlef

Lidiia **Galliamova** Ural Federal University <u>lida2201@gmail.com</u>

Marc Garcia Civit Rovira i Virgili Univeristy marc.garcia@urv.cat

**EUROBORON 7** 

September 4-8, 2016

## Dmitrv

Gruzdev Institute of Organic Synthesis of the Russian Academy of Sciences, Ural Branch aruzdev-da@ios.uran.ru

#### Ekaterina Gulvaeva

A.N.Nesmevanov Institute of Organoelement Compounds of Russian Academy of Sciences elenor.kagami@gmail.com

Flla

Gurkova State Research Institute of Chemistry and Technology of Organoelement Compounds carboran@mail.ru

> Martin Heida University of Pardubice st23755@student.upce.cz

Drahomir Hnvk Institute of Inorganic Chemistry of the ASCR, vvi hnyk@iic.cas.cz

Josef

Holub

Institute of Inorganic Chemistry, v.v.i., AS CR

holub@iic.cas.cz

Tomas

Jelinek

Katchem s r.o. t.ielinek@seznam.cz

Naiwrit Karmodak Indian Institute of Science knaiwrit@gmail.com

> Roman Keder Katchem spol. s r.o. keder@katchem.cz

Alexander Kisin State Research Institute of Chemistry and Technology of Organoelement Compounds kisin@eos.su

> Christian Kleebera

Technische Universitat Braunschweig, Institut fur Anorganische und Analvtische Chemie ch.kleeberg@tu-braunschweig.de

Valentin Kochnev N.S. Kurnakov Institute of General and Inorganic Chemistry valentine878@gmail.com

Irina Kochneva Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences Ira.kochneva@gmail.com

> Yulia Korostey

jkorostei@mail.ru

Sergey Korvakin

A. Tsyb Medical Radiological Research Centre branch of the National Medical Research Radiological Centre of the Ministry of Health of the Russian Federation, Obninsk korsernic@mail.ru

.lohn Jones

Heriot Watt University jjj2@hw.ac.uk

#### Anastasiya Koryakina

A. Tsyb Medical Radiological Research Centre – branch of the National Medical Research Radiological Centre of the Ministry of Health of the Russian Federation, Obninsk korsernic@mail.ru

### Irina

Kosenko A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences kosenko@ineos.ac.ru

Alexandr Kostukovich Institute of Organoelement Compounds dftblyp@gmail.com

#### Konrad Kowalski

Institute of Immunology and Experimental Therapy, Polish Academy of Sciences konrad.kowalski@iitd.pan.wroc.pl

> Aleksandra Kozlova

A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences kozlova@mitht.ru

Vladlen

Krasnikov Unifest twinkysmen93@gmail.com

#### Alexey

Kubasov Kurnakov institute of general and inorganic chernistry fobosax@mail.ru

## Radim

Kucera Charles University in Prague, Faculty of Pharmacy in Hradec Kralove radim.kucera@faf.cuni.cz Alexander Kudinov A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences arkudinov@ineos.ac.ru

#### Marianna

Kuznetsova State Research Institute of Chemistry and Technology of Organoelement Compounds <u>mary20031@yandex.ru</u>

> Enrico La Cascia Rovira I Virgili University enrico.lacascia@urv.cat

> > Julia

Laskova A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences laskova@ineos.ac.ru

Dmitry

Loginov A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences dloginov@ineos.ac.ru

Pingping Lou Institute of Chemistry , Chinese Academy of Sciences pingpinglou@iccas.ac.cn

#### Elena

Malinina Kurnakov Institute of General and Inorganic Chemestry Russian Academy of Science malinina@igic.ras.ru

> lvan Merenkov

Merenkov@niic.nsc.ru

Philippe **Miele** European Institute of Membranes - UMR5635 philippe.miele@umontpellier.fr

> Sergey Milenin

CepHe@mail.ru

Nuria Miralles Prat Rovira i Virgili University nuria.mirallesp@urv.cat

Dmitry

Muratov A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences <u>muratov@ineos.ac.ru</u>

> Hiroyuki Nakamura Tokyo Institute of Technology <u>hiro@res.titech.ac.jp</u>

Daoud **Naoufal** Lebanese University, Faculty of Sciences, Inorganic and Organometallic Coordination Laboratory

dnaoufal@ul.edu.lb

Lev

Nikitin Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences nikitin.lev@rambler.ru

> Rosario Nunez ICMAB-CSIC rosario@icmab.es

Aleksandr Ogarkov Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences ogarkov\_al@rambler.ru

Valentina Ol'shevskaya A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences olshevsk@ineos.ac.ru

Elena Oleshkevich Institute of Material Science of Barcelona (ICMAB-CSIC) eoleshkevich@icmab.es

Elena Oleshkevich Institute of Material Science of Barcelona (ICMAB-CSIC) eoleshkevich@icmab.es

Josep Oliva Spanish National Research Council (CSIC) j.m.oliva@iqfr.csic.es

Elena Osipova A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences aosipova92@gmail.com

> Thilagar Pakkirisamy Indian Institute of Science thilagar@ipc.iisc.ernet.in

Vladimir Pasko State Research Institute of Chemistry and Technology of Organoelement Compounds carboran@mail.ru

Sofia Pasynkova Moscow Technological University pasynkova.sofiya@gmail.com

Albina Petrova Moscow Technological University <u>albishapetrova@yandex.ru</u>

> Silvia **Plana** *urv* silvia.plana@urv.cat

Dmitry **Rudakov** The Institute of Physical Organic Chemistry of the NAS of Belarus <u>deach@list.ru</u>

Andrea Rossin

ICCOM-CNR

a.rossin@iccom.cnr.it

Arpita Saha Institut de Ciencia de Materials de Barcelona arpitasaha666@gmail.com

Cristina Prandi University of Turin cristina.prandi@unito.it

Mikhail **Prezent** Zelinsky Institute of Organic Chemistry <u>pre1962@mail.ru</u>

> Laura **Riley** Heriot-Watt University <u>ler30@hw.ac.uk</u>

Alasdair Robertson Heriot-Watt University ar35@hw.ac.uk

> Tatyana Rokitskaya

Belozersky Institute of Physico-Chemical Biology, Lomonosov Moscow State University rokitskaya@genebee.msu.ru Abhishek **Saini** Institut de Ciencia de Materials de Barcelona <u>ab76779@gmail.com</u>

Vitaly Saldin Institute of Chemistry of Far-Eastern Branch of Russian Academy of Science sald@ich.dvo.ru

Salem Ould Amara Institut Europeen des Memebranes Salem.Ould-Amara@iemm.univ-montp2.fr

Benedikt Schwarze Leipzig University bene.schwarze@googlemail.com

Andrey Semioshkin A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences semi@ineos.ac.ru

Alexandr Shafir Unstitute of Chemical Research of Catalonia <u>ashafir@iciq.es</u>

> Vladimir Shayapov

shayapov@niic.nsc.ru

Akim Shmal'ko A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences <u>akimbend@yandex.ru</u>

> Alexander Shtil Blokhin Cancer Center shtilaa@yahoo.com

> > Elena

Shubina A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences shu@ineos.ac.ru

Igor

Sivaev A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences sivaev@ineos.ac.ru

### Daria

Smirnova Faculty of Chemistry, Lomonosov Moscow State University S\_mir\_nova@mail.ru

## Boris

Spitsyn Institute of Physical Chemistry and Electrochemistry, named after A.N.Frumkin, Russian Academy of Sciences bspitsyn@yahoo.com Alexander Spokoyny UCLA spokoyny@chem.ucla.edu

Andrzej **Sporzynski** Warsaw University of Technology <u>spor@ch.pw.edu.pl</u>

> Olga Stepanova Ural Federal University stepashka809@mail.ru

Alexey Sukhorukov N.D. Zelinsky Institute of Organic Chemistry <u>a.yu.sukhorukov@gmail.com</u>

Grigoriy Sukhorukov Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences ogarkov\_al@rambler.ru

Yerlan **Suleimen** L.N. Gumilev Eurasian National University suleimen em@enu.kz

Veronica Sulyaeva Nikolaev Institute of Inorganic Chemistry Siberian Branch of Russian Academy of Sciences veronica@niic.nsc.ru

Sergey Taskaev Budker Institute of Nuclear Physics taskaev@inp.nsk.su Francesc Teixidor ICMAB-CSIC teixidor@icmab.es

Sergey Tikhonov Far Eastern Federal University <u>allser@bk.ru</u>

> Ekaterina Titova

A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences <u>e.m.kozinets@gmail.com</u>

#### Stepan Ulyanenko

A. Tsyb Medical Radiological Research Centre – branch of the National Medical Research Radiological Centre of the Ministry of Health of the Russian Federation, Obninsk <u>ustev@mail.ru</u> Liliya

#### Ulyanenko

A. Tsyb Medical Radiological Research Centre – branch of the National Medical Research Radiological Centre of the Ministry of Health of the Russian Federation, Obninsk oulianenko@yandex.ru

Yulia

Vatutina Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences yuliy.vatutina@yandex.ru

> Clara Vinas CS/C clara@icmab.es

Alan Welch Heriot-Watt University a.j.welch@hw.ac.uk

Yuying Wu Shandong University wuyuying@sdu.edu.cn

Pascal Yot University of Montpellier pascal.yot@umontpellier.fr

Andrei

Zaitsev A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences porphyrin@yandex.ru

lgor Zavarzin Zelinsky Institute of Organic Chemistry igorzavarzin@yandex.ru

Xuezhong Zhang Institute of Chemistry Chinese Academy of Science zhangxuezhong@iccas.ac.cn

#### Andrey

Zhdanov Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences zhdanov@igic.ras.ru

Konstantin

Zhizhin Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences zhizhin@igic.ras.ru

Dorothy Welch University of Glasgow dorothy.welch@glasgow.ac.uk

**EUROBORON 7** 





## **Лабораторное оборудование ВUCHI** Решения для научных исследований

В течение более 75 лет BUCHI является ведущим экспертом в области лабораторного оборудования. Универсальные, проверенные и надежные решения охватывают широкий диапазон областей применения для научных исследований и разработок.. Они позволяют существенно экономить время и средства при выполнении различных задач.

«Quality in your hands» – это основной принцип, определяющий нашу философию и нашу деятельность. С момента своего основания BUCHI следует этой идеологии для успешной разработки передовых продуктов для упаривания, очистки и создания частиц в лабораторных условиях.

Контакты представительства BUCHI в России/СНГ: Тел. +7 495 36 36 495 russia@buchi.com | www.buchi.ru



Очистка



## Ротационный испаритель Rotavapor® R-300

Передовая система упаривания Rotavapor<sup>®</sup> R-300 используется для работы с различными объемами образца. Благодаря уникальному датчику вспенивания и датчику уровня возможна полная автоматизация процесса упаривания без необходимости наблюдения оператора. Режимы работы: ручной, таймер, непрерывный, автоматическая дистилляция, сушка (попеременное вращения колбы в обе стороны), библиотека растворителей.



### Препаративный хроматограф Reveleris® Prep

Система очистки Reveleris<sup>®</sup> PREP представляет собой мощную высокопроизводительную систему, объединяющую флэш-хроматографию и препаративную ВЭЖХ в одном приборе с интуитивно понятным управлением. Благодаря встроенным ELSD и UV-Vis детекторам Reveleris<sup>®</sup> PREP распознает как хромофоры, так и нехромофоры. Давление до 120 бар гарантирует высокоэффективную очистку целевого соединения.

Распылительная сушка



### Распылительная сушилка В-290

Распылительная сушилка позволяет в одну стадию получать порошок как из водных, органических и даже кислотных растворов в лабораторных масштабах. Короткое время пребывания образца в осушительной камере и охлаждающий эффект испарения делает возможным высушивание термолабильных соединений. Процесс распылительной сушки отличает высокая скорость, экономичность и корректирование размера частиц на выходе.

# www.buchi.ru

# Quality in your hands

18:40 Sigma-Aldrich	18:25 YO6 Gozzi	18:10 YO5 Saha	17:55 YO4 Riley	17:40 YO3 Bennour	17:25 YO2 Schwarze	17:10 YO1 Chan	16:40 Coffee break	16:20 O11 Cuenca	16:00 O10 Sukhorukov	15:40 O9 Prandi	15:10 I3 Bubnov	13:15 Lunch	12:55 O8 Taskaev	12:35 O7 Nakamura	12:15 O6 Robertson	11:55 O5 Grishin	11:35 04 Welch	11:05 I2 Grüner	10:30 Coffee break	10:10 O3 Spitsyn	09:50 O2 Carbó	09:30 O1 Beckett	09:00 I1 Sporzyński	08:45 Opening Ceremony	Monday
		15:00- 18.00 Excursion										13:10 Lunch	12:50 019 Kochnev	12:30 O18 Dudenkov	12:10 017 <b>Oliva</b>	11:50 O16 Teixidor	11:20 I5 Fox	10:50 Coffee break	10:30 O15 Deagostino	10:10 O14 Shtil	09:50 O13 Ol'shevskaya	09:30 O12 Semioshkin	09:00 14 Viñas	1 ucsuay	Tupeday
		19:00 POSIEL SESSION	16:50- Dector Consistent				16:30 030 Thilagar	16:10 029 Fojt	15:50 O28 Sivaev	15:30 O27 Goszczyński	15:00 I7 Bernhardt	13:10 Lunch	12:40 F1-F5	12:20 O26 Spokoyny	12:00 O25 Núñez	11:40 O24 Naoufal	11:20 023 Gabel	10:50 Coffee break	10:30 INTERTECH	10:10 O22 Shayapov	09:50 O21 Yot	09:30 O20 Rossin	09:00 I6 Demirci	w cuitesuay	Wedneeday
19:30 and Conference Dinner	Closing ceremony	17:00 YO15 Oleshkevich	16:45 YO14 Merenkov	16:30 YO13 Sulyaeva	16:15 YO12 Vatutina	16:00 YO11 Civit	15:45 YO10 Fuentes	15:30 YO9 La Cascia	15:15 YO8 Osipova	15:00 YO7 Miralles	13:20 Lunch	13:00 ETI Products	12:40 O39 Aksu	12:20 O38 Kučera	12:00 O37 Fanfrlik	11:40 O36 Titova	11:20 O35 Golub	10:50 Coffee break	10:30 O34 Muratov	10:10 O33 Chrostowska	09:50 O32 Tikhonov	09:30 O31 Kleeberg	09:00 I8 Fernández	inursuay	Thursday