

SCIENTIFIC PROGRAM

9:00

Prof. Jozef Drabowicz/Prof. Anna Wypych-Gawrońska, Rector JDU

OPENING

Chairman: Dr Tomasz Girek

9:15

Prof. Ludger Wessjohann

RAPID ACCESS TO FUNCTIONAL MACROCYCLES

10:00

Prof. Hansjörg Grützmacher

FUNCTIONAL GROUPS FOR ORGANOPHOSPHORUS CHEMISTRY

10:45-11.15

Coffee break

Chairman: Prof. Wojciech Ciesielski

11:15

Prof. Marc Gingras

POLYFUNCTIONALIZED ASTERISKS, DENDRIMERS AND HELICENES OF USES IN NANOSCIENCE AND IN NANOMEDICINE

12:00

Prof. Aleš Růžička

DIRECT GUANYLATION OF CARBODIIMIDES AND USE OF GUANIDINATE(1-) AND (2-) COMPLEXES

12:45

Prof. Jozef Drabowicz

CLOSING

XX INTERNATIONAL SYMPOSIUM

on

SELECTED PROBLEMS OF CHEMISTRY OF ACYCLIC AND CYCLIC HETEROORGANIC COMPOUNDS

The second symposium under the Project:
“Doskonała Nauka” – “Klaster 3 międzynarodowych sympozjów”
(DNK/SP/514249/2021; 2022-02-11)
Ministry of Education and Sciences
POLAND

Jan Dlugosz University in Czestochowa
(JDU)

CZĘSTOCHOWA, October 27, 2022

**XX INTERNATIONAL SYMPOSIUM
on
SELECTED PROBLEMS
OF CHEMISTRY OF ACYCLIC AND CYCLIC HETEROORGANIC COMPOUNDS**

NOTES

organized by

Team of Organic Chemistry
Institute of Chemistry
Jan Dlugosz University in Czestochowa

Division of Organic Chemistry
Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz

Section of Heteroorganic Chemistry, Polish Chemical Society

Polish Chemical Society, Czestochowa Branch

Scientific and Organizing Committee

Prof. Józef DRABOWICZ (CBMM PAN Lodz; JDU Czestochowa)
Dr hab. prof. JDU Wojciech CIESIELSKI (JDU Czestochowa)
Dr Tomasz GIREK (JDU Czestochowa)

Date

October 27, 2022

Location

Institute of Chemistry
lecture hall 139,
Armii Krajowej 13/15 Ave.,
42-200 Częstochowa

phone: 48 (34) 361 51 54
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DIRECT GUANYLATION OF CARBODIIMIDES AND USE OF GUANIDINATE(1-) AND (2-) COMPLEXES

Lukáš Vlk, Tomáš Chlupatý, Aleš Růžicka

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Guanidines are a diverse class of compounds able to bear up to five substituents on the central CN₃ moiety, thus offering considerable tunability of steric and electronic effects contributed by the substituents. Important uses are as ligands in coordination chemistry, basic/(non)nucleophilic catalysts or recognition agents in organic synthesis and as pharmaceuticals thanks to biological activity of the guanidyl group.¹

With the growing demand for these compounds the lack of an appropriate synthetic pathway becomes more obvious. So far, a plethora of (transition) metal catalysts for direct guanylation of carbodiimides with amines has been reported with usually excellent yields, but limited scope of substrates. The main drawback is the price, low stability, or sensitivity of these complexes.^{1,2}

Here we present a universal, simple method leading to tri- and tetrasubstituted guanidines which uses cheap hydrogen chloride as a catalyst. Guanylation reactions were carried out successfully for all combinations of aromatic and aliphatic substrates (both amines and carbodiimides) with mostly good yields. The reaction mechanism was further studied by supplemental experiments confirmed by DFT calculations.

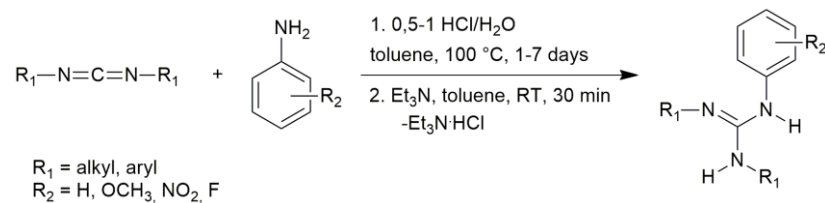


Figure 1 - General reaction conditions used for guanylation of carbodiimides and primary aromatic amines

Major part of the presentation will be devoted to the preparation of various guanidinate metal complexes.

Acknowledgements: We thank the Czech Science Foundation for financial support (grant number 21-02964S).

References:

- 1 a) Alonso-Moreno, C.; Antinolo, A.; Carrillo-Hermosilla, F.; Otero, A. Chem. Soc. Rev. 2014, 43, 3406–3425. b) Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts. Ishikawa, T. Wiley, Chhippenham, 2009.
- 2 a) Zhang, W.-X., Nishiura, M., Hou, Z. Synlett, 2006, 8, 1213–1216. b) Bhattacharjee, J.; Sachdeva, M.; Banerjee, I. et al. J. Chem. Sci. 2016, 128, 875–881.

RAPID ACCESS TO FUNCTIONAL MACROCYCLES

Ludger Wessjohann

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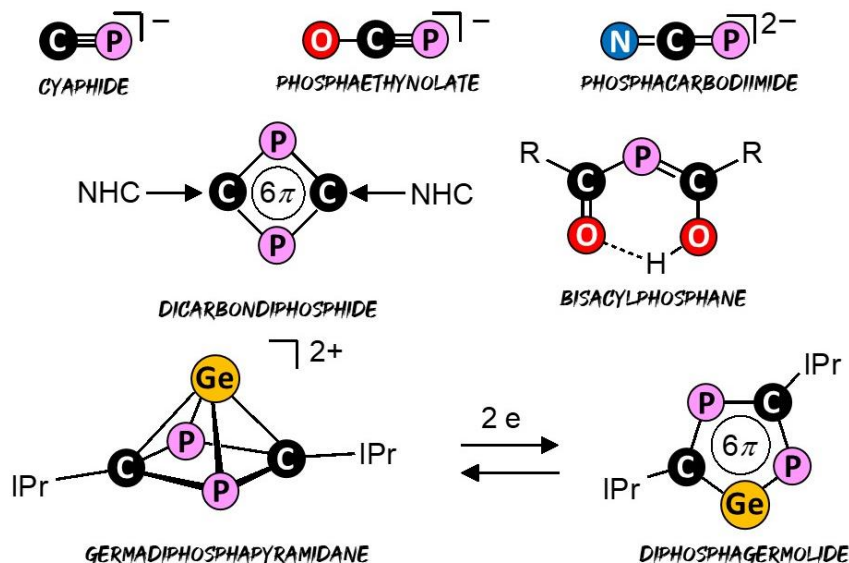
I will present our MiB-Concept (MCR-macrocyclization including bifunctional building blocks) for the rapid assembly of diverse heterocyclic macrocycles including cage compounds, medicinal macrocycles or such controlling peptide conformations (stapled peptides).

FUNCTIONAL GROUPS FOR ORGANOPHOSPHORUS CHEMISTRY

Hansjörg Grützmacher

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From the elements C,H,N,O the realm of organic chemistry is built and their combination leads to an endless array of molecules. A set of very well established functional groups allows organic chemists to synthesize these conveniently. In main group element chemistry, a very different situation is met and the mutual substitution of "homologous" elements - like nitrogen for phosphorus - looks simple only on paper. The lecture will give an overview on our efforts to generate new functional groups such as cyaphide, phosphoethynolate, or phosphacarbodiimide (as analogues of [CN]₂, [OCN]₂, or [CN₂]₂). Not surprisingly, everything turned out differently than one thought. But some of these "funny" molecules help to solve fundamental problems in chemistry, such as the mutual conversion of cluster into planar aromatic compounds, while others like bis(acyl)phosphanes assist in the solution of practical problems.

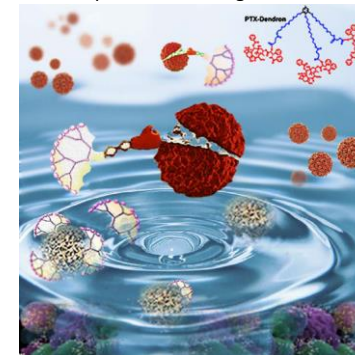


POLYFUNCTIONALIZED ASTERISKS, DENDRIMERS AND HELICENES OF USES IN NANOSCIENCE AND IN NANOMEDICINE

Marc Gingras

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Polyfunctionalized molecular architectures of various topologies will be presented, along with their synthesis and a survey of some applications in chemical-biology, in materials science and in nanomedicine. They comprise asterisks, dendrimers and helicenes, which often incorporate sulfur and aromatic units,[1] leading to multifunctional and luminescent (phosphorescent and fluorescent) nano-objects.[2] They represent an underexploited class of macromolecules with attractive features, rich supramolecular interactions, chiroptical and electronic properties, which could be modulated by some metal interactions,[3-4] by some cation- π -interactions and by some π - π complexes. Some applications of these asterisks and dendrimers will be presented in life sciences towards some studies in lectin-carbohydrate interactions,[5,6] drug delivery (slow drug release)[7-8] and nanomedicine (especially against cancer).[9-11] Their uses as nanomaterials will also be discussed.



References:

- (1) M. Gingras, J.-M. Raimundo, Y. M. Chabre, *Angew. Chem. Int. Ed.* 2006, 45, 1686.
- (2) "Molecular asterisks with a persulfurated benzene core are among the strongest organic phosphorescent emitters in the solid state", A. Fermi, G. Bergamini, R. Peresutti, E. Marchi, M. Roy, P. Ceroni, M. Gingras, *Dyes and Pigments* 2014, 110, 113.
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- (4) "Bright Phosphorescence of All-Organic Chromophores Confined within Water-Soluble Silica Nanoparticles", M. Villa; B. Del Secco; L. Ravotto; M. Roy; E. Rampazzo; N. Zaccheroni; L. Prodi; M. Gingras; S. Vinogradov; P. Ceroni *J. Phys. Chem. C* 2019, 123, 49, 29884.
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- (11) "Gold nanoparticles prepared by laser ablation in aqueous biocompatible solutions: assessment of safety and biological identity for nanomedicine applications", F. Correard, K. Maximova, M.A. Esteve, C. Villard, M. Roy, A. Alkattan, M. Sentis, M. Gingras, A.V. Kabashin, D. Braguer, *Intern. J. Nanomedicine* 2014, 9, 5415.