New Bonding and Reactivity:

Chemistry of N-Cations and N-Radicals

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The lecture will consist of two parts. The first part will focus on chemistry of cationic nitrogen compounds. We will demonstrate that nitrenium cations, which are isostructural and isoelectronic to ubiquitous N-heterocyclic carbenes, can serve as ligands for a wide range of transition metals.[1] It represents a missing link in the coordination behavior of carbenes and other main group carbene-like species. The chemistry of these systems will be discussed. Formation of a stable bond between the positively charged nitrenium ligands and cationic metal centers, providing an extremely rare example of cation-cation binding, will be also presented and discussed.[2] In addition, we will disclose a novel class of Lewis acids based on nitrogen. Discovery of this class of Lewis acids allowed us a first synthesis of triazanes.

In the second part of the lecture, new efficient and robust *methods and reagents* to the preparation of iodo-, chloro-, bromo- and fluoroorganic compounds, as well as straightforward approach to the preparation of geminal dihaloalkanes, will be presented. We will demonstrate that the geminal dihaloalkanes have a great potential for facile functionalization to produce valuable complex organic compounds. Specifically, two new efficient catalytic methods utilizing geminal dihaloalkanes will be presented: (a) stereoconvergent enantioselective synthesis of tailor-made organic fluorides, which are not easy to prepare by other synthetic methods,[3] and (b) enantio- and chemoselective assembly of tertiary stereocenters from the carboxylic acids just in few steps.[4]

[1] *Nature Chem.* **2011**, *5*, 525.

[2] (a) *Chem.Sci.* **2014**, *5*, 1305. (b) *Chem. Eur. J.* ***2015****, 21, 7099*

[3] (a) *J. Am. Chem. Soc.* **2014**, *136*, 1305. (b) *J. Am. Chem. Soc.* **2015**, *137*, 2542.

[4] *Chem.Sci.* **2016**, **DOI:** 10.1039/C5SC04378F