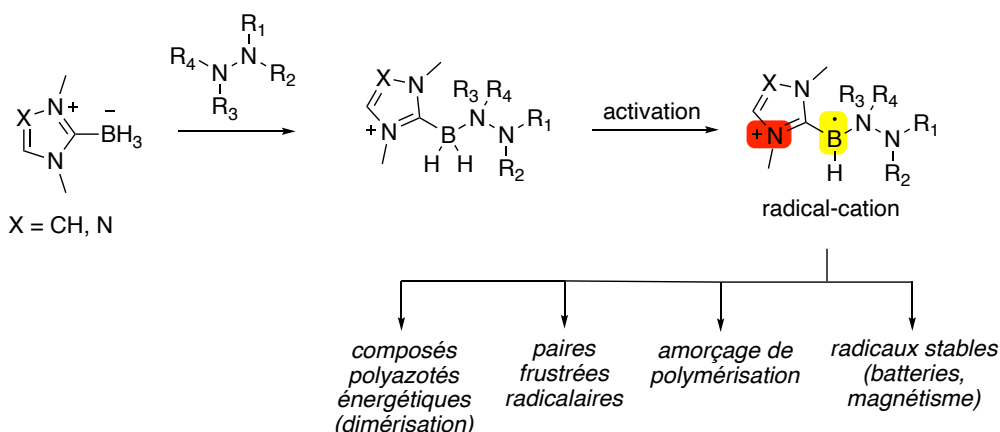


Réactivité de radicaux-cations borés / Reactivity of boryl radical-cations

Emmanuel Lacôte & Anne Renault

The aim of the present thesis is to characterize and exploit boron-centered radical-cations. These reactive intermediates are poorly understood because of a lack of access to them, and their reactivity is largely unknown. Our group has shown that NHC-boryl radicals are very useful reagents for use in organic and macromolecular synthesis as they are able to build C–B bonds and initiate radical polymerizations. Today, ligated boryl radicals have become essential tools for synthesis at large.

Our next goal is to examine how an additional charge on the boron atom will change the reactivity of NHC-boryl radicals, or even create new reaction modes. It is however necessary to first be able to access these intermediates. Inspired by our work on NHC-Boranes, we consider accessing radical-cations by hydrogen atom abstraction from a boronium cation (isoelectronic to alkanes), stabilized by both an NHC and a hydrazine or an aromatic amine.



The radical-cations will be engaged in different applications, depending on their lifetime. This will depend on steric hindrance and/or electronic effects and conjugation around the Boron atom.

- if they are fleeting, they might lead to the synthesis of energetic molecules (by dimerization) or the initiation of radical polymerizations to obtain polymers with a positively charged chain end.
- if they are stable (that is thermodynamically stabilized by delocalization) or persistent (ie prevented from dimerizing because of steric strain) they might be inserted into 3D networks for use in magnetism or redox reactions.

The thesis will be carried out within the LHCEP - which is a joint academic/industrial unit (UCBL, CNRS, CNES, ArianeGroup) whose core competence is in the chemistry of main block derivatives, in particular towards the synthesis of energetic derivatives. It will be placed under the direction of Dr. E. Lacôte, a specialist in boron chemistry and Dr. A. Renault, specialist in polyazo compounds. The laboratory is located on the campus of La Doua (Université Claude Bernard-Lyon 1) in Villeurbanne and has modern synthesis laboratories, with all the equipment necessary for the synthesis and study of these new compounds (NMR, DSC, etc.). The thesis will thus offer a training in organic chemistry at the interface of the materials domain.

Laboratoire des Hydrazines et Composés Énergétiques Polyazotés (LHCEP), UMR 5278, Univ Lyon, Université Claude Bernard Lyon 1, campus LyonTech – La Doua, 2 rue Victor Grignard, Villeurbanne, France, emmanuel.lacote@univ-lyon1.fr