Guillaume BERIONNI
Namur Institute of Structured Matter (NISM)
University of Namur, 61 rue de Bruxelles,
B-5000 Namur, Belgium
guillaume.berionni@unamur.be

Reprogramming Main-Group Compounds: Toward New Superelectrophilic and Superacidic Catalysts

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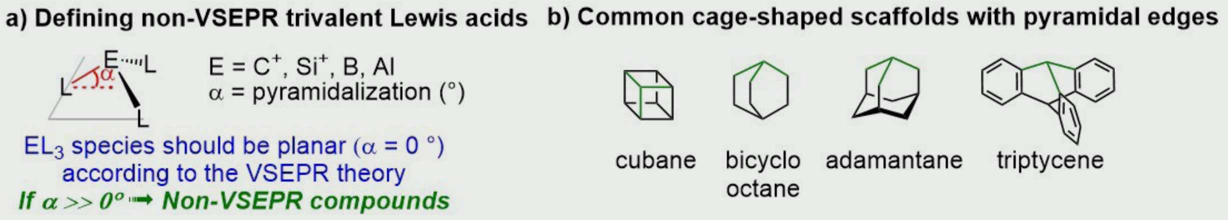
The Valence Shell Electron Pair Repulsion (VSEPR) theory predicts the geometry of molecules from the number of electron pairs surrounding their central atoms. It describes all trivalent electrophiles and Lewis acids EL_3 (L = ligand) from group XIII (E = B, Al, Ga) and all trivalent cationic species from group XIV (E = C^+, Si^+) as trigonal planar species (Scheme 1a). However, a number of geometrically constrained trivalent species embedded in cage-shaped scaffolds such as those represented in Scheme 1b are known and have generally been referred to as “non-VSEPR” Lewis acids [1].

Rare but impressive examples of pyramidal boranes and isoelectronic carbenium ions have been generated in solution or in gas phase, and a few have even been structurally characterized in the solid-state (Scheme 2a) [2]. These textbook examples of main-group species escaping the general chemical structural rules are illustrating that other non-VSPER Lewis acids could potentially be generated *in-situ*, or even isolated. Many non-planar trivalent Lewis acids and electrophiles were computationally evaluated (Scheme 2b) [3], and quantum-chemical calculations are revealing that their central element pyramidalization considerably reduce the enthalpic cost of structural reorganization when forming a Lewis adduct with a Lewis base (Scheme 2c) or when reacting with a substrate. This has in particular a tremendous importance for boron Lewis acids possessing the largest reorganization energy in the group XIII series (E = B, Al, Ga, In) [4], which considerably hampers many of their potential applications in chemistry [5].



Scheme 1. a) Defining the geometry of trivalent EL_3 species (E = element, L = ligand or subsitutent) with the pyramidalization angle α; b) Common cage-shaped scaffolds.

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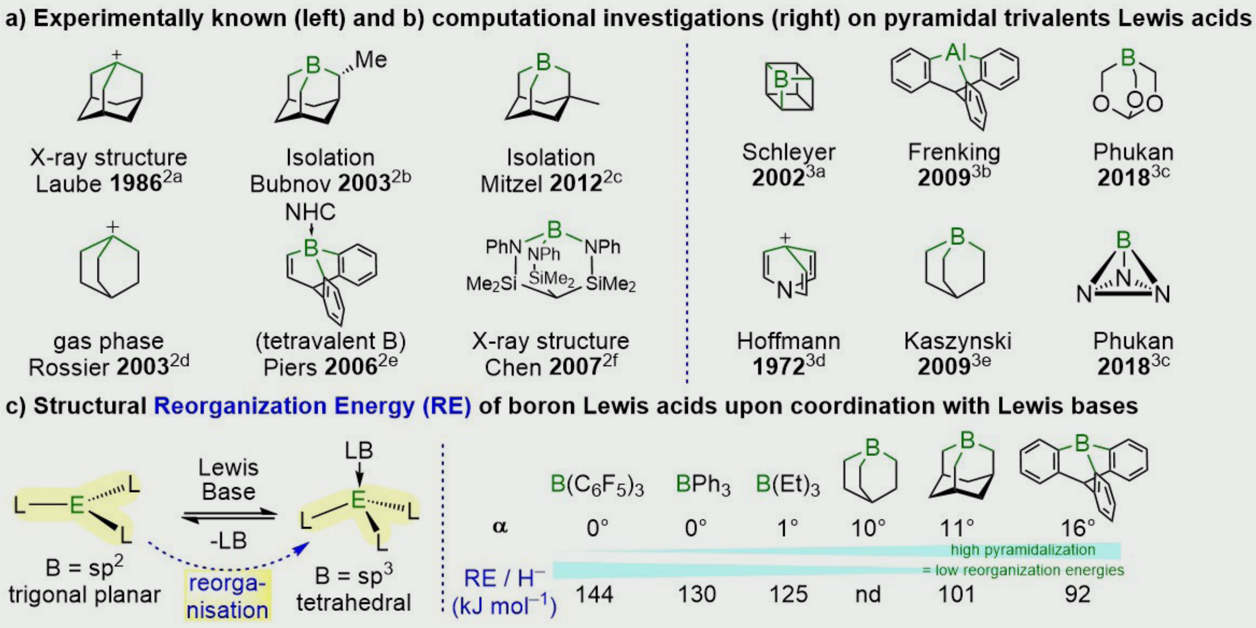

Scheme 2. Overview on experimentally known non-planar Lewis acids with low structural reorganization energies and high pyramidalizations at the reactive central element E.

Such uncommon reactive species are expected to open new paths to reach unexpected chemical reactivities, with interesting perspectives in the area of superelectrophiles, superacids and Lewis superacids chemistry [6]. The applications of these non-VSEPR species in bonds activation are nearly unexplored, although quantum-chemical investigations leave no doubts on their promising modes of bonds activation [7].

We recently reported the unrivalled reactivity of pyramidal boron Lewis acids [8], which exhibited unforeseen Lewis acidity strength surpassing that of all reported boron Lewis acids so far [9]. By expanding the current boundaries of the Lewis acidity scale and decreasing the reorganization energies of boron Lewis acid, our research group future goals are to considerably expand the applications of main-group Lewis superacids in chemistry and catalysis [10].

Accessing even more reactive species will open a whole new range of opportunities for the activation of inert molecules, and the extraordinary structures, reactivities and robustness of these new type of p-block reactive entities show that they are the forerunners of novel and unique properties and applications in catalysis and in coordination chemistry. This research will be developed during the next five-years at the University of Namur within the context of the ERC consolidator grant “B-YOND” entitled “Reprogramming main-group compounds for capturing and activating methane and dinitrogen”.

Acknowledgments

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Additional information on Prof. Guillaume Berionni, his research group, and the ERC consolidator grant "B-YOND" starting in October 2022.

Prof. Guillaume Berionni (Namur Institute of Structured Matter - University of Namur) has been recently awarded an ERC consolidator grant.

With this funding instrument, the European Research Council enables outstanding scientists to implement pioneering concepts over a period of five years and thus strengthens the European research landscape.

The ERC received 2652 consolidator grant proposals, and a total of 313 laureates were funded in Europa. In the physical sciences and engineering PE5 panel (Synthetic Chemistry and Materials), a total of 12 ERC CoG grants were awarded this year in Europa, among which only one (this project B-YOND) was awarded in Belgium. ERC Consolidator Grants are designed to support excellent research programs which must demonstrate ground-breaking nature and multidisciplinary ambition.

Inspired by transition-metal catalysis and main-group chemistry, the recently funded ERC project "B-yond" aims at reprograming molecular systems based on s and p block elements to overstep current chemistry reactivity rules.

A milestone of this project is the formulation of acids and bases with minimal reorganization energies suitable for promoting new catalytic processes. The development of ground-breaking main-group catalysts based on the most abundant elements in the earth crust will have a wide impact on chemical materials transformation, as well as on bulk and fine chemical synthesis.

The research outcomes will lay the basis for developing new energy and resources management strategies, notably through novel approaches to catalysts design and sustainable materials development, by avoiding the use of precious transition-metal elements.

Thus, the research project B-YOND addresses important challenges in the quest for a sustainable future, since Prof. Berionni and his working group (see Prof. Berionni research group picture on May 2022 below) will develop new reactive species and catalysts that benefit a variety of chemical technologies.

Figure 1. Prof. Berionni research group on May 2022 (copyright © Geoffroy LIBERT). From left to right : Damien Mahaut – Lucie Pedussaut – Ali BenSaida – Guillaume Berionni – Thu-Hong Doan – Nicolas Niessen – Arnaud Osi – Aurélien Chardon – Bruno Dicarlo – Julien Habrard. (Missing: Antoine Willems and Esteban Danloy).

Additional links

- Prof. Berionni research group website: Laboratory of Reactivity and Organic Catalysis
- A recent interview of Prof. Berionni: Young Career Focus presents Guillaume Berionni, Synform (Thieme Chemistry, 2021).
- A recent highlight (Namur Institute of Structured Mater, 2022) on the applications of new pyramidal Lewis acids developed in the Berionni group: here
- A description of a former research program supported by the Belgian National Fund for Scientific Research (Fonds National de la Recherche Scientifique FNRS): here
- Link to the ERC consolidator grant webpage: here