Theme Issue of Chemical Reviews

Introduction: Frontiers in Main-Group Chemistry

2019 celebrates the 150th anniversary of the discovery of the periodic system by Dmitri Mendeleev. The periodic table of the chemical elements is arguably one of the most important cornerstone in Science, and definitely the reference notion when dealing with chemical species and chemical transformations. The main group elements, *ie* the s and p-block elements, play a prominent role among the periodic table. They are abundant on Earth, they form compounds of broad structural diversity, of generally low toxicity and of versatile properties. These features make main-group elements ideal candidates for a broad range of applications, from fine chemistry to materials science.

Main-group chemistry has tremendously advanced since the last Special issue on the topic appeared in Chemical Reviews in 2010 (earlier issues have been published in 1985 and 1990). This Issue aims at highlighting this progress and the new possibilities main-group elements offers. It collects reviews on diverse topics that illustrate the broadness and effervescence of this field of research.

From a fundamental standpoint, main-group elements are unique in forming highly reactive species and unusual compounds with non-classical electronic structures and bonding situations. These species are interesting in their own, as new chemical entities, and they often raise question about chemical bonding and bonding models. Here the interplay between experiment and theory is of major interest. Modern theoretical methods are extremely useful in order to rationalize and predict the structure and properties of the new main-group species, both known and unknown.

Main-group compounds also possess rich reactivity and major discoveries has been made recently regarding their ability to activate small essential molecules. Such chemical bond activations were long considered achievable under mild conditions only with transition metals. It is now clear that smart design enables main-group compounds to activate key molecules such as H₂, CO₂ or even N₂ and applications into catalysis are rapidly developing.

Combination of main-group elements (homo or heteronuclear) in well-defined polyfunctional compounds as well as clusters also attract much interest with the aim to create and take advantage of synergism between multiple sites. Such cooperativity is very promising to enhance reactivity and ultimately to enable transformations which are otherwise impossible or very challenging to perform.

In addition, main group elements are very valuable in materials science and properties ranging from electron- and ion-conduction, photophysics, magnetism... can be triggered and finely tuned playing with the specific properties of the p-block elements. As illustrated by some reviews, chirality is also playing an important role in main-group chemistry, in asymmetric synthesis of course, but also in chiral materials with electrochemical and/or chiroptical properties.

All the contributing expert authors are warmly acknowledged for providing comprehensive and stimulating reviews covering a wide span of topics. This Issue aims at highlighting the progress achieved in the field and the associated opportunities for the future. Hopefully, it will also foster studies to push forward main-group chemistry and explore unknown territories.

To end up, I wish to express my gratitude to Prof. Guy Bertrand who has served as an Associate Editor for this Thematic Issue. It has been a pleasure to work with him and his Assistant, Michèle Soleilhavoup.

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