Introduction to Main Group Chemistry

In October 1985, the first-ever thematic issue of *Chemical Reviews* appeared. It was entitled "Main-Group Chemistry". In January 1990, in the introduction of the second thematic issue dedicated to this topic, Josef Michl and John Gladysz wrote: "The chemistry of main-group elements was chosen (in 1985) since it seemed to be in the initial phases of a renaissance. This relatively rapid return to a subject reflects the continued growth of interest in this subdiscipline". Some 20 years later, main group chemistry continues to blossom, and there are many reasons for that. The main group elements, sometimes termed s- and p-block elements, are the most diverse in the Periodic Table and represent the most prevalent components of the Earth's crust. Their abundance, availability, and diversity make them useful for a myriad of applications of enormous industrial, economic, and environmental importance. These elements play key roles in nearly all fields of chemistry, and recent years have witnessed spectacular developments, ranging from fundamental aspects such as unprecedented binding motifs to the design and application of new materials and alternative energy sources.

Following the columns of the Periodic Table, from the metals to nonmetals via semimetals, this issue begins with an article by Harder dealing with a novel aspect of the alkaline earth metals, namely catalytic reactions mediated by calcium complexes, with relevant examples of similar strontium and barium catalysts. This is an excellent demonstration that, although transition metal chemistry still forms the heart of homogeneous catalysis, main group organometallic chemistry is not limited to classical Lewis-acidic or -basic catalysis.

Group 13, 14, and 15 elements are well represented, beginning with an article on very fundamental aspects. Fischer and Power show that unlike the second row elements, heavier analogues belonging to these three groups still allow for the discovery of novel bonding arrangements and unprecedented structures.

Three contributions emphasize boron chemistry and its applications. Braunschweig, Dewhurst, and Schneider focus on molecular compounds featuring "electron-precise" two-center metal−boron bonds, with a special attention to the very recent developments in boron-transition metal chemistry. Wade, Broomsgrove, Aldridge, and Gabbaï show the pros and cons of boron-based Lewis acids, compared to organic receptors, as fluoride sensors. Jäkle reviews the advances in boron-containing organic−inorganic polymers and details applications of these macromolecules as optical, sensory, and electronic device materials.

Heavier analogues of group 13 are also represented in this thematic issue. Schnöckel analyzes the structure and properties of metal rich aluminum and gallium clusters. The reader quickly realizes that the highly mixed valent states of their metal atoms offer challenges not only for chemists, but also for physicists.

White phosphorus (P_4) is readily available, and the most reactive allotrope of the element. It is the classical starting material for the industrial preparation of organophosphorus derivatives. To meet the growing demand in phosphorus derivatives and the increasingly stringent environmental regulations, new processes using white phosphorus but avoiding chlorine are highly desirable. This short statement readily explains why three articles deal with the activation of P_4. Cossairt, Piro, and Cummins first summarize recent results using early transition metal complexes (groups 3−7), lanthanides and actinides. Then, Caporali, Gonsalvi, Rossin, and Peruzzini detail the coordination behavior of white phosphorus with late transition metals (groups 7−11), a more mature topic, since it started in the early 1970s. Last, Scheer, Balázs, and Seitz provide insight into the current stage of research on the use of main group element derivatives (groups 1, 2, 13−17) for P_4 activation. Another article deals with phosphines, the most conventional ligands for transition metals. When the phosphorus center is part of a ring, the ligand properties can be significantly tuned, as described by Kollár and Keglevich. They present the synthesis of three- to seven-membered P-heterocycles, as well as their coordination chemistry and the catalytic properties of the ensuing complexes.

Two articles deal specifically with group 16 elements. Wojaczyńska and Wojaczyński discuss the numerous chemical and biological methods allowing the preparation of nonracemic sulfoxides developed since 2000. Then, Mukherjee, Zade, Singh, and Sunoj emphasize the hypervalent nature of selenium, with applications in the fields of organic synthesis, biochemistry, and even in transition metal chemistry.

The last two reviews to appear in this issue are perfect examples of the diversity and usefulness of main group elements. Malik, Afzaal, and O'Brien present an overview concerning the preparation of semiconducting materials based on the combination of different main group elements, 2 and 16, 13 and 15, 13 and 16, 14 and 16, and 15 and 16. Gleiter and Werz discuss the preparation and properties of alkynes substituted by almost all main group elements from right to left, and top to bottom of the periodic table—even the noble gases are there. They do not analyze only simple alkynes, but they show that the rigidity of the CC triple bonds in oligoalkynes allows for building complex structural motifs.

The field is so broad that a single issue of *Chemical Reviews* cannot cover all aspects and even all elements. We simply hope that this collection of articles, written by a broad and internationally diverse spectrum of experts, vividly conveys the creative vision of the main group community and illustrates how an art is reduced to practice.

I began this introduction quoting John Gladysz and Josef Michl. I would like to end by wishing John to be as successful as the Editor-in-Chief of Organometallics as he was as the Associate Editor of Chemical Reviews. This marks the last issue where his name will appear on the masthead. I am proud to be John's successor and hope that I will be able to assist Josef as John did for so many years.

Guy Bertrand
UCR, Chemistry

CR1001657

10.1021/cr1001657
Published on Web 07/14/2010