

Preface: Forum on Main-Group Chemistry from Synthesis to Applications

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The study of the main-group elements and their compounds is one of the major themes in inorganic chemistry. Nonetheless, it is a theme that has often been overshadowed by the intense interest in transition-metal derivatives. There are a variety of reasons for this, not the least of which is the perception that, in general, main-group compounds are less interesting—or possibly more predictable—in their chemical behavior because of their closed-shell propensity, more restricted electron counts, and fewer available oxidation states. However, over the past 3 decades, there has been a growing interest in main-group compounds, extending across all members of the s and p blocks, which has resulted in the discovery of numerous new classes of compounds with previously unknown structures and bonding. Arguably, the major motivation for many workers associated with these developments has been the construction of novel molecular architectures and the discovery of previously unknown bonding modes or reactivities. These investigations have now blossomed into a very large and diverse field. In this Forum, we provide a selection of articles on some of the new topics in main-group chemistry. This selection is only a sampler of the recent activity and newly envisioned challenges in this increasingly rich field. Additionally, while these articles are mostly fundamental by their nature, it is hoped that they will also stimulate further interest in the use and application of these new systems in synthesis and catalysis.

In s-block derivatives, the structural chemistry of alkali and alkaline-earth benzyl derivatives is showcased by Ruhlandt-Senge, who describes the structural versatility of this family of compounds and the hard-to-predict dependence of these structures on the nature of the specific s-block element or the coligands present. s-Block element chemistry also presents some striking opportunities in the development of novel organometallic synthetic pathways as developed by Mulvey and Robertson in an account of their extensive studies of synergic metalation chemistry. In their article, they present a series of new results on the direct ortho-alumination of various aromatic substrates using the putative $\text{Bu}_2\text{Al}(\mu\text{-TMP})_2\text{Li}\cdot\text{THF}$ base (TMP = anion of 2,2,6,6-tetramethylpiperidine). Their contribution, which establishes the crucial role played by lithium as a “mediator” and “director” in these reactions, illustrates the ever-expanding importance of s-block and early p-block bases and their impact in organic synthesis.

In the past few years, related efforts in the chemistry of group 2 and 12 elements have afforded compounds that feature a covalent linkage between two electropositive elements. While originally regarded as laboratory curiosities, such species are now surfacing as potentially useful reducing agents, a prospect nicely exemplified by the contribution of Jones, Frenking, and Stasch on the use of magnesium(I) dimers for the reduction of

group 14 complexes. This contribution illustrates the emergence of new reagents; it also provides an elegant illustration of the use of uninegative bidentate ligands for stabilization of low-valent group 14 compounds such as tin(I).

Another example of curiosity-driven research directed toward the discovery of new structures is provided by Schrobilgen, who describes how a well-known main-group molecule such as thiazyl trifluoride $\text{N}\equiv\text{SF}_3$ can be used to access a variety of xenon–nitrogen complexes including $[\text{F}_3\text{S}\equiv\text{NXeF}]^+$, which isomerizes into $[\text{F}_4\text{S}=\text{NXe}]^+$ in anhydrous HF. This contribution also illustrates a continuing effort among the inorganic community to develop the chemistry of high-oxidation-state main-group compounds. While much of this activity can be regarded as purely academic, one should bear in mind the growing importance of main-group compounds such as hypervalent iodine derivatives as oxidants in organic chemistry.

At the other extreme of the “redox spectrum” lies a rich collection of low-valent main-group compounds, which have been targeted by many researchers. While applications of this chemistry are still forthcoming, the advances made in this area have led to the revision of accepted bonding paradigms, such as the so-called “double-bond rule”. In this Forum, these vibrant developments are captured in two articles that describe some aspects of low-valent group 13, 14, and 15 chemistry. In one of these two papers, Lee and Sekiguchi present the chemistry of geminal dianionic silicon, tin, and germanium derivatives and their reaction chemistry to access a variety of unsaturated main-group compounds including heavy analogues of cyclobutadiene dianions and transition-metal carbene complexes. One of the key aspects of this contribution is the demonstration that highly reduced main-group dianionic compounds can be handled as versatile reagents to access a range of thus-far unprecedented structures. The geminal dianionic group 14 reagents evoked by Lee and Sekiguchi can be regarded as group 14 compounds with the group 14 element in the zero formal oxidation state. As such, these compounds can be related to the bis(carbene) silicon species described by Robinson in his contribution to this Forum issue. In this didactic article, Robinson describes how nucleophilic carbene ligands can stabilize not only neutral $\text{Si}=\text{Si}$ and $\text{P}=\text{P}$ units but also diborene ($\text{H}=\text{B}=\text{B}=\text{H}$) or the parent phosphinidene ($\text{H}=\text{P}=\text{P}=\text{H}$). By presenting these leading efforts, Robinson opens a window on a much larger field of contemporary main-group chemistry concerned with the use of nucleophilic two-electron donor ligands for the stabilization of otherwise highly reactive intermediates.

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As in transition-metal chemistry, the electronic and steric properties of a ligand may be exploited to stabilize and thus observe unprecedented main-group species. This approach has proved especially important in the domain of low-valent main-group chemistry, where, for example, bulky ligands have been key “enablers”. Parkin, Yurkerwich, and Yurkerwich underscore the importance of this approach in an article dealing with the chemistry of the tris(2-mercaptoimidazolyl)hydroborato ligand. This article shows how this unusual ligand type can be used to probe a variety of phenomena ranging from mercury detoxification to the formation of complexes with transition-metal-to-ligand $M \rightarrow B$ dative bonds. The article also presents a series of new results that underscore the power of these ligands for stabilization of a variety of complexes including low-valent group 13 compounds.

The use of main-group compounds as precursors to inorganic phases has important ramifications in the processing or the discovery of new materials for energy and catalysis applications. Given the importance of III/V semiconductors in electronic and solar energy conversion, the design of group 13 compounds that could be potential precursors to such semiconductors continues to be an important topic. The structurally fascinating group 13 hydrazide cage compounds described by Uhl in his paper highlight the continuing advances made in this field of research and offer a glimpse into a family of possible low-temperature precursors for group 13 nitrides. Molecular main-group chemistry may also afford important models for extended inorganic solids, as demonstrated by Frenking and Fischer, who show how transition-metal-centered clusters decorated at their periphery by low-valent zinc and gallium ligands relate to Hume–Rothery-type alloys. This contribution validates the structural analogy that exists between these molecular compounds and the extended solid analogues; it also illustrates how understanding the electronic structure of a finite cluster compound can provide a model for the corresponding extended intermetallic phase.

In addition to providing models or precursors for inorganic materials, transition-metal complexes bearing main-group ligands have also attracted a great deal of attention in the area of metal–metal or metal–element multiple bonding. This field of research has witnessed some exciting developments over the years, as exemplified by the contribution of Cummins et al., who report on the activation of P_4 by a niobium complex with an $Nb \equiv P$ triple bond. Their work also shows how new main-group species such as a substituted pentaphosphacyclopentadienide can be crafted in the coordination spheres of transition metals.

Although the physical properties of main-group elements have been central to the development of modern electronics, they are also becoming key constituents of molecular materials. In a review article dedicated to the synthesis, structure, and electronic properties of boron complexes featuring pyrrolyl ligands, Brothers demonstrates how a light inorganic element such as boron can be incorporated in polydentate pyrrole-based ligands to afford a broad collection of unprecedented conjugated materials with unique photophysical properties. This review also identifies some exciting dinuclear boron species such as $[B_2(\text{porphine})]^{2+}$ and its two-electron reduction products, which are certain to attract further attention for their potential in materials chemistry. Similar themes are evoked by Wang and co-workers, who review the synthesis and optoelectronic properties of four-coordinate organoboron compounds with π -conjugated chelate ligands. This review

shows how a single class of main-group molecules may present attractive leads in different technological fields ranging from new emissive materials for light-emitting diodes to the design of new anion sensors. This review also emphasizes new exciting work from Wang’s laboratory on the properties of N,C-chelated boron compounds that isomerize and thus change color upon exposure to specific visible wavelengths. As duly noted by the authors, these new “photochromic” materials may find use in applications ranging from optical memory devices to smart windows.

Stephan’s contribution to this Forum issue shows how his group has been able to apply their 2006 discovery on the heterolytic splitting of H_2 by frustrated Lewis pairs (FLPs) to the design of new hydrogenation catalysts that can be used with a variety of substrates including imines, enamines, and silylenol ethers, among others. The demonstrated versatility of these FLP-based hydrogenation catalysts suggests their continuous growth and broader applicability in terms of both substrates and asymmetric hydrogenation reactions. On the same general topic, Piers, Marwitz, and Mercier recount the seminal mid-1990s discovery that $B(C_6F_5)_3$ can be used for the hydrosilylation of a variety of carbonyl and imine substrates. By analyzing the lessons learned from mechanistic studies, these authors conclude that the activations of Si–H and H_2 by Lewis pairs are chemically related and both rely on the phenomenon of frustration. These independent contributions by Piers and Stephan validate the emerging notion that main-group compounds or combinations thereof may compete advantageously with transition-metal catalysts.

As mentioned in the opening paragraph, this Forum highlights only a limited number of new and exciting investigations in main-group chemistry. As a consequence, several important areas have not been covered. Not the least among these is the vast area of molecular clusters of main-group elements, which could occupy several volumes without difficulty (*Molecular Clusters of Main Group Elements*; Driess, M., Nöth, H., Eds.; Wiley-VCH: Weinheim, Germany, 2004). The importance of aluminum alkyls in several catalytic processes is another important area that has not been included. We recognize that catalysis by main-group element compounds, the aspects of which have been covered in the reviews of Piers and Stephan, and the direct interaction of several main-group compounds with important small molecules are topics of increasing interest and importance. It is our hope that, as a sampler of exciting new chemistry, this Forum will serve to stimulate further development in the renewed blossoming of main-group chemistry.

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