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## **Editorial: Earth-abundant metals**

Why Earth-abundant metals? Their low cost, ready availability, comparatively low toxicity and greater sustainability are all factors leading to a major renaissance in the study of the organometallic chemistry of Earth-abundant metals over the last few years.

Traditionally, second and third row transition metals are extensively exploited in organometallic chemistry, especially in catalytic applications, where platinum group metals (PGMs) and, to a lesser extent heavier coinage metals, play a particularly prominent role. However, there are significant and growing issues associated with the longer-term use of PGMs. The first of these is cost and supply: PGMs are not only expensive, but their prices can vary wildly depending on the balance between availability and exploitation. Significant competition from the bulk chemical, automotive and consumer electronics sectors can and does impact markedly on the price. Moreover, the low natural abundance of PGMs, and the fact that their production is confined to a very few regions globally, can lead to supply and cost issues. The British Geological Survey maintains a 'risk list' (<http://www.bgs.ac.uk/mineralsuk/statistics/risklist.html>) that delineates the supply risk index for chemical elements or element groups that are of economic value, and platinum group metals feature high on this.

A second issue associated with the use of platinum group metals is their relatively high toxicity. Nature has not exploited these elements to any great extent in evolution, due to their low abundance, and many of them show pronounced deleterious effects on biological systems. Consequently their use in the preparation of pharmaceuticals is subject to strict regulatory control in order to minimize (typically to the low ppm level) the presence of PGMs in the final products.

In addition to these economical and ecological arguments, the investigation of Earth-abundant metal complexes constitutes an intriguing endeavor also from a purely scientific

perspective: Nature is able to utilize first-row transition metals for catalyzing some of the most challenging transformations such as the selective activation of non-polar aliphatic C-H or C-C bonds, nowadays considered as 'holy grails' of homogeneous catalysis. In natural systems, these processes generally follow a single electron transfer (SET)-type radical mechanism, in which the metal plays a central role. Organometallic chemists have tried to understand the unique properties of these natural catalysts by preparing and analyzing model complexes. As a consequence, a significant knowledge base has evolved over time, which triggered a renewed interest in Earth abundant metal complexes for catalysis. The mechanistic manifolds adopted by first row metals are often significantly more complex than those of their heavier metal counterparts. Thus while the latter typically undergo well-defined 2-electron redox processes, first row transition metals such as Cr, Mn, Fe, Co, and Ni are prone to facile single-electron transfer pathways. The associated radical chemistry often involves electron redistribution between the central metal and electronically non-innocent ligands and hence frequently entails ill-defined open-shell configurations. These electronic and structural uncertainties impact structural analyses and spectroscopic monitoring, and mechanistic elucidations become a formidable challenge. Nonetheless, one-electron redox processes are likely to open entirely new perspectives in organometallic catalysis and bond making and breaking processes.

Apart from these synthetic challenges, there are of course significant spectroscopic issues with the study of Earth abundant element organometallic chemistry. First row metal chemistry in particular not least many of the organometallic starting materials, products and intermediates are paramagnetic. This can severely hamper their routine analysis and necessitates the use of specialist instrumentation and expertise, such as EPR spectroscopy and SQUID magnetometry, which is not always available in research institutes. In addition, many first row metal complexes are substitutionally far more labile than their second and third row

counterparts and hence, isomerization, substitution, and rearrangement reactions are considerably more frequent and less controllable than with the more inert precious metals of the platinum group or the coinage series. As a consequence, structural features can be much less well defined, as exemplified by the lability of bpy in  $[\text{Fe}(\text{bpy})_3]^{2+}$  complexes, compared with  $[\text{Ru}(\text{bpy})_3]^{2+}$  which exists in distinct  $\Lambda$  and  $\Delta$  forms. This lability can also lead to a marked decrease in stability of organometallic species compared with second and third row congeners.

Even though Nature routinely exploits first row transition metals in metal-mediated processes, the synthetic usage of these metals has developed comparatively little. We organometallic chemists tend to be drawn towards the charms of heavier metals, in particular the platinum group metals, as evidenced by the fact that around half of all papers submitted to *Organometallics* last year focused on PGM chemistry. However it is readily apparent from the above discussion that there are major drivers for the organometallics community to wean itself off an over-reliance on platinum group and heavier coinage metals, and move instead towards more Earth-abundant elements, particularly first row transition metals.

It is fair to say the complications associated with the study of Earth abundant elements outlined above constitute a key reason why the organometallic community has largely concentrated its efforts on precious and coinage metals. However the need to develop sustainable synthetic processes that address cost, supply, toxicity and the minimizing of environmental impact means that, as a community, we organometallic chemists need to increase our focus on the study Earth abundant metal's chemistry. We need to address the perceived challenges and realize that these in fact provide opportunities for creative, intellectually stimulating endeavor.

Over the last few years, it has become apparent that this process has begun in earnest and that significant progress has been made in this previously underdeveloped area, including

both classic coordination chemistry and organometallic systems. The aim of this themed issue is to highlight the diversity of efforts in the organometallic chemistry of Earth-abundant metals, including their application to synthesis, catalysis and biochemically relevant processes. With excellent contributions from all over the world encompassing a high diversity of organometallic species based on iron, nickel, aluminum, calcium, chromium, cobalt, copper and magnesium, this issue reflects the global efforts to move towards more sustainable processes and showcases the lively activities in this field, as well as the continuous challenges and excitement that this branch of organometallic chemistry entails. The issue is grouped primarily by application (synthesis, mechanistic studies, catalysts and biological applications) and then by metal. It is our hope that this compilation will act as a catalyst for further activity in this demanding, yet exciting and intellectually stimulating area of organometallic chemistry.

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### **About the Cover:**

While a considerable amount of organometallic research has revolved around precious metals with comparatively little focus on Earth-abundant metals such as Ni, Co, and Fe, more recent times have seen a burst of activity with these elements. Spurred by a number of attractive triggers such as their inherently low toxicity, their cost effectiveness, a shift to more sustainable processes, and probably above all by the tremendous intellectual challenge, these metals have become central to many most creative research programs and begin to sparkle in a various areas of classical organometallic chemistry. This Special Issue aims to showcase the diverse efforts to advance the understanding and utilization of Earth-abundant metals and to stimulate further research in this burgeoning area.