Small molecule activation

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The activation of small molecules has become an increasingly popular area of research over the last years, and there are many reasons to be captivated by this fascinating topic. For some, small molecule activation may be a purely academic challenge. Others may be spell-bound by the vast opportunities that emerge for synthesis, like the ability to use N_2 or O_2 as synthons for the formation of C–N or C–O bonds. Again a different focus is of course imposed by the pressing environmental issues like the depletion of fossil fuel feedstocks and the associated accumulation of methane and CO_2. Within the same context, small molecule activation has played a central role in all major attempts to store renewable yet transient energy into chemical bonds, as in artificial photosynthesis or in modern fuel cells.

All efforts share the same fundamental questions: how can fairly unreactive and typically very strong bonds such as C–H or N–N bonds be activated? What conditions and perturbation is needed to move an otherwise inert molecule such as N_2 or CO_2 out of its comfort zone to become a reagent? As organometallic and coordination chemists, we probably wonder most what concept and what strategy is required to induce the appropriate configuration on the metal center to bind such small molecules, and eventually to perturb their ground state to such an extent that a reaction starts to occur, ideally in a catalytic manner. Clearly, such questions require a concerted and holistic approach, including synthetic skills for ligand design and fabrication, an in-depth understanding of mechanistic and kinetic aspects of the interaction of small molecules with the activating entity, and explanatory as well as predictive support from theoretical expertise. The importance of such a concerted and collaborative approach has been recognized by the foundation and support of a variety of consortia and networks, such as the COST Action on "Catalytic Routines for Small Molecule Activation (CARISMA)", which pools about 60 European experts in a network to address many of the challenges associated with small molecule activation, and to enforce collaborative approaches to meet these challenges. This themed issue of *Dalton Transactions* features a number of contributions from members of CARISMA and hence highlights the benefits of collaborative and integrative approaches to advance this field.

This themed issue provides an overview of current activities with 39 papers, authored by well-recognized experts in their field, and we are truly grateful for their splendid contributions. The issue also emphasizes the large diversity of topical aspects within the area of small molecule activation, highlighting various domains as demonstrated by several articles on the activation of CO_2 (with a far end goal to reduce global CO_2 levels), a set of contributions directed towards new methodologies and a better understanding of H_2 evolution (to provide a chemical approach for energy storage), exciting prospects in NH_3 and N_2 bonding and activation, and more than a dozen contributions that provide new insights into O_2 activation, or its reverse, the oxidation of H_2O or H_2O_2, key processes for example for generating a sustainable artificial photosynthetic device.

From reading the many outstanding contributions, it becomes clear that while impressive progress has been and continues to be made, many challenges remain to be tackled. Low turnover numbers and/or turnover frequencies are prohibitive for a wide application and need to be improved. Many processes such as water oxidation continue to rely on precious metals for being efficient—can Earth-abundant metal centers be tailored to reach similar or better catalytic performance? Then of course, many processes will need to be placed into a more interdisciplinary context, maybe involving engineers and materials scientists in order to fabricate proper and efficient devices, and certainly also involving completely different disciplines in order to address the various steps for

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implementation, such as legal, economic, and societal aspects. Whether optimizing well-established reactivity patterns or discovering fundamentally new (catalytic) processes for small molecule activation, this field remains a burgeoning area of research and a fascinating ground for exciting developments. We trust that this issue with its impressive contributions succeeds in sharing some of this fascination and excitement.