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Editorial

Diversity in Small-Molecule Activation: The Adventure Continues

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The sustainable transformation of small molecules such as CO_2, N_2, O_2, and CH_4 into other products has always been central to endeavors in chemical science. Indeed, from an inorganic chemistry perspective, the catalytic activation of typically inert small molecules has had an evergreen presence in the research community. For instance, although established for more than a century, the Haber−Bosch process to convert N_2 and H_2 into NH_4 is still one of the highlights of catalytic transformations and remains an area of active research, whether that be developments in new heterogeneous catalysts or in small-molecule homogeneous catalysts, or, indeed, theory.

Despite the long history, the modern challenges of climate change, energy sustainability, and resource efficiency perhaps make the activation of small molecules more important than ever before. It is in this context that this curated *Inorganic Chemistry* Forum on Advances in Small-Molecule Activation is presented, one that we hope makes a timely contribution to the discussion of this critical and dynamic topic. This edition sits alongside other key works in the area, including a multivolume set of *Inorganic Chemistry* Forums,[1−3] which are the foundations of the present issue, an edited book summarized by the editor of this journal in 2006,[4] and a themed collection of *Dalton Transactions* issued in 2016.[5]

Herein, we have taken the view that there is no sharp definition of a small molecule, not least because recent fundamental and applied work has broadened the scope of small-molecule activation beyond the classical examples. Moreover, the nature of catalysts has been significantly extended; besides transition-metal complexes, we have seen lanthanide and actinide metals, main-group metals, and nonmetals such as frustrated Lewis pairs (FLPs) intensively investigated as suitable reagents for small-molecule activation.

Accordingly, with this Forum Issue, we showcase some recent developments, which include both classical challenges, such as nitrogen, oxygen, hydrogen, and C−H activation, and emerging fields, like FLPs. For instance, Borovik and co-workers address modern C−H bond activation with an emphasis on nonheme iron enzymes (DOI: 10.1021/acs.inorgchem.1c01754). An emerging field of small-molecule activation centers on the use of FLPs as activators, which Hevia and co-workers demonstrate through the use of a NHC/GaR_3 FLP for the catalytic hydroboration of unsaturated organic molecules (DOI: 10.1021/acs.inorgchem.1c01276). A theoretical approach to the nature of the bonds in FLPs of oxorhenium and nitridorhenium complexes with $B(C_6F_5)_3$ is presented by Ison and Tubb (DOI: 10.1021/acs.inorgchem.1c00911). Further, Szymczak and co-workers report on weak intramolecular Lewis acid/base interactions (DOI: 10.1021/acs.inorgchem.1c01382).

Within the area of bioinspired N_2 activation, Neidig, Song, and co-workers report a diferric [2Fe−2S] cluster, which displays catalytic activity toward dinitrogen reduction (DOI: 10.1021/acs.inorgchem.1c00683). Another bioinspired work presented by Latifi, de Visser, Tahsini, and co-workers focuses on a biomimetic nonheme iron(IV) oxo complex and its reactivity upon changing axial ligand coordination (DOI: 10.1021/acs.inorgchem.1c01312). A bimolecular O_2 activation induced by a sterically encumbered polyoxovanadate-alkoxide is described by Matson and co-workers (DOI: 10.1021/acs.inorgchem.1c00887). A different activation of O_2 by nickel(I) is shown by Limberg and co-workers (DOI: 10.1021/acs.inorgchem.0c03761). Among other examples, they present the formation of a superoxide nickel complex. Both topics, N_2 and O_2 activation, are covered in theoretical studies dealing with the multiple-bond character of pseudotetrahedral Co^{III} oxo and imide complexes presented by Anderson and co-workers (DOI: 10.1021/acs.inorgchem.1c01022). The activation of heavier chalcogens is described by Roesky and co-workers (DOI: 10.1021/acs.inorgchem.0c03609). Another approach to bioinspired chemistry is presented by Shafaat and Lewis. They report on the reversible electron transfer of a metalloprotein model for carbon monoxide dehydrogenase (DOI: 10.1021/acs.inorgchem.1c01323).

Hydrogen activation, formation, and transformation is key for modern energy conversion. Karlin, Dey, and co-workers report on the nature of proton-transfer groups for the hydrogen evolution reaction in the presence of iron porphyrins (DOI: 10.1021/acs.inorgchem.1c01079). The role of electrocatalysts with redox-active ligands for H_2 evolution is outlined by de Vivie-Riedle, Hess, and co-workers (DOI: 10.1021/acs.inorgchem.1c01157), while the reaction of η^2-alkene complexes with H_2 is addressed by Weller and co-workers (DOI: 10.1021/acs.inorgchem.0c03687). Xiang, Chen, and co-workers describe the reactivity of divalent ytterbium hydrido complexes (DOI: 10.1021/acs.inorgchem.1c00686), while Morris and Tsui outline the difference between transition

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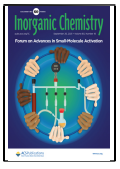

metals and main group element hydrogen bonds (DOI: 10.1021/acs.inorgchem.1c00801).

The topic of small-molecule activation is a large and ongoing research topic in which inorganic chemistry plays a critical role in the development of activators and catalysts. It is not possible to fully cover this broad field within this *Inorganic Chemistry* Forum. Our intention was rather to give insight into the cutting-edge research work from first-class authors working in different areas of small-molecule activation. Also, we hope this collection of research articles inspires others to contribute to this field of inorganic chemistry and to expand it with new ideas.

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Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

Biographies

Peter W. Roesky obtained his diploma in 1992 from the University of Würzburg and his doctoral degree from the Technical University of Munich (with Prof. W. A. Herrmann) in 1994. He was as a postdoc with Prof. T. J. Marks at Northwestern University (1995−1996). In 1999, he completed his habilitation at the University of Karlsruhe. As a full professor, he joined the faculty of chemistry and biochemistry at the Freie Universität Berlin in 2001. Since 2008, he has held the chair for inorganic functional materials at the University of Karlsruhe Institute of Technology. In 1999, Prof. Roesky received a Heisenberg scholarship from the German Science Foundation and, in 2000, a Karl-Winnacker scholarship. Since 2014, he has been a fellow of the Royal Society of Chemistry and, since 2020, a fellow of the European Academy of Science (EurAsc). In 2019, he received a JSPS Invitational Fellowships for Research in Japan and, in 2020, a Reinhart Koselleck Project from the German Science Foundation.

Alison R. Fout graduated with a B.S. from Gannon University (2002) and a M.S. from the University of North Carolina, Charlotte (with Daniel Rabinovich in 2004). Alison obtained her Ph.D. from Indiana University under the tutelage of Daniel J. Mindiola (2009). She was a NIH Ruth Kirschstein and Mary Fieser Postdoctoral Fellow with Theodore A. Betley at Harvard University. She joined the faculty at the University of Illinois, Urbana−Champaign, in 2012, where she is currently an associate professor. Prof. Fout has been the recipient of an NSF CAREER award and a DOE Early Career Award and is a Sloan Scholar and a Camille Dreyfus Scholar. In 2018, she was also awarded the Emergent Investigator in Bioinorganic Chemistry including Medicinal Chemistry sponsored by the ACS Division of Inorganic Chemistry.

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