Molecular Donor-Acceptor Systems for Small Molecules Activation

Dr. Antoine Simonneau
LCC-CNRS, Université de Toulouse, CNRS, UPS, 31077 Toulouse, France
antoine.simonneau@lcc-toulouse.fr

After studying at Chimie ParisTech and Sorbonne University, AS completed his PhD under the supervision of Profs. M. Malacria and L. Fensterbank (2008–2012). He earned the Springer thesis prize for his work on gold catalysis. He continued his training with a post-doctoral internship at the Technical University of Berlin under the direction of Prof. M. Oestreich (2012–2015), thanks to a fellowship from the Alexander von Humboldt Foundation. At the end of 2015, he joined the Prof. M. Etienne at LCC as a CNRS researcher to develop a theme on the transformation of N_2. In 2017, he obtained a Starting Grant from the European Research Council (ERC). Since 2018, he has been co-managing the team "Activation of Small Molecules" with Dr. Sébastien Bontemps. In 2022, the Institute of Chemistry of Toulouse awarded him the "Young Investigator" prize and in January 2025 he will receive the Young Researcher Award of the Coordination Chemistry Division of the French chemical Society.

Activation of small molecules by donor-acceptor systems is conceptually important as many catalytic processes rely on the synergistic action of electron-rich and -poor sites to activate and cleave bonds. This pertains to both the biological and industrial chemistry contexts. Focusing on dinitrogen, the two major processes that converts it into ammonia do not escape this donor-acceptor paradigm. Biological nitrogen fixation by the nitrogenase enzymes have been proposed to be facilitated by secondary-sphere acidic residues that further activate the diatomic, when bound to the electron-rich iron-sulphur cluster of the active site, through a push-pull mechanism.[1] In industrial nitrogen fixation, alkali promoters have been shown to facilitate N_2 dissociation on the surface of the Haber-Bosch catalyst thanks to electrostatic effects.[2] However, the complexity of these two catalytic systems prevents from finely appreciating the impact and consequences of the push-pull activation in action. In this presentation, an overview of the Lewis acid adducts of low-valent N_2-complexes we have prepared and characterized will be given, with an emphasis on measuring and understanding the factors that lead to enhanced N_2 activation in these donor acceptor systems.[3] The reactivity of these new objects was also examined with the aim of devising new elementary steps en route to nitrogen fixation, taking inspiration from the recent frustrated Lewis pair chemistry.[4]

[1] P. C. Dos Santos, R. Y. Igarashi, H.-I. Lee, B. M. Hoffman, L. C. Seefeldt, D. R. Dean, *Acc. Chem. Res.* **2005**, *38*, 208–214.
[2] Q. Wang, J. Guo, P. Chen, *Chem* **2021**, *7*, 3203–3220.
[3] A. Coffinet, A. Simonneau, D. Specklin, in *Encycl. Inorg. Bioinorg. Chem.* (Ed.: R.A. Scott), Wiley-VCH Verlag GmbH & Co. KGaA, **2020**, pp. 1–25.
[4] D. W. Stephan, *Science* **2016**, *354*, aaf7229.