

LABORATOIRE DE CHIMIE DE COORDINATION DU CNRS,
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Équipe d'accueil : N (SMAC • Small Molecule Activation)

Responsables de stage : Dr. N. Queyriaux & Dr. V. César

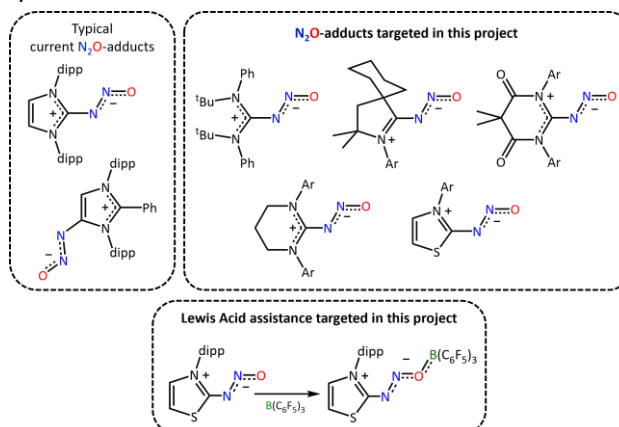
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ELECTROCHEMICAL BEHAVIOUR OF MOLECULARLY PRE-ACTIVATED N₂O

Nitrous oxide (N₂O) is a minor constituent of the atmosphere (332.1 ± 0.4 ppb, in 2019). Its tropospheric concentration is constantly rising when compared to pre-industrial levels (270.1 ± 6.0 ppb, in 1750), driven by anthropogenic perturbations of the biogeochemical nitrogen cycle: large-scale use of synthetic fertilizers in modern agriculture, chemical-processing manufactures, fossil fuels burning...^[1] *Increased atmospheric nitrous oxide levels are of particular concern*, both because of its contribution to anthropogenic radiative forcing and its ability to serve as a strong ozone-depleting agent. **Its valorisation is a prime target and new methodologies relying on nitrous oxide are thus needed.** However, N₂O is poorly reactive due its kinetic reluctance arising from the high activation barrier required to break its linearity.^[2]

Some **N-Heterocyclic Carbenes (NHCs)** are known to react with N₂O under mild conditions (*Scheme 1, upper left*). In the resulting stable, **covalent adducts**, the N₂O motif is linked to the carbene moiety through its terminal nitrogen atom, adopting a bent configuration. This results in a significant weakening of both N-N and N-O bonds, capable to enable new reactivities. This has been carefully explored by the group of K. Severin at the Swiss Federal Institute of Technology, Lausanne (EPFL) with important achievements.^[3,4] **In this internship, alternative carbene families will be explored to tune the degree of activation of the N-N-O motif.** Primarily targets are six-membered analogues, acyclic diaminocarbenes (ADC), diamidocarbenes (DAC), cyclic(alkyl)(amino)carbenes (CAAC) and thiazole-based carbenes, that span over a wide range of σ -donation and π -accepting characters. Once the NHC precursors synthesized according to literature procedures, the NHC-N₂O adducts will be synthesized and characterized (*Scheme 1, upper right*). Special attention will be given to the study of their electrochemical behaviours (one-electron reduction, reversibility, reduction locus). Further activation of the N-N-O motifs will be sought by the addition of Lewis acid partners (B(C₆F₅)₃, typically). Such species are expected to interact with terminal oxygen, initiating electronic push-pull processes capable to foster polarization of the N₂O fragment in a FLP-type activation (*Scheme 1, lower right*).



The internship will be supervised by Dr. N. Queyriaux and Dr. V. César. Solid skills in synthesis, handling and characterisation of air-sensitive species (glove box work, vacuum ramp,) will be acquired, as well as a background in analytical chemistry (NMR, UV-Vis and infrared spectroscopy, X-ray diffraction). The student will also become familiar with electrochemical tools.

To apply, please attach a CV, M1 results and the most recent internship report to your application.

- [1] V. Masson-Delmotte, P. Zhai, A. Pirani, S. L. Connors, C. Péan, S. Berger, N. Caud, Y. Chen, L. Goldfarb, M. I. Gomis, M. Huang, K. Leitzell, E. Lonnoy, J. B. R. Matthews, T. K. Maycock, T. Waterfield, Ö. Yelekçi, R. Yu, B. Zhou, Eds., *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, **2021**.
- [2] K. Severin, *Chem. Soc. Rev.* **2015**, *44*, 6375–6386.
- [3] A. G. Tskhovrebov, B. Vuichoud, E. Solari, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2013**, *135*, 9486–9492.
- [4] A. G. Tskhovrebov, E. Solari, M. D. Wodrich, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2012**, *51*, 232–234.