

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

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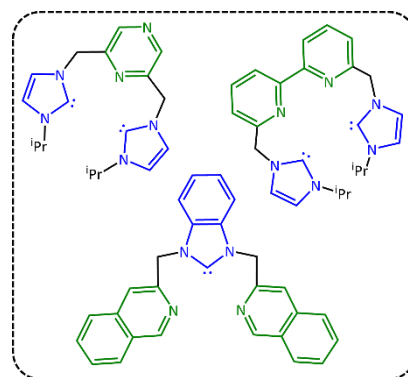


ELECTRO-ASSISTED REDUCTION OF NITROUS OXIDE (N₂O): USE OF MIXED-ELECTRONICS LIGANDS

Nitrous oxide 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]

Electron-rich metal centres are essential to foster interaction of catalysts with nitrous oxide. So far, this has been achieved through the use of low-valent metal complexes, synthesized as such or *in situ*-generated by addition of sacrificial reductants. The lower oxidation states, however, may be responsible for the occurrence of degradation pathways or unwanted reactions that alter the efficiency of the catalytic process.^[3] This is particularly true for first-row late transition metal complexes, that are targeted in this Master project. Such low-valent late transition metal complexes are indeed prone to disproportionate with formation of metallic assemblies (films, nanoparticles, etc). In this project, an original decorrelation strategy will be followed, allowing nucleophilicity and formal oxidation state of the metal centre to be regarded independently.^[4] Through a judicious ligand design, scaling relationships may be avoided, granting stable, electron-rich late transition metal centres.

The use of N-Heterocyclic Carbenes (NHCs) as ligands for transition metals has resulted in major achievements in homogeneous catalysis, thanks to a unique combination of properties. Strong σ -donor, tuneable sterics, oxidation-resistant, synthetically accessible, these ligands are also reported to ensure catalysts stability due to excellent binding ability. This project aims to assemble polydentate ligands associating those carbene motifs with redox-active moieties. The resulting bifunctional ligands will be associated with first-row transition metals and the electrocatalytic properties of the resulting complexes towards N₂O reduction investigated.



The internship will be supervised by Dr. N. Queyriaux. Solid skills in ligand synthesis, coordination chemistry and common electrocatalytic tools will be acquired, as well as a background in analytical chemistry (NMR, UV-Vis and infrared spectroscopy, X-ray diffraction).

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] D. P. Hickey, C. Sandford, Z. Rhodes, T. Gensch, L. R. Fries, M. S. Sigman, S. D. Minter, *J. Am. Chem. Soc.* **2019**, *141*, 1382–1392.
- [4] S. Gonell, M. D. Massey, I. P. Moseley, C. K. Schauer, J. T. Muckerman, A. J. M. Miller, *J. Am. Chem. Soc.* **2019**, *141*, 6658–6671.