Project Title	**Homogeneous hydrocarbon oxidation using nitrous oxide as a sustainable feedstock**
University (where student will register)	University of Warwick
Which institution will the student be based at?	As above
Theme (Max. 2 selections)	Climate & Environmental Sustainability ☒ Organisms & Ecosystems ☐ Dynamic Earth ☐
Key words	Nitrous oxide; homogeneous catalysis; synthetic inorganic chemistry; computational modelling
Supervisory team (including institution & email address	**PI:** Adrian Chaplin; Department of Chemistry, University of Warwick; a.b.chaplin@warwick.ac.uk **Co-I:** Tobias Krämer; Department of Chemistry, Maynooth University, Ireland; Tobias.Kraemer@mu.ie

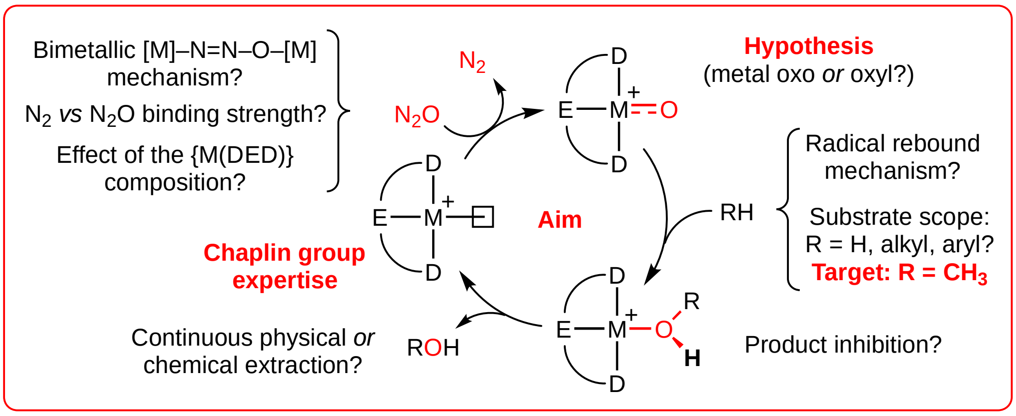
Project Highlights:

- Exploring the potential of nitrous oxide as a sustainable oxidant
- Homogeneous transition-metal-based catalysts for the transformation of hydrocarbons
- Student co-developed targets, informed by *in silico* evaluation

Overview:

Nitrous oxide (N_2O) is a potent greenhouse gas, with a half-life of 114 years in the atmosphere and global warming potential 300 times greater than carbon dioxide, and the dominant ozone depleting substance emitted in the 21st century. As an abundant and sustainable resource, the use of N_2O as an oxidant in chemical manufacture is an attractive prospect, liberating environmentally benign dinitrogen N_2, but encumbered by the robust triatomic formulation of this gas. Whilst application of heterogenous catalysts under extreme conditions does permit reactions with N_2O to be performed, such systems are energy intensive, unselective and ultimately not commercially viable.

This project will seek to establish the science underpinning the activation of N_2O by homogeneous transition-metal complexes with the ultimate objective of translating these findings into impactful catalytic applications. Using group 9 and 10 metal complexes supported by robust *mer*-tridentate 'pincer' ligands, the formation and onward reactivity of intact M–N_2O adducts will be leveraged to gain fundamental understanding of how N_2O can be most effectively exploited in chemical synthesis, with the prospect for generating reactive terminal oxo/oxyl derivatives rigorously examined in particular. The resulting structure-property and structure-activity relationships generated from these studies will be harnessed to enable the rational design of new catalysts and achieve step-changes in performance for transformations employing N_2O as a selective hydrocarbon oxidant. The upgrading of methane to methanol is one notable and industrially coveted transformation that will be targeted, with world demand for methanol approaching 100 million metric tons annually (MMSA data).



M = Co, Rh, Ir, Ni, Pd, Pt; D = phosphine, imine, NHC; E = N, C^-, N^-, B^-

Scheme 1: Conceptual overview of the project

Methodology:

Building upon ongoing experimental work in the Chaplin group and drawing parallels with the chemistry of the early transition elements, this proposal will systematically investigate the activation of N_2O using group 9 and 10 group metal pincer complexes, that is hypothesised to result in the formation of reactive terminal oxo/oxyl derivatives. Using a synergistic combination of experimental (with Chaplin) and computational (with Krämer) approaches, group 9 and 10 metal catalyst targets will be investigated to establish structure-property and structure-activity relationships underlying the coordination and activation of N_2O. These findings will be harnessed to propel subsequent catalyst design, with the most promising leads rigorously examined experimentally.

Training and skills:

All the necessary specialist training in organic and organometallic synthesis, air-sensitive techniques, homogeneous catalysis, and computational methods will be provided throughout the project by the PI, Co-I and senior members of their research teams.

Partners and collaboration (including CASE):

Results from the project will be used to engage with relevant industries, working with Warwick Ventures to protect emerging Intellectual Property.

<u>COVID-19 Resilience of the Project:</u>

The computational component of the work will not enable an efficient and broad survey of chemical space but help mitigate against the effects of the COVID-19 pandemic. This work can be carried out remotely during any necessary periods of laboratory shutdown.

Possible timeline:

Year 1: Synthesis of a representative cross-section of ca. 10 pincer complexes, followed by evaluation of their reactivity with nitrous oxide and catalytic activity in hydrocarbon oxidation reactions. Simultaneous *in silico* evaluation of these complexes.

Year 2: Detailed experimental mechanistic studies and a wide-ranging computational survey of catalyst targets. Continuous experimental catalyst evaluation and reaction optimisation.

Year 3: Iterative catalyst design, preparation, and evaluation based on experimental and computational findings.

Further reading:

Ravishankara, A.R., Daniel, J.S. & Portmann, R.W., 2009. Nitrous oxide (N_2O): the dominant ozone-depleting substance emitted in the 21st century. *Science*, 326(5949), pp.123–125.

Hansen, J. & Sato, M., 2004. Greenhouse gas growth rates. *Proceedings of the National Academy of Sciences of the United States of America*, 101(46), pp.16109–16114.

Tolman, W.B., 2010. Binding and activation of N_2O at transition-metal centers: recent mechanistic insights. *Angew. Chem. Int. Ed*, 49(6), pp.1018–1024.

Severin, K., 2015. Synthetic chemistry with nitrous oxide. *Chemical Society Reviews*, 44(17), pp.6375–6386.

Gyton, M.R., Leforestier, B. & Chaplin, A.B., 2019. Rhodium(I) Pincer Complexes of Nitrous Oxide. *Angew. Chem. Int. Ed*, 58(43), pp.15295–15298.

Delony, D. et al., 2019. A Terminal Iridium Oxo Complex with a Triplet Ground State. *Angewandte Chemie International Edition*, 58(32), pp.10971–10974.

Further details:

Further information about the Chaplin group can be found at: http://go.warwick.ac.uk/chaplingroup

Before starting the project, applications must hold an honours degree (at least II.1 or equivalent) in Chemistry, or other relevant discipline.

Enquires are welcomed and applications should be directed to Dr Adrian Chaplin (a.b.chaplin@warwick.ac.uk); please include a current CV that details any past research work.