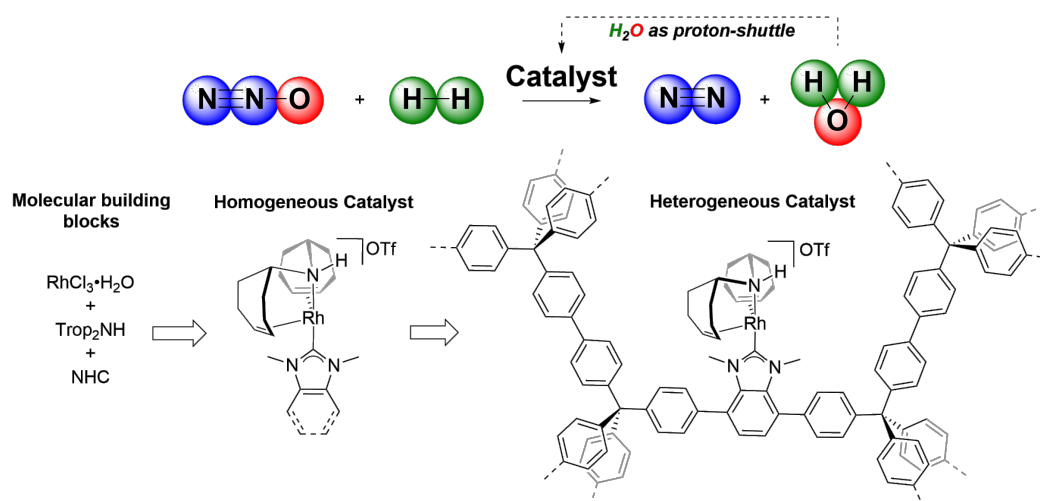


Metal-ligand Cooperative Rhodium Complexes as Highly Active N₂O Hydrogenation Catalysts

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Nitrous oxide (N₂O), more commonly known as laughing gas, is no laughing matter in view of its significance as an atmospheric pollutant. In recent times, N₂O has been identified as the most ozone depleting agent of the 21st century (comparable to that of CFC's) and a potent greenhouse gas.^[1] The 'simple on-paper' reaction: N₂O + H₂ → N₂ + H₂O can be a promising mitigation strategy, but in reality this reaction is difficult to perform. Activation of N₂O is challenging, in addition, the catalyst must remain robust and selective towards the oxidizing (N₂O) and reducing (H₂) conditions. N₂O have been, and generally still is, broadly overlooked compared to its isoelectronic and isostructural more well known molecule, CO₂. In the past decades we have seen strong research forces yielding several CO₂ hydrogenation catalysts with turnover numbers (TON's) up to millions.^[2] Meanwhile the homogeneous N₂O hydrogenation catalysts in the scientific literature today are very few in numbers and only reaches TON's of hundreds.^[3]



We can now report that we have found a catalyst that shows unprecedented activity (~ 200'000 TON's) in the hydrogenation of N₂O at mild conditions (2-5 bars, 65 °C). Rhodium as the metal and NHC's as ancillary ligands combined with a tridentate bis-olefine amine ligand^[4] was found to be the best among the tested candidates. The credit cannot be given to the catalyst design alone as evidence suggests a more holistic process. Our combined experimental and theoretical study of the reaction mechanism concludes that the process is autocatalytic. In a bottom-up approach the catalyst could be heterogenized, and the activity and stability of the well-defined single-site heterogeneous catalyst was evaluated and compared with the molecular version.

[1] Akkihebbal Ramaiah Ravishankara, Daniel John, Robert Portmann, *Science*, **2009**, 326, 123-125.

[2] Duo Wei, Matthias Beller, et. al., *Nature Energy*, **2022**, 7, 438-447.; and literature cited therein.

[3] Isabel Ortega-Lepe, Andrés Suárez, et. al., *Inorg. Chem.*, **2022**, 61, 18590-18600.; and literature cited therein.

[4] Thomas L. Gianetti, Hansjörg Grützmacher, et. al., *Angewandte Chemie*, **2016**, 55, 1854-1858.; and literature cited therein.