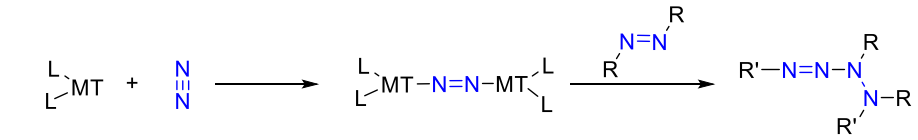
Activation du N_2 pour la synthèse de dérivés polyazotés pour la propulsion

N_2 activation for the synthesis of polynitrogen derivatives for propulsion

Context: Today, there is a strong need for research to improve propellant performance. It is crucial to be able to offer systems with a better on-board payload/total weight ratio, and therefore longer operating ranges and/or better operating and marketing costs. The aim of the present project is to develop new upstream nitrogen activation methods, enabling us to design new routes to High Energy Density Materials (HEDMs), which could lead to specific impulse gains of over 30%. HEDMs would be breakthrough propellants that could also reduce the environmental impact of launchers, as these "green" propellants would not require a stoichiometric oxidizer to react.

Thesis aims : The LHCEP laboratory is particularly interested in the synthesis of extended hydrazine analogues and their cyclic analogues. With this in mind, we plan to use dinitrogen as the basic building block for the construction of ultrahigh nitrogen-content molecules. The activation and functionalization of nitrogen represents a major challenge in organic synthesis, let alone use it as a building block for energetic materials.

First, we will use first period-transition metal complexes known for their efficiency in the activation of dinitrogen to bimetallic diazo intermediates.[1,2] These diimidometal species feature nucleophilic nitrogen atoms. Addition of these complexes to electrophilic diazo compounds would install N-N bonds, giving access to 1,2-tetrazenes. While the stoichiometric reactions will have to be examined first, the ultimate goal is to develop a catalytic method(s). It would be of further interest to examine whether/how the tetrazene can be isomerized by migration of the N=N bond along the skeleton, and whether this can be controlled by the metal complexes.



MT: Métal de transition
(Ti, Fe...)

Work context. The thesis will be carried out at the LHCEP in Villeurbanne. The LHCEP is a joint CNRS/Université Claude Bernard Lyon 1 unit with industrial partnership (CNES, ArianeGroup), whose aim is to design and develop new energetic compounds for propulsion.

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[2] a) Y. Nakanishi, Y. Ishida, H. Kawaguchi, *Angew. Chem. Int. Ed.* **2017**, *56*, 9193; b) Y. Ishida, S. Hasegawa, H. Kawaguchi, *Angew. Chem. Int. Ed.* **2023**, *62*, e202304700.

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