

Making N-C bonds directly from dinitrogen: Summary and perspective

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As the most abundant constituent in Earth's atmosphere, dinitrogen (N_2) is the main nitrogen source of N-containing compounds in the Earth. Therefore, N_2 fixation and activation are essential both for nature and

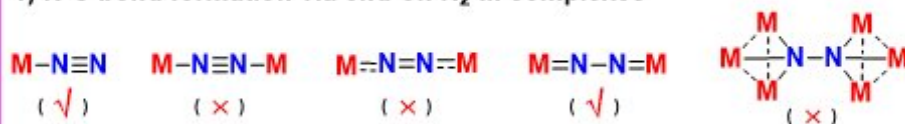
humans. Nevertheless, the high bond dissociation energy (942 kJ/mol) and large HOMO-LUMO gap (10.82 eV) make N_2 exhibit extremely low reactivity and may be regarded as an inert gas.

Currently, the N_2 activation and conversion in nature and industry mainly rely on two pathways, in which ammonia (NH_3) is the product. In nature, nitrogenase metalloenzymes transfer N_2 into NH_3 at ambient temperature and pressure. In industry, more than 170 million metric tons of NH_3 is produced from the Haber-Bosch process annually, in which N_2 reacts with dihydrogen (H_2) under harsh condition in the presence of metal catalysts. This NH_3 synthesis process consumes about 1-2% of the world's annual energy supply along with the huge CO_2 emission.

Compared to NH_3 -based N_2 fixation process, an alternative route of N_2 fixation is the direct conversion of N_2 into N-containing organic [compounds](#) under mild condition. This approach is always targeted because it provides the potential solution to develop a sustainable system with reduced fossil-fuel requirements.

In a new review published in the *National Science Review*, Zhenfeng Xi et al. summarize the previous works of transition-metal mediated direct conversion of N_2 into organic compounds via N-C [bond](#) formation at metal dinitrogen complexes. The review is organized by the coordination modes of the complexes (end-on, side-on, end-on-side-on, etc.) that are involved in the N-C bond formation steps, and each part is arranged in terms of reaction types (N-alkylation, N-acylation, cycloaddition, insertion, etc.) between metal dinitrogen complexes and carbon-based substrates. Besides, earlier works on one-pot synthesis of organic compounds from N_2 via ill-defined intermediates are also briefed by the authors.

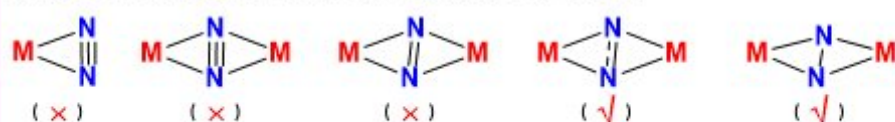
1) N-C bond formation via end-on N₂-M complexes



Reaction types

- N-Alkylation
- N-Acylation
- Cycloaddition and insertion
- N-Protonation/carbonylation
- ...

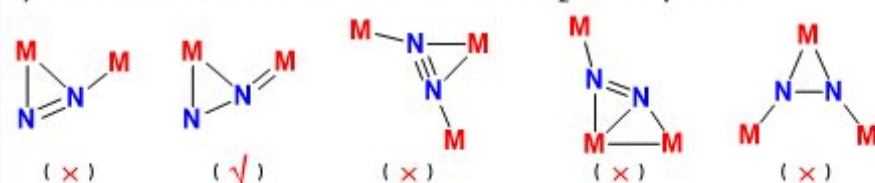
2) N-C bond formation via side-on N₂-M complexes



Reaction types

- N-Alkylation
- Cycloaddition and insertion
- CO-Induced N₂ functionalization and cleavage
- ...

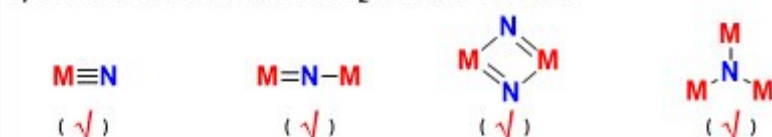
3) N-C bond formation via end-on-side-on N₂-M complexes



Reaction types

- N-Alkylation
- Cycloaddition and insertion
- ...

4) N-C bond formation via N₂-derived nitrides



Reaction types

- N-Alkylation
- N-Acylation
- N-Acylation/elimination
- Redox-coupled N-atom transfer
- N-Silylation/imido transfer
- ...

5) N-C bond formation via uncharacterized N₂-M intermediates

Typical reactions

- $PhLi + Cp_2TiCl_2 \xrightarrow[2) H_2O]{1) N_2} PhNH_2$
- $Cp_2TiCl_2 + Mg + N_2 \xrightarrow[2) H_2O]{1) R_2CO} R_2CHNH_2 + (R_2CH)_2NH$
- $TiCl_4 + xs Li + xs TMSCl + N_2 \xrightarrow{\text{Diketones}} \text{Nitric heterocycles}$

The relationship between coordination modes of dinitrogen complexes and the reaction types of N-C bond formation. The N-C bond formation is reported (√) or not reported (×). Credit: ©Science China Press

Besides the homogeneous stoichiometric thermochemical reaction systems, the sporadically reported syntheses involving photochemical, electrochemical, heterogeneous thermo-catalytic reactions are also discussed in this overview.

In the review, the authors point out that some synthetic cycles about direct conversion of N₂ into organic compounds have also been developed in recent decades. However, all of these reactions are stoichiometric and the catalytic system for the direct introduction of N₂ into organic compounds has not been realized yet. The main factors that prevent these complete synthetic cycles from becoming catalytic process are the rigorous reaction conditions of the N-C bond formation and N-containing organic compounds releasing steps in these cycles, which are incompatible with the preparation steps for metal dinitrogen complexes.

To provide readers with perspectives of future research particularly in direct catalytic and efficient conversion of N₂ into N-containing organic compounds under mild conditions, the authors likewise outline the potential development directions. They forecast that the research topics of 'new reaction types and systems for N-C bond formation,' 'polynuclear metal species cooperative N₂ scission and functionalization,' 'main group elements promoted N-C bond formation,' 'photochemistry and electrochemistry involved N-C bond formation,' 'heterogeneous catalysis systems for conversion of N₂ into [organic compounds](#)' would get more attention in the future.

More information: Ze-Jie Lv et al, Direct transformation of dinitrogen: synthesis of N-containing organic compounds via N–C bond formation, *National Science Review* (2020). [DOI: 10.1093/nsr/nwaa142](https://doi.org/10.1093/nsr/nwaa142)

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