

Photochemical Dinitrogen Functionalization with an Iridium Porphyrin Hydride as a Hydrogen Activation Catalyst

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The splitting of multinuclear, N₂-bridged transition metal complexes is a potential entry into synthetic nitrogen fixation that has attracted considerable interest in recent years.^[1] As the molecular nitrides that result from thermal N₂ splitting often suffer from low reactivity,^[1] photochemical strategies are desirable to drive N₂ activation and functionalization.^[2] However, compared with thermal pathways, only a small number of well-defined systems have been reported that undergo light-driven N₂-splitting and functionalization. Recently, photo induced hydrogen atom transfer from metal hydride complexes gained remarkable attention.^[3]

Our group reported the light-driven N–N bond scission of the N₂ bridged dirhenium complex **2** (Figure 1).^[4,5] The resulting Re^V nitride **3** can undergo N-atom transfer in the presence of organic electrophiles (e.g., acid halides) upon chemical or electrochemical reduction at mild potentials.^[5] Here, hydrogen activation by an iridium hydride porphyrin complex is introduced which facilitate the catalytic formation of benzamide, where visible light enables a thermodynamic endergonic reaction.

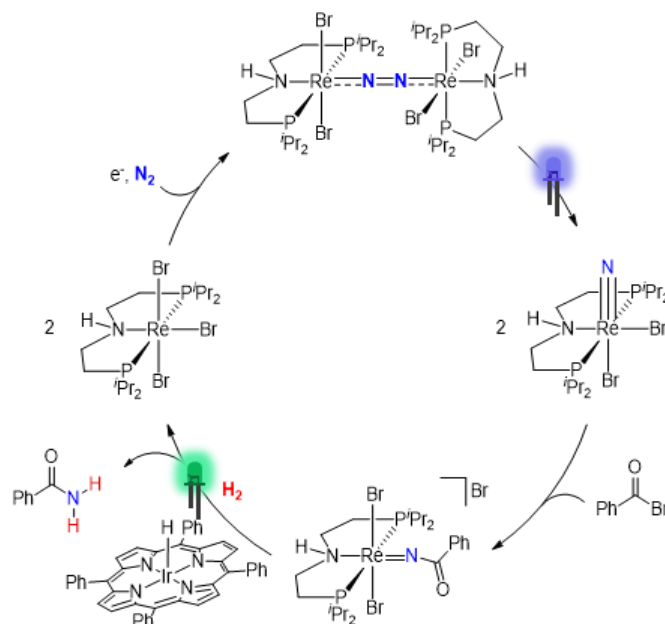


Figure 1: Photochemical N₂ functionalization to benzamide.

References:

- [1] Forrest, S. *et al.*, *Chem. Rev.*, 2021, **121**, 6522–6587. DOI: 10.1021/acs.chemrev.0c00958.
- [2] Schluschaß, B. *et al.*, *JACS Au*, 2021, **1**, **6**, 879–894. DOI: 10.1021/jacsau.1c00117.
- [3] C. K. Prier, *et al.*, *Chemical Reviews* 2013, **113**, 5322–5363. DOI: 10.1021/cr300503r
- [4] Schendzielorz, F. *et al.* *Angew. Chem. Int. Ed.*, 2019, **58**, 830–834. DOI: 10.1002/anie.201812125
- [5] Fritz, M. *et al.* *Angew. Chem. Int. Ed.*, 2022, **61**, e202205922. DOI: 10.1002/ange.202205922