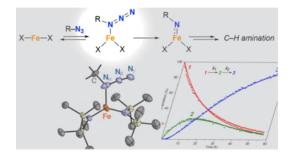
## Synthesis and Reactivity of a Stable Organoazide Iron Complex and its Relevance to C-H Bond Amination

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The formation of C-N bonds is of paramount importance for synthesis of pharmaceuticals, agrochemicals and natural products.<sup>[1]</sup> Complexes with organic azides are critical precursors for the formation of nitrene systems en route to the direct C-H amination, forming C-N bonds very efficiently and sustainably. Despite their relevance, first-row transition metals with  $\alpha$ -organoazide coordinated are extremely rare,<sup>[2,3]</sup> and they have been elusive so far for iron, even though iron complexes are by far the most active C-H amination catalysts with organic azides.<sup>[4-6]</sup>



In this contribution we will show the first example of the full characterization of such an organoazide iron complex. We will demonstrate the further reactivity to a transient nitrene intermediate and discuss reactivity of the azide both in solution and in crystallo. The characterization of both these intermediates is of paramount importance for understanding the catalytic C-H amination reaction and for designing new and improved catalytic systems.

[1] Ryan Hili, Andrei K. Yudin, *Nat. Chem. Biol.*, **2006**, 2, 284–287.

[2] Lauren N. Grant, Maria E. Carroll, Patrick J. Carroll, Daniel J. Mindiola, *Inorg. Chem.*, **2016**, 55, 7997-8002.

[3] Yunjung Baek, Anuvab Das, Shao-Liang Zheng, Joseph H. Reibenspies, David C. Powers, Theodore A. Betley, *J. Am. Chem. Soc.*, **2020**, 142, 11232–11243.

[4] Wowa Stroek, Martin Keilwerth, Daniel M. Pividori, Karsten Meyer, Martin Albrecht, J. Am. Chem. Soc., **2021**, 143, 20157–20165.

[5] Wowa Stroek, Lilian Hoareau, Martin Albrecht, Catal. Sci. Technol. 2023, 13, 958-962

[6] Wowa Stroek, Martin Albrecht, Chem. Sci. 2023, 14, 2849-2859