Mechanistic insight into N=N cleavage by a low-coordinate iron(II) hydride

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A Low-coordinate iron(II) hydride, [LFeH]₂ has been synthesized by reacting LFeCl with KBEt₃H. Considering the possibility of Fe-H intermediates in FeMoco, studying the reactivity of low-coordinate iron hydride complexes is highly relevant to potential nitrogenase mechanisms. [LFeH]₂ reacts with azobenzene to afford the hydrazido complex, LFeN(Ph)NHPh, which in turn forms the anilidoiron(II) complex, LFeNHPh, upon heating at 80 °C. This unique transformation shows that the low-coordinate iron(II) hydride has the ability to cleave an N-N bond. In order to gain mechanistic understanding of this unusual transformation kinetics and labeling experiments were pursued. The results of the mechanistic study will be described with synthetic and spectroscopic details.

$$[LFeH]_{2} \xrightarrow{2 \text{ PhN=NPh}} 2 LFe-N$$

$$Ph$$

$$Ph$$

$$Ph \longrightarrow Ph$$

$$Ph \longrightarrow Ph$$