

# SEVERELY BENT DINITROGEN BINDING IN A HIGHLY PREORGANIZED DINUCLEAR COBALT COMPLEX

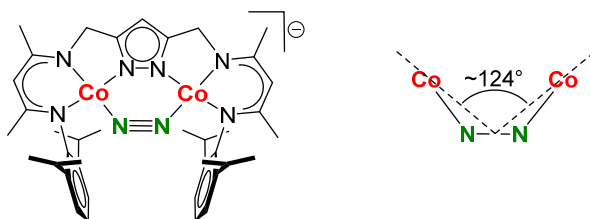
Yue Wang<sup>a</sup>, Sandeep K. Gupta<sup>a</sup>, Sebastian Dechert<sup>a</sup>, Vera Krewald<sup>b</sup> and Franc Meyer<sup>a</sup>

<sup>a</sup> Institut für Anorganische Chemie, Universität Göttingen, Göttingen, Germany

<sup>b</sup> Fachbereich Chemie, Theoretische Chemie, Technische Universität Darmstadt, Darmstadt, Germany

Dinitrogen reduction in the industrial Haber-Bosch process and in the biological enzyme nitrogenase is key to the production of ammonia and the downstream synthesis of other nitrogen-containing compounds.[1] In both processes the inert N<sub>2</sub> molecule is activated at multimetallic sites, either at the metallic surface of the Haber-Bosch iron catalyst or at the FeMo-cofactor of nitrogenase.[2,3] Binding and activation of N<sub>2</sub> is proposed to proceed via several intermediates prior to N-N bond cleavage, including a severely bent end-on bridging mode. However, synthetic model complexes featuring such non-linear end-on N<sub>2</sub> binding geometry are rare.[4]

Here we present the isolation and comprehensive characterization of a series of dicobalt(I)-dinitrogen complexes based on a dinucleating ligand[5] featuring a central pyrazolate bridge and two β-diketiminato chelate arms. Crystallographic analyses reveal that the preorganized bimetallic core induces a highly constrained geometry of the N<sub>2</sub> substrate with an acute Co-CtN<sub>2</sub>-Co angle of around 124° (see Figure), very close to the angle estimated for the key α-N<sub>2</sub> intermediate during N<sub>2</sub> adsorption and splitting on the iron surface of the Haber-Bosch catalyst. Crystallographic and spectroscopic data suggest that the bound N<sub>2</sub> in these dicobalt(I) complexes is moderately activated, and theoretical studies indicate an unusual bonding situation distinct from the bonding in common linear M-NN-M complexes. The syntheses, properties and initial reactivity studies of these novel N<sub>2</sub> complexes will be discussed.



**Figure 1.** Dicobalt complex with severely bent N<sub>2</sub> coordination in the bimetallic pocket.

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