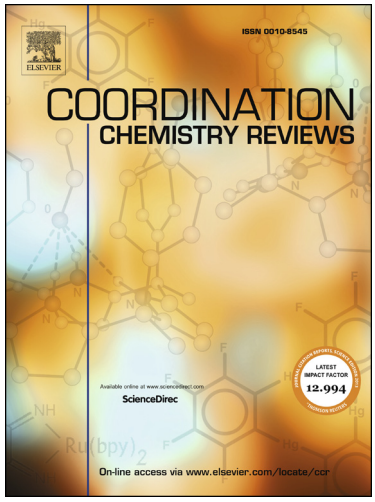

Review

Synthetic nitrogen fixation with mononuclear molybdenum complexes: electronic-structural and mechanistic insights from DFT

Benedikt M. Flöser, Felix Tuczek

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Synthetic nitrogen fixation with mononuclear molybdenum complexes: electronic-structural and mechanistic insights from DFT

*Benedikt M. Flöser and Felix Tuczek**

**Institute of Inorganic Chemistry, Christian Albrechts University of Kiel, Max-Eyth-Str. 2, D-24118 Kiel, Germany*

e-mail: ftuczek@ac.uni-kiel.de

Abstract

Synthetic nitrogen fixation continues to be a topic of high interest. Besides the synthesis and mechanistic investigation of small-molecule model systems of nitrogenase quantum chemical studies are required to provide a mechanistic understanding and help in the design of new systems. This article revisits DFT treatments of existing mononuclear Mo(0) pentaphosphine-based model complexes. Moreover, it considers a recently published Mo(0)-N_2 complex coordinated by a pentadentate phosphine ligand. This complex as well as its possible role in the conversion from N_2 to NH_3 are thoroughly analyzed by DFT and its properties are compared to those of other molybdenum pentaphosphine systems. Also a proposition is made for another target complex showing even more promise regarding the catalytic fixation of nitrogen.

Keywords: Nitrogen fixation, Chatt-cycle, model systems, DFT, Intrinsic bonding orbitals

1. Introduction

Nitrogen is an essential element for every living organism. The by far biggest reservoir of it exists in the form of highly inert dinitrogen in the earth's atmosphere. Nature's elaborate way of fixing dinitrogen consists of its enzymatic reduction to ammonia, mediated by the enzyme nitrogenase [1-3]. Industrially, ammonia is synthesized through the reaction of H_2 and N_2 by the Haber-Bosch process [4]. Since this process requires high temperatures and pressures it is of significant interest to devise a way of producing ammonia from dinitrogen under ambient conditions, in analogy to the biological process [5]. This is the foundation of synthetic nitrogen fixation which aims at making use of coordination compounds to bind, activate and catalytically reduce dinitrogen to ammonia, more or less mimicking nitrogenase [6-7]. Additionally, since the natural process is still not fully understood