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Review

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

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

24 Synthetic nitrogen fixation continues to be a topic of high interest. Besides the synthesis and 25 mechanistic investigation of small-molecule model systems of nitrogenase quantum chemical studies 26 are required to provide a mechanistic understanding and help in the design of new systems. This 27 article revisits DFT treatments of existing mononuclear Mo(0) pentaphosphine-based model 28 complexes. Moreover, it considers a recently published $Mo(0)-N_2$ complex coordinated by a 29 pentadentate phosphine ligand. This complex as well as its possible role in the conversion from N₂ to 30 NH₃ are thoroughly analyzed by DFT and its properties are compared to those of other molybdenum 31 pentaphosphine systems. Also a proposition is made for another target complex showing even more 32 promise regarding the catalytic fixation of nitrogen.

33

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

35 1. Introduction

36 Nitrogen is an essential element for every living organism. The by far biggest reservoir of it exists in 37 the form of highly inert dinitrogen in the earth's atmosphere. Nature's elaborate way of fixing 38 dinitrogen consists of its enzymatic reduction to ammonia, mediated by the enzyme nitrogenase [1-39 3]. Industrially, ammonia is synthesized through the reaction of H_2 and N_2 by the Haber-Bosch 40 process [4]. Since this process requires high temperatures and pressures it is of significant interest to 41 devise a way of producing ammonia from dinitrogen under ambient conditions, in analogy to the 42 biological process [5]. This is the foundation of synthetic nitrogen fixation which aims at making use 43 of coordination compounds to bind, activate and catalytically reduce dinitrogen to ammonia, more or 44 less mimicking nitrogenase [6-7]. Additionally, since the natural process is still not fully understood

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