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Review

Molybdenum(0) dinitrogen complexes with polydentate phosphine ligands for synthetic nitrogen fixation: Geometric and electronic structure contributions to reactivity

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ABSTRACT

Synthetic nitrogen fixation with molybdenum phosphine complexes has witnessed a renaissance recently due to the discovery that such systems are competent to catalytically convert N_2 to ammonia. In the framework of this research area, we have prepared the molybdenum bis(dinitrogen) complexes *cis*- and *trans*-$[Mo(N_2)_2(prP_4)]$ which contain the linear tetraphos ligand prP_4 (1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane). More recently, the synthesis and physicochemical properties of the molybdenum monodinitrogen complexes $[Mo(N_2)(tdppme)(dmpm)]$ and $[Mo(N_2)(tdppme)(dppm)]$ have been achieved. These complexes are facially coordinated by the tripod ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (tdppme) and contain the bidentate coligands dppm (bis(diphenylphosphino)methane) and dmpm (bis(dimethylphosphino)methane), respectively. They are related to the complexes $[Mo(N_2)(dpepp)(diphos)]$ which have been investigated earlier (dpepp = $PhP(CH_2CH_2PPh_2)_2$). The structural, electronic and vibrational properties of all of these dinitrogen complexes have been investigated by NMR, IR and Raman spectroscopy, and their reactivities in a nitrogen fixing cycle have been evaluated. To this end, protonated derivatives have been investigated as well. On the basis of DFT calculations, these systems are promising candidates for the catalytic conversion of N_2 to ammonia.

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1. Introduction

One of the big challenges in biological, inorganic and organometallic chemistry is the conversion of molecular dinitrogen to ammonia under ambient conditions [1]. In nature, this process is catalyzed by the enzyme nitrogenase according to the equation [2]:

$$N_2 + 8H^+ + 8e^- + 16MgATP \rightarrow 2NH_3 + H_2 + 16MgADP + 16P_i$$

This process is highly energy consuming [3], and during the reduction not only ammonia but also H_2 is developed. Nitrogenase consists of two proteins. The larger one, called molybdenum-iron (MoFe) protein, is an $\alpha_2\beta_2$-tetramer which contains two iron-sulfur clusters, the P-clusters and two iron-molybdenum cofactors (FeMoco) which are the active site of the enzyme where the reduction of dinitrogen occurs [4–7]. The electrons needed are provided by the iron (Fe) protein by forming a complex with the MoFe protein. One electron is transferred from the Fe-protein; then the Fe-protein dissociates and is recharged, so it is able to reduce the MoFe protein again. After accomplishing this process eight times, one catalytic cycle is completed [8]. To find out how nitrogenase works on a molecular level, detailed spectroscopic studies have been performed [9–12]. Moreover, many theoretical studies on the binding and reduction of N_2 at the FeMoco have been published [13–17]. Out of these investigations a few plausible mechanistic scenarios for the biological nitrogen fixation reaction have emerged.

Synthetic nitrogen fixation focuses on the binding, activation and reduction of dinitrogen on mono-, di- and polynuclear metal centers. These systems also contribute important information on the elementary reaction steps of ammonia formation in the biological process. So far two classes of transition metal-complexes have emerged that involve a full set of well-defined intermediates on the way of N_2 to NH_3. These systems form the basis of the Chatt and the Schrock cycle [18,19]. While the Chatt cycle is based on zerovalent molybdenum or tungsten bis(dinitrogen) complexes $[M(N_2)_2(diphos)_2]$ (M = Mo/W) with diphosphine coligands (diphos = dppe or depe), the Schrock cycle is based on a trivalent molybdenum mono(dinitrogen) complex, $[Mo(N_2)(HIPTN_3N)]$, which is supported by the sterically shielding ligand $HIPTN_3N$ = hexaisopropylterphenyl-triamidoamine. Yandulov and Schrock were able to catalytically generate ammonia by the addition of the weakly coordinating acid 2,6-dimethylpyridinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($LutHBAr^F{}_4$) as proton source and the strong reducing agent decamethyl chromocene in four turnovers and 66% yield with respect to the reducing equivalents [20]. Many years before, Pickett and Talarmin had succeeded in using the Chatt-type complex $[W(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and tosylic acid to electrochemically generate ammonia in three cycles; however, the yield was only 36% with respect to the metal complex [21].

There has been a renaissance of molybdenum-phosphine systems in synthetic nitrogen fixation recently, as evidenced by such complexes as $[Mo(PNP)(N_2)_2]_2(\mu\text{-}N_2)$ (where PNP = 2,6-bis(di-tert-butylphosphinomethyl)pyridine) or $[(t\text{-BuPOCOP})MoI_2]$ (where t-BuPOCOP = C_6H_3-1,3-$[OP(t\text{-Bu})_2]_2$) [22,23]. Importantly, the first of these systems enabled the generation of NH_3 from N_2 with a yield of 49% based on the reducing agents or 12 equiv. per molybdenum atom. Although the mechanism of this reaction has not been fully elucidated, it can be expected that it will differ from that of the Chatt and Schrock cycles.

1.1. Improving Chatt-type catalysts

In a historic breakthrough, the Schrock system has proven the feasibility of catalytic NH_3 formation under ambient conditions, in analogy to the enzyme nitrogenase. More recently, a yield of 12 equiv. of NH_3 based on the metal catalyst or 49% based on the reducing agent has been achieved by employing as a catalyst the dinuclear zerovalent molybdenum complex $[Mo(PNP)(N_2)_2]_2(\mu\text{-}N_2)$ which contains the extremely bulky pincer ligand PNP [22]. A problem of amine and amide donor containing ligands is the Brønsted basicity of these N-containing groups which tend to get protonated under acidic reaction conditions, leading to ligand dissociation and eventually loss of the catalytically active species. Phosphine based ligands have the advantage of lower Brønsted basicity and thus higher stability against acids. On the other hand, due to the relative softness of phosphine donors, metal–ligand bonding of phosphines is considerably weakened in higher-valent molybdenum intermediates, such as Mo nitrido complexes. To compensate the lower affinity of phosphine donors to higher oxidation state molybdenum centers, multidentate phosphine ligands should be employed. These ligands could render molybdenum-phosphine complexes comparably effective catalysts for the reduction of nitrogen as the Mo(III)-triamidoamine system. The tridentate ligand dpepp (bis(2-diphenylphosphinoethyl)phenylphosphine) and the tetradentate ligand *prP*$_4$ (1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane) also follow this concept.

Another intrinsic problem of the Chatt cycle is a disproportionation of two $[MoX(N_2)(diphos)_2]$ intermediates to one still catalytically active $[Mo(N_2)_2(diphos)_2]$ and one inactive $[MoX_2(diphos)_2]$ species (X^- = conjugate anion of the employed acid). This reaction is equivalent to the loss of 50% of the catalyst per cycle. One strategy to prevent such side reactions is the synthesis of monodinitrogen complexes employing tridentate ligands that occupy the pivotal *trans* position of N_2. This approach has first been pursued by George and co-workers with the synthesis of complexes of the type $[Mo(N_2)(dpepp)(L_2)]$ (where $L_2 = (PMe_2Ph)_2$ or $Me_2PCH_2PMe_2$, $Ph_2PCH_2PPh_2$, $Ph_2PCH_2CH_2PPh_2$) which are supported by the tridentate ligand dpepp [24]. The stoichiometric formation of ammonia by protonation of these systems with various acids has been studied in detail. In the corresponding dinitrogen complexes the dpepp ligand can (in principle) coordinate in a *mer* or *fac* geometry, and in the *fac* geometry the central P donor can bind *trans* or *cis* to the N_2 ligand (*ortho*/*iso* isomerism) [25,26]. By use of the tripodal ligand tdppme (1,1,1-tris(diphenylphosphanylmethyl)ethane) our group created the new molybdenum mono(dinitrogen) complexes $[Mo(N_2)(tdppme)(dppm)]$ (**21**) and $[Mo(N_2)(tdppme)(dmpm)]$ (**19**) to realize the expected enhancement in stability and the retention of the pentaphosphine coordination in protonation reactions [27]. The ability of tripodal ligands to enforce facial coordination and in doing so to sterically protect one hemisphere of a complex makes them eligible building blocks for catalyst design in small-molecule activation chemistry.

2. Linear P_3 and P_4 ligands

An obvious strategy to reach a higher thermal stability of Chatt-type complexes in higher oxidation states is the coordination of a tri- or tetraphos ligand instead of the two diphosphines used in the original Chatt systems. The chelating effect should render the complexes more stable so that less of the catalyst is lost in protonation reactions.