

## Review

## Transition metal hydride complexes as mechanistic models for proton reduction catalysis

Rebecca E. Adams, Tod A. Grusenmeyer, Audrey L. Griffith, Russell H. Schmehl\*

Department of Chemistry, Tulane University, New Orleans, LA, USA

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## ABSTRACT

The paper presents a brief overview of the role of metal hydride complexes in understanding the dynamics of hydrogen generation in homogeneous water reduction catalysts. In addition, the kinetics of protonation of  $[\text{Os}(\text{phen})_2(\text{CO})(\text{H})]^+$  and the one-electron reduced form of the complex,  $[\text{Os}(\text{phen})(\text{phen}^-)(\text{CO})(\text{H})]$ , in acetonitrile solution were examined. The monocationic complex reacted with tosylic acid to form a distinct intermediate species which was found to be a dihydrogen complex; this went on to produce hydrogen and the solvento complex. The one-electron reduced complex was prepared by reduction of the photoexcited monocationic complex with the sacrificial donor BIH. Protonation of the reduced complex by tosylic acid occurred with a rate constant approximately 100 million times larger. The results are used to address possible mechanistic pathways of existing homogeneous catalysts.

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## Contents

1. Introduction	44
1.1. Catalytic cycles for $\text{H}_2$ generation	45
1.2. Cobalt catalysts	45
1.3. Fe–Ni hydrogenase models	46
2. Metal hydride complex reactivity and photochemistry	46
2.1. Hydricity measures	46
2.2. Kinetics of metal hydride reactivity	46
2.3. Basics of metal hydride complex photochemistry	47
3. Photochemical and electrochemical properties of $[\text{Os}(\text{phen})_2(\text{CO})(\text{H})]^+$	47
3.1. Complex synthesis	47
3.2. Photophysical properties	48
3.3. Redox behavior	48
3.4. Excited state reductive quenching	49
4. Protonation of $[\text{Os}(\text{phen})_2(\text{CO})(\text{H})]^+$	49
4.1. Protonation of $[(\text{phen})_2\text{Os}(\text{CO})(\text{H})]^+$ in $\text{CH}_3\text{CN}$	49
4.2. Protonation following one electron photoreduction	50
5. Effect of redox state on protonation kinetics and subsequent reactions	51
Acknowledgements	52
Appendix A. Supplementary data	52
References	52

## 1. Introduction

The mechanistic investigation of proton reduction catalysis is complicated by the fact that two electrons are required to reduce two protons to one equivalent of dihydrogen. The multi-electron

\* Corresponding author.

E-mail address: [russ@tulane.edu](mailto:russ@tulane.edu) (R.H. Schmehl).

redox process of catalyzed proton reduction thus requires the study of intermediate species to gain mechanistic insight. Intermediates formed within catalytic cycles are often unstable and difficult to characterize. The use of metal hydrides in kinetic and thermodynamic studies to model proton reduction is attractive because the hydride is capable of H<sub>2</sub> evolution when protonated.

A rich variety of transition metal hydride complexes have been prepared and employed in studies of catalytic processes [1,2]. A significant portion of this work involves analyses of metal hydride protonation to ultimately yield dihydrogen; such studies highlight the requirements necessary for efficient transition metal-catalyzed proton reduction. An intriguing possibility for kinetic studies of metal hydrides is to use photolysis to reduce a metal hydride in the presence of an appropriate proton source. Recently, the photochemistry of transition metal hydrides was thoroughly reviewed by Perutz et al. [3]. Examples of photo-reactive metal hydrides can be found for complexes of group 4 through group 11 transition metals, although few have been reported to have emissive, long-lived (>100 ns) excited states that are non-dissociative [3].

A number of years ago Meyer and coworkers found that [Os<sup>II</sup>(diimine)<sub>2</sub>(CO)(H)]<sup>+</sup> complexes are luminescent in room temperature solution, have lifetimes on the order of hundreds of nanoseconds, and are relatively inert in solutions containing weak proton donors (i.e., acetic acid, phenol) [4,5]. The aim of this article is to highlight the use of transition metal hydride complexes to assess the mechanistic details of proton reduction. The influence of electron density within a metal hydride structure will be discussed, along with the effect of one-electron reduction of a metal hydride on the rate of protonation. As a case study, reaction of [Os(phen)<sub>2</sub>(CO)(H)]<sup>+</sup> with tosylic acid in acetonitrile is compared with protonation of the one-electron reduced species generated via photoinduced electron transfer.

### 1.1. Catalytic cycles for H<sub>2</sub> generation

Many transition metal-based homogeneous catalysts have been developed that efficiently generate hydrogen in both photochemical and electrochemical systems [6]. Typically, metal hydride species are proposed as intermediates in proton reduction cycles. In a 2011 review, Artero and Fontecave illustrated possible catalytic cycles for water reduction involving cobalt complexes (Fig. 1) [7]. Homolytic paths involve disproportionation of metal hydrides while, in heterolytic paths, the metal hydride is protonated to ultimately yield H<sub>2</sub>. Metal hydrides can be formed through direct protonation of a reduced metal center, resulting in an increase of the formal charge of the metal center by two electrons. This process has been observed in many catalytic systems where reducing equivalents are readily available.

Loss of hydrogen from M–H can occur by hydride transfer, H-atom transfer, or proton transfer depending upon the relative acidity or basicity of the metal and the oxidation state of the metal. In transition metal-catalyzed generation of H<sub>2</sub>, heterolytic reaction of the hydride by protonation or homolytic bond dissociation via disproportionation are the typical mechanisms (Fig. 1). These two pathways can be distinguished by differing rate laws. An excellent description of methods to unravel the mechanism of proton reduction through electrochemical experiments was devised by Saveant and coworkers [8] and has been used quite effectively [9–12].

Catalysts of cobalt and hydrogenase-mimicking structures containing iron and nickel have been the subject of numerous studies; intermediates in the catalytic cycles of these complexes have been identified and in some cases, directly prepared. Metal hydride formation typically occurs by protonation of a low-valent metal complex, resulting in a metal hydride with a two-electron oxidized metal center. The formation of metal hydrides is common in nearly all mechanisms for proton reduction catalyzed by Co, Fe–Fe and

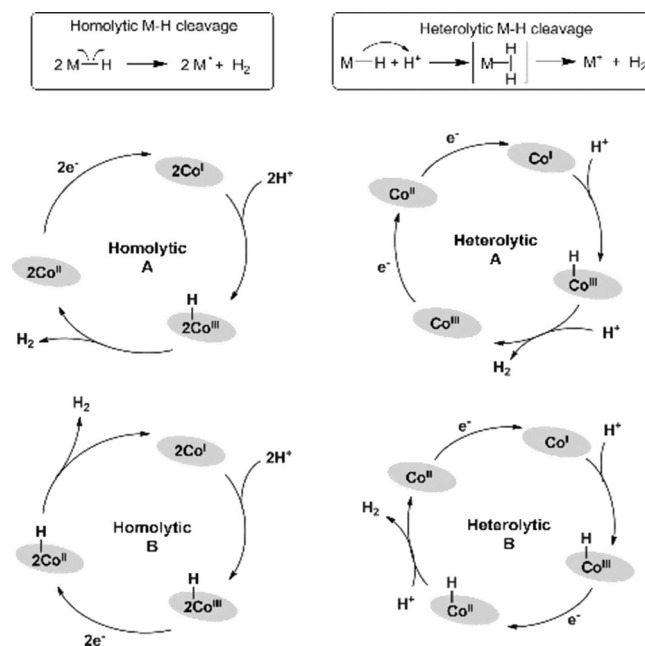


Fig. 1. Proposed schemes for hydrogen generation with Co(III) water reduction catalysts. (Used with permission from Ref. [7]. Copyright 2011 John Wiley and Sons.)

Ni–Fe complexes. A nickel metalloporphyrin complex appended with a carboxylic acid hanging group offers a rare example of a metal complex that catalyzes proton reduction without the involvement of a metal hydride intermediate; protonation and H<sub>2</sub> generation occurs at the *meso* carbon of the porphyrin with no evidence of nickel hydride formation. Combining experimental and computational results, the authors concluded that formation of a nickel hydride was thermodynamically unfavorable compared to formation of a phlorin intermediate. The authors postulate that the C–H bond of the phlorin can react with protons to generate H<sub>2</sub> in a manner similar to metal hydrides [13,14].

### 1.2. Cobalt catalysts

A study of a difluoroboryl bridged Co<sup>II</sup>–diglyoxime complex was done utilizing the photoacid <sup>B</sup>rNaphOH [15]. The investigators employed the reduced form of the complex (Co<sup>I</sup>) to probe the mechanism of H<sub>2</sub> generation in acetonitrile. Upon excitation of the photoacid, the triplet excited state generated has a pK<sub>a</sub> of 14.6 (as compared to 26.1 in the ground state). The ground state of the acid is not strong enough to protonate Co<sup>I</sup>, but the photoacid triplet reacts with the diglyoxime complex to produce the hydride (Co<sup>III</sup>H) on the microsecond time scale. Following this reaction by transient absorption, a slow kinetic process is also observed on the millisecond time scale. It was found that the initially formed Co<sup>III</sup>H is not basic enough to be protonated by the weakly acidic ground state of the photoacid. The slow kinetic process was attributed to the reduction of Co<sup>III</sup>H by excess Co<sup>I</sup> ( $k_{red} = 9.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ), forming the very reactive Co<sup>II</sup>H. This hydride is then protonated by the very weakly acidic ground state of <sup>B</sup>rNaphOH to yield H<sub>2</sub> and Co<sup>II</sup> ( $k_{H_2} = 4.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ). It was noted by the authors that this heterolytic pathway will dominate in catalytic studies containing low concentrations of Co<sup>III</sup>H and excess reducing equivalents.

A later electrochemical and photochemical study of a pentapyridine cobalt complex was done to gain understanding of the proton reduction pathway [16]. They found that protonation of the complex to form a hydride occurs after reduction to Co<sup>I</sup>, yielding

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