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# Solar Fuels

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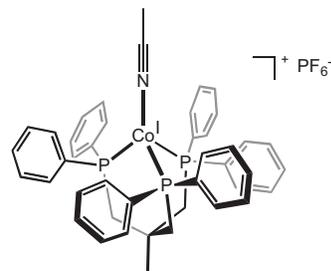
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**Abstract.** *The generation of hydrogen from water and sunlight may provide the clean, renewable fuel that solves our planet's growing demand for energy. However, for any approach to be practical, we will need to develop robust catalysts containing earth-abundant elements for the efficient reduction of protons to H<sub>2</sub> and oxidation of water to O<sub>2</sub>.*

Molecular hydrogen has emerged as an attractive candidate for a clean, renewable fuel to meet the world's skyrocketing demand for energy.<sup>1,2</sup> Hydrogenase enzymes that contain iron and nickel cofactors evolve H<sub>2</sub> catalytically from water with turnover frequencies as high as 9000 s<sup>-1</sup> at 30 °C.<sup>3</sup> However, the relative instability of these enzymes under aerobic conditions has led to the search for robust inorganic catalysts that can produce hydrogen from water. Platinum is an excellent catalyst for proton reduction and hydrogen oxidation, but scarcity and high cost limit its widespread use.

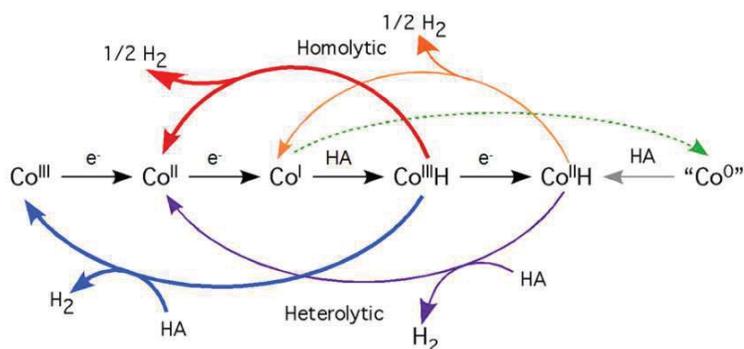
These considerations have led to the development of catalysts for hydrogen evolution that employ earth-abundant metals. Promising heterogeneous catalysts include MoS<sub>2</sub> and Ni–Mo, which reduce protons in aqueous solutions with catalytic efficiencies near that of platinum.<sup>4,5</sup> While homogeneous catalysts typically degrade faster than their heterogeneous counterparts, molecular systems are much easier to study mechanistically. DuBois recently reported the production of H<sub>2</sub> with turnover frequencies above 100,000 s<sup>-1</sup> for a family of mononuclear nickel-phosphine complexes containing pendant proximal bases.<sup>6</sup> The proposed mechanism of proton reduction and hydrogen oxidation involves the cooperative interaction of H<sub>2</sub> with both the metal center and multiple proton relays incorporated in the second coordination sphere.<sup>7</sup> More recently, Chang and Long reported that a high-valent molybdenum-oxo species can catalytically generate hydrogen from water at neutral pH.<sup>8</sup> Related cobalt complexes enable electrocatalytic production of H<sub>2</sub> from neutral water with high turnover frequencies, albeit at high overpotentials.<sup>9,10</sup> Co-diglyoxime complexes, reported by groups at Caltech and elsewhere, generate H<sub>2</sub> from protic solutions at overpotentials as low as 40 mV.<sup>11</sup> For all of the cobalt complexes reported, proton reduction occurs near the Co<sup>III/I</sup> potential.

$\text{Co}^{\text{I}}$  complexes also have been targeted as molecular catalysts for proton reduction, including a variety of  $\text{Co}^{\text{I}}$ (triphos) species.<sup>12</sup>  $\text{Co}^{\text{II}}$  iodide undergoes spontaneous reduction upon treatment with phosphine to give **1**,  $\text{Co}^{\text{I}}$  (triphos) (Figure 1), which can be converted to the cationic adduct **2**,  $[\text{Co}(\text{triphos})(\text{MeCN})][\text{PF}_6]$ .



**Fig. 1.**  $\text{Co}^{\text{I}}$ (triphos)(MeCN) cation for proton reduction.

Proton reduction to  $\text{H}_2$  is electrocatalyzed by **2** in an acetonitrile solution containing an organic acid. We have shown that the mechanism involves a  $\text{Co}^{\text{III}}\text{-H}$  intermediate formed by protonation of  $\text{Co}^{\text{I}}$



**Scheme 1.** Homolytic and heterolytic pathways for  $\text{H}_2$  evolution catalyzed by cobalt complexes.

another path, a  $\text{Co}^{\text{II}}$  hydride could react in a homolytic fashion to generate  $\text{H}_2$  and  $\text{Co}^{\text{I}}$ , or in a heterolytic process to generate  $\text{H}_2$  and  $\text{Co}^{\text{II}}$ .<sup>14</sup> The latter path is dominant in the  $\text{Co}^{\text{I}}$ (triphos) catalyzed reaction, as we have found that hydrogen is formed mainly by protonation of  $\text{Co}^{\text{II}}\text{-H}$ .<sup>12</sup>

For hydrogen to be the solution to our planet's growing demand for a clean, renewable fuel, we will need an inexpensive and abundant source of protons and electrons. Water is an obvious stockpile of these components, but mining  $\text{H}_2\text{O}$  for its protons and electrons introduces the problem of finding efficient catalysts for the oxidation of water to molecular oxygen.

The challenge of water oxidation in many ways eclipses that of proton reduction. The oxidation reaction involves the rearrangement of more protons and electrons, and fewer good catalysts for the reaction exist that are made of earth-abundant materials. There is, of course, one striking example of an earth-abundant system for evolving oxygen from water: photosystem II (PSII), a protein assembly found in plants, algae, and cyanobacteria. Recent high-resolution X-ray diffraction studies have elucidated the structure of PSII and its oxygen-evolving complex (OEC).<sup>15,16</sup> The OEC is a  $\text{Mn}_4\text{CaO}_5$  cluster that adopts a cubane-like structure of metals bridged by oxo ligands. One of the Mn atoms dangles from the central, distorted cube, and four water molecules are bound to the OEC—at least one of which is presumably ripe for oxidation. The

groups of Agapie and Christou have recently reported synthetic models of the manganese cluster, but so far, none has emulated its reactivity.<sup>17,18</sup>

Functional systems for the oxidation of water typically rely on precious metals, but several notable catalysts made of earth-abundant elements have recently been reported. Nocera and coworkers have developed a heterogeneous Co-phosphate material that forms on conductive surfaces under mild conditions and shows high activity in aqueous media. Structural characterization of the material indicates that, like PSII, the metal and oxygen atoms adopt a cubane arrangement.<sup>19,20</sup> Photoanodes containing BiVO<sub>4</sub>/FeOOH and Mn<sub>3</sub>O<sub>4</sub>/CoSe<sub>2</sub> also have shown great promise for solar-driven water splitting.<sup>21,22</sup>

Many promising catalysts for water oxidation are metal oxides. These heterogeneous catalysts are typically resistant to further oxidation and lack organic ligands that can react and erode the activity of the material. There is a vast number of combinations of metal oxides that can be prepared from the thermolysis of mixtures of metal nitrate salts, so our team has developed a system for distributing the labor of screening these catalysts. The Solar Hydrogen Activity Research Kit (SHArK) and Solar Materials Discovery (SMD) kit empower high-school and college students to assist in our exploration of this vast catalyst space.<sup>23,24</sup> Students prepare electrodes spotted with combinations of metal oxides, scan the catalysts for activity in the solar-driven oxidation of water, and share their data on a central Web site. With the screening outsourced to eager youngsters, our team can focus its resources on pursuing the most promising candidates.

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