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Unexpected ligand effect on the catalytic reaction rate acceleration for hydrogen production using biomimetic nickel electrocatalysts with 1,5-diaza-3,7-diphosphacyclooctanes



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ABSTRACT

The two new nickel complexes $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{Ph}(\text{CH})_2\text{Ph}_2})_2]^{2+}$ (where R = Ph or *o*-Py) with cyclic 1,5-diaza-3,7-diphosphacyclooctane ligands have been synthesized. All complexes are effective electrocatalysts for hydrogen production using $[(\text{DMF})\text{H}]^+$ as proton source in acetonitrile. The bulky benzhydryl substituent at nitrogen atom leads to higher catalytic activity comparison to benzyl. The introduction *o*-Py substituents at phosphorus as additional basic center is caused by the changing of voltage–current picture and significantly catalytic current enhancement. TOFs being 100 and 15200 s^{-1} for R = Ph and *o*-Py, respectively.

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Introduction

The development of renewables is important for the future of the energy frontiers, partly because of mitigating increasing CO₂ concentrations in the atmosphere resulting from the burning of mineral fuels [1]. One of the simplest reactions for storage of renewable energy is the formation of H₂ from two protons and two electrons. Platinum and the hydrogenase enzymes are excellent catalysts for both production and oxidation of hydrogen.

Platinum, however, is a precious metal with high cost and low abundance [2]. Hydrogenase enzymes being remarkably efficient catalysts in nature [3–5], are expensive to be obtained commercially, unstable and difficult to adapt to large-scale commercial applications. These considerations have motivated efforts to design molecular catalysts that employ more abundant metals, such as nickel [6–11], cobalt [12–20], iron [21–34], or molybdenum

[35–37], as electrochemical catalysts for the production and oxidation of dihydrogen [38,39].

The [FeFe]-hydrogenase enzyme can both produce and oxidize H₂ at turnover frequencies of $\geq 9000 \text{ s}^{-1}$ [3,4,40,41]. Recent advances in Ni-based bio-inspired catalysts [6–11], such as $[\text{Ni}(\text{P}^{\text{R}}_2\text{N}^{\text{R}_n})_2]^{2+}$, demonstrated the possibility of cleaving H₂ or generating H₂ heterolytically with turnover frequencies comparable or superior to those of hydrogenase enzymes. In these catalysts the transformation between H₂ and protons proceeds via an interplay between proton, hydride and electron transfer steps, and involves the interaction of a dihydrogen molecule with both a Ni(II) center and pendent amine bases incorporated in six-, seven or octa-membered rings, which function as proton relays. The catalysts with ligand 8-membered ring achieved the high electrocatalytic H₂ production rates, up to 1540 s^{-1} in dry acetonitrile and up to 6700 s^{-1} in water-acetonitrile solutions with $[(\text{DMF})\text{H}]\text{OTf}$ acid [42–45] as proton source.

In this communication we report new data on the unexpectedly high activity of nickel complexes with 8-membered ring 1,5-diaza-3,7-diphosphacyclooctane ligands with the diphenylmethyl

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