Design of Molecular Electrocatalysts for the Production and Oxidation of Hydrogen

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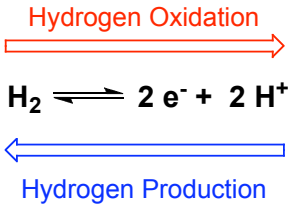
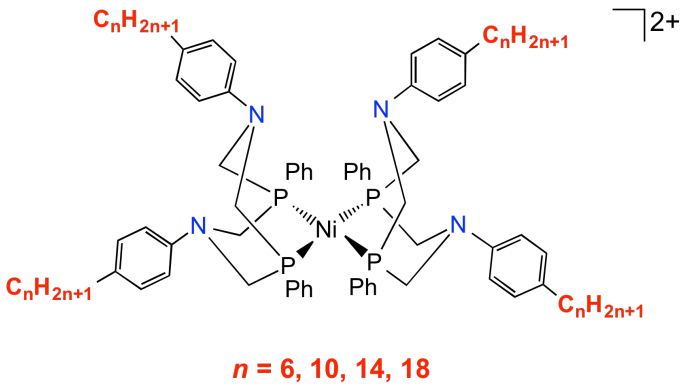
Solar and wind are carbon-neutral, sustainable energy sources, but their intermittent nature requires energy storage. Catalysts that efficiently interconvert between electrical energy and chemical bonds (fuels) are needed for sustainable, secure energy in the future. Electrocatalysts based on inexpensive, earth-abundant metals ("Cheap Metals for Noble Tasks") are needed since low-temperature fuel cells generally use platinum, an expensive, precious metal. We developed nickel(II) complexes for the electrocatalytic production of H_2 by reduction of protons.[1] Pendant amines in the ligand function as proton relays, facilitating intramolecular and intermolecular proton mobility. Turnover frequencies up to 10^7 s^{-1} have been observed,[2] though some have a high overpotential. For a series of $[Ni(P^{Ph}_2N^{C6H4\text{-}R}_2)_2]^{2+}$ complexes (R = C_6 – C_{18} hydrocarbon chains), the turnover frequency of H_2 production is inversely correlated with the rates of ring inversion (chair-boat isomerization) of the six-membered ring of the Ni-P_2N_2 group, as this dynamic process governs protonation at either the catalytically productive or non-productive sites.





Iron complexes with pendant amines in diphosphine ligands have been developed for the opposite reaction, oxidation of H_2 (1 atm).[3] The proposed mechanism involves binding of H_2, heterolytic cleavage of H_2, and removal of two protons and two electrons. These results document the rational design of catalysts based on abundant, inexpensive metals as alternatives to precious metals.

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[1] Bullock, R. M.; Appel, A. M.; Helm, M. L. *Chem. Commun.* **2014**, *50*, 3125-3143.
[2] Cardenas, A. J. P.; Ginovska, B.; Kumar, N.; Hou, J.; Raugei, S.; Helm, M. L.; Appel, A. M.; Bullock, R. M.; O'Hagan, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 13509-13513.
[3] Bullock, R. M.; Helm, M. L. *Acc. Chem. Res.* **2015**, *48*, 2017-2026.