

Metal Complexes with a Proton-Responsive PNP Pincer-Type Ligand as a Proton-Coupled Electron Transfer Reagent

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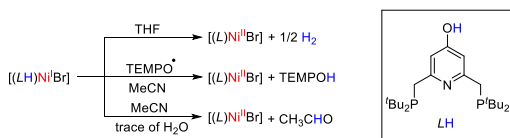
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Proton-coupled electron transfer (PCET) reactions have widespread importance in e.g., hydrogenation reactions.^[1] Since the initially formed XH bond in such C=C or C=O moieties is very weak, it necessitates the use of catalysts with low BDFE. However, such PCET reagents are also prone to homolytic H₂ evolution. To solve this problem, the spatial separation of the reduction and protonation sites was recently explored, as this polarity mismatch can slow the competing hydrogen evolution reaction.^[2]

This inspired us to synthesize Ni and Co pincer complexes with a proton-responsive acid/base site in the backbone. The thermochemical parameters of the PCET reaction as well as the kinetics of 1H⁺/1e⁻ transfer reactions have been determined in combination with electronic structure calculations, which will be presented.^[3]



Scheme 1: 1H⁺/1e⁻ Reactivity of In Situ Prepared PCET Reagent.^[3]

[1] T. J. Meyer *et al.*, Chem. Rev., 2012, **112**, 4016–4093, DOI. 10.1021/cr200177j, R. R. Knowles. *et al.*, Acc. Chem. Res., 2016, **49**, 1546–1556, DOI. 10.1021/acs.accounts.6b00272.

[2] J. C. Peters *et al.*, Science, 2020, **369**, 850–854, DOI. 10.1126/science.abc1607, J. M. Mayer *et al.*, Inorg. Chem. 2023, **62**, 10031–10038, DOI. 10.1021/acs.inorgchem.3c01241.

[3] I. Siewert *et al.*, Organometallics 2023, **42**, 3258–3265, DOI. 10.1021/acs.organomet.3c00378.