Photochemically Driven Reverse Water-Gas Shift Reactivity

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Hydrogen transfer from transition metal hydride (TMH) complexes is pivotal as elementary reaction in many catalytic chemical and biochemical transformations. Combination of formal proton and electron transfer can result in net proton, hydrogen atom or hydride transfer.\(^1\) While ground state hydrogen transfer reactions are well examined, photochemical reactivity of group 10 TMH complexes is rare.\(^2\)

Herein we report carbon dioxide activation by PNP Nickel(II) hydride 1 (PNP = N(CH\(\text{CH}_{\text{P}}\text{Bu}_2\))\(_2\)), giving formate 2 under thermal conditions and hydroxycarbonyl 3 via unprecedented abnormal CO\(_2\) insertion upon photolysis (figure 1).\(^3\) Mechanistic investigation by transient UV/Vis and infrared spectroscopy, DFT calculations, kinetic studies and trapping experiments suggest initial population of a Ni-H dissociative excited state followed by reductive N-H bond formation giving a Ni(0) photoproduct which undergoes subsequent CO\(_2\) coordination.

Reformation of hydride 1 via carbonyl 5 is a net 2H\(^+\)/2e\(^-\) process and can be performed by stepwise addition of acid and hydride donors or reductants, respectively, showing formation of a rare Ni(II) formyl as intermediate in both cases. Using H\(_2\) as electron and proton source, starting from imine hydride 4 a two-step synthetic cycle for the reverse water-gas shift reaction on a PNP Ni(II) platform is established (figure 1).\(^4\)

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\(^1\) Jeffrey J. Warren, Tristan A. Tronic, James M. Mayer. (2010). *Chem. Rev.*, 12, 6961. DOI: 10.1021/cr100085k

\(^2\) Robin N. Perutz, Barbara Procacci. (2016). *Chem. Rev.*, 15, 8506. DOI: 10.1021/acs.chemrev.6b00204


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