MECHANISTIC INVESTIGATION INTO COPPER(I) HYDRIDE CATALYZED FORMIC ACID DEHYDROGENATION

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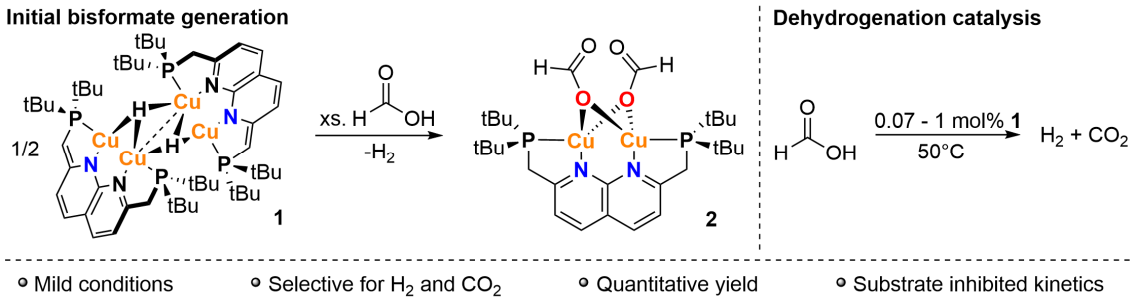
For decades, copper hydrides have been widely used as homogeneous catalysts in reduction reactions.[1] Despite this, mechanistic understanding of these catalysts is limited since their nuclearity in solution is often unknown. Copper hydrides are also known to reduce CO_2 both stoichiometrically and catalytically. However, recently it has been found that some copper hydrides exhibit the opposite reactivity, and can catalytically dehydrogenate formic acid.[1,2] Understanding the mechanism of this reaction and the reasons leading to the change in directionality could aid rational catalyst design for either type of reactivity. Currently, however, the dehydrogenation reactivity is sluggish and the mechanism for the reported complexes is unknown. We have found that our tetranuclear $[PNNP^*Cu2H]_2$ complex (**1**)[3] can also catalyze formic acid dehydrogenation selectively and under mild conditions. This is surprising, since the deprotonated anionic analogue of this complex reacts with CO_2, forming various species amongst which potassium formate.[4] In contrast with reported systems, our catalyst is well-defined during the formic acid dehydrogenation reaction, which enables us to study the mechanism. We were able to isolate bisformate complex **2** as catalytic intermediate and to monitor the kinetics of the reaction using an inline GC for gaseous products. These kinetic measurements revealed that the reaction is inhibited by the formic acid substrate. In this work we investigated the origins of this inhibition as well as the general mechanism using isotopic labeling and various catalyst analogues, which provides new insights into this unusual reaction.



[1] Tanase, T., et al., *J. Am. Chem. Soc.* **2019**, *141* (22), 8732–8736.

[2] Tilley, T. D., et al., *Angew. Chemie–Int. Ed.* **2020**, *59* (31), 12769–12773.

[3] Broere, D. L. J., et al., *Chem.–A Eur. J.* **2019**, *25* (58), 13280–13284.

[4] Broere, D. L. J., et al., *Angew. Chemie–Int. Ed.* 2022, 61 (29), 1–6.