TOWARDS THE ELECTRIFICATION OF METAL-LIGAND COOPERATIVE CATALYSTS

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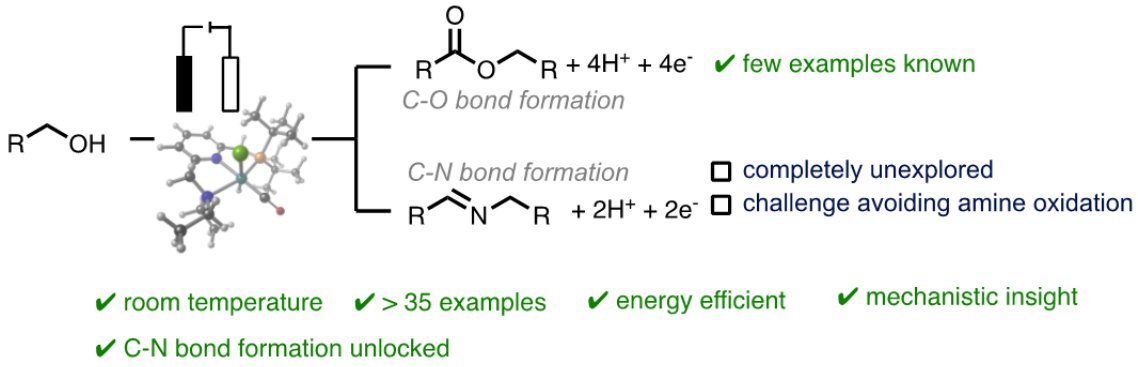
The development of energy and atom efficiency processes is thought to play an important role for a sustainable chemical industry of the future. One opportunity could be the electrification of thermal processes to benefit from the inherent advantages of electrochemistry, such as safety, scalability, a cheap and traceless redox agent (electrons), and the possibility to directly control the energy input of a given reaction through the applied potential. In recent years, the construction of novel C-N bonds from simple and potentially renewable feedstock (alcohols and amines) spurred interest in the community.[1,2]



This is a particular challenge due to the redox labile nature of amines, making undesired amine oxidation both thermodynamically and kinetically more facile. Here, we demonstrate that our recent efforts to electrify aromatic pincer complexes,[3] known to catalyze acceptor-less dehydrogenation reactions, can be extended to formation of C-N bonds directly from alcohols and amines. We demonstrate that such catalysts are indeed robust candidates, that allow to avoid high working potentials to access the coupling of a variety of amines substrates with benzyl alcohols.[4] By understanding possible side-reactions and the possibility to fine-tune working potentials, also simple alkyl alcohols can be coupled. With over 35 examples, TON > 90, temporal control and the possibility to easily recover unreacted alcohols, we hope that this work will spur novel developments in the field of molecular electrocatalytic alcohol oxidation. A rational for the beneficial role of electricity in such MLC-type catalyzed systems will be discussed.

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[1] J. Li, Y. Zhang, K. Kuruvinashetti, N. Kornienko, *Nat Rev Chem* **2022**, *6*, 303–319.

[2] J. Shao, N. Meng, Y. Wang, B. Zhang, K. Yang, C. Liu, Y. Yu, B. Zhang, *Angewandte Chemie International Edition* **n.d.**, *n/a*, e202213009.

[3] D. Tocqueville, F. Crisanti, J. Guerrero, E. Nubret, M. Robert, D. Milstein, N. von Wolff, *Chem. Sci.* **2022**, DOI 10.1039/D2SC04533H.

[4] S. Kasemthaveechok, N. von Wolff, **2022**, DOI 10.26434/chemrxiv-2022-n306b.