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The Origin of Anion−π Autocatalysis

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This study explores the mechanism behind the autocatalysis of epoxide-opening ether cyclisation reactions on the aromatic surface of anion−π catalysts. Despite a proposed working hypothesis, the mechanism of anion−π autocatalysis has not been fully understood. This research shows that peripheral crowding in substrate and product does not have a major influence on anion−π autocatalysis. The inclusion of water between substrate and product on the catalytic aromatic surface is necessary for efficient anion−π autocatalysis. Computational models suggest that two water molecules serve as proton shuttles to stabilise charge density in the transition state. This new transition-state model offers a plausible mechanism that explains experimental results and brings anion−π catalysis to a new level of sophistication.

Authors’ comments:
“Interested in emergent properties from unorthodox interactions, we found anion-π autocatalysis literally wonderful: Thinking about asymmetric versions, how could substrate and product on the catalytic π surface interact without physically touching each other? Even if we made them bigger and bigger?”

Nickel-Catalyzed Enantioselective Electrochemical Reductive Cross-Coupling of Aryl Aziridines with Alkenyl Bromides

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Chiral β-functionalized homoallylic amines are important structural motifs found in pharmacologically and biologically active molecules. In this paper, the authors developed a new method using nickel-catalyzed asymmetric electrochemical reductive cross-coupling of aryl aziridines with alkenyl bromides to construct enantioenriched β-aryl homoallylic amines with excellent E-selectivity. The method employs constant current electrolysis in an undivided cell with triethylamine as a terminal reductant and does not require heterogeneous metal reductants or sacrificial anodes. Detailed mechanistic studies indicate that this transformation proceeds through a stereocongruent mechanism. The method offers a versatile and cost-effective alternative to classic methods for accessing chiral homoallylic amines, with excellent functional group compatibility and broad substrate scope.

Authors’ comments:
“We hope that the combination of electro-reduction with organic reductants presented here will inspire the development of enantioselective electrochemical reductive cross-coupling reactions in the future.”

Prepared by Cesare Berton, Patrick A. Cieslik, Fan Liu, Stanislav Prytuliak, Simon Klinger, Jonas Genz, Dominik Roth, Samy Kichou, Eda Nisli, and Jason P. Holland*

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Theory-guided development of homogeneous catalysts for the reduction of CO₂ to formate, formaldehyde, and methanol derivatives

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This article explores the use of organometallic catalysts made of earth-abundant metals in the catalytic reduction of carbon dioxide to formic acid, formaldehyde, and methanol. The goal was to identify molecular control parameters that steer selectivity to these three distinct reduction levels. The authors developed linear scaling relationships to predict catalyst activity and selectivity in CO₂ hydrosilylation based on the hydride affinity of the catalysts. They found that cobalt complexes with bis(phosphino)triazine PNP-type pincer ligands could selectively reach all three reduction levels under different reaction conditions. Experimental studies successfully validated the composite volcano picture using selected catalysts, with one cobalt complex producing formaldehyde in over 80% yield. The collaborative study demonstrates the potential of combining computational and experimental approaches to design catalysts for CO₂-based chemical transformations.

Authors’ comments:
“Using molecular volcano plots, we successfully predicted selectivity trends in first-row transition metal-catalyzed CO₂ reduction. These predictions were then experimentally validated, leading to systematic improvements in catalyst design.”

Synthetic Receptors with Micromolar Affinity for Chloride in Water

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The selective capture of chlorides in neutral water is a challenging task due to their high hydration energy and the lack of ligands that can overcome this obstacle. In their publication, Severin and co-workers prepared a water-soluble, dinuclear palladium cage that displays an unprecedented micromolar affinity towards chloride via an anion-exchange mechanism with nitrate. The stability of the chloride adduct facilitated detailed characterisation of the supramolecular complex providing insights into the attractive C-H···Cl interactions within the cavity of the host. These findings are general and offer new possibilities for the selective recognition of halides in neutral water creating a solid starting point for designing the next generation of synthetic anion receptors.

Authors’ comments:
“We were surprised that C-H···Cl hydrogen bonds and electrostatic interactions are sufficient to achieve tight chloride binding in water.”