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A CHIMIA Column
Short Abstracts of Interesting Recent Publications of Swiss Origin

Redox Reactions in Palladium Catalysis: On the Accelerating and/or Inhibiting Effects of Copper and Silver Salt Additives in Cross-Coupling Chemistry Involving Electron-rich Phosphine Ligands


ETH Zürich
Palladium-catalyzed cross-coupling reactions are ubiquitous in the formation of C–C and C–heteroatom bonds. The widely accepted mechanism relies on a Pd⁰/Pd⁴ reductive elimination/oxidative addition sequence. The synergistic effect of added copper salts is well documented but poorly understood. Schoenebeck and co-workers propose a mechanism in which the copper promotes the formation of a more active Pd⁰ dimer and an inert copper-cubane. The Pd-dimer is more active than Pd(i-Bu,P) for the Suzuki cross-coupling of ArCl, a notoriously difficult substrate, with Ar²B(OH)₂.

Sialy Lewis*: A 'Pre-Organized Water Oligomer'? 


University of Basel
Among lectins, selectins, being key players in the early stages of inflammation, are most prominently investigated as drug targets. Despite the progress made in understanding the structural interactions between E-selectin with the tetrasaccharide sialyl Lewis⁴, the driving force behind it has previously not been fully characterized. Unexpectedly, the binding is largely entropy driven, since sialyl Lewis⁴ represents a 'pre-organized water oligomer', mounted on a presentation scaffold. The impetus for binding to E-selectin is the high degree of pre-organization and the entropic benefit of the release of water molecules from the binding interface to bulk water. The thermodynamic study highlights structural modifications that can be made in glycomimetics to improve significantly their enthalpic contribution to binding while maintaining a similar entropy term.

In Vitro Selection of Functional Lantipeptides


Massachusetts General Hospital, MPI Dortmund, and University of Basel
Lantipeptides are posttranslationally modified peptides containing lanthionine moieties, which consist of two alanines sharing a common sulfur atom. The resulting intramolecular cross-link is important for bioactivity and stability. Lantipeptides are characterized by potent antibacterial activities, suggesting that this class of molecules provides a promising platform for the development of peptide-based therapeutics. In order to systematically identify artificial lantipeptides with tailor-made function, the authors developed an in vitro selection method for the production of up to 10⁸ different lantipeptides. This diversity can be screened for functional molecules using mRNA-lantipeptide display. The validation of this approach was performed by isolating binders toward Sortase A, a transamidase which is required for virulence of Staphylococcus aureus. The interaction of selected lantipeptides with Sortase A is highly dependent on the presence of a (2S,6R)-lanthionine in the peptide.

Formation of Quaternary Stereogenic Centers by NHC–Cu-Catalyzed Asymmetric Conjugate Addition Reactions with Grignard Reagents on Polyconjugated Cyclic Enones


Université de Genève, and ENSC de Rennes
The enantioselective generation of quaternary centers by conjugate addition remains a synthetic challenge. Relying on NHC-based copper catalysts, the authors report on the regioselective 1,4-addition of Grignard reagents onto polyconjugated enones and enyones to yield all-carbon stereogenic centers. The observed regioselectivity stands in sharp contrast to that observed with either dialkylzinc or trialkylaluminium reagents that usually favor 1,6-addition.

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