doi:10.2533/chimia.2015.638

Swiss Science Concentrates

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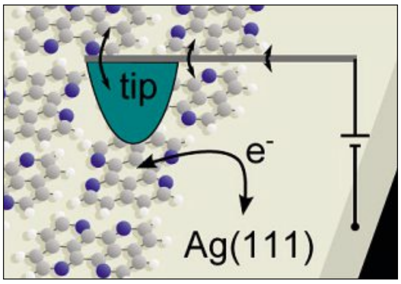
Short Abstracts of Interesting Recent Publications of Swiss Origin

Periodic Charging of Individual Molecules Coupled to the Motion of an Atomic Force Microscopy Tip

N. Kocić, P. Weiderer, S. Keller, S. Decurtins, S.-X. Liu*, and J. Repp*, *Nano Lett.* **2015**, *15*, 4406. University of Bern

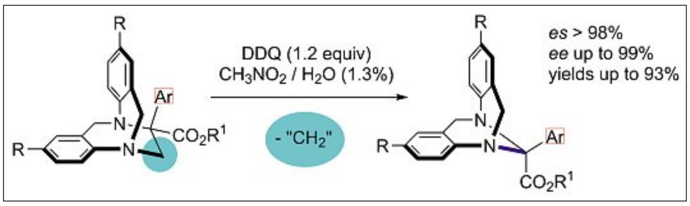
Single-electron charging is critical for many areas of nanoscience. Liu and her collaborators have identified that individual molecules at the edges of self-assembled islands grown on Ag(111) can be deliberately switched in their charge state with the electric field from a scanning-probe tip. Notably, the oscillatory motion of a cantilever in atomic force microscopy (AFM) can be directly coupled to a charge-state transition of single molecules. In analogy to previous experiments on quantum dots, this may also be used in the future to access excited state properties of single molecules from AFM experiments.



A Mild and Efficient CH_2-Extrusion Reaction for the Enantiospecific Synthesis of Highly Configurationally Stable Tröger Bases

S. A. Pujari, C. Besnard, T. Bürgi, and J. Lacour*, *Angew. Chem. Int. Ed.* **2015**, *54*, 7520. University of Geneva

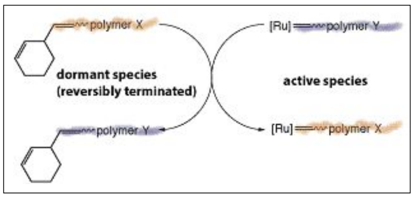
Only few CH_2 extrusions are hitherto reported using metal-free conditions and activated benzylamines and α-hydroxy carbonyl compounds as substrates. Lacour and collaborators report here a novel, high-yielding CH_2-extrusion reaction leading to the transformation of ethano-Tröger bases into disubstituted methano derivatives. Under mild and metal-free oxidative conditions, loss of CH_2 and ring contraction are provoked. Despite two bond cleavages at stereogenic nitrogen and carbon centers and a temporary rupture of the bicyclic structure, a very high enantiospecificity (*es* 98%) is observed for this unusual reaction. A reaction mechanism involving a conformationally locked iminium intermediate is proposed. Interestingly, the products of ring contraction are significantly more configurationally stable than regular Tröger bases.



Catalytic Living Ring-Opening Metathesis Polymerization

A. A. Nagarkar and A. F. M. Kilbinger*, *Nat. Chem.* **2015**, *7*, 718. University of Fribourg

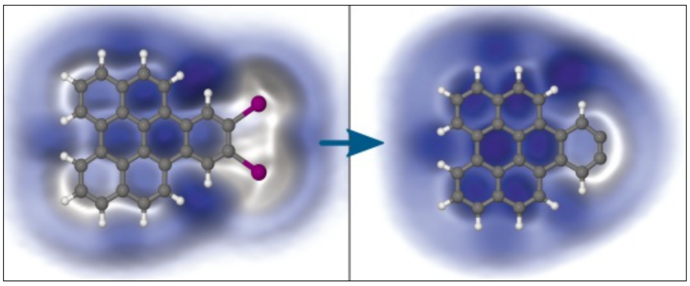
In living ring-opening metathesis polymerization (ROMP), a transition-metal–carbene complex polymerizes ring-strained olefins with very good control of the molecular weight of the resulting polymers. Because one molecule of the initiator is required for each polymer chain, however, this type of polymerization is expensive for widespread use. Nagarkar and Kilbinger now designed a chain-transfer agent (CTA) capable of reducing the required amount of metal complex. They demonstrate that substituted cyclohexene rings are good CTAs, and thereby preserve the 'living' character of the polymerization using catalytic quantities of the metal complex. This new technique provides access to well-defined polymers for industrial, biomedical and academic use at a fraction of the current costs and significantly reduced levels of residual ruthenium catalyst.



On-Surface Generation and Imaging of Arynes by Atomic Force Microscopy

N. Pavliček*, B. Schuler, S. Collazos, N. Moll, D. Pérez, E. Guitián, G. Meyer, D. Peña*, and L. Gross, *Nat. Chem.* **2015**, *7*, 623. IBM Research-Zurich

Arynes, formally derived from arenes by the removal of two hydrogen atoms from adjacent carbon atoms, are prominent reactive intermediates that have been hypothesized for more than a century. Here, Pavliček, Peña and co-authors demonstrate the generation and characterization of individual polycyclic aryne molecules on an ultrathin insulating film by means of low-temperature scanning tunnelling microscopy and atomic force microscopy. Bond-order analysis suggests that a cumulene resonance structure is the dominant one, and the aryne reactivity is preserved at cryogenic temperatures. The results provide important insights into the chemistry of these elusive intermediates and their potential application in the field of on-surface synthesis.



Prepared by Caroline D. Bösch, Markus Probst, Yuliia Vyborna, Mykhailo Vybornyi, Simon M. Langenegger and Robert Häner

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