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Swiss Science Concentrates

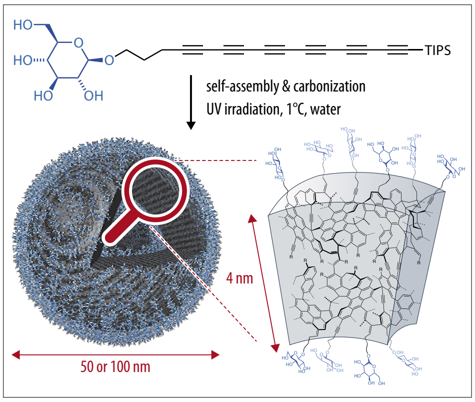
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Low-Temperature Preparation of Tailored Carbon Nanostructures in Water

R. Szilluweit, T. N. Hoheisel, M. Fritzsche, B. Ketterer, A. Fontcuberta i Morral, D. Demurtas, V. Laporte, R. Verel, S. Bolisetty, R. Mezzenga, and H. Frauenrath*, *Nano Lett.* **2012**, *12*, 2573.
EPF Lausanne and ETH Zürich

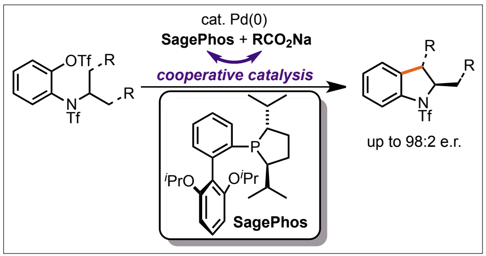
Carbon nanostructures have found widespread interest in applications ranging from high performance composites, to fuel cells and electrode materials. Conventional synthetic pathways to such materials make it difficult to tailor their morphology or their surface chemistry. The authors now report a route to carbon nanostructures in aqueous solution at 1 °C. Oligo(ethynylene)-derived amphiphiles dissolved in water, self-assemble into vesicles. UV-irradiation triggers carbonization. Carbon vesicles with a carbohydrate-decorated, graphite-like amorphous carbon membrane were obtained. This versatile strategy will allow the preparation of many functional carbon nano-structures for various applications.



Chiral Monodentate Phosphines and Bulky Carboxylic Acids: Cooperative Effects in Palladium-Catalyzed Enantioselective C(sp³)-H Functionalization

T. Saget, S. J. Lemouzy, and N. Cramer*, *Angew. Chem. Int. Ed.* **2012**, *51*, 2238.
EPF Lausanne

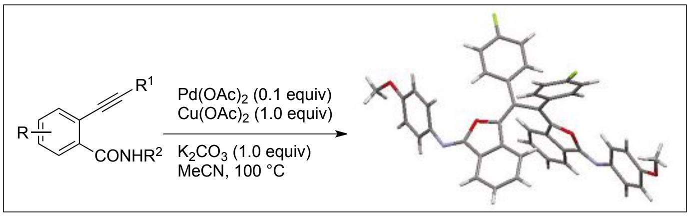
The direct enantioselective functionalization of unactivated C(sp^3)-H bonds is a prime challenge in asymmetric catalysis. Towards this objective, Cramer and coworkers report on a new class of sterically demanding, electron-rich yet air-stable, monodentate chiral phosphines. These ligands in conjunction with a bulky carboxylate base are competent for the palladium-catalyzed enantioselective intramolecular arylation of unactivated methyl and methylene C(sp^3)-H bonds with high selectivities. The reaction displays a promising substrate scope and allows for the simultaneous creation of up to three stereocenters.



Synergistic Effect of Palladium and Copper Catalysts: Catalytic Cyclizative Dimerization of *ortho*-(1-Alkynyl) benzamides Leading to Axially Chiral 1,3-Butadienes

B. Yao, C. Jaccoud, Q. Wang, and J. Zhu*, *Chem. Eur. J.* **2012**, *18*, 5864.
EPF Lausanne

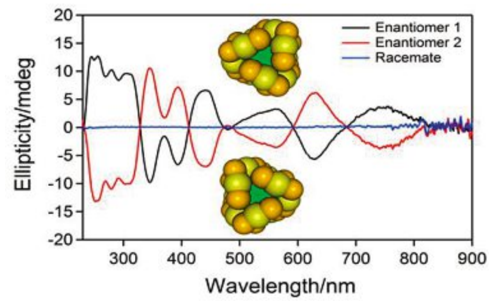
Synergistic catalysis can enable previously unknown transformations or improve the efficiency of existing reactions. In this context, the authors report on the dimerization of *o*-(1-alkynyl) benzaminedes in the presence $Pd(OAc)_2$ and $Cu(OAc)_2$ leading to chiral *E*,*E*-1,3-dienes, a frequently appearing structural motif in natural products. The concurrent formation of vinylpalladium and vinylcopper species followed by transmetalation is key step in this transformation. The coexistence of both Pd and Cu-catalysts was found to be essential for both the cyclizative dimerization process and for the observed unusual cyclization mode.



First Enantioseparation and Circular Dichroism Spectra of Au_{38} Clusters Protected by Achiral Ligands

I. Dolamic, S. Knoppe, A. Dass, and T. Bürgi*, *Nature Commun.* **2012**, *3*, 798.
Universities of Geneva and Mississipi, USA

Several forms of chirality are well known to chemists. One of these arises from the adsorption of achiral substrates on a surface. In this context, thiolate-decorated gold clusters were recently reported to be chiral. In this communication, Bürgi and coworkers present the synthesis and enantiomer separation of $Au_{38}(SCH_2CH_2Ph)_{24}$. The racemic nanoparticles were subjected to semi-preparative chiral HPLC, allowing the separation of the enantiomers. Importantly, the authors show that i) the chirality stems only from the asymmetric arrangement of the achiral adsorbates on the nanoparticle and ii) the nanoparticles are configurationally stable for several days at −5 °C.



Prepared by Nico Bruns, Adnan Ganic, Valentin Köhler, Fabien Monnard, Mark R. Ringenberg and Thomas R. Ward
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