



# Swiss Science Concentrates

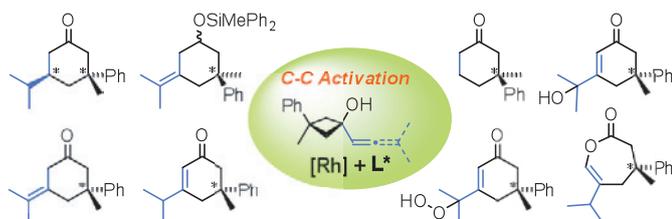
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

## Rhodium(I)-Catalyzed Enantioselective Activation of Cyclobutanols: Formation of Cyclohexane Derivatives with Quaternary Stereogenic Centers

T. Seiser and N. Cramer\*, *Chem. Eur. J.* **2010**, *16*, 3383  
ETH Zürich

The activation of carbon–carbon bonds is a complementary method to access uncommon organometallic species. The authors describe an enantioselective activation of *tert*-cyclobutanols through an insertion of a chiral rhodium(I) complex into the C–C bond of the cyclobutane, forming a quaternary stereogenic center and an alkyl–rhodium species initiating ring-closing reactions. High yields and excellent enantioselectivities of up to 99% *ee* are obtained. This technology provides access to substituted cyclohexane derivatives with quaternary stereogenic centers.

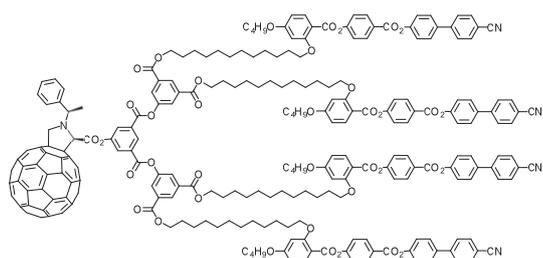


## Diastereoisomerically Pure Fulleropyrrolidines as Chiral Platforms for the Design of Optically Active Liquid Crystals

S. Campidelli, P. Bourgun, B. Guintchin, J. Furrer, H. Stoeckli-Evans, I. M. Saez, J. W. Goodby\*, and R. Deschenaux\*, *J. Am. Chem. Soc.* **2010**, *132*, 3574

University of Neuchâtel; University of York

In this article, the authors report the synthesis, characterization and liquid-crystalline properties of four optically active fullerodendrimers. The fullerodendrimers display chiral nematic (N\*) phases which exhibit supramolecular helicoidal organizations. The formation and nature of the mesophase arises from the combination of the chirality of the fulleropyrrolidine units with the nematogenic behavior of the dendritic liquid-crystalline promoter. Therefore, each subunit plays a complementary role in order to generate the desired mesophase in each final material. This result suggests that the self-organization of such supermolecular materials can be controlled at the molecular level by the introduction of only one chiral centre.



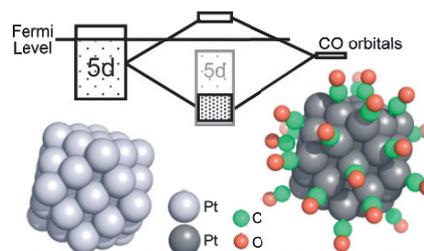
(*R,R*)-fullerodendrimer, Tg: 68 °C, N\* → I: 108 °C

## In Situ Characterization of the 5d Density of States of Pt Nanoparticles upon Adsorption of CO

P. Glatzel\*, J. Singh, K. O. Kvashnina, and J. A. van Bokhoven\*, *J. Am. Chem. Soc.* **2010**, *132*, 2555

European Synchrotron Radiation Facility; ETH Zürich.

The authors performed an element-specific study of the occupied and unoccupied density of electronic states in Pt nanoparticles using hard X-ray resonant inelastic X-ray scattering (RIXS). An opening in the valence d band is observed when CO is adsorbed on Pt nanoparticles. The gap originates as a result of newly formed bonding and antibonding orbitals between Pt and CO. The adsorption of CO blocks the active sites and changes the electronic structure, thus passivating the catalytic activity of Pt. The experimental results are supported by full multiple scattering calculations.



## Atomistic Simulation of NO Dioxygenation in Group I Truncated Hemoglobin

S. Mishra and M. Meuwly\*, *J. Am. Chem. Soc.* **2010**, *132*, 2968

University of Basel

In this paper, the oxidation of nitric oxide to nitrate by oxygen-bound truncated hemoglobin (trHbN) was studied using Adiabatic Reactive Molecular Dynamics (ARMD). The simulations reveal that the reaction favors a pathway including i) NO binding to oxy-trHbN, followed by ii) rearrangement of peroxynitrite-trHbN to nitrate-trHbN, and finally iii) nitrate dissociation from nitrate-trHbN. The simulations elucidate the experimentally determined kinetics of the reaction. Active site residues Tyr33 and Gln58 were found to considerably affect and slow down the dioxygenation reaction.

