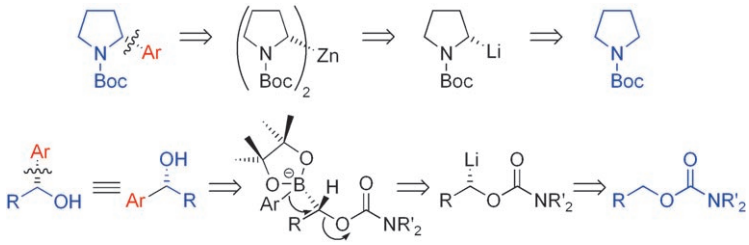
VIP *The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:*

News

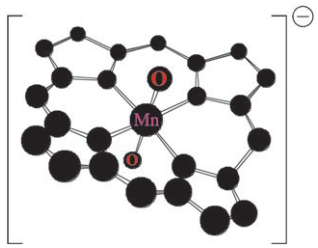
Books

Highlights



Aryl unplugged: Two conceptually new disconnections are equivalent to arylation of enantioenriched carbanions obtained by asymmetric deprotonation. One retrosynthesis (see scheme, above) involves *N*-Boc pyrrolidine (Boc = *tert*-butoxycarbonyl, Ar = aryl) and an organozinc intermediate, and the other (below) *O*-alkyl carbamates with organoboron intermediates.

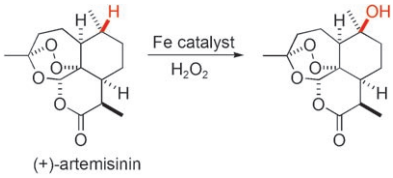
Carbanion Arylations



Double O agents: The first definitive spectroscopic evidence for *trans*-dioxomanganese(V) porphyrins (see picture) has been reported by Groves, Spiro, and co-workers. Their work extends the scope of oxo-coordination chemistry and opens the way for the exploration of reactivity patterns of *trans*-dioxo complexes of first-row transition-metal ions.

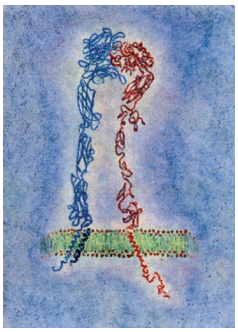
Dioxo Complexes

Contents



Tamed cat: Iron-catalyzed selective C–H oxidation reactions present new possibilities in the synthesis and modification of natural products. As a model reaction of a possible C–H oxidation as part of a total synthesis, the natural product (+)-artemisinin was converted into (+)-10β-hydroxyartemisinin in 34% yield (see scheme). The combination of nontoxic metal catalyst with H_2O_2 is an environmentally friendly process.

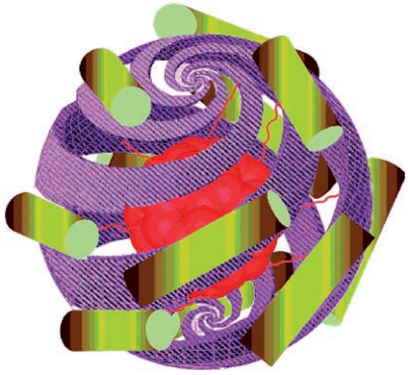
Minireviews



Over the limit: Despite accounting for about one third of all proteins encoded in the human genome, the functions and structures of the transmembrane domains of membrane proteins are poorly understood. Major advances have recently been made in the development of exogenous agents that can recognize these domains, which have laid the groundwork for targeting protein–protein interactions in the membrane bilayers (see picture).

Reviews

Tune in your crystal set: Design of molecular shape, deformable molecular topologies, self-assembly, and self-organization combine together to yield super- and supramolecular liquid crystals (such as the nanomolecular "Boojum" shown in the picture) that are capable of exhibiting "superphases". Transmission and amplification of physical properties are often observed for such systems.



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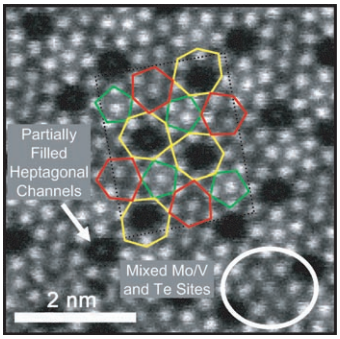
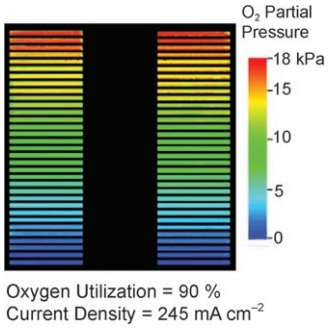
Communications



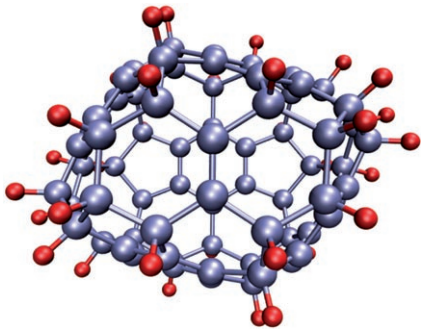
Seeing is believing: Aberration-corrected STEM imaging allows direct visualization of the orthorhombic M1 phase primary component of the MoVNbTeO propane ammoxidation catalyst. Atomic coordinates and site occupancies are obtained, and the beam-sensitive Te chains in the hexagonal and heptagonal channels are successfully imaged. These results suggest that HR-HAADF imaging may provide improved starting models for Rietveld analysis of complex structures.

STEM Imaging



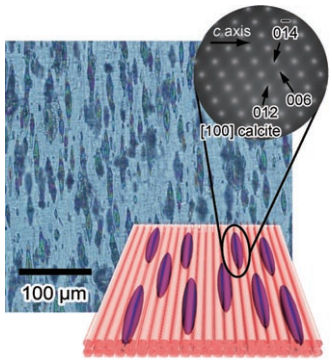
Cell diagnosis: The oxygen distribution in the interior of operating fuel cells can be visualized by using dye films painted on the transparent gas flow field (see image). The spatial and time resolutions are 300 μm and 500 ms, respectively. The oxygen distribution in a polymer electrolyte membrane fuel cell was not in accordance with that expected from the current, suggesting a significant contribution from water.

Fuel Cell Analysis



Feeling the pressure: Hydrogenation of C_{70} at 100 bar H_2 pressure and 400 °C for 72 h has enabled isolation of $C_{70}H_{38}$. Full structural assignment was achieved by 2D NMR spectroscopic studies, which show $C_{70}H_{38}$ to have C_2 symmetry and contain five benzenoid rings and two protonated carbon atoms on the equator (see picture). The proposed protonation scheme for the formation of this isomer shows a high similarity to reported $C_{70}F_{38}$isomers.

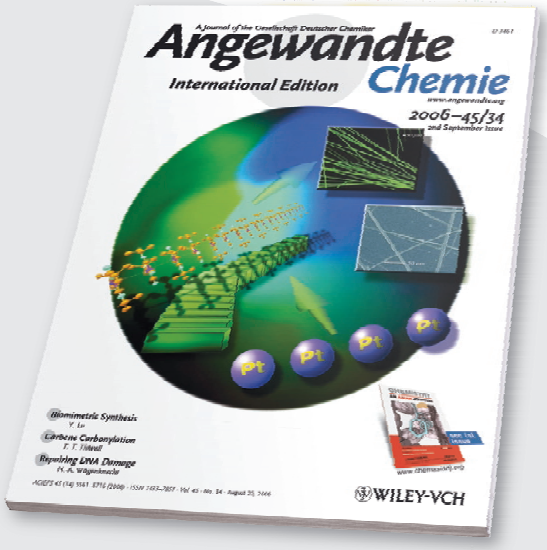
Fullerenes



Unidirectionally aligned hybrids consisting of chitin and calcite were obtained by template crystallization of $CaCO_3$ in an ordered chitin film with nematic liquid-crystalline molecular alignment. The picture shows the resulting chitin matrix containing $CaCO_3$ rods, schematically and in the form of an optical micrograph, and the selected-area electron diffraction pattern of a thin section of a single rod.

Self-Organized Hybrids

Incredibly international!



Although *Angewandte Chemie* is owned by the German Chemical Society (Gesellschaft Deutscher Chemiker, GDCh) and is published by Wiley-VCH in a charming small town in southwest Germany, it is international in every other respect. Authors and referees from around the globe contribute to its success. Most of the articles are submitted from China (20%), USA (16%), and Japan (13%) - only then comes Germany (12%). Most of the referee reports come from Germany and the USA, but Japan and Western Europe are also well represented.

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GDCh Gesellschaft Deutscher Chemiker

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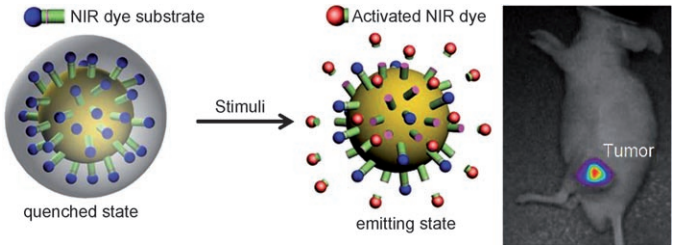
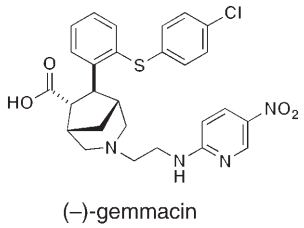


Nanodiagnosis: A matrix-metalloproteinase (MMP) sensitive gold-nanoparticle (AuNP) imaging probe quenches conjugated near-infrared (NIR) dyes with high efficiency and is specifically activated by the target MMPs (see picture, left). With this system, nanomolar amounts of protease can be detected—both in vitro and in vivo. Experiments disclose an apparent positive contrast in MMPs-positive tumor-bearing mice (right).

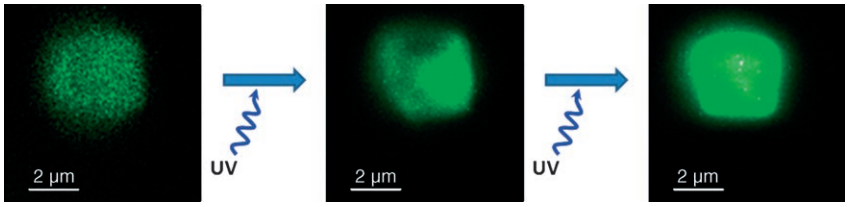
Gold Nanoprobes

Beating the superbugs: Diversity-oriented synthesis using a solid-supported phosphonate unit to synthesize 242 drug-like compounds based on 18 natural-product-like scaffolds led to the discovery of gemmacin (see scheme). This new structural class of antibiotic is active towards methicillin-resistant *Staphylococcus aureus* (MRSA).



(–)-gemmacin

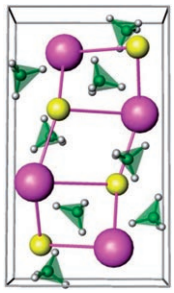
Combinatorial Chemistry



The right bright light: Silver-exchanged zeolite 3A crystals show remarkable luminescent properties. Upon irradiation with high-power UV light, a strong photoactivation process takes place which results in an emission increase of up to two orders of magnitude (see picture). The crystals of interest—or even small domains within one crystal—can be selectively activated by using a confocal microscope.

Silver in Zeolites

Variegated decomposers: The synthesis of the first mixed alkali metal borohydride, which contains lithium and potassium, is presented. $LiK(BH_4)_2$ (see picture; K crimson, Li yellow, B green, H gray) has a crystal structure similar to $LiBH_4$, and a thermal decomposition temperature between those of $LiBH_4$ and KBH_4. Using this route, the hydrogen desorption thermodynamics of complex hydrides can be easily tailored.



Hydrogen Storage

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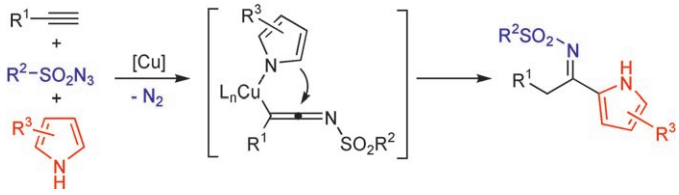
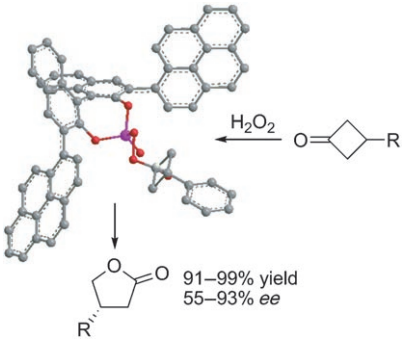


Making rings: A new Cu-catalyzed three-component coupling reaction between 1-alkynes, sulfonyl azides, and pyrrole derivatives has been developed for making 2-functionalized pyrrole rings (see scheme). This C–C bond formation offers high efficiency and selectivity, mild reaction conditions, and a wide substrate scope.

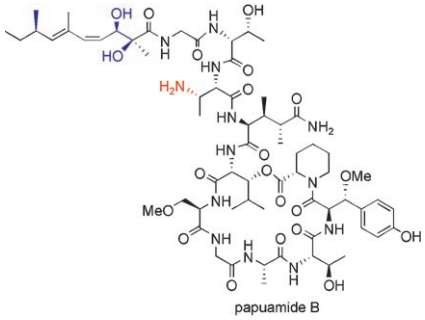
Pyrrole Functionalization



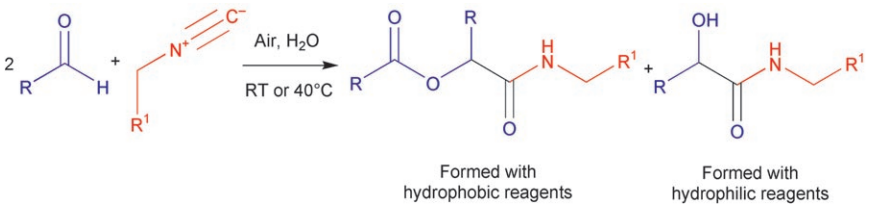
A catalytic amount of a chiral Brønsted acid with aqueous H_2O_2 as the oxidant is sufficient for the enantioselective Baeyer–Villiger oxidation of 3-substituted cyclobutanones to give the corresponding γ-lactones in excellent yields and up to 93% *ee*. The method employs benign aqueous H_2O_2 instead of stoichiometric amounts of a dangerous peracid.

Asymmetic Catalysis

Synthesis in stereo: The first total synthesis of papuamide B, a cyclic peptide isolated from a marine sponge, has been achieved. The configuration of three stereogenic centers of its dienoic acid unit has been established by comparison to a series of stereoisomers of known configuration, and the stereochemistry of its 2,3-diaminobutanoic acid segment has been revised.



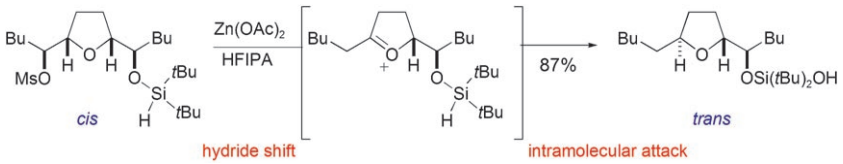
Natural Product Synthesis



Wet, wet, wet: Hydrophobic aldehydes are cleanly oxidized upon stirring with water in air. Addition of hydrophobic isocyanides to aqueous suspensions of such aldehydes results in the formation of Passerini reaction products, with the aldehyde being the source of both carbonyl and ester functions. Partially water-soluble reagents reacted slower than water-insoluble ones. Isotope labeling studies show that water participates in these "on water" reactions.

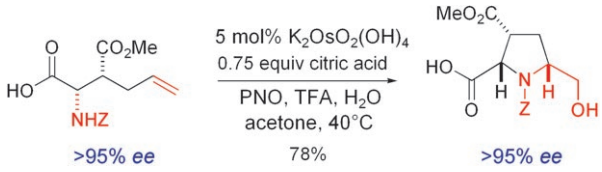
Organic Synthesis

Contents



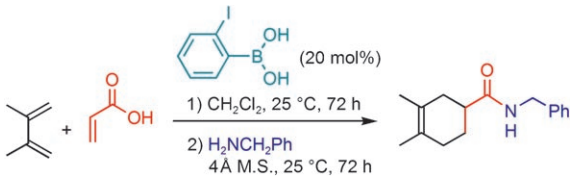
Stereoselective Synthesis

Switching sides: *cis* THF derivatives produced from the oxidative cyclization of dienes and diols can be transformed into the corresponding *trans* heterocycles through a 1,2-hydride shift and intramolecular trapping with a hydride nucleophile (see scheme). Moreover, organometallic compounds can be used to trap the oxonium ion generated in this way so that it is possible to introduce various groups at the C-2 position with control of stereochemistry.



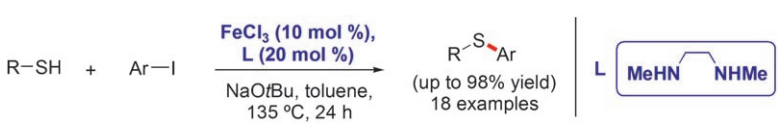
Oxidative cyclization

The PNOman can: The use of pyridine-*N*-oxide (PNO) transforms the catalytic oxidative cyclization to include the formation of pyrrolidines from N-Z-protected amino alcohols and amino acids (see scheme; Z = $PhCH_2OCO$). This new method expands the scope of the oxidative cyclization as illustrated with the synthesis of a range of di- and trisubstituted pyrrolidines with complete control of stereochemistry.



Organocatalysis

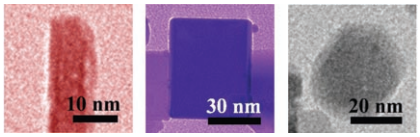
Taming carboxylic acids: *ortho*-Iodo- and *ortho*-bromophenylboronic acids are exceptional organocatalysts in atom-economical amidations between free carboxylic acids and amines, including functionalized ones, and can also provide LUMO-lowering activation in [4+2] cycloadditions of α,β-unsaturated carboxylic acids.



Cross-Coupling Reactions

Strike while the iron is hot: An efficient iron-catalyzed protocol for the S-arylation of aromatic and heteroaromatic thiol derivatives has been developed, which involves an inexpensive catalyst system formed by combining $FeCl_3$ and *N*,*N*′-dimethylethylenediamine at 135 °C. This method avoids the use of expensive and/or air-sensitive ligands and provides in most cases the desired sulfide in high yields.

Contents



A two-step synthesis method is used to prepare gold-on-ceria nanorods, nanocubes, and nanopolyhedra (see picture), and a strong shape-effect of CeO_2 on the water–gas shift reaction activity of the catalysts is identified. Gold on the (110) facets of ceria nanorods shows the highest activity.

Supporting information is available on www.angewandte.org (see article for access details).

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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