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:

Author Profile

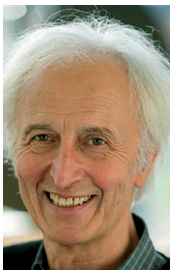
"The biggest problem that scientists face is the pursuit of fame and fortune.
If I won the lottery, I would stop applying for grants and concentrate on oxidative coupling research just for fun! …"
This and more about Aiwen Lei can be found on page 12136.

News


D. Chen


D. Spiegel

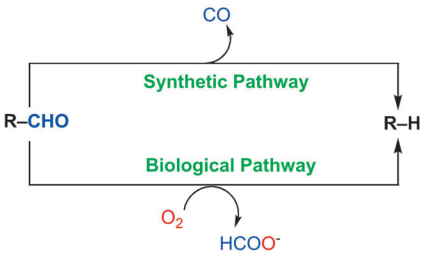

F. Schüth


H. Schwarz

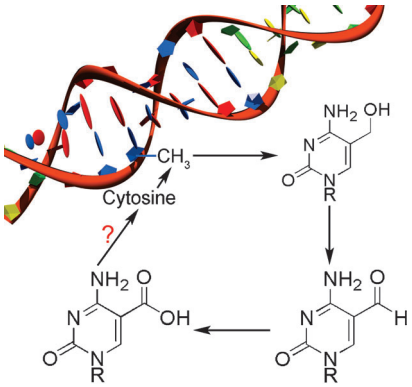
Books

Contents

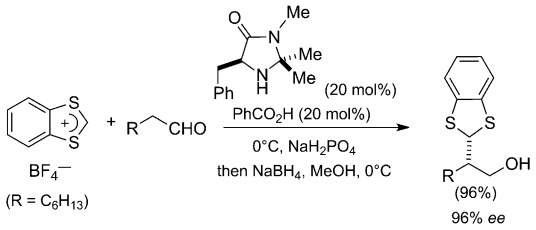
Highlights



No two ways about it: The title reaction is immensely important in synthesis and biology. Whereas biological systems oxygenate aldehydes to generate formate and alkanes or alkenes, synthetic deformylation reactions primarily rely on rapid oxidative addition into the C(O)—H bond and subsequent rate-determining extrusion of CO.



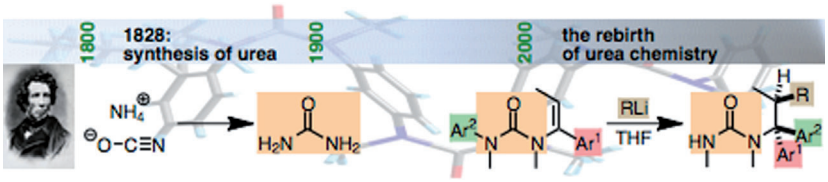
DNA methyltransferases catalyze the transfer of methyl groups to cytosines within DNA. Afterwards, 5-methylcytosine is oxidized to 5-hydroxymethylcytosine. Two further cytosine derivatives, 5-formylcytosine and 5-carboxycytosine, have been discovered recently. The existence of the seventh and eighth nucleobase provides new hints for deciphering the process of active DNA demethylation (see scheme).



Simple and practical: Direct intermolecular α alkylation reactions by S_N1-type transformations have been developed and offer flexible and robust routes to major compound classes, for which the direct preparations were unavailable before.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

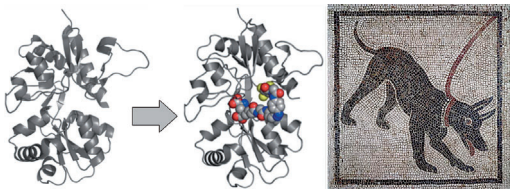
Minireviews



It's back: This Minireview summarizes the development of urea chemistry during the last few years by taking examples to illustrate each of the themes associated with this renaissance—ureas as lithiation directors, the design of urea-based catalysts and supramolecular structures, the increased reactivity that is characteristic of more hindered ureas, and the electrophilicity disguised within electron-rich aromatic ureas (see picture).

Synthetic Methods

Reviews

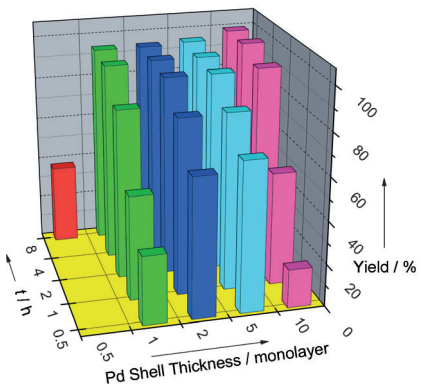


Light of my life: The merger of natural transmembrane proteins with synthetic photoswitches creates hybrid receptors that can be integrated into complex systems and regulated with the precision that only light provides. This strategy allows for the optical control of single cells, neural systems, and can even be used to control animal behavior.

Chemical Genetics

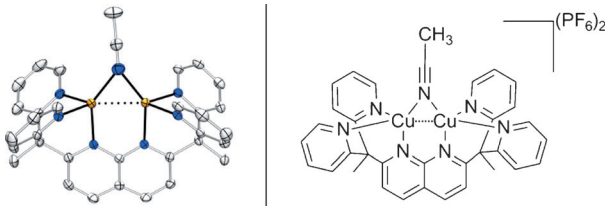
Communications

Away from the surface: Novel nanoparticles (NPs) consisting of 16 nm Au cores surrounded by Pd shells of various thicknesses catalyze Suzuki–Miyaura cross-coupling reactions in water at room temperature. NPs having shells of two to five Pd monolayers thick exhibit the highest catalytic activity. Catalysis was attributed to the leaching of Pd species from the NPs through the synergistic action of the carbonate base and the arylboronic acid.



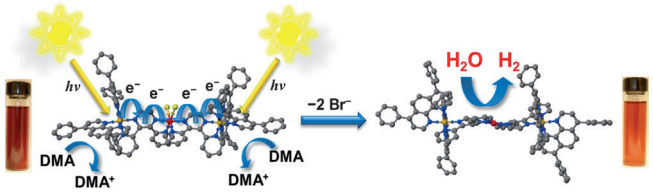
Nanoparticle Catalysis

Contents



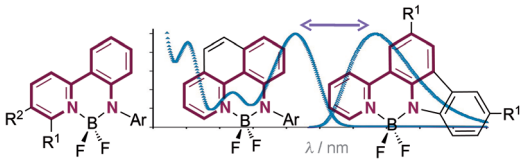
Unusual bonding: A ligand system that promotes formation of a rare μ-η¹:η¹ acetonitrile-bridged dicopper(I) complex (see picture) has been developed. The acetonitrile ligand is involved in a three-center two-electron bond supported by a cuprophilic interaction. The labile acetonitrile ligand can be substituted with xylyl isocyanide or CO.

Electron-Deficient Bonding



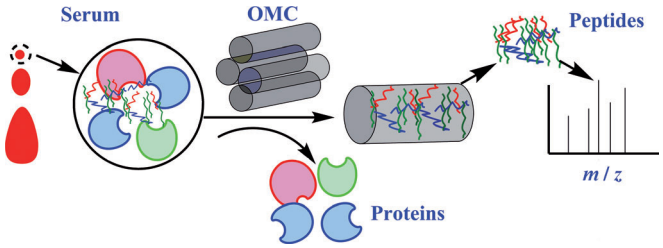
Small changes go a long way: Modification of the terminal ligand to incorporate 4,7-diphenyl-1,10-phenanthroline has generated superior Ru,Rh,Ru photocatalysts (see scheme; ochre Ru, red Rh, blue N, yellow Cl or Br) displaying significantly enhanced photocatalytic H_2 production from H_2O with long-term functioning: H_2O is reduced to H_2 with over 1300 turnovers per Rh site and a maximum efficiency of 7.3%.

Photocatalysis



To dye for: Three related families of fluorescent dyes, rigidified by boron difluoride and based on bidentate anilido-pyridyl donor ligands, are reported (see picture). The dyes show quantum yields up to 0.75 and improved Stokes shifts of >100 nm relative to the widely employed BODIPY family of dyes. Furthermore, the new dyes are exceptionally photostable and membrane-specific.

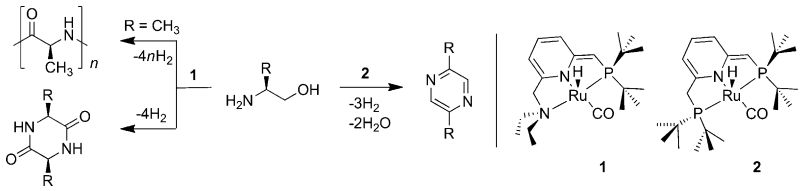
Fluorescence



Size matters: A highly ordered mesoporous carbon material (OMC) was synthesized by a soft-template method, and was applied as an adsorbent for the highly efficient extraction of endogenous peptides from human serum (see scheme). A total of 3402 different peptides were identified from only 20 μL of human serum.

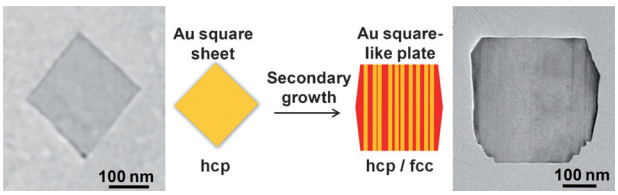
Mesoporous Materials

Contents



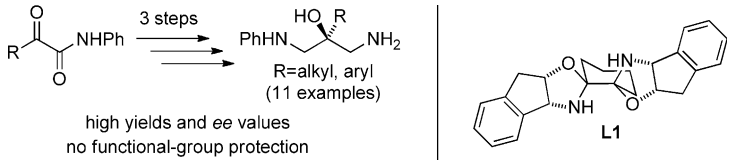
Your choice: The choice of the Ru-pincer-complex catalyst determines if peptides or pyrazines are formed from β-amino alcohols. Use of PNN complex **1** leads to linear poly(alanine) or to cyclic dipeptides, depending on the R group (see scheme). With the PNP complex **2**, pyrazines are formed. These reactions are homogeneously catalyzed under neutral conditions and are environmentally benign.

Homogeneous Catalysis



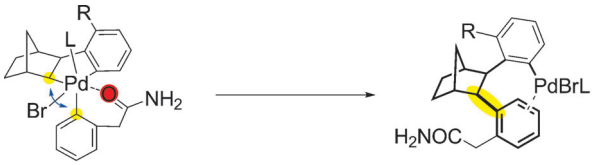
It's hip to be square: Gold square-like plates exhibit alternating hexagonal close-packed (hcp, see picture, yellow) and face-centered cubic (fcc, red) structures in the center and defect-free fcc structures at one pair of the opposite thick edges. They can be synthesized from Au square sheets in a secondary growth process. For the first time, the hcp-to-fcc phase transformation associated with shape variation in Au nanostructures is demonstrated.

Gold Nanoplates



Three high-yielding steps lead to the formation of chiral 1,3-diaminopropanols from aliphatic and aromatic α-keto amides. In this approach, a nitroaldol reaction, which is catalyzed by Cu-$(SO_2CF_3)_2$ and the bisoxazolidine ligand **L1**, is followed by two mild reduction reactions (see scheme). Laborious protection and deprotection steps can be avoided by using this method.

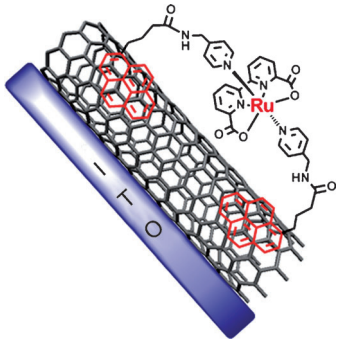
Asymmetric Catalysis



Out of the norm: The first deviation from the *ortho* effect in palladium/norbornene catalysis, as evidenced by the resulting products, is reported (see scheme). DFT calculations indicate that this deviation is likely to originate from a distortion, caused by specific chelation, in the reductive-elimination pathway from the Pd^{IV} intermediate initially formed. Addition of water restores the normal selectivity, but also it leads to dearomatization.

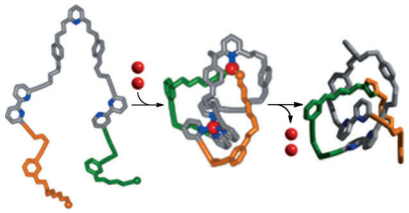
C–C coupling

Contents



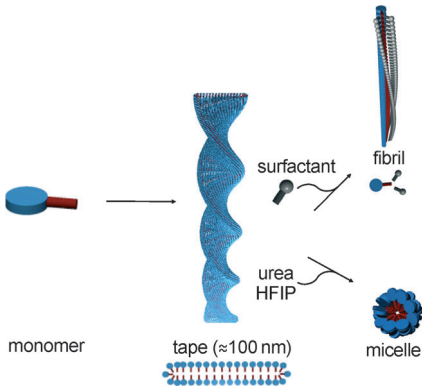
A successful team: A molecular device based on multiwalled carbon nanotubes functionalized by a mononuclear ruthenium catalyst has been shown to split water electrochemically (see picture; ITO = indium tin oxide). The readily prepared electrode showed excellent electrocatalytic activity for the oxidation of water, a high current density, and a low overpotential, and constitutes one step forward in the design of artificial photosynthetic systems.

Water Splitting



Tying the knot: The marriage of catalysis and coordination chemistry enables two Cu^{I} ions (red; see picture) to work in partnership for the synthesis of a molecular trefoil knot. One ion entangles an acyclic building block to create a loop in the ligand, and the other gathers the ligand's reactive end-groups, threads the loop, and catalyzes the covalent capture of the knotted architecture by an alkyne–azide "click" reaction.

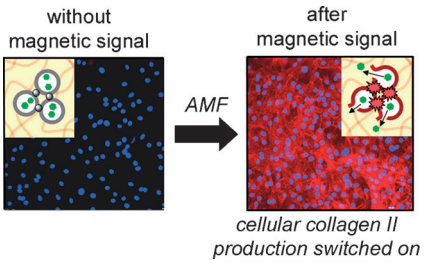
Chemical Topology



A multisegment amphiphile, made of a gelator and a surfactant, self-assembles into architectures with properties inherited from both segments. By addition of a surfactant, the surfactant segment of the amphiphile is selectively switched off, leading to the formation of fibrils. The addition of urea or hexafluoroisopropyl alcohol (HFIP) switches off the gelator segment, giving micelles.

Morphological Transitions

Crosslinking vesicles with magnetic nanoparticles produced MNPVs, self-assembled "nanopills" that can be "unlocked" by an alternating magnetic field (AMF), releasing chemical messengers stored within the vesicles. When MNPVs are co-immobilized with cells in a hydrogel matrix, exposure to an AMF magnetic signal releases the chemical messengers, which then induce a cellular response.



Magnetoresponsive Biomaterials

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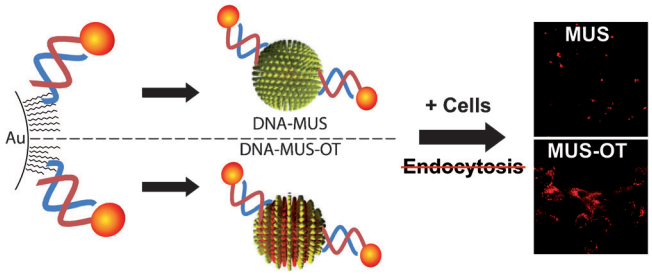
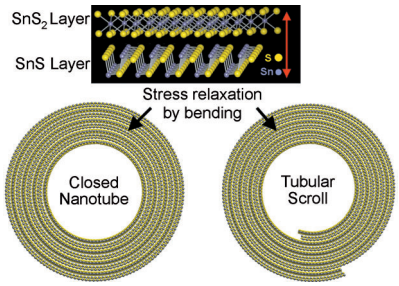


Gold nanoparticles coated with homogeneous (MUS) or "striped" (MUS-OT) ligand shells can be conjugated with double or single stranded DNA, and particles with either ligand configuration effectively carry DNA into melanoma tumor cells. When endocytosis is inhibited, however, MUS-OT particles continue to mediate DNA delivery, while the delivery ability of MUS particles is abolished.

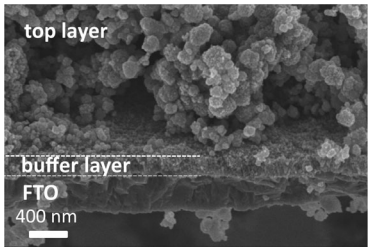
Delivery Platforms



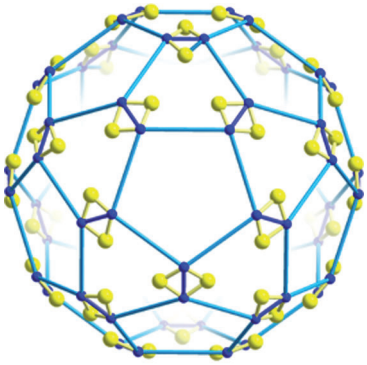
Roll 'em up, move 'em out: The growth of SnS_2 and SnS_2/SnS nanotubes and nanoscrolls with ordered superstructures is promoted by the relaxation of stress between adjacent SnS_2 and SnS layers. Partial decomposition of the SnS_2 precursor to more sulfur-deficient SnS was manifested in the exfoliation of layers and scrolling. The presence of the two main structures (see picture) was confirmed by HRTEM and Raman spectroscopy.

Nanotube Structures

Spray pyrolysis is effective in the formation of a nanoengineered photoanode. An unprecedented photoconversion efficiency of 7.5% for ZnO-based dye-sensitized cells was achieved on a photoelectrode consisting of polydispersed ZnO aggregates of nanocrystallites over a compact ZnO buffer layer at a firing temperature of 450 °C. FTO = fluorine-doped tin oxide.



Dye-Sensitized Solar Cells

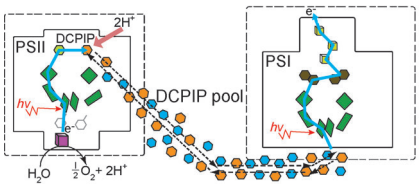


A hard capsule gets soft: The exchange of 60 oxide by 60 sulfide ligands (see picture) in a well-known porous metal-oxide capsule skeleton conataining 132 metal atoms changes the interior properties as well as pore sizes, reactivities, flexibilities and affinities to guest molecules.

Porous Capsules

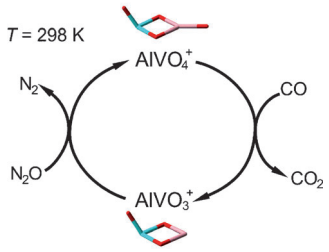
Contents

Happily coupled: Photosystem II and photosystem I can be coupled in a sol–gel system so that electron flow can be directly mediated from photooxidized water at the donor side of photosystem II to the highly reducing acceptor side of photosystem I. The electron transfer pathway is set up by addition of the amphipathic quinone analogue 2,6-dichlorophenolindophenol (DCPIP) to the sol–gel mixture to provide a pool of redox carriers (see picture).

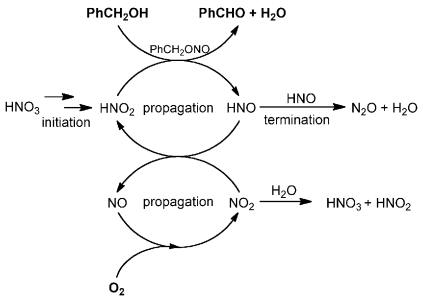


Photosynthesis

Exhaustive studies: The exact reaction pathway of catalytic conversion of automobile exhaust gases, such as N_2O and CO, into N_2 and CO_2 is still not completely understood. Studying this reaction at room temperature using the bimetallic oxide cluster couple $AlVO_3^+/AlVO_4^+$ in the gas phase shows that the active M-$O_t^\bullet$ site is located at the Al-bound and not the V-bound oxygen atom (see scheme, Al pink).



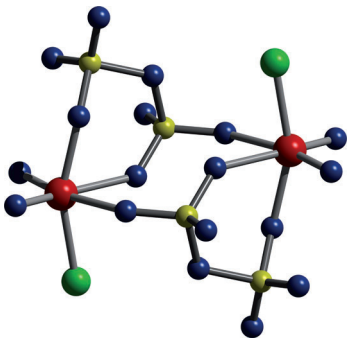
Gas-Phase Reactions



A touch of acid: Catalytic amounts of HNO_3 can trigger the aerobic oxidation of alcohols in the presence of the solid acid amberlyst-15. The desired oxidation cycle, mediated by (H)NO_x species, is in kinetic competition with the detrimental formation of N_2O by HNO dimerization (see scheme). In situ water removal in a gas recirculation reactor increases the reaction rate and the end-conversion by minimizing N_2O formation and increasing the (H)NO_x turnover.

Shuttling Oxygen

A molecular metal disulfate, $Re_2O_4Cl_2(S_2O_7)_2$ forms in the reaction of $ReCl_5$ and oleum (65% SO_3) under harsh conditions. The first of its kind, this unique Re^{VII} compound contains two ReO_2Cl fragments linked by two disulfate groups, leading to C_i-symmetric molecules (see picture; Re red, O blue, S yellow, Cl green).



Molecular Disulfate

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).

This article is available online free of charge (Open Access)

Service

Corrigendum

Hydrogen-Independent Reductive Transformation of Carbohydrate Biomass into γ-Valerolactone and Pyrrolidone Derivatives with Supported Gold Catalysts

X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao,* H. Y. He, K. N. Fan **7815–7819**

Angew. Chem. Int. Ed. **2011**, *50*

DOI: 10.1002/anie.201100102

The authors of this Communication have noticed an error in the Supporting Information. In Figure S1 e, the same TEM image was inadvertently used as in Figure S1 a. The correct Figure S1 e is shown below. This error does not affect the interpretation of results in the Communication. The authors sincerely apologize for this oversight and any inconvenience it may have caused.

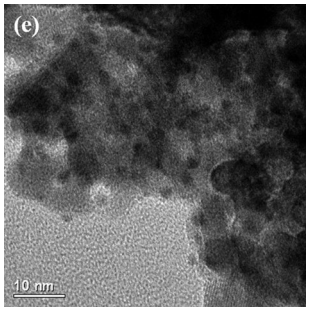


Figure S1. TEM image of e) Au/ZrO_2-VS (after five runs).