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:

*J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao**
Single Fused Gene Approach to Photo-Switchable and Fluorescent Biliproteins

Y. Sohma, Q. Hua, J. Whittaker, M. A. Weiss, S. B. H. Kent**
Design and Folding of [GluA4(OβThrB30)]Insulin (Ester Insulin), a Minimal Proinsulin Surrogate Chemically Convertible into Human Insulin

*A. C. Stelzer, J. Kratz, Qi Zhang, H. Al-Hashimi**
RNA Dynamics by Design: Biasing Ensemble towards Ligand-Bound States

*T. Ikawa, A. Takagi, Y. Kurita, K. Saito, K. Azechi, M. Egi, K. Kakiguchi, Y. Kita, S. Akai**
Preparation of Borylbenzynes and their use in the Regioselective Diels–Alder Reaction: Synthesis of Functionalized Arylboronates

*Z. Zhang, Z. Wang, R. Zhang, K. Ding**
Extremely Efficient Titanium Catalyst for the Enantioselective Cyanation of Aldehydes by Using Cooperative Catalysis

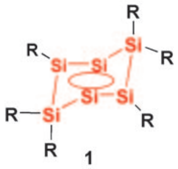
*Qi Wang, M. Zhang, C. Chen, W. Ma, J. Zhao**
Photocatalytic Aerobic Oxidation of Alcohols on TiO_2: The Acceleration Effect of Bronsted Acids

Ye Fu, Q. Dai, W. Zhang, J. Ren, T. Pan, C. He**
AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA

C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R. Haire, J. Rebizant, F. Bruchertseifer, T. Fanghänel*
$[An(H_2O)_9](CF_3SO_3)_3$ (An=U–Cm, Cf): Exploring Their Stability, Structural Chemistry, and Magnetic Behavior of by Experiment and Theory

Books

Highlights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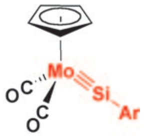

2

Elegant synthesis! Recent progress in synthetic methods has allowed the preparation and isolation of novel silicon compounds with multiple bonds. A cyclic conjugated isomer **1** of the elusive hexasilabenzene and a silylidyne complex **2** with a genuine molybdenum–silicon triple bond have been synthesized.

Silicon Chemistry

Essays

A classic that hasn't lost its charm: The historical origins and current status of the vinylcyclopropane–cyclopentene rearrangement and the corresponding transformations of heteroatom-containing analogues (see scheme) are described in the context of methodology development and natural products synthesis. Several important events that greatly influenced the author's own research program some 30 to 40 years ago are recounted as personal recollections.

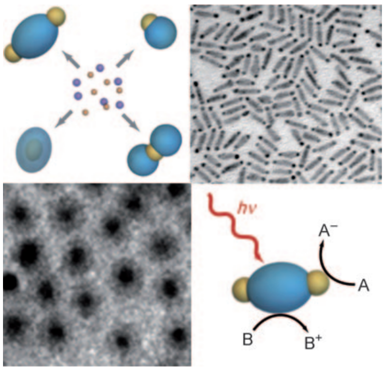
A, B, C, D, E = carbon, oxygen, nitrogen, sulfur, and/or other elements as permitted by valence

History of Chemistry

Contents

Reviews

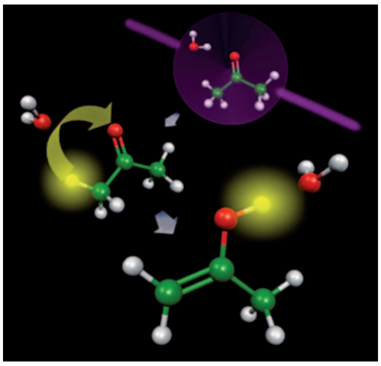
Multicomponent Nanoparticles



One goal of nanocrystal research is the development of methods to control composition and shape. The ability to selectively arrange nanosized domains of metallic, semiconducting, and magnetic materials into a hybrid nanoparticle offers a route to nanomaterials with multiple functionalities or the enhanced properties of one domain. This Review focuses on recent synthetic strategies, properties, and applications of semiconductor–metal hybrid nanoparticles.

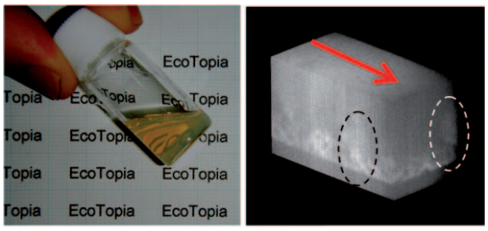
Communications

Keto–Enol Tautomerization



Baby steps: The mechanism of proton migration in an ionized acetone–water cluster was studied by IR spectroscopy. After the ionization, water abstracts a proton from the methyl group of the acetone moiety and transfers it to the carbonyl group (see picture).

Nanocomposite Fluid



A smart fluid containing $BaTiO_3$ nanoparticles was synthesized by a chemical solution process. The transparent and homogeneous fluid (see picture) changes its rheological properties in response to an electric field. Formation of aligned structures from nanoparticles under shear stress (arrow) was confirmed by 3D confocal fluorescence microscopy (white dots: fluorescein-modified nanoparticles).

For the USA and Canada:
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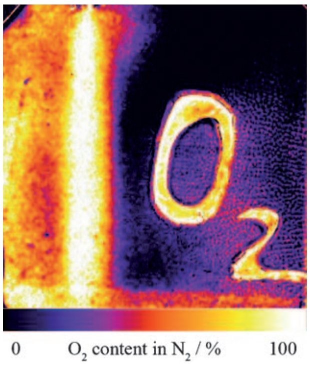
Oxygen Detection

X. D. Wang, R. J. Meier, M. Link,
O. S. Wolfbeis* ———— 4907 – 4909

Photographing Oxygen Distribution

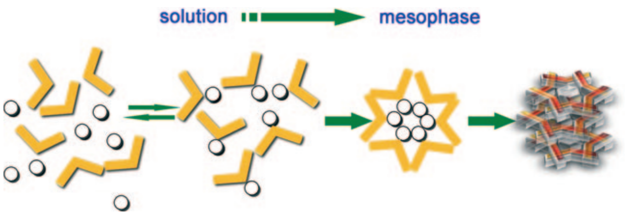


O_2, where are you? The spatial distribution of oxygen can be imaged with a conventional digital camera by making use of a specially designed fluorescent sensor film containing a quenchable red-emitting probe for oxygen along with a green-emitting reference fluorophore. The technique exploits the RGB channels involved in digital photography (see picture) to deliver a simple method for quantitative sensing and imaging of this important species.

Supramolecular Chirality

F. Vera, J. Barberá, P. Romero,
J. L. Serrano, M. B. Ros,
T. Sierra* ———— 4910 – 4914

Orthogonal Action of Noncovalent Interactions for Photoresponsive Chiral Columnar Assemblies

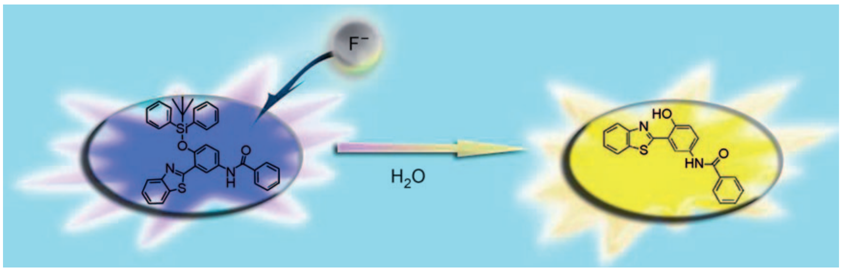


Making a stack: Helical columnar architectures are prepared by a hierarchical self-assembly process involving H-bonding, π–π, and ion–dipole interactions (see picture). The strategic combination of these supramolecular interactions within mesomorphic systems yields materials in which photoinduced chirality and the incorporation of ions can be used to design multifunctional liquid crystals.

Sensors

R. Hu, J. Feng, D. H. Hu, S. Q. Wang,
S. Y. Li,* Y. Li,* G. Q. Yang* 4915 – 4918

A Rapid Aqueous Fluoride Ion Sensor with Dual Output Modes

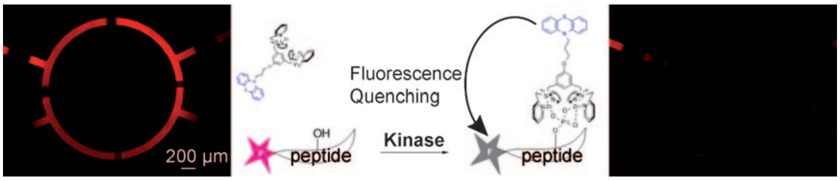


The color purple: A siloxy-functionalized benzamide (see picture) is a highly efficient fluoride ion sensor in water. The sensor, which is activated when the O–Si bond is cleaved by fluoride ions, provides two independent modes for signal recognition. In colorimetric mode, the fluoride ion concentration is transformed into a fluorescence signal that can be observed directly with the naked eye.

Kinase Assay

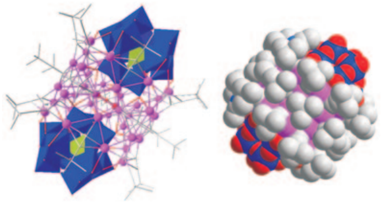
H.-W. Rhee, S. H. Lee, I.-S. Shin, S. J. Choi,
H. H. Park, K. Han, T. H. Park,*
J.-I. Hong* ———— 4919 – 4923

Detection of Kinase Activity Using Versatile Fluorescence Quencher Probes



Turn off the light! A kinase assay system employs fluorescent peptides and a phosphate-selective fluorescence quencher probe, and can be placed on a microfluidic chip (see picture). The system can be used for real-time kinase monitoring, kinase inhibitor screening, and cancer diagnosis based on abnormal kinase activity observed in patients' samples.

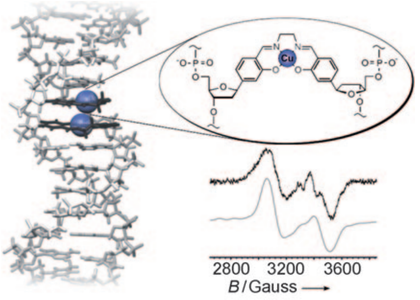
Cluster Compounds



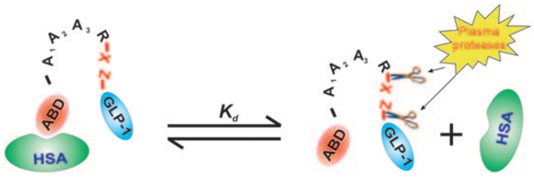
The Earl of Sandwich: The first intercluster sandwich compound was obtained from silver alkynyl clusters and $[CoW_{12}O_{40}]^{6-}$ in a one-pot reaction. The silver block has a toroidal shape with direct contacts to two polyoxometalate anions, which close its open ends.

DNA Nanomaterials

A pretty couple: Two copper–salen metal–base pairs were incorporated into a DNA double helix in neighboring positions (see picture). The two paramagnetic Cu^{II} ions are antiferromagnetically coupled, and the exchange coupling constant is $-2J = 22.4\ cm^{-1}$. The dipolar coupling constant yielded a Cu···Cu distance of 3.7 Å, which is comparable to the base-pair distance in natural B-type DNA.

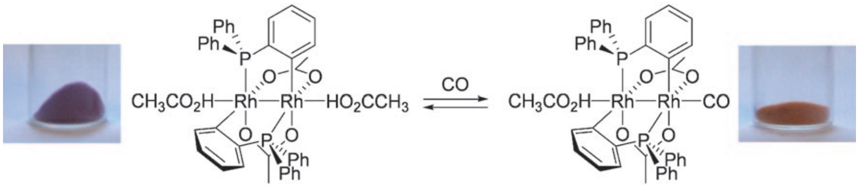


Drug Delivery



A polypeptide containing an albumin-binding domain (ABD), an amino acid sequence linker, and glucagon-like peptide-1 (GLP-1), a potential antidiabetic agent, is designed to slowly release GLP-1 through sequential cleavage by native plasma proteases (see picture). The half-life of the polypeptide in the bloodstream is extended by its association with human serum albumin (HSA).

Sensors

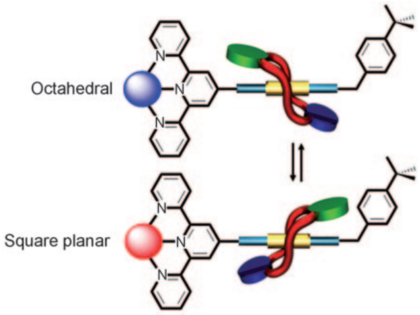


CO-catcher: Carbon monoxide can be detected selectively and sensitively by the binuclear rhodium complex *cis*-$[Rh_2(C_6H_4PPh_2)_2(O_2CCH_3)_2](HO_2CCH_3)_2$. This complex, which contains two cyclometalated phosphine ligands, coordinates CO axially and undergoes a color change from violet to orange-yellow (see picture).

Molecular Switches

G. J. E. Davidson, S. Sharma,
S. J. Loeb* ______ 4938–4942

A [2]Rotaxane Flip Switch Driven by Coordination Geometry



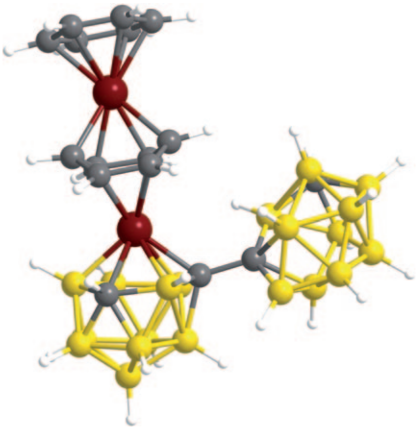
The carrot is better than the stick! Changes in the metal coordination geometry of the capping group in a [2]rotaxane ligand results in molecular switching by reorienting a trapped macrocyclic component (see picture). Switching was successfully initiated when the metal coordination site was made more attractive (square planar), but not when the metal coordination site was made less attractive (octahedral).

Metallacarboranes

D. Ellis, D. McKay, S. A. Macgregor,*
G. M. Rosair, A. J. Welch* ______ 4943–4945

Room-Temperature C–C Bond Cleavage of an Arene by a Metallacarborane

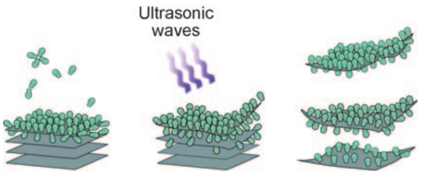
On the fly: Reduction of 1,1′-bis(*o*-carborane) and subsequent reaction with a source of {Ru(*p*-cymene)}$^{2+}$ fragments yields a fly-over bridge species resulting from room-temperature C–C bond cleavage of a *p*-cymene ligand. DFT calculations suggest that the arene is sandwiched between two Ru atoms as part of a metallacarborane (see picture; C gray, B yellow, Ru red) and reduced by the second, pendant, carborane.



Functional Protein Coatings

P. Laaksonen,* M. Kainlauri,
T. Laaksonen, A. Shchepetov, H. Jiang,
J. Ahopelto, M. B. Linder ______ 4946–4949

Interfacial Engineering by Proteins: Exfoliation and Functionalization of Graphene by Hydrophobins



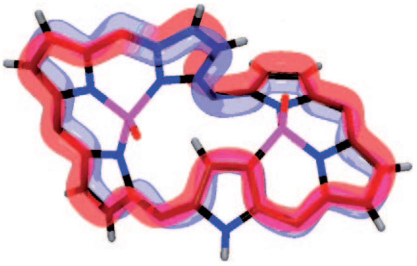
Simply peel off the layers: Functionalities from nature may be used to meet the demands of contemporary materials science in terms of the efficient and safe production of high-quality, versatile materials. Thus, the spontaneous absorption on graphite of small amphiphilic proteins known as hydrophobins from an aqueous phase, followed by sonication, led to the exfoliation and stabilization of graphene sheets (see picture).

Aromaticity

T. Higashino, J. M. Lim, T. Miura, S. Saito,
J.-Y. Shin, D. Kim,*
A. Osuka* ______ 4950–4954

Möbius Antiaromatic Bisphosphorus Complexes of [30]Hexaphyrins

Aromaticity with a twist: The reversal of Möbius aromaticity occurs by changing the number of π electrons between [4*n*+2] and [4*n*] in monophosphorus complexes of [28]hexaphyrins and bisphosphorus complexes of [30]hexaphyrins. The 30π Möbius antiaromatic bisphosporus[30]hexaphyrins (see picture) were determined to be the first structurally characterized Möbius antiaromatic systems, which are rigid, neutral, and stable.

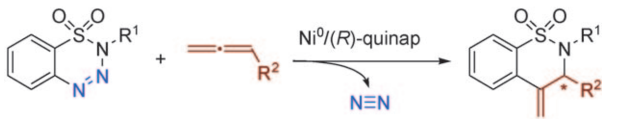


Contents

Asymmetric Synthesis

T. Miura, M. Yamauchi, A. Kosaka, M. Murakami* ____ **4955–4957**

Nickel-Catalyzed Regio- and Enantioselective Annulation Reactions of 1,2,3,4-Benzothiatriazine-1,1(2*H*)-dioxides with Allenes



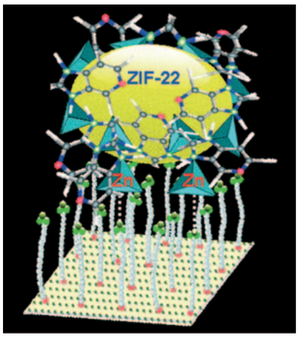
Extrusion of N_2: 1,2,3,4-Benzothiatriazine-1,1(2*H*)-dioxides reacted with allenes in the presence of a nickel(0)/(*R*)-quinap complex to produce a variety of substituted 3,4-dihydro-1,2-benzothiazine-1,1(2*H*)-dioxides in a regio- and enantioselective fashion. An intermediate nickelacycle was generated through denitrogenative activation of the triazo moiety which allowed the intermolecular incorporation of an allene group. quinap = 1-(2-diphenylphosphino-1-naphthyl)isoquinoline.

Microporous Membranes

A. Huang,* H. Bux, F. Steinbach, J. Caro* ____ **4958–4961**

Molecular-Sieve Membrane with Hydrogen Permselectivity: ZIF-22 in LTA Topology Prepared with 3-Aminopropyltriethoxysilane as Covalent Linker

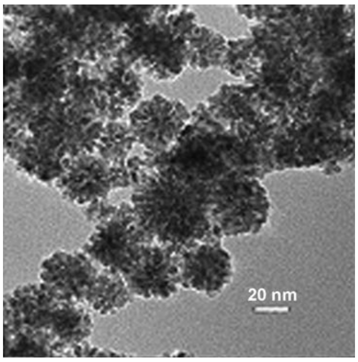
High hydrogen selectivity and thermal stability are displayed by a membrane of zeolitic imidazolate ZIF-22 grown on porous ceramic supports by using 3-aminopropyltriethoxysilane (APTES) as covalent linker (see picture). At 323 K, H_2/CO_2 selectivity of 7.2 and H_2 permeance of 1.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1} were achieved.



Nanoflowers

A. Mohanty,* N. Garg, R. Jin* ____ **4962–4966**

A Universal Approach to the Synthesis of Noble Metal Nanodendrites and Their Catalytic Properties



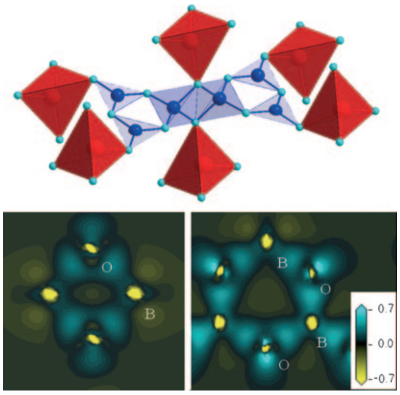
Flower power: A universal approach is presented for high-yield synthesis of Au, Pt, and Pd nanoflowers using the surfactant sodium *N*-(4-*n*-dodecyloxybenzoyl)-L-isoleucinate (SDBIL). The pH-dependent self-assembly using SDBIL is critical for nanoflower growth. The Pt and Pd nanoflowers show superior catalytic activity for Suzuki–Miyaura and Heck coupling reactions over spherical counterparts.

Solid-State Structures

S. F. Jin, G. M. Cai, W. Y. Wang, M. He, S. C. Wang, X. L. Chen* ____ **4967–4970**

Stable Oxoborate with Edge-Sharing BO_4 Tetrahedra Synthesized under Ambient Pressure

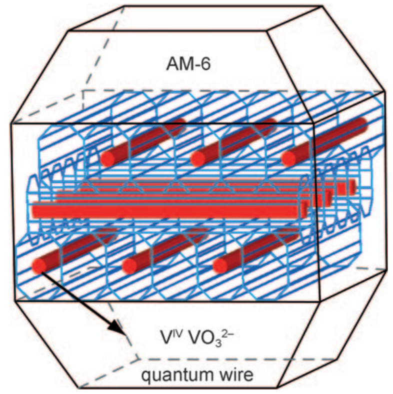
Back from the extreme: The formation of edge-sharing BO_4 tetrahedra is excluded from borate structure chemistry and only rarely presents itself under extremely high pressure. Now this structure has been observed in an ambient pressure borate. Unlike high-pressure metastable phases, the title compound is stable up to its melting point. The tunnel structure of the compound is also accessible to mobile ions.



Quantum Wires

S. J. Datta, K. B. Yoon* ______ 4971 – 4975

Synthesis of Ideal AM-6 and Elucidation of V^{4+}-to-O Charge Transfer in Vanadate Quantum Wires

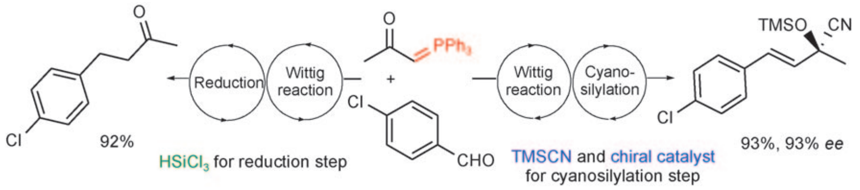


Vanadosilicate zeolite AM-6, which contains a 3D array of vanadate ($V^{IV}O_3^{2-}$) quantum wires (see picture), was prepared as high-quality crystals (free from V^{V}, titanosilicate seeds, and pore-blocking organic template cations) from inexpensive V_2O_5. The linear dependence of λ_{max} and band-gap energy E_g on the partial charge on the framework O atoms reveal that the UV band of AM-6 is due to V^{IV}-to-O metal-to-ligand charge transfer.

Sustainable Chemistry

J.-J. Cao, F. Zhou, J. Zhou* _ 4976 – 4980

Improving the Atom Efficiency of the Wittig Reaction by a "Waste as Catalyst/Co-catalyst" Strategy

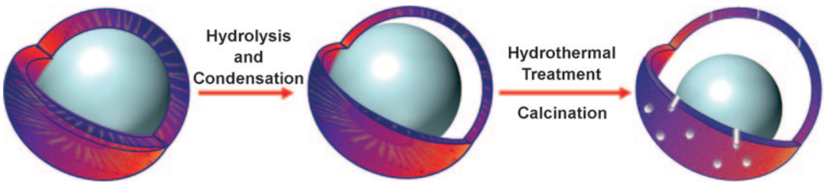


Waste not want not: Reported is a strategy to improve the atom economy of the Wittig reaction by using it in tandem reactions that directly employ the waste Ph_3PO as an in-situ-generated Lewis base catalyst/co-catalyst in the next step (see scheme).

Nanostructures

J. Liu, S. Z. Qiao,* S. Budi Hartono,
G. Q. Lu* ______ 4981 – 4985

Monodisperse Yolk–Shell Nanoparticles with a Hierarchical Porous Structure for Delivery Vehicles and Nanoreactors

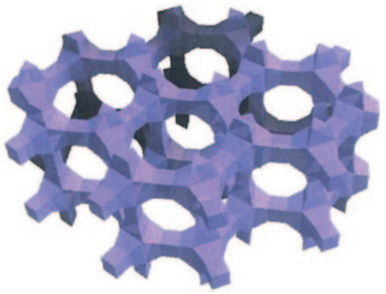


A good egg: A general and facile template strategy is presented for the fabrication of yolk–shell structures (see picture) with various types of movable cores, such as gold, SiO_2, and magnetic Fe_3O_4. The vesicle template, formed of a fluorocarbon surfactant, is built up around the core.

Extra-Large-Pore Zeolites

J. Jiang, J. L. Jorda, M. J. Diaz-Cabanas,
J. Yu, A. Corma* ______ 4986 – 4988

The Synthesis of an Extra-Large-Pore Zeolite with Double Three-Ring Building Units and a Low Framework Density

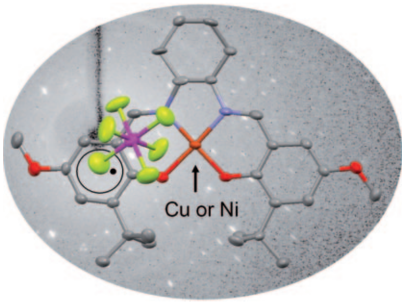


The great wide open: High-throughput techniques have allowed an extra-large-pore zeolite to be obtained that has an 18×12×12 ring pore system. This material (see picture) has the lowest framework density for a silica-based fully-connected zeolite, and is the first example with double three-ring units in its framework.

Metal Radical Complexes

M. Orio, O. Jarjayes, H. Kanso,
C. Philouze, F. Neese,
F. Thomas* **4989 – 4992**

X-Ray Structures of Copper(II) and Nickel(II) Radical Salen Complexes: The Preference of Galactose Oxidase for Copper(II)

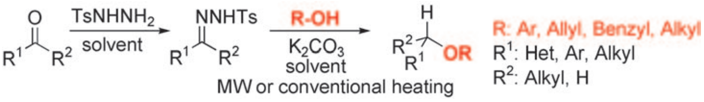


Copper or nickel? The depicted Cu^{II} salen complex, an active-site model of galactose oxidase (GO), is a localized radical in the solid state with a quinoid distribution of bond lengths in one ring. While the ligand-radical structure is not metal-dependent, the composition of the radical SOMO is. This feature may explain the much lower reactivity of the Ni complex and nature's preference for a Cu^{II} center in GO.

Synthetic Methods

J. Barluenga,* M. Tomás-Gamasa,
F. Aznar, C. Valdés* **4993 – 4996**

Straightforward Synthesis of Ethers: Metal-Free Reductive Coupling of Tosylhydrazones with Alcohols or Phenols



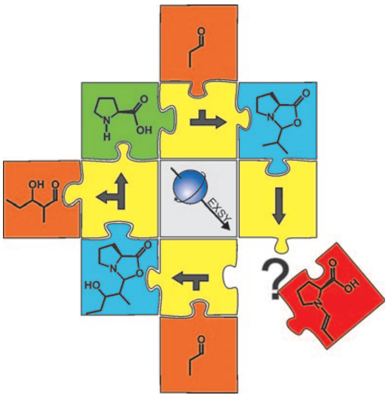
Ethers made easy: Heating a solution containing a tosylhydrazone and either a phenol or an alcohol in the presence of K_2CO_3 leads to the corresponding ethers (see scheme; MW = microwave, Ts = tosyl). The reaction is fairly general for the preparation of aryl alkyl and alkyl alkyl ethers, and represents a new method for the reductive etherification of carbonyl compounds.

Organocatalysis

M. B. Schmid, K. Zeitler,
R. M. Gschwind* **4997 – 5003**

The Elusive Enamine Intermediate in Proline-Catalyzed Aldol Reactions: NMR Detection, Formation Pathway, and Stabilization Trends

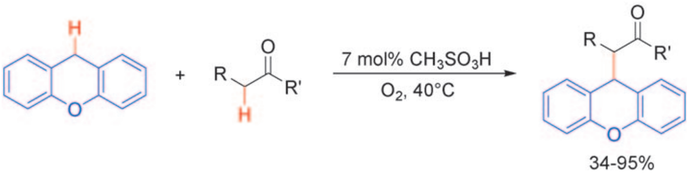
The missing link: The elusive enamine intermediate of nucleophilic proline catalysis was detected and stereochemically characterized by NMR analysis of the aldehyde self-aldolization reaction in dipolar aprotic solvents. NMR exchange spectroscopy (EXSY) was used to observe direct enamine formation from oxazolidinones. Additionally, the stabilization of the intermediate by the appropriate choice of solvent and substitution pattern on the aldehyde is presented.



Oxidative Coupling

Á. Pintér, A. Sud, D. Sureshkumar,
M. Klussmann* **5004 – 5007**

Autoxidative Carbon–Carbon Bond Formation from Carbon–Hydrogen Bonds



Only oxygen and acid! The oxidative coupling of xanthene and other activated benzylic compounds with carbon nucleophiles such as ketones, can be performed under ambient conditions without solvent by simply using oxygen and catalytic amounts of methanesulfonic acid. The proposed reaction mechanism involves substrate activation by formation of hydroperoxides; the method can therefore be regarded as an "autoxidative coupling reaction".

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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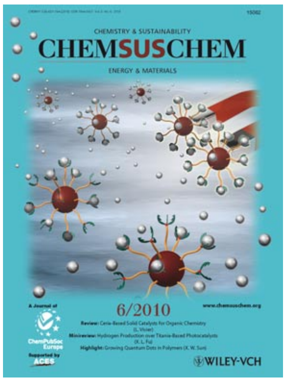
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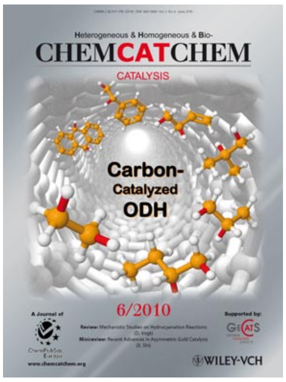
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