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:

*A. Schlossbauer, S. Warncke, P. E. Gramlich, J. Kecht, A. Manetto, T. Carell, T. Bein**
A Programmable DNA-Based Molecular Valve for Colloidal Mesoporous Silica

*M. Walz, M. Schirmer, F. Vollnhals, T. Lukasczyk, H.-P. Steinrück, H. Marbach**
Electrons as "Invisible Ink"! Fabrication of Nanostructures by Local Electron Beam Induced Activation of SiO_x

*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

D. Sišak, L. B. McCusker, G. Zandomeneghi, B. Meier,* D. Bläser, R. Boese,* W. B. Schweizer, R. Gilmour, J. D. Dunitz**
The Crystal Structure of Ribose – At Last!

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

M. W. Powner, J. D. Sutherland
Phosphate-Mediated Interconversion of Ribo- and Arabino-Configured Prebiotic Nucleotide Intermediates

S. Yang, X. Feng, L. Wang, K. Tang, J. Maier, K. Müllen**
Graphene-Based Nanosheets with Sandwich Structure

J. Esteban, J. V. Ros-Lis, R. Martínez-Máñez, M. D. Marcos, M. Moragues, J. Soto, F. Sancenón*
Sensitive and Selective Chromogenic Sensing of Carbon Monoxide Using Metalated Binuclear Rhodium Complexes

Author Profile

"My favorite subject at school was philosophy. The most exciting thing about my research is facing new challenges everyday …"
This and more about Teresa Carlomagno can be found on page 4162.

Teresa Carlomagno ______ **4162**

Books

Radical and Radical Ion Reactivity in Nucleic Acid Chemistry — Marc Greenberg — *reviewed by B. Giese* ______ **4163**
Chiral Ferrocenes in Asymmetric Catalysis — Li-Xin Dai, Xue-Long Hou — *reviewed by R. Peters* ______ **4163**

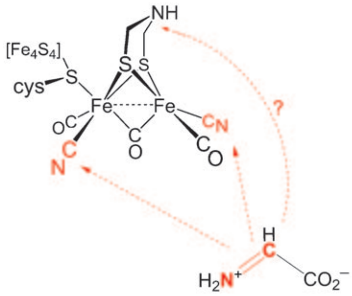
Highlights

Cofactor Biosynthesis

T. B. Rauchfuss* ______ **4166–4168**

Unraveling the Biosynthesis of Nature's Fastest Hydrogenase

Take two cyanides and report to work! Cyanide is an essential ingredient of the [FeFe]-hydrogenases. Recent studies have revealed how nature makes these cyanide ligands coordinated to the diiron core of the active site (see structure). Rapidly unfolding research on the maturation process is revealing new dimensions of biosynthesis. The transformations discovered may lead to the development of useful organometallic reactions.



Contents

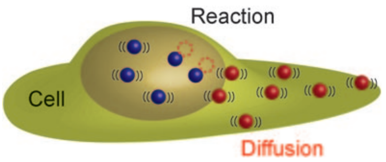
Reviews

Reaction-Diffusion Systems

S. Soh, M. Byrska,
K. Kandere-Grzybowska,
B. A. Grzybowski* ________ **4170 – 4198**

Reaction-Diffusion Systems in Intracellular Molecular Transport and Control

Both prokaryotic and eukaryotic cells couple chemical reactions with diffusion (in reaction-diffusion or RD systems) to achieve spatially and temporally coordinated delivery of the molecules to intracellular reaction sites. These cellular RD systems are based on several common architectures and motifs that enable cells to build, operate, and position structures for cell division, gradient sensing, signal transduction and amplification, and cell motility.



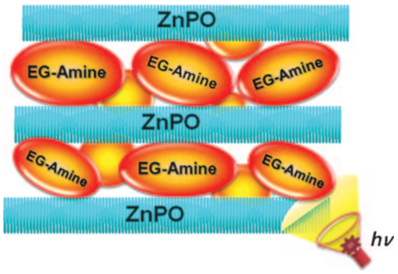
Communications

Ionothermal Synthesis

P. C. Jhang, N. T. Chuang,
S.-L. Wang* ____________ **4200 – 4204**

Layered Zinc Phosphates with Photoluminescence and Photochromism: Chemistry in Deep Eutectic Solvents

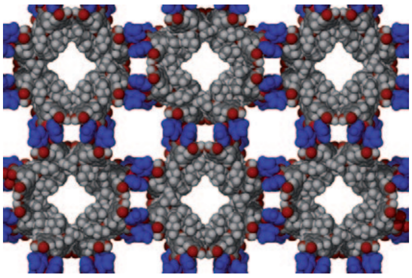
A metal-activator-free orange phosphor was synthesized from ZnO/H_3PO_3/diamine in choline chloride/oxalic acid deep eutectic solvent, which also acted as methylating agent and source of ethylene glycol (EG) by dissociation of choline ions. Interlayer incorporation of a dimethylated amine made the resulting layered zinc phosphate ("ZnPO", see picture) photochromic, and their interaction with EG formed fluorophores with orange photoluminescence.



Self-Assembled Nanotubes

S. Kennedy, G. Karotsis, C. M. Beavers,
S. J. Teat, E. K. Brechin,*
S. J. Dalgarno* _________ **4205 – 4208**

Metal–Organic Calixarene Nanotubes



Control over molecule conformation and transition metal cluster formation has been combined to afford metal–organic calixarene building blocks that induce nanotube formation in the solid state. The resulting assembly type can have chosen magnetic properties, and has three types of solvent filled channel that differ in diameter and shape (see picture).

For the USA and Canada:
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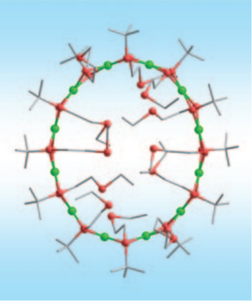
Tiara Structures

C. Zhang,* T. Matsumoto, M. Samoc, S. Petrie, S. C. Meng, T. Christopher Corkery, R. Stranger, J. F. Zhang, M. G. Humphrey,* K. Tatsumi* ______ **4209 – 4212**

Dodecanuclear-Ellipse and Decanuclear-Wheel Nickel(II) Thiolato Clusters with Efficient Femtosecond Nonlinear Absorption



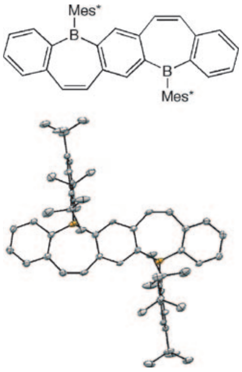
Crowned with success: Stepwise coordination of two kinds of thiolate ligands to a nickel(II) center affords a dodecanuclear ellipse (see structure) and two decanuclear wheel-like Ni^{II}–thiolato clusters. The wavelength-dependent nonlinear optical behavior of these tiara-like compounds was investigated and supported by theoretical studies. The results suggest that Ni–S π bonds play a crucial role.

Organic Materials

A. Caruso, Jr., M. A. Siegler, J. D. Tovar* ______ **4213 – 4217**

Synthesis of Functionalizable Boron-Containing π-Electron Materials that Incorporate Formally Aromatic Fused Borepin Rings

Not a natty B–OH: Borepin-based extended π-electron molecules contain bulky substituents that shield the vacant boron p orbitals and allow synthetic manipulation and purification under ambient conditions. These borepin-containing compounds (see picture; Mes* = 1,3,5-tris(*tert*-butyl)phenyl; B orange, C gray) display reversible cathodic electrochemistry and can be viewed as n-type analogues to bent acene hydrocarbons.

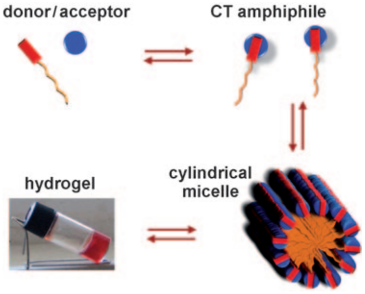


Self-Assembly

K. V. Rao, K. Jayaramulu, T. K. Maji, S. J. George* ______ **4218 – 4222**

Supramolecular Hydrogels and High-Aspect-Ratio Nanofibers through Charge-Transfer-Induced Alternate Coassembly

Gelling together: The alternate coassembly of a noncovalent donor–acceptor (D–A) amphiphilic pair in water results in very long nanofibers that form hydrogels (see scheme). Microscopic and single-crystal studies have provided an insight into the hierarchical self-assembly of the charge-transfer (CT) amphiphile, which consists of coronene and a viologen derivative, into cylindrical micelles and gels as the concentration of the D–A pair is increased.

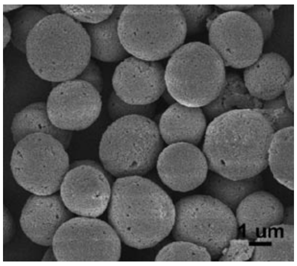


Microspheres

D. Z. Ni, L. Wang, Y. H. Sun, Z. R. Guan, S. Yang,* K. B. Zhou* ______ **4223 – 4227**

Amphiphilic Hollow Carbonaceous Microspheres with Permeable Shells

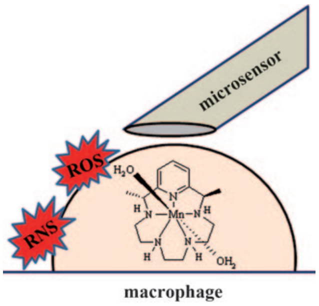
An inside job: Porous hollow carbonaceous microspheres can be easily fabricated by hydrothermal treatment of *Saccharomyces cerevisiae* cells. An amphiphilic surface and porous shell structure endow these microspheres with phase-transfer features and the ability to enrich proteins inside their hollow interiors. These characteristics will enable their application in drug delivery, active ingredients encapsulation, adsorption, and separation techniques.



Macrocyclic Ligands

M. R. Filipović,* A. C. W. Koh, S. Arbault,*
V. Niketić, A. Debus, U. Schleicher,
C. Bogdan, M. Guille, F. Lemaître,
C. Amatore,*
I. Ivanović-Burmazović* **4228–4232**

Striking Inflammation from Both Sides: Manganese(II) Pentaazamacrocyclic SOD Mimics Act Also as Nitric Oxide Dismutases: A Single-Cell Study



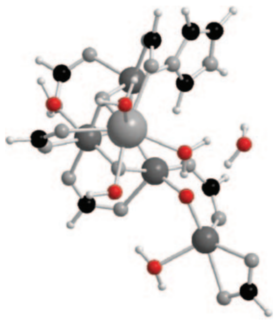
Removing cytotoxics: A Mn^{II}–pentaazamacrocycle removes $NO^{\bullet}$, $O_2^{\bullet -}$, and their $ONOO^-$ product as shown by real-time amperometry at single cells (see picture). This is the first compound able to completely abolish the cytotoxic effects of reactive oxygen (ROS) and reactive nitrogen species (RNS) in inflammation.

Photosystem II

S. Petrie, R. Stranger,*
R. J. Pace **4233–4236**

Location of Potential Substrate Water Binding Sites in the Water Oxidizing Complex of Photosystem II

Water divining: DFT calculations are applied to a set of Mn_4Ca cluster models of the water oxidizing complex (WOC) in photosystem II (see picture; O red, H white, Ca light gray, Mn dark gray, C black). The calculations uncover a model of the active site which rationalizes recent experimental data probing substrate interaction with the WOC and identifies the most likely substrate water binding sites.



Analytical Methods

I. M. Kempson,*
D. A. Henry **4237–4240**

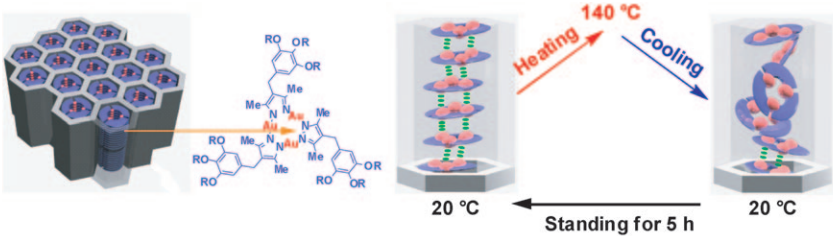
Determination of Arsenic Poisoning and Metabolism in Hair by Synchrotron Radiation: The Case of Phar Lap

Fresh physical evidence about the demise of the racehorse Phar Lap (see photograph) has been gathered from the study of mane hair samples by synchrotron radiation analysis with high resolution X-ray fluorescence (XRF) and X-ray absorption near edge structure (XANES) analyses. The results are indicative of arsenic ingestion and metabolism, and show that the racing champion died from arsenic poisoning.

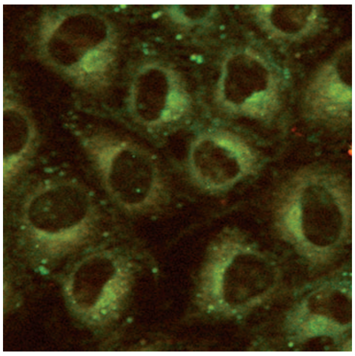
Mesoporous Materials

H. O. Lintang, K. Kinbara,* K. Tanaka,
T. Yamashita, T. Aida* **4241–4245**

Self-Repair of a One-Dimensional Molecular Assembly in Mesoporous Silica by a Nanoscopic Template Effect



Upon confinement of a trinuclear gold(I) pyrazolate complex in a hexagonal silicate channel, the luminescence center formed by a Au^I–Au^I metallophilic interaction is not only protected against thermal disruption but also strongly encouraged to self-recover from a heat-induced structural damage. This nanoscopic template effect is negligible for a lamellar silica framework.

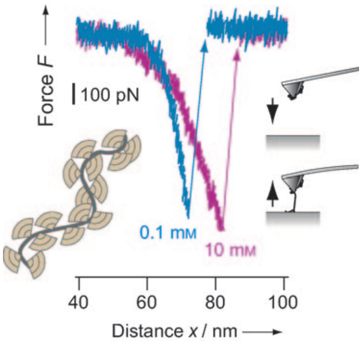


A ratiometric fluorescent nanogel can sense pH over a range that is applicable to physiological studies. It can be easily prepared and made pH-responsive by addition of a pH probe and a FRET system that utilizes the gel to hold dyes in close proximity (see picture; overlay of coumarin dye and Nile Red fluorescence in kidney cells).

Cellular Sensing

H. Peng,* J. A. Stolwijk, L. Sun, J. Wegener, O. S. Wolfbeis* ——— **4246 – 4249**

A Nanogel for Ratiometric Fluorescent Sensing of Intracellular pH Values



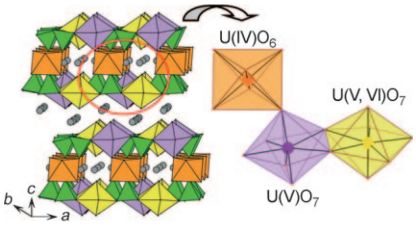
The mechanical properties of single cationic dendronized polymers can be strongly modified in aqueous solutions by the ionic strength. Given the possibility to tune the elasticity of dendronized polymers significantly through the solvent properties, such polymers may become ideal building blocks for single-molecule machines, especially as actuators or motors.

Single Polymers

I. Popa, B. Zhang, P. Maroni, A. D. Schlüter,* M. Borkovec* ——— **4250 – 4253**

Large Mechanical Response of Single Dendronized Polymers Induced by Ionic Strength

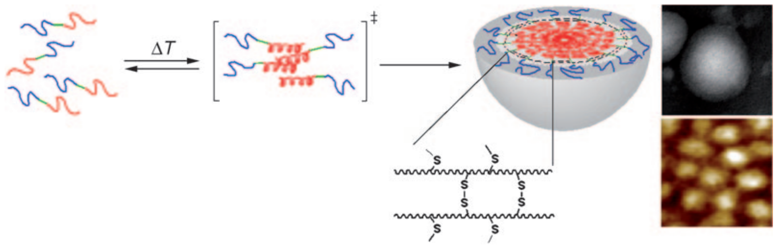
For U′r eyes only: A mixed-valence uranium silicate containing three different valence states of uranium has been synthesized under high-temperature, high-pressure hydrothermal conditions. The structure contains uranium silicate sheets with uranophane anion topology that are connected by UO_6 octahedra to form a 2D layered structure with Na^+ ions within and between the layers.



Mixed-Valence Compounds

C.-S. Lee, C.-H. Lin, S.-L. Wang,* K.-H. Lii* ——— **4254 – 4256**

$[Na_7U^{IV}O_2(U^{V}O)_2(U^{V/VI}O_2)_2Si_4O_{16}]$: A Mixed-Valence Uranium Silicate



Stable micellar structures were synthesized containing cysteine residues at the diblock interface to stabilize micellar structure (see picture). Self-assembly of these copolypeptides affords a new class of protein nanoparticles with potential applications in drug-delivery and bioimaging.

Micelles

W. Kim, J. Thévenot, E. Ibarboure, S. Lecommandoux, E. L. Chaikof* ——— **4257 – 4260**

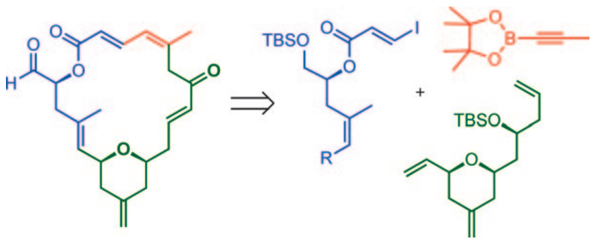
Self-Assembly of Thermally Responsive Amphiphilic Diblock Copolypeptides into Spherical Micellar Nanoparticles

Contents

Natural Product Synthesis

S. Y. Yun, E. C. Hansen, I. Volchkov,
E. J. Cho, W. Y. Lo, D. Lee* **4261 – 4263**

Total Synthesis of (−)-Dactylolide

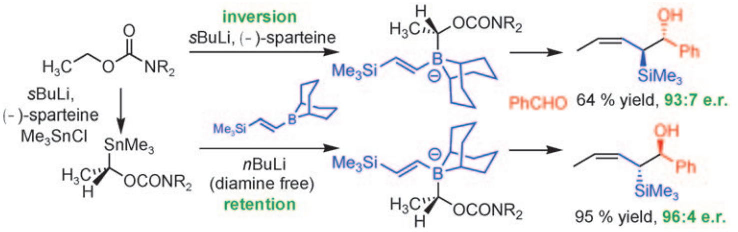


Multiple metals in action: Relying on the prowess of various metal-catalyzed C−O and C−C bond-forming reactions, a concise asymmetric total synthesis of (−)-dactylolide has been achieved (see scheme). The formation of a *Z*-trisubstituted vinylboronate through an Alder–ene reaction and subsequent rhenium-mediated regioselective transposition of an allylic alcohol are the key features of this convergent synthesis.

Asymmetric Synthesis

M. Binanzer, G. Y. Fang,
V. K. Aggarwal* **4264 – 4268**

Asymmetric Synthesis of Allylsilanes by the Borylation of Lithiated Carbamates: Formal Total Synthesis of (−)-Decarestrictine D

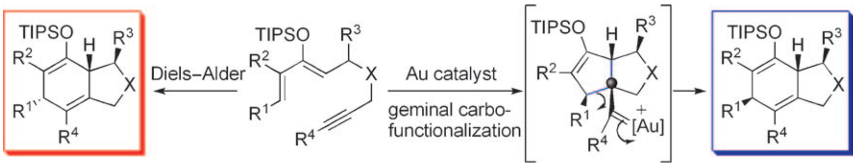


The flip side: (−)-Sparteine-complexed lithiated carbamates react with β-silylvinylboranes with inversion of configuration, whereas the diamine-free lithiated carbamates react with retention of configuration, thereby providing enantiocomplementary routes to β-hydroxy allylsilanes (see scheme). The methodology has been applied in a concise formal total synthesis of (−)-decarestrictine D.

Cyclization Reactions

H. Kusama, Y. Karibe, Y. Onizawa,
N. Iwasawa* **4269 – 4272**

Gold-Catalyzed Tandem Cyclization of Dienol Silyl Ethers for the Preparation of Bicyclo[4.3.0]nonane Derivatives

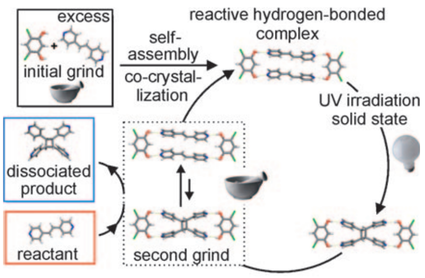


Tandem bicycle: A gold-catalyzed geminal carbo-functionalization reaction of 3-siloxy-1,3-dien-8-ynes proceeded smoothly to give bicyclo[4.3.0]nonanes stereoselectively through ring expansion of the bicyclic carbene complex intermediates. The product configuration was different from that of the thermal Diels–Alder adduct.

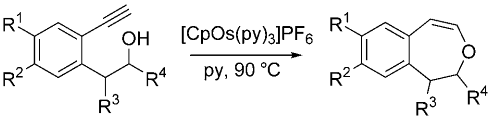
Supramolecular Catalysis

A. N. Sokolov, D.-K. Bučar, J. Baltrusaitis,
S. X. Gu, L. R. MacGillivray* **4273 – 4277**

Supramolecular Catalysis in the Organic Solid State through Dry Grinding



Chemical mechanics: Hydrogen-bond-driven self-assembly and mechanochemistry are used to facilitate supramolecular catalysis in the solid state. Mortar-and-pestle grinding proves to be an efficient means to achieve co-crystal formation and turnover using a physical mixture composed of an olefin and catalytic amounts of a ditopic template (see scheme).



The wizard of Os: Regioselective osmium-catalyzed 7-*endo* heterocyclization of aromatic alkynols affords benzoxepines in good yields. The proposed catalytic cycle involves the key formation of osmium–vinylidene complexes via an alkynyl-hydride–osmium(IV) complex from the starting alkynol.

Heterocyclization

A. Varela-Fernández, C. García-Yebra,
J. A. Varela, M. A. Esteruelas,*
C. Saá* ______________ **4278 – 4281**

Osmium-Catalyzed 7-*endo* Heterocyclization of Aromatic Alkynols into Benzoxepines

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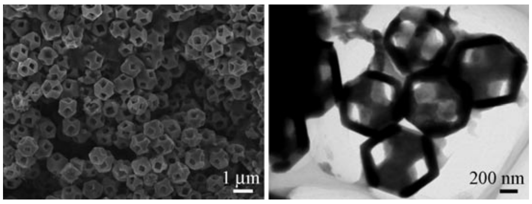


Hollow Cu_2O nanostructures with uniform size (see SEM and TEM images) were obtained by oxidative etching of truncated octahedral particle precursors. A unique feature of the as-synthesized nanoframes is that the six {100} faces are absent, and thus they are constructed of eight hexagonal {111} faces, which are expected to be more catalytically active.

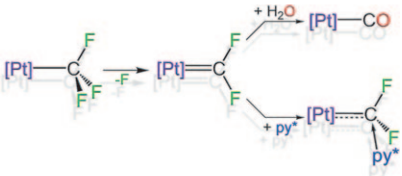
Hollow Structures

Y. Sui, W. Fu, Y. Zeng, H. Yang,* Y. Zhang,
H. Chen, Y. Li, M. Li, G. Zou **4282 – 4285**

Synthesis of Cu_2O Nanoframes and Nanocages by Selective Oxidative Etching at Room Temperature

---

Caught in the act: Evidence for the intermediacy of difluorocarbene–platinum species along the acidic degradation of Pt−CF_3 bonds was gained by trapping a base-stabilized Pt=CF_2 moiety (see scheme). Attack of an N nucleophile (py*) to the highly electrophilic and extremely reactive difluorocarbene carbon atom takes place with C−N bond formation.



Carbenes

S. Martínez-Salvador, B. Menjón,
J. Forniés,* A. Martín,
I. Usón ______________ **4286 – 4289**

Trapping a Difluorocarbene–Platinum Fragment by Base Coordination

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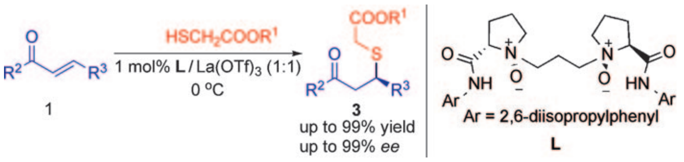


Ramping it up: The titled reaction has been developed using a chiral *N*,*N*′-dioxide–La^{III} complex as the catalyst. The reaction proceeded with high yield and enantioselectivity. Remarkably, a high asymmetric amplification was observed, as 98 % *ee* was achieved using 1 mol % **L**/La(OTf)$_3$ in which the *ee* value of **L** was 2 % *ee*. Tf = trifluoromethanesulfonyl.

Asymmetric Synthesis

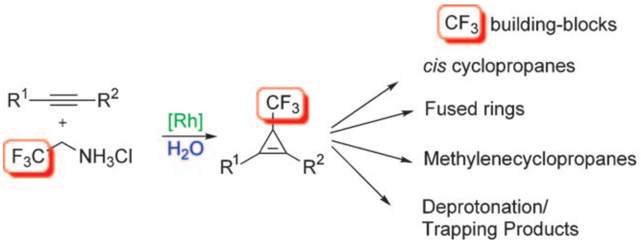
Y. H. Hui, J. Jiang, W. T. Wang, W. L. Chen,
Y. F. Cai, L. L. Lin, X. H. Liu,
X. M. Feng* ______________ **4290 – 4293**

Highly Enantioselective Conjugate Addition of Thioglycolate to Chalcones Catalyzed by Lanthanum: Low Catalyst Loading and Remarkable Chiral Amplification

Cyclopropenation

B. Morandi, E. M. Carreira* **4294 – 4296**

Rhodium-Catalyzed Cyclopropenation of Alkynes: Synthesis of Trifluoromethyl-Substituted Cyclopropenes



Make it strained and fluorinated! A rhodium-catalyzed domino diazotization/cyclopropenation reaction involving trifluoroethylamine hydrochloride and alkynes has been developed for the synthesis of trifluoromethyl cyclopropenes that can be easily functionalized to afford useful CF_3-containing building blocks for drug discovery.

Rearrangement

K. Moriya, S. Saito,
A. Osuka* ———— **4297 – 4300**

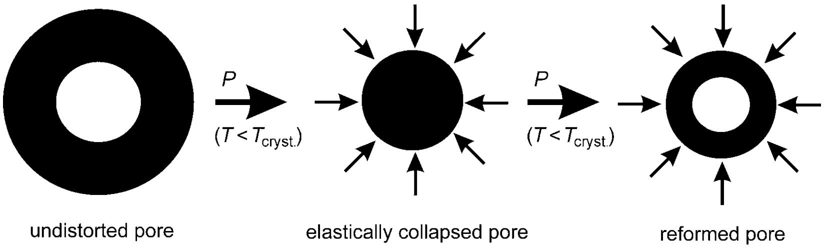
Boron(III) Induced Skeletal Rearrangement of Hexaphyrin(1.1.1.1.1.1) to Hexaphyrin(2.1.1.0.1.1)

Who eight all the πs? Hexaphyrin(1.1.1.1.1.1) rearranges into figure-of-eight hexaphyrin(2.1.1.0.1.1) upon B^{III} complexation (see scheme). Redox reactions convert between 30π and 28π electron systems requiring the B^{III} coordination to change between trigonal and tetrahedral. Removal of the B^{III} centers allows hexaphyrin(2.1.1.0.1.1) to complex two Pd^{II} centers.

High-Pressure Chemistry

P. Mohanty, V. Ortalan, N. D. Browning,
I. Arslan, Y. Fei,
K. Landskron* ———— **4301 – 4305**

Direct Formation of Mesoporous Coesite Single Crystals from Periodic Mesoporous Silica at Extreme Pressure

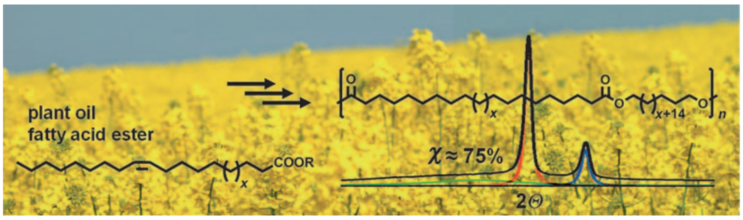


Under an extreme pressure of 12 GPa, mesoporous coesite can be formed directly from periodic mesoporous silica without the aid of a template. The porous coesite particles obtained from SBA-16 are single crystalline, with a pore size of about 4 nm and about 50% porosity. The formation can be attributed to the kinetically controlled crystallization of a nonporous elastically strained glasslike silica intermediate (see scheme).

Renewable Resources

D. Quinzler, S. Mecking* — **4306 – 4308**

Linear Semicrystalline Polyesters from Fatty Acids by Complete Feedstock Molecule Utilization



Complete and linear incorporation of fatty acids into polyesters is achieved by isomerizing carbonylation to give polymerization-quality diesters and their polycondensation with the corresponding diols obtained by reduction. The strictly linear and long-chain hydrocarbon nature of these polyesters results in a high degree of crystallinity and melting behavior akin to common thermoplastics.

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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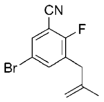
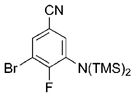
Preview ———— *4313*

Corrigendum

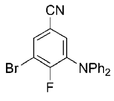
More detailed NMR studies of experiments carried out in this Communication (DOI:10.1002/anie.200903505) have revealed that the manganation of compounds **6i** and **6k** occurs at the *ortho* position relative to the fluorine substituent, and not *ortho* to the cyano group as originally mentioned. Therefore, the compounds **12a** and **12c–f** derived from **6k** bear the amino functionality in the *ortho* position relative to the fluorine substituent (see corrected structures and the corrected structure of **8i**). The authors apologize for this oversight.



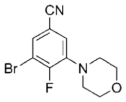
8i



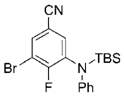
12a



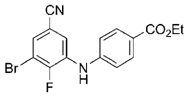
12c



12d



12e



12f

Directed Manganation of Functionalized Arenes and Heterocycles Using $tmp_2Mn{\cdot}2\,MgCl_2{\cdot}4\,LiCl$

S. H. Wunderlich, M. Kienle, P. Knochel* ———— **7256–7260**

Angew. Chem. **2009**, *48*

DOI 10.1002/anie.200903505