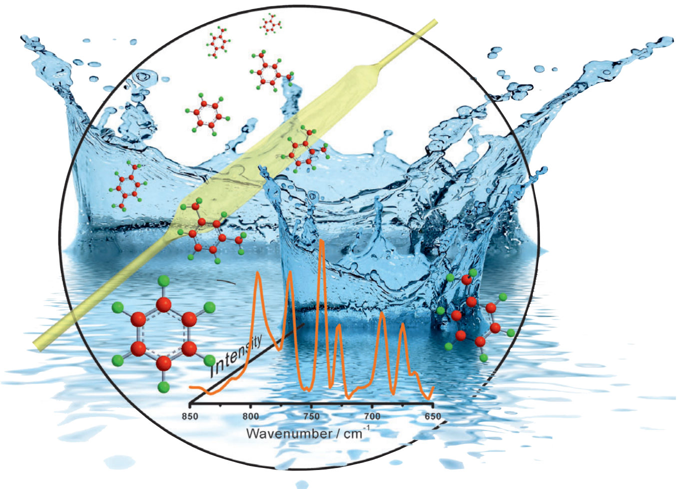
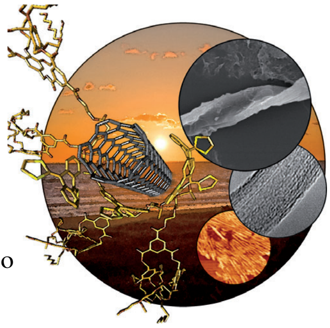
Rapidly responding ...

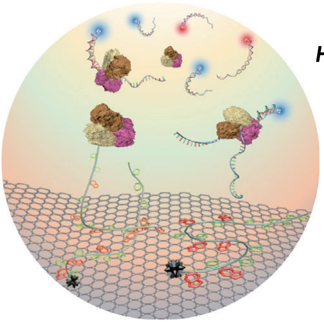


… in situ analysis methods, such as mid-infrared optochemical sensors utilizing evanescent field absorption techniques, may inherently provide qualitative and quantitative information on multiple volatile organic contaminants in water. In their Communication on page 2265 ff., B. Mizaikoff et al. describe a planar infrared attenuated total reflection (IR-ATR) fiberoptic sensor that was coated with an ethylene/propylene copolymer. Such a system may be used for continuous monitoring of the water quality.



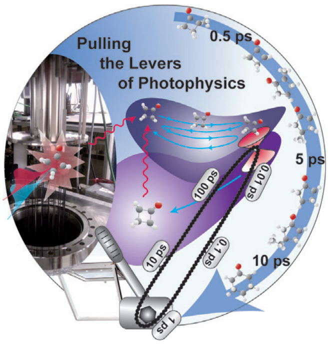
Carbon Nanotubes

In their Communication on page 2180 ff., D. M. Guldi, N. Martín, et al. report the immobilization of a photo- and redox-active 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-based dipeptide onto single-walled carbon nanotubes.



High-Throughput Screen

Graphene oxide was used as the substrate for a screen for inhibitors of DNA helicases by D.-H. Min et al. in their Communication on page 2340 ff. Several inhibitors of disease-related helicase targets were identified using this method.



Photophysics

In their Communication on page 2247 ff., T. I. Sølling, K. B. Møller, et al. show the influence of small structural variations in the nuclear arrangement on the rate of internal conversion processes of cyclic ketones.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 6201–606-332
Telephone: (+49) 6201–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 6201–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 6201–606-550
Telephone: (+49) 6201–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

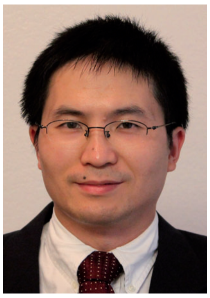
Get the Angewandte App International Edition

Available on the App Store

Enjoy Easy Browsing and a New Reading Experience on the iPad
- Keep up to date with the latest articles in Early View.
- Download new weekly issues automatically when they are published.
- Read new or favorite articles anytime, anywhere.

Service

Author Profile



"In a spare hour, I check out the latest news and listen to some folk music.
My favorite name reaction is the Ferrier rearrangement …"
This and more about Liming Zhang can be found on page 2156.

News

B. Schmidt

J. Cheon

F. Seela

C. Schultz

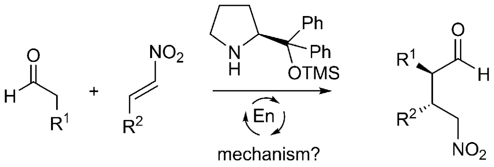
Books

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY ONLINE LIBRARY

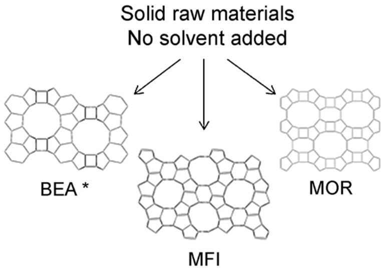
Highlights

Organocatalysis



Two views: The mechanism of the conjugate addition of linear aldehydes to nitro olefins has been investigated by two research groups. In spite of extensive experimental data, important questions remain unanswered (see scheme; TMS = trimethylsilyl, En = enamine).

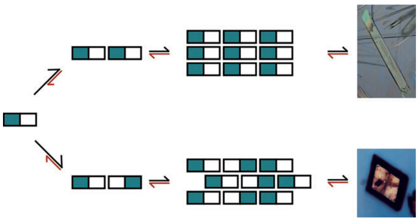
Zeolite Synthesis



No added solvent means no waste solvent or recycling costs. Understandably the chemical industry is interested in developing approaches to increase the product to solvent ratio in synthesis. In recent work various zeolites were prepared by grinding the dry materials and then heating to 180 °C, and this method could lead to significant savings in zeolite synthesis.

Reviews

Mechanisms of Crystallization

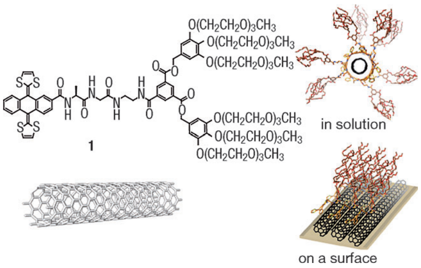


Everything starts out small: The synthesis of organic materials depends strongly on the first steps of molecular self-assembly during crystal nucleation. This Review summarizes current knowledge on these processes. Self-association in different solvents can lead to the creation of different building blocks, which form differently packed nuclei and thus in each case specific crystalline phases.

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.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Communications



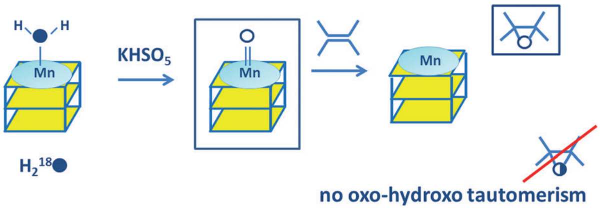
From nano- to macroscale: The immobilization of photo- and redox-active 9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene-based dipeptide **1** onto SWCNTs resulted in a high order of self-alignment among **1**/SWCNTs (see picture). The assembly of the **1**/SWCNTs is the key for stabilizing long-lived charge-separated states that are formed upon photoexcitation of the SWCNTs.

Donor–Acceptor Nanohybrids

F. G. Brunetti, C. Romero-Nieto,
J. López-Andarias, C. Atienza, J. L. López,
D. M. Guldi,* N. Martín* **2180 – 2184**

Self-Ordering Electron Donor–Acceptor Nanohybrids Based on Single-Walled Carbon Nanotubes Across Different Scales

Frontispiece

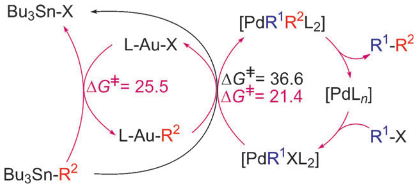


On the flip side: A free manganese porphyrin, when activated into a high-valent metal-oxo species, mediates O atom transfer (epoxidation) from both faces. This results in a mixed labeling of epoxide in labeled water. When the porphyrin (blue oval, see scheme) is bound to G-quadruplex DNA (yellow boxes), the O atom transfer reaction takes place only on the accessible face of the porphyrin. This shows the binding mode of the porphyrin to the G-quadruplex DNA.

G-Quadruplex Ligands

V. Pradines, G. Pratviel* **2185 – 2188**

Interaction of Cationic Manganese Porphyrin with G-Quadruplex Nucleic Acids Probed by Differential Labeling of the Two Faces of the Porphyrin

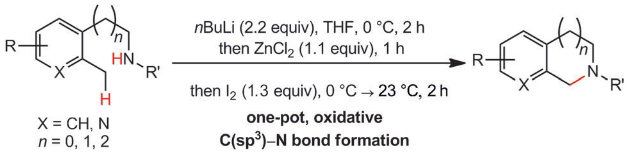


Gold shuttle: Bulky groups, which will not (or only very sluggishly) undergo Stille coupling with stannanes and inexpensive ligands, can be efficiently coupled using bimetallic catalysis. A gold cocatalyst serves as an efficient shuttle to convey the bulky group from tin to palladium by reducing the steric crowding in the transition-states (see scheme).

Cross-Coupling

J. delPozo, D. Carrasco,
M. H. Pérez-Temprano,
M. García-Melchor, R. Álvarez,
J. A. Casares,* P. Espinet* **2189 – 2193**

Stille Coupling Involving Bulky Groups Feasible with Gold Cocatalyst



What a couple! An intramolecular, $C(sp^3)$–N coupling to afford azacycles is reported. This reaction proceeds through the oxidation of benzylic C,N-dianions with iodine and builds on an earlier discovery during the synthesis of the natural product lyconadin A. The current study employs conformationally unbiased substrates with less acidic C–H bonds and less reactive nitrogen nucleophiles. $ZnCl_2$ was identified as an important additive.

Heterocycle Synthesis

J. L. Jeffrey, E. S. Bartlett,
R. Sarpong* **2194 – 2197**

Intramolecular $C(sp^3)$–N Coupling by Oxidation of Benzylic C,N-Dianions

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

The German Chemical Society (GDCh) invites you to:

Angewandte Anniversary Symposium

125 JAHRE

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

GDCh

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

Speakers


Carolyn R. Bertozzi


François Diederich


Alois Fürstner


Roald Hoffmann
(Nobel Prize 1981)


Susumu Kitagawa


Jean-Marie Lehn
(Nobel Prize 1987)


E.W. “Bert” Meijer


Frank Schirrmacher
(Publisher, *FAZ*)


Robert Schlögl


George M. Whitesides


Ahmed Zewail
(Nobel Prize 1999)

Freie Universität Berlin

Register now:

angewandte.org/symposium

WILEY-VCH

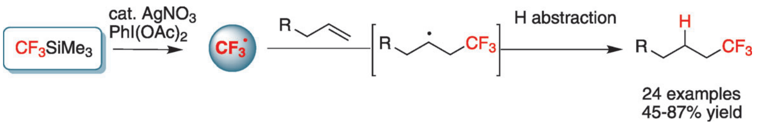
GDCh
GESELLSCHAFT
DEUTSCHER CHEMIKER

PSJ-12-50223_gu

Radical Reactions

X. Wu, L. Chu, F.-L. Qing* **2198 – 2202**

Silver-Catalyzed Hydrotrifluoromethylation of Unactivated Alkenes with CF_3SiMe_3

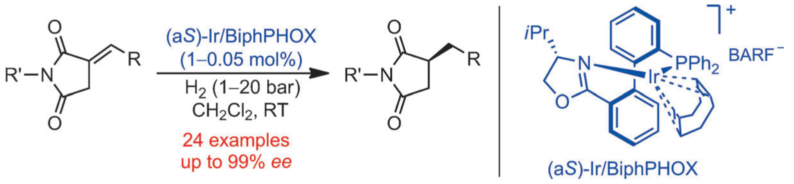


A silver bullet: The title reaction results in selective formation of trifluoromethylated alkanes, and is in contrast to the previously reported transition-metal-catalyzed trifluoromethylation of olefins to generate a series of trifluoromethylated allylic compounds. Preliminary mechanistic investigations indicate that the current hydrotrifluoromethylation proceeds through a pathway involving a CF_3 radical species.

Synthetic Methods

Y. Liu, W. Zhang* **2203 – 2206**

Iridium-Catalyzed Asymmetric Hydrogenation of α-Alkylidene Succinimides

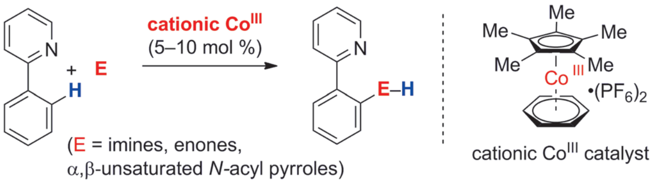


Not to be out PhOXed! The title reaction provides a new approach to chiral succinimide derivatives with excellent yields and *ee* values by using a low catalyst loading (0.05 mol %) and mild reaction conditions. Chiral 3-benzyl pyrrolidines and 1-hydroxypyrrolidine-2,5-diones, important structural motifs in natural products and pharmaceuticals, could be readily prepared. $BARF^- =$ tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

C–H Activation

T. Yoshino, H. Ikemoto, S. Matsunaga,*
M. Kanai* **2207 – 2211**

A Cationic High-Valent Cp^*Co^{III} Complex for the Catalytic Generation of Nucleophilic Organometallic Species: Directed C–H Bond Activation

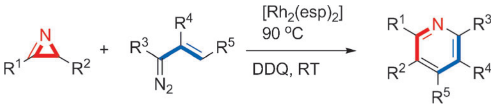


Active without activation: In an inexpensive and atom-economical approach to C–H bond functionalization, a cationic Co^{III} complex (see scheme) was used to generate nucleophilic organometallic species in situ without additional activating reagents. Under these conditions, aryl C–H bonds underwent efficient addition to polar electrophiles, including α,β-unsaturated *N*-acyl pyrroles as β-substituted ester and amide surrogates.

Heterocycles

N. S. Y. Loy, A. Singh, X. Xu,
C.-M. Park* **2212 – 2216**

Synthesis of Pyridines by Carbenoid-Mediated Ring Opening of 2*H*-Azirines



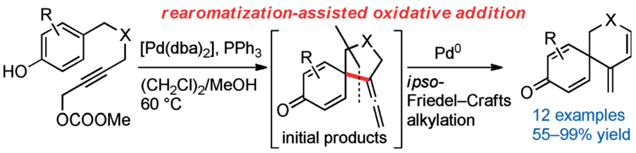
Roaming the range: The title reaction tolerates a wide range of substituents on the resulting pyridine ring using mild reaction conditions (see scheme; esp = α,α,α′,α′-tetramethyl-1,3-benzenedipropionic acid). The formation of the key intermediate is catalyst-controlled, and subsequent cyclization and oxidation affords pyridines in excellent yields. The method has been used for the efficient synthesis of polyarylpyridines.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Homogeneous Catalysis

T. Nemoto, Z. Zhao, T. Yokosaka,
Y. Suzuki, R. Wu,
Y. Hamada* ______________ **2217 – 2220**

Palladium-Catalyzed Intramolecular *ipso*-Friedel–Crafts Alkylation of Phenols and Indoles: Rearomatization-Assisted Oxidative Addition

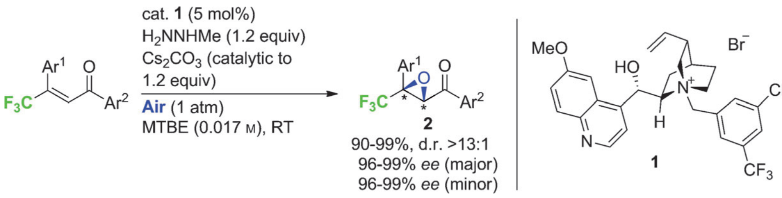


Inspiroation: A novel synthesis of spirocycles based on a palladium-catalyzed intramolecular *ipso*-Friedel–Crafts alkylation of phenols (see scheme; dba = dibenzylideneacetone) and indoles is described. Mechanistic studies show that the reaction proceeds through an unprecedented rearomatization-assisted oxidative addition.

Synthetic Methodology

H. Kawai, S. Okusu, Z. Yuan, E. Tokunaga,
A. Yamano, M. Shiro,
N. Shibata* ______________ **2221 – 2225**

Enantioselective Synthesis of Epoxides Having a Tetrasubstituted Trifluoromethylated Carbon Center: Methylhydrazine-Induced Aerobic Epoxidation of β,β-Disubstituted Enones



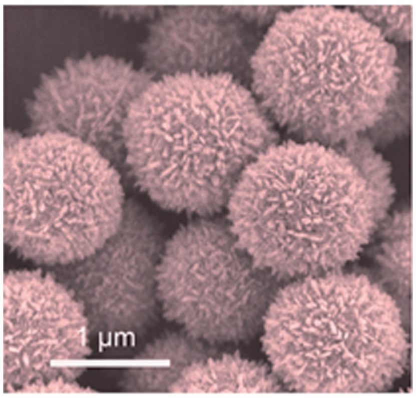
The unprecedented title reaction is catalyzed by a methylhydrazine/base/organocatalyst (**1**) system. Biologically attractive epoxides (**2**) having a tetrasubstituted trifluoromethylated carbon center were obtained with excellent enantioselectivity for the first time. ^{18}O-labeling experiments suggest a mechanism involving the activation of molecular oxygen. MTBE = methyl *tert*-butyl ether.

Synthetic Methods

A. Q. Pan, H. B. Wu, L. Yu,
X. W. Lou* ______________ **2226 – 2230**

Template-Free Synthesis of VO_2 Hollow Microspheres with Various Interiors and Their Conversion into V_2O_5 for Lithium-Ion Batteries

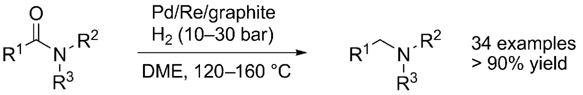
Getting a charge out of microspheres: Uniform VO_2 microspheres with various complex interiors, such as yolk-shelled and multi-shelled hollow structures, have been synthesized through a template-free solvothermal method. After annealing in air, the derived V_2O_5 microspheres manifest improved electrochemical performance as a high-capacity cathode material for lithium-ion batteries.



Amide Hydrogenation

M. Stein, B. Breit* ________ **2231 – 2234**

Catalytic Hydrogenation of Amides to Amines under Mild Conditions



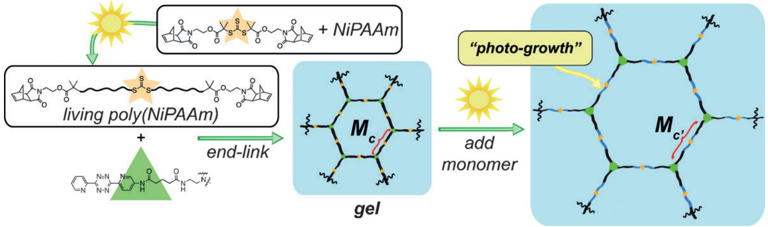
Under (not so much) pressure: A general method for the hydrogenation of tertiary and secondary amides to amines with excellent selectivity using a bimetallic Pd–Re catalyst has been developed. The reaction proceeds under low pressure and comparatively low temperature. This method provides organic chemists with a simple and reliable tool for the synthesis of amines.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Photo-Responsive Materials

H. Zhou, J. A. Johnson* ____ 2235 – 2238

Photo-controlled Growth of Telechelic Polymers and End-linked Polymer Gels

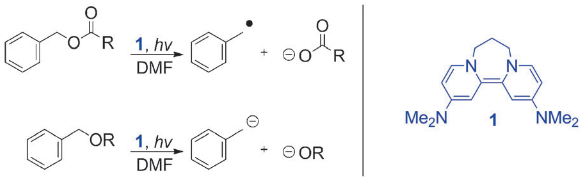


Growing pores: Exposure of a bis-norbornene trithiocarbonate to long-wavelength UV light, or sunlight, in the presence of *N*-isopropylacrylamide (NiPAAm) led to well-defined norbornene–telechelic poly(NiPAAm) macromers. The macromers were end-linked with a tris-tetrazine via inverse-electron-demand Diels–Alder cycloaddition to generate polymer gels. Addition of new monomer, followed by exposure to sunlight, led to "photo-growth" of the network pores.

Radical Reactions

E. Doni, S. O'Sullivan, J. A. Murphy* ____ 2239 – 2242

Metal-Free Reductive Cleavage of Benzylic Esters and Ethers: Fragmentations Result from Single and Double Electron Transfers

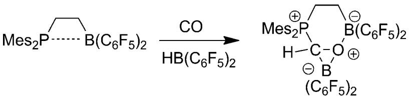


The mechanisms for the reductive cleavage of benzylic esters and ethers by neutral organic electron donor **1** are different (see scheme). Products isolated from the cleavage of benzylic ethers result from the transfer of two electrons, without the intermediacy of benzyl radicals, which are believed to be intermediates in the reductive cleavage of benzylic esters.

Activation of Small Molecules

M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr, G. Erker* ____ 2243 – 2246

Facile Carbon Monoxide Reduction at Intramolecular Frustrated Phosphane/Borane Lewis Pair Templates



A new reaction pathway: Carbon monoxide is readily reduced by Piers' borane at a frustrated Lewis pair (FLP) to yield a formylborane stabilized by the FLP (see picture). This reaction may be considered a typical example of efficient activation of a small molecule by a FLP.

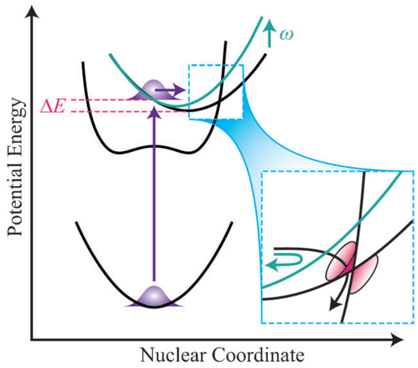
Gas-Phase Chemistry

T. S. Kuhlman, M. Pittelkow, T. I. Sølling,* K. B. Møller* ____ 2247 – 2250

Pulling the Levers of Photophysics: How Structure Controls the Rate of Energy Dissipation

Back Cover

Internal conversion: The energy difference between the Franck–Condon and equilibrium geometries and the vibrational frequency of one or a few modes determine the relative importance of adiabatic and nonadiabatic dynamics and thus the rate of electronic energy dissipation (see picture). In the cycloketones, variations in these quantities lead to a difference in the timescale for the $S_2 \rightarrow S_1$ transition.

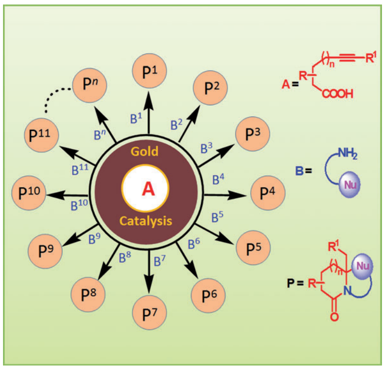


© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Diversity-Oriented Synthesis

N. T. Patil,* V. S. Shinde,
B. Sridhar ______________ **2251 – 2255**

Relay Catalytic Branching Cascade: A Technique to Access Diverse Molecular Scaffolds

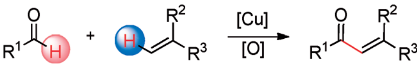


Skeletal diversity: The reactions of alkynoic acids (**A**, common type of substrates) with various scaffold-building agents (**B**) under gold catalysis produce a series of multifunctional polyheterocyclic structures (see scheme). The approach enables the preparation of compound libraries with high skeletal diversity.

Oxidative Coupling

J. Wang, C. Liu, J. Yuan,
A. Lei* ______________ **2256 – 2259**

Copper-Catalyzed Oxidative Coupling of Alkenes with Aldehydes: Direct Access to α,β-Unsaturated Ketones

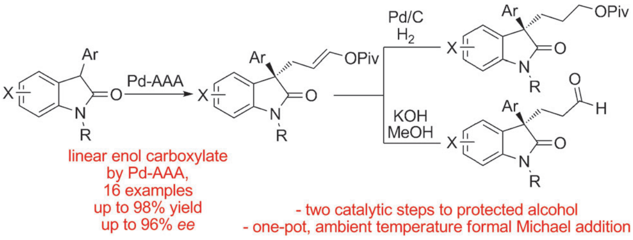


Let's get radical: The first copper-catalyzed oxidative coupling of alkenes and aldehydes was developed. Various aldehydes were utilized as substrates to construct α,β-unsaturated ketones. A preliminary mechanistic study indicated that this reaction is likely to proceed through a single-electron transfer.

Asymmetric Catalysis

B. M. Trost,* J. T. Masters,
A. C. Burns ______________ **2260 – 2264**

Palladium-Catalyzed Asymmetric Allylic Alkylation of 3-Aryloxindoles with Allylidene Dipivalate: A Useful Enol Pivalate Product

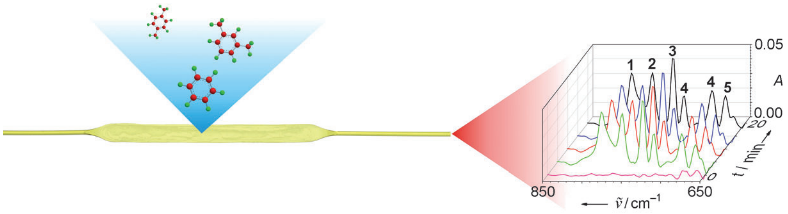


Triple A: The catalytic asymmetric allylic alkylation (AAA) of 3-aryloxindoles with allylidene dipivalate is described. This reaction affords stable, synthetically useful enol pivalates in high yield and with excellent regio- and enantioselectivity. A broad range of substrates is tolerated, including unprotected and 3-heteroaryl nucleophiles.

Analytical Methods

R. Lu, G. Sheng, W. Li, H. Yu, Y. Raichlin,
A. Katzir, B. Mizaikoff* ______ **2265 – 2268**

IR-ATR Chemical Sensors Based on Planar Silver Halide Waveguides Coated with an Ethylene/Propylene Copolymer for Detection of Multiple Organic Contaminants in Water



Sensitive: Several monocyclic aromatic hydrocarbons, for example *p*-, *m*-, *o*-xylene, toluene, and benzene (**1**–**5**), were detected in a single measurement by using a planar infrared attenuated total reflection (IR-ATR) fiberoptic sensor that was coated with ethylene/propylene copolymer. Compared to conventional IR sensing systems, this device exhibits a large dynamic detection range.

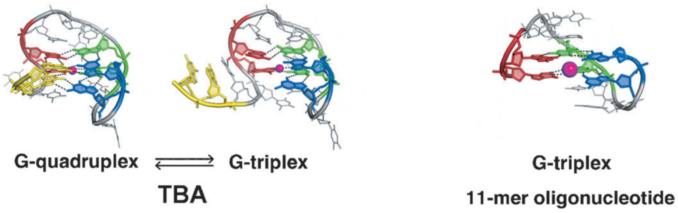
Front Cover

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

DNA Structures

V. Limongelli, S. De Tito, L. Cerofolini, M. Fragai, B. Pagano, R. Trotta, S. Cosconati, L. Marinelli, E. Novellino, I. Bertini, A. Randazzo,* C. Luchinat,* M. Parrinello* ______ **2269 – 2273**

The G-Triplex DNA



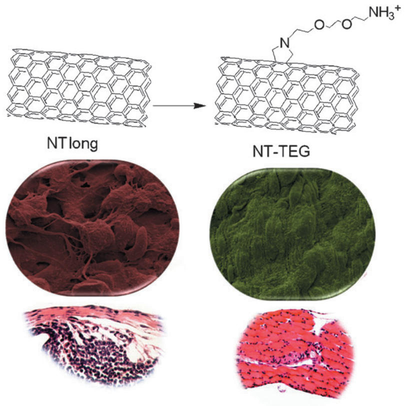
Triplex with a twist: Through metadynamics calculations, the thrombin binding aptamer (TBA) has been shown to adopt a stable G-triplex structural motif, in addition to the usual G-quadruplex (see scheme). An 11-mer oligonucleotide was also shown to form a stable G-triplex, whose structural and thermodynamic properties have been characterized.

Nanotube Toxicology

H. Ali-Boucetta, A. Nunes, R. Sainz, M. A. Herrero, B. Tian, M. Prato,* A. Bianco,* K. Kostarelos* _ **2274 – 2278**

Asbestos-like Pathogenicity of Long Carbon Nanotubes Alleviated by Chemical Functionalization

Inside Cover

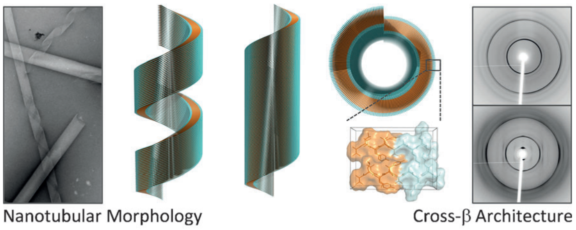


Sometimes shorter is better: The apparent similarity between multi-walled carbon nanotubes (MWNTs) and asbestos fibers has generated serious concerns about their safety profile. The asbestos-like pathogenicity observed for long, pristine nanotubes (NTlong, see scheme) can be completely alleviated if their effective length is decreased as a result of chemical functionalization, such as with tri(ethylene glycol) (TEG).

Self-Assembled Peptide Architecture

K. L. Morris, S. Zibaee, L. Chen, M. Goedert, P. Sikorski, L. C. Serpell* ______ **2279 – 2283**

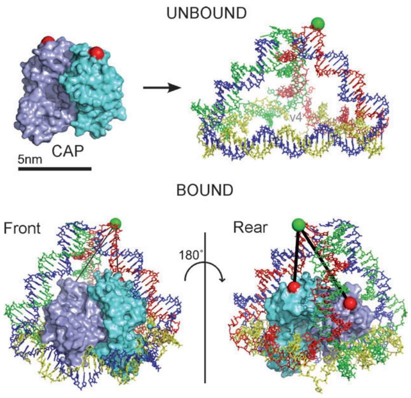
The Structure of Cross-β Tapes and Tubes Formed by an Octapeptide, αSβ1



Elaborate morphology: The αSβ1 peptide, a fragment of α-synuclein, assembles into flat tapes consisting of a peptide bilayer, which can be modeled based on the cross-β structure found in amyloid proteins. The tapes are stabilized by hydrogen bonding, whilst the amphiphilic nature of the peptide results in the thin bilayer structure. To further stabilize the structure, these tapes may twist to form helical tapes, which subsequently close into nanotubes.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

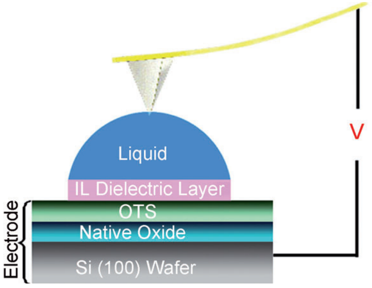
DNA Nanotechnology



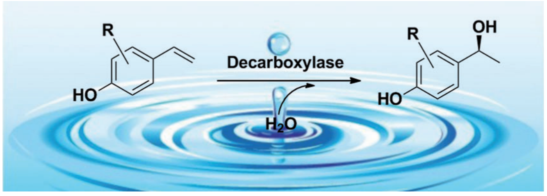
CAP-turing the moment: A cage made from DNA can be used to encapsulate a transcription factor (catabolite activator protein, CAP; see figure) without covalent attachment. CAP is shown to stably bind inside the DNA cage at a 1:1 ratio by bending one edge to accommodate the protein. Single-molecule fluorescence measurements confirm the orientation of CAP within the cage.

Surface Chemistry

Electrowetting was achieved on an ionic-liquid-coated (IL) dielectric layer at a driving voltage of just 70 mV and 5 V in AC and DC mode, respectively. AFM studies suggest that the high capacitance density of the ionic-liquid dielectric layer is the reason for the low voltage electrowetting (see picture; OTS = octadecyltrichlorosilane).

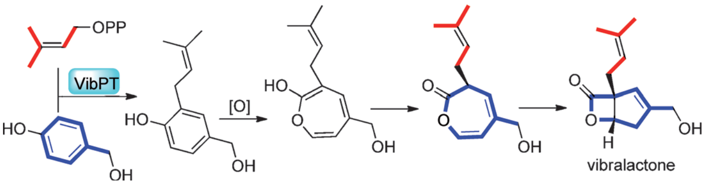


Enzyme Catalysis



More than one activity: Owing to their hydratase activity, phenolic acid decarboxylases catalyze the regio- and stereoselective addition of H_2O across the C=C double bond of hydroxystyrene derivatives yielding (*S*)-4-(1-hydroxyethyl)phenols with up to 82 % conversion and 71 % *ee*. Based on structure analysis and molecular docking simulations, a catalytic mechanism for this novel enzymatic reaction is proposed.

Natural Products



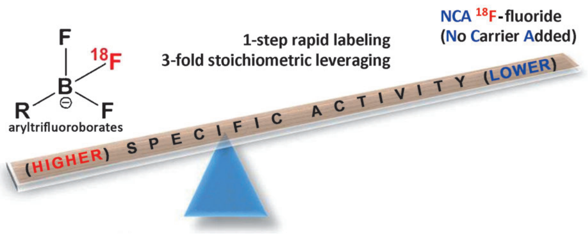
Not so simple: Evidence from ^{13}C-labeling studies, metabolite profiling, and cell-free conversion established that the bicycle skeleton of vibralactone is derived from an aryl ring moiety and both shikimate and phenylalanine pathways may contribute. VibPT was found to be potentially involved in vibralactone biosynthesis, as well as an aromatic PTase, which was first characterized in basidiomycete fungi. OPP = pyrophosphate.

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Radiochemistry

Z. Liu, Y. Li, J. Lozada, P. Schaffer,
M. J. Adam, T. J. Ruth,
D. M. Perrin* ______ 2303 – 2307

Stoichiometric Leverage: Rapid ^{18}F-Aryltrifluoroborate Radiosynthesis at High Specific Activity for Click Conjugation

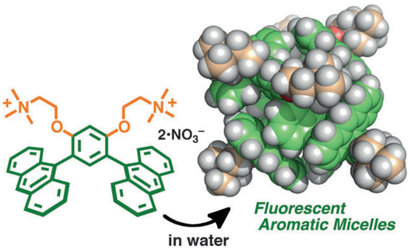


Raising the $^{18}F_3$-BAr: Specific activities of most ^{18}F-labeled radiotracers fall below 2 Ci µmol^{-1}, yet ^{18}F-aryltrifluoroborate synthesis affords specific activities as high as 15 Ci µmol^{-1}. This has been confirmed by using click chemistry to link an [^{18}F]-$ArBF_3^-$ to rhodamine and thereby demonstrating a rapid and generalizable one-pot method for preparing a fluorescent tracer with about 10-fold higher specific activity than usual.

Molecular Capsules

K. Kondo, A. Suzuki, M. Akita,
M. Yoshizawa* ______ 2308 – 2312

Micelle-like Molecular Capsules with Anthracene Shells as Photoactive Hosts

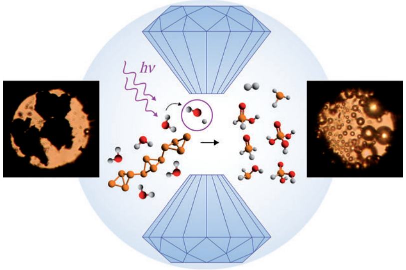


Aromatic micelles: Hydrophobic and aromatic–aromatic interactions promoted the spontaneous formation of micelle-inspired molecular capsules with large aromatic shells from bent bisanthracene amphiphiles (see picture). The micellar capsules could accommodate fluorescent-dye guests in water, and the resultant nanocomposites exhibited strong fluorescence through efficient energy transfer from the host shells to the encapsulated guests.

Red Phosphorus

M. Ceppatelli,* R. Bini, M. Caporali,
M. Peruzzini ______ 2313 – 2317

High-Pressure Chemistry of Red Phosphorus and Water under Near-UV Irradiation

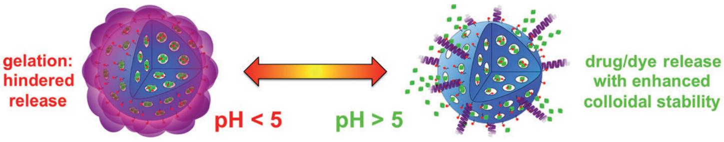


A high-pressure job: Under high-pressure conditions, within a diamond anvil cell, irradiation of red phosphorus (see scheme, orange) and water was found to lead to a reaction that gives H_2, PH_3, H_3PO_2, H_3PO_4, and H_3PO_4 (H gray, O red, P orange). This reaction can be easily monitored using Raman spectroscopy and presents an interesting method for H_2 generation.

Nanosize Bioconjugates

R. Guillet-Nicolas, A. Popat, J.-L. Bridot,
G. Monteith, S. Z. Qiao,*
F. Kleitz* ______ 2318 – 2322

pH-Responsive Nutraceutical–Mesoporous Silica Nanoconjugates with Enhanced Colloidal Stability



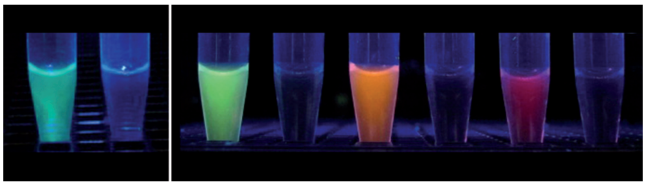
An innovative platform for targeted oral drug delivery is proposed based on the functionalization of drug/dye-loaded mesoporous silica nanoparticles (MSNs) with a biodegradable nutraceutical (β-lactoglobulin). The attachment of the nutraceutical not only protects the drug/dye from leaching in acidic environment, but also effectively allows their release in desired basic sites (pH 7.4).

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Fluorescent Sensors

Q. Wang, M. A. Priestman,
D. S. Lawrence* ______ 2323 – 2325

Monitoring of Protein Arginine Deiminase Activity by Using Fluorescence Quenching: Multicolor Visualization of Citrullination

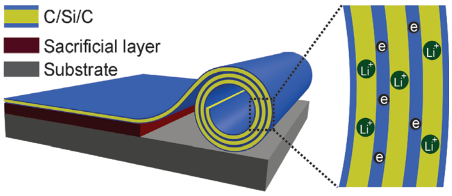


Colorful: The protein arginine deiminases are members of the enzyme family that catalyze posttranslational histone modification and consequent changes in gene expression. A visual readout of catalytic activity was developed that yields large fluorescence changes across the visible spectrum. The use of different fluorophores (see picture) enables the simultaneous multicolor monitoring of a mixture of histone-modifying enzymes.

Anode Nanotubes

J. W. Deng, H. X. Ji, C. L. Yan,* J. Zhang,
W. Si, S. Baunack, S. Oswald, Y. F. Mei,
O. G. Schmidt ______ 2326 – 2330

Naturally Rolled-Up C/Si/C Trilayer Nanomembranes as Stable Anodes for Lithium-Ion Batteries with Remarkable Cycling Performance

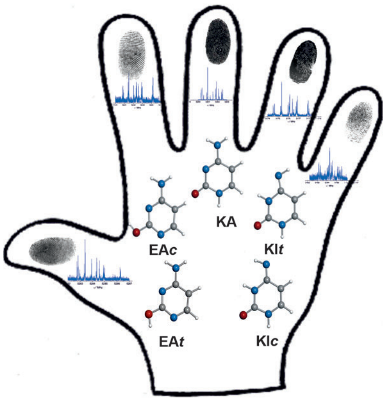


Rolling their own: Naturally rolled-up C/Si/C trilayer nanomembranes (see scheme) exhibit a high reversible capacity of about 2000 mAh g^{-1} at 50 mA g^{-1}, and 100 % capacity retention at 500 mA g^{-1} after 300 cycles. This technique is general and could be applied to the fabrication of other battery materials that undergo large volume changes.

Gas-Phase Tautomers

J. L. Alonso,* V. Vaquero, I. Peña,
J. C. López, S. Mata,
W. Caminati ______ 2331 – 2334

All Five Forms of Cytosine Revealed in the Gas Phase

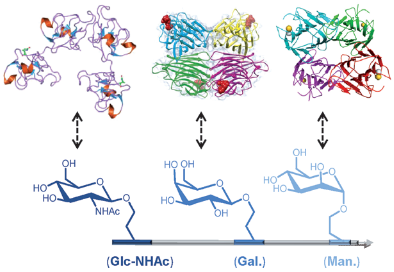


Give me five! All five tautomers and conformers of cytosine were characterized in the gas phase by laser ablation molecular beam Fourier transform microwave spectroscopy. The spectra were assigned unambiguously on the basis of the hyperfine structure due to the three ^{14}N nuclei (see picture; N blue, O red). The relative energies of the identified species were estimated from the relative intensities of the spectra.

Single-Chain Technology

N. Baradel, S. Fort, S. Halila, N. Badi,
J.-F. Lutz* ______ 2335 – 2339

Synthesis of Single-Chain Sugar Arrays



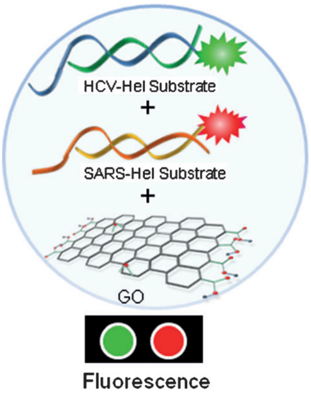
Polymers that toe the line: Well-defined linear polystyrene chains containing precisely positioned hexose moieties (mannose, galactose, and *N*-acetylglucosamine) were synthesized by a sequence-controlled polymerization approach followed by a series of site-selective modification steps. Such multifunctional single-chain hexose arrays associate specifically with complementary lectins (see picture).

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Drug Discovery

H. Jang, S.-R. Ryoo, Y.-K. Kim, S. Yoon, H. Kim, S. W. Han, B.-S. Choi, D.-E. Kim, D.-H. Min* **2340 – 2344**

Discovery of Hepatitis C Virus NS3 Helicase Inhibitors by a Multiplexed, High-Throughput Helicase Activity Assay Based on Graphene Oxide



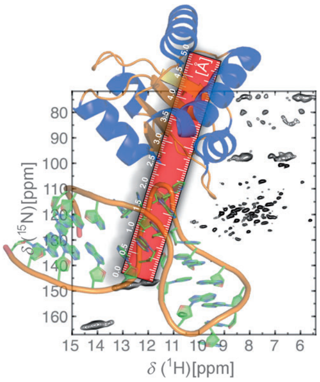
A GO-to solution: A simple graphene oxide (GO)-based assay to screen for selective inhibitors of a hepatitis C virus (HCV) helicase along with inhibitors of a severe acute respiratory syndrome coronavirus (SARS CoV) helicase was tested (see scheme). A single screen found five inhibitors highly selective for the HCV helicase orthologous to the SARS CoV helicase. Some of these hits were validated using the same GO-based assay.

Inside Back Cover

Protein–RNA Interactions

S. Asami, M. Rakwalska-Bange, T. Carlomagno, B. Reif* **2345 – 2349**

Protein–RNA Interfaces Probed by ^{1}H-Detected MAS Solid-State NMR Spectroscopy



Both protonated and deuterated samples were employed in the study of the L7Ae box C/D RNA complex by ^{1}H-detected solid-state NMR spectroscopy. This approach yielded high-resolution spectra and was used to determine the intermolecular interface and extract structural parameters with high accuracy.

Noncovalent Interactions

E. Hartmann, R. M. Gschwind* **2350 – 2354**

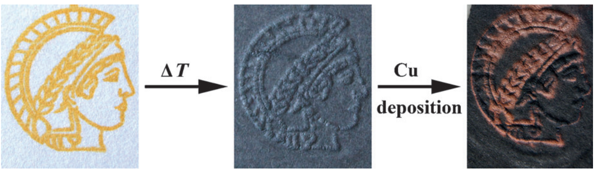
The Supramolecular Balance for Transition-Metal Complexes: Assessment of Noncovalent Interactions in Phosphoramidite Palladium Complexes

The virtue of enantiomers: A general method has been developed for measuring the individual contributions of noncovalent interactions within transition-metal complexes and dissecting them from electronic effects. On Pd complexes with one enantiopure and two enantiomeric phosphoramidite ligands, it was experimentally shown that modulations in extended CH–π and π–π interaction interfaces provide a $\Delta\Delta G$ value that is significant for stereoselection.

Printed Electronics

S. Glatzel, Z. Schnepp, C. Giordano* **2355 – 2358**

From Paper to Structured Carbon Electrodes by Inkjet Printing



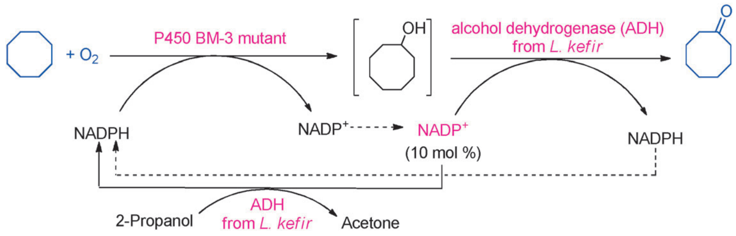
Electrodes from the ink-jet printer: Cellulose sheets can be transformed into mesostructured graphene nanostructures by a simple and general method. Since the iron catalyst can be printed on paper with an ink-jet printer, the products can be prepared with 2D patterns. Subsequent Cu deposition results in further functionalization of the microstructured electrodes (see picture).

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Alkane Oxidation

S. Staudt, E. Burda, C. Giese, C. A. Müller, J. Marienhagen, U. Schwaneberg, W. Hummel, K. Drauz, H. Gröger* ______ **2359 – 2363**

Direct Oxidation of Cycloalkanes to Cycloalkanones with Oxygen in Water

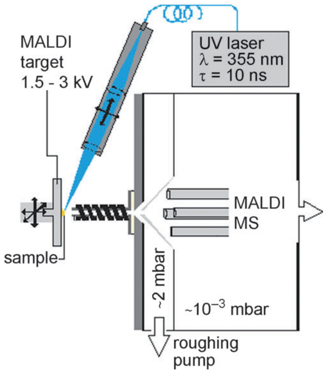


It doesn't take much to oxidize cycloalkanes directly to the corresponding cyclic ketones: molecular oxygen as the oxidant, water as the solvent, the cofactor $NADP^+$ (and a little 2-propanol to reduce it), as well as two catalytic enzymes—a hydroxylating P450 monooxygenase and an alcohol dehydrogenase (see scheme).

Biological Mass Spectrometry

R. Cramer,* A. Pirkl, F. Hillenkamp, K. Dreisewerd ______ **2364 – 2367**

Liquid AP-UV-MALDI Enables Stable Ion Yields of Multiply Charged Peptide and Protein Ions for Sensitive Analysis by Mass Spectrometry



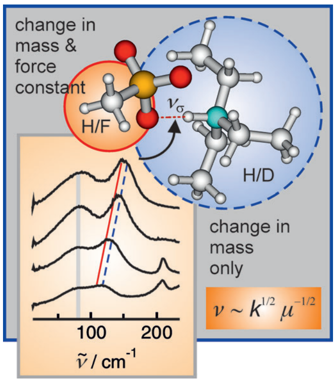
All charged up: High and prolonged yields of multiply charged peptide and protein ions can be formed in MALDI mass spectrometry using liquid UV-MALDI matrices and a heated ion-transfer tube. The key features are low laser energies of 1–10 μJ, resulting in fluences of less than 200 to 2000 J m^{-2} and low sample ablation, high sensitivity, and continuous ion generation over tens of thousands of laser shots.

Interaction Energy

K. Fumino, V. Fossog, K. Wittler, R. Hempelmann, R. Ludwig* ______ **2368 – 2372**

Dissecting Anion–Cation Interaction Energies in Protic Ionic Liquids

The strength of the interaction between anions and cations in protic ionic liquids (PILs) can be extracted from far-IR spectra. A suitable set of specially synthesized PILs was used to correct the frequency shifts of these low vibrational modes for contributions resulting from changing reduced masses only. The experimental results were confirmed by DFT calculations.



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).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Angewandte Corrigendum

The authors of this Communication wish to correct the author information in reference [10c]. The authors also wish to add a new citation as reference [10e] with regard to the polymer synthesis. The correct reference [10] should be as follows:

---

[10] See, for example: D. M. Lynn, R. Langer, *J. Am. Chem. Soc.* **2000**, *122*, 10761–10768; b) Y.-L. Lin, G. Jiang, L. K. Birrell, M. E. H. El-Sayed, *Biomaterials* **2010**, *31*, 7150–7166; c) L. V. Christensen, C.-W. Chang, W. J. Kim, S. W. Kim, Z. Zhong, C. Lin. J. F. J. Engbersen, J. Feijen, *Bioconjugate Chem.* **2006**, *17*, 1233–1240; d) R. S. Burke, S. H. Pun, *Bioconjugate Chem.* **2010**, *21*, 140–150; e) C. Lin, C.-J. Blaauboer, M. M. Timoneda, M. C. Lok, M. van Steenbergen, W. E. Hennink, Z. Zhong, J. Feijen, J. F. J. Engbersen, *J. Controlled Release* **2008**, *126*, 166–174.

A Bioreducible Polymer for Efficient Delivery of Fas-Silencing siRNA into Stem Cell Spheroids and Enhanced Therapeutic Angiogenesis

M. S. Shim, S. H. Bhang, K. Yoon,
K. Choi, Y. Xia* **11899–11903**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201206595

Angewandte Corrigendum

While the two reported organometallic reactions (**2**→**4** and **4**→**5**) mediated by cage **1** are new, the overall reaction (**2**→**5**) in a common solvent has been reported by Knox and co-workers for R = Ph.[13,14] Therefore, reference [14] is cited as an additional paper and the following sentence must be deleted from the introduction: "The overall reaction provides the first example of a photochemical organometallic transformation of a Ru_2 dinuclear complex that occurs across the two metal centers."

---

[14] J. N. L. Dennett, S. A. R. Knox, K. M. Anderson, J. P. H. Charmant, A. G. Orpen, *Dalton Trans.* **2005**, 63–73.

A Remarkable Organometallic Transformation on a Cage-Incarcerated Dinuclear Ruthenium Complex

S. Horiuchi, T. Murase,
M. Fujita* **12029–12031**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201206325

Angewandte Corrigendum

The authors of this Communication unintentionally provided the incorrect recommended name "9β-presilphiperfolan-1α-ol" for the natural product isolated by König and Leitão. The correct name should instead be "9β-presilphiperfolan-1β-ol" to reflect the *syn* orientation of the hydroxy group relative to the C9-methyl group of the natural product. This error appears in the table-of-contents graphic, a portion of the article text, and a portion of the Supporting Information.

Enantioselective Total Synthesis of the Reported Structures of (−)-9-*epi*-Presilphiperfolan-1-ol and (−)-Presilphiperfolan-1-ol: Structural Confirmation and Reassignment and Biosynthetic Insights

A. Y. Hong, B. M. Stoltz* **9674–9678**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201205276

Angewandte Corrigendum

Low-Valent Ge_2 and Ge_4 Species Trapped by N-Heterocyclic Gallylene

A. Doddi, C. Gemel, M. Winter,
R. A. Fischer,* C. Goedecke,
H. S. Rzepa, G. Frenking* ____ **450–454**

Angew. Chem. Int. Ed. **2013**, *52*

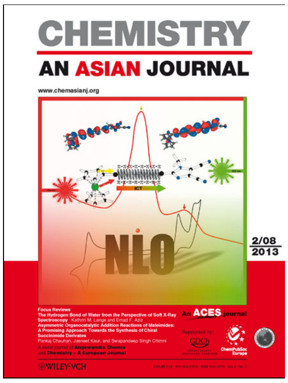
DOI: 10.1002/anie.201204440

After publication of this Communication, the authors learned about theoretical and experimental studies of four-membered cyclic compounds containing a B_2E_2 moiety (E = N, P, As) which possess a similar bonding situation as in their Ge_2Ga_2 species.[1–3] In particular, the isolated and structurally characterized 1,3-dibora-2,4-diphosphoniocyclobutane-1,3-diyl which has a cyclic B_2P_2 fragment exhibits a transannular B–B π bond without a B–B σ bond.[1] Thus, the Ge_2Ga_2 compound described in the Communication is not the first example of a stable species which exhibits a π bond between two atoms without a σ bond. The authors are grateful to Didier Bourissou for drawing their attention to these precedents.

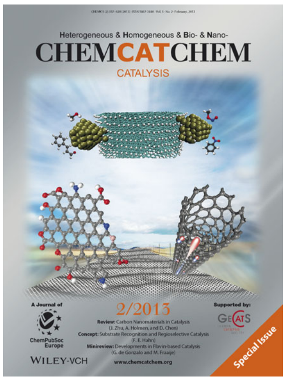
---

[1] D. Scheschkewitz, H. Amii, H. Gornitzka, W.W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880.
[2] W. W. Schoeller, A. Rozhenko, D. Bourissou, G. Bertrand, *Chem. Eur. J.* **2003**, *9*, 3611.
[3] G. Fuks, N. Saffon, L. Maron, G. Bertrand, D. Bourissou, *J. Am. Chem. Soc.* **2009**, *131*, 13681.

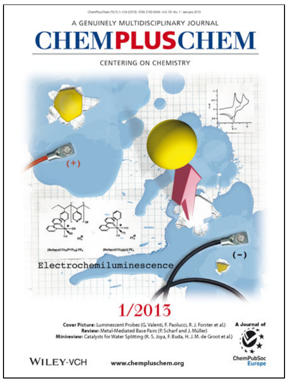
Check out these journals:



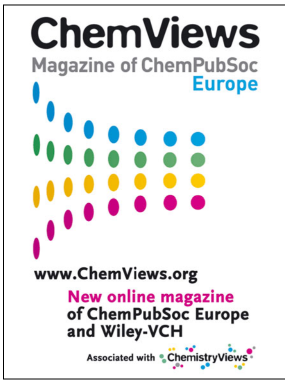
www.chemasianj.org



www.chemcatchem.org



www.chempluschem.org



www.chemviews.org

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim