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

*T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey**
Preparation of a Dihydrogen Complex of Cobalt

X. Zeng, H. Beckers, H. Willner,* J. F. Stanton*
Elusive Diazirinone, N_2CO

*J. H. Schrittwieser, V. Resch, J. Sattler, W.-D. Lienhart, K. Durchschein, A. Winkler, K. Gruber, P. Macheroux, W. Kroutil**
Biocatalytic Enantioselective Oxidative C–C Coupling by Aerobic C–H Activation

Z. Zhao, E. L. Jacovetty, Y. Liu, H. Yan**
Encapsulation of Gold Nanoparticles in a DNA-Origami Cage

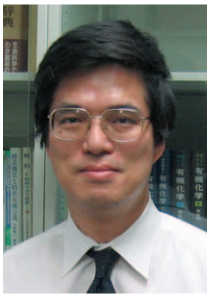
*T. Reiner, E. J. Keliher, S. Earley, B. Marinelli, R. Weissleder**
Synthesis and In Vivo Imaging of an ^{18}F-Labeled PARP1 Inhibitor by a Chemically Orthogonal Scavenger-Assisted High-Performance Method

*D. T. Cohen, B. Cardinal-David, K. A. Scheidt**
Lewis Acid Activated Synthesis of Highly Substituted Cyclopentanes by the N-Heterocyclic-Carbene-Catalyzed Addition of Homoenolate Equivalents to Unsaturated Ketoesters

M. Barsukova-Stuckart, N. V. Izarova, G. B. Jameson, V. Ramachandran, Z. Wang, J. v. Tol, N. S. Dalal, R. N. Biboum, B. Keita, L. Nadjo, U. Kortz**
The Dicopper(II)-Containing 22-Palladate(II) $[Cu^{II}_2Pd^{II}_{22}P^{V}_{12}O_{60}(OH)_8]^{20-}$

F. Liao, Y. Huang, J. Ge, W. Zheng, K. Tedsree, P. Collier, X. Hong, S. C. Tsang**
Morphology-Dependent Interactions of ZnO with Cu Nanoparticles at the Materials Interface in the Selective Hydrogenation of CO_2 to CH_3OH

Author Profile

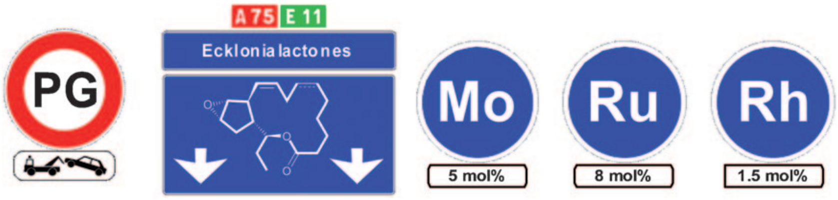


"When I was eighteen I wanted to be an organic chemist, although I didn't know what it really meant.
The biggest challenge facing scientists is how to deal with the depletion of energy sources and other resources. …"
This and more about Nobuharu Iwasawa can be found on page 1224.

Books

Highlights

Total Synthesis



Meet the challenge! The time has come for organic chemists to devise more economically and ecologically sustainable strategies for multistep synthesis. One way to meet this challenge is to achieve protecting-group-free total synthesis. The recent progress accomplished in the field of catalyzed reactions will help chemists to meet this challenge (see figure; PG = protecting group).

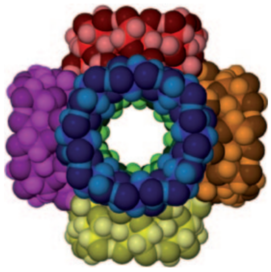
Contents

Metal–Organic Frameworks

K. T. Holman* ______ **1228 – 1230**

Molecule-Constructed Microporous Materials: Long under Our Noses, Increasingly on Our Tongues, and Now in Our Bellies

Emerging roles for MOFs: Crystalline microporous materials constructed from molecular components have been known for over four decades, and are increasingly utilized in the context of materials design. Recent developments in the field of metal–organic frameworks (MOFs) further highlight the roles of design and serendipity at the crossroads of emerging applications for this family of materials, from robust dynamics to food science.

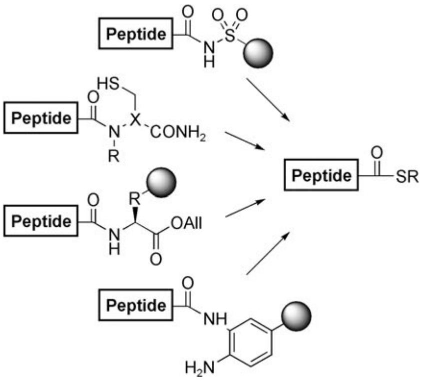


Minireviews

Solid-Phase Synthesis

F. Mende, O. Seitz* ______ **1232 – 1240**

9-Fluorenylmethoxycarbonyl-Based Solid-Phase Synthesis of Peptide α-Thioesters



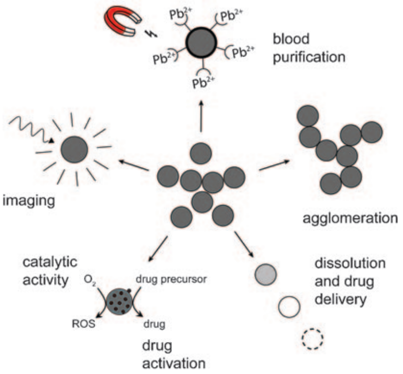
Fast ways to Rome: Peptide thioesters are key intermediates in convergent protein synthesis. Fmoc-based solid-phase synthesis usually provides rapid and reliable access to peptide derivatives; however, the base-lability of the thioester bond presents a formidable challenge. Intensive research efforts have led to the development of new methods which overcome limitations in yield and practicability.

Reviews

Nanomedicine

W. J. Stark* ______ **1242 – 1258**

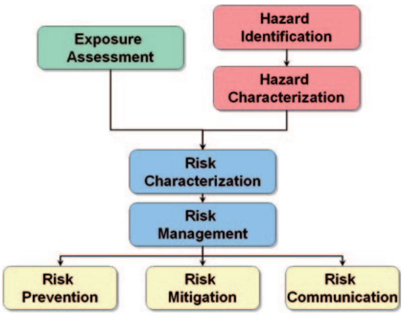
Nanoparticles in Biological Systems



Particles in motion: Nanoparticles combine the properties of a traditional solid (magnetic, optic, mechanic, radiation) with the mobility of molecules, including the ability to diffuse inside an organism. This combination opens up fascinating opportunities for medical treatments, industrial processes, and improved consumer products—but the environmental aspects must also be considered.

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$ 9442/8583 (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.

Nanotechnology safety research combines biology, chemistry, and physics with workplace hygiene and material sciences into a substantial interdisciplinary field of research. Sustainability and reliability are the pillars of the success of this new technology, and the safety of applications is founded on findings that are based on robust, reliable testing strategies.



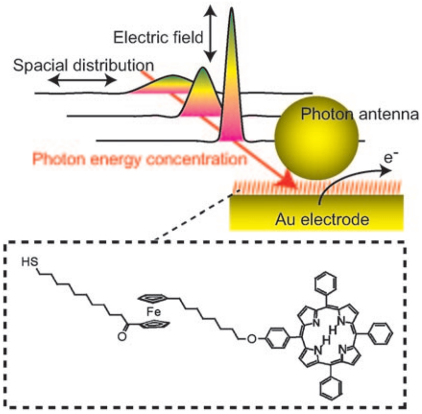
Nanotoxicology

H. F. Krug,* P. Wick ______ **1260 – 1278**

Nanotoxicology: An Interdisciplinary Challenge

Communications

Feeling the squeeze: The performance of a molecular-based photoenergy conversion system is substantially enhanced by addition of plasmonic photon-absorbing antennae that enable incoming light to be “squeezed” in the photosensitive organic monolayer (see picture). The antenna structure is optimized for use in self-assembled monolayers formed on an atomically smooth metal electrode.



Energy Conversion

K. Ikeda,* K. Takahashi, T. Masuda, K. Uosaki* ______ **1280 – 1284**

Plasmonic Enhancement of Photoinduced Uphill Electron Transfer in a Molecular Monolayer System

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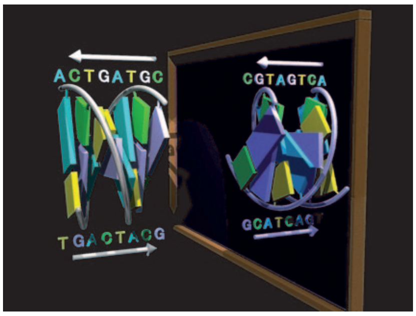


Mimicking the masters: An artificial nucleic acid, serinol nucleic acid (SNA), formed oligomers in which natural nucleobases were tethered through its 2-amino-1,3-propanediol (serinol) scaffold. These SNA oligomers have two unique properties: their chirality is controllable by sequence design and can be inverted by reversing the sequence (see picture), and they can cross-hybridize with DNA and RNA with sufficient thermal stability.

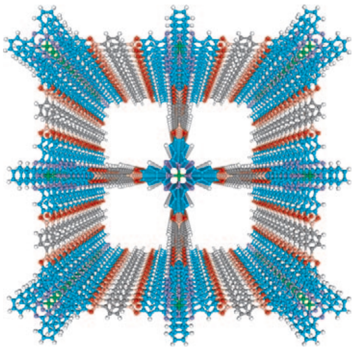
Artificial Nucleic Acids

H. Kashida, K. Murayama, T. Toda, H. Asanuma* ______ **1285 – 1288**

Control of the Chirality and Helicity of Oligomers of Serinol Nucleic Acid (SNA) by Sequence Design

---

A light COF: Two-dimensional covalent organic frameworks of a nickel phthalocyanine have been synthesized. Owing to well-ordered stacking of the phthalocyanine units, the resulting 2D framework provides enhanced and broad light absorbance and facilitates charge transport. The material becomes highly photoconductive and is exceptionally sensitive to deep-red visible and near-infrared light.



Organic Frameworks

X. Ding, J. Guo, X. Feng, Y. Honsho, J. Guo, S. Seki, P. Maitarad, A. Saeki, S. Nagase, D. Jiang* ______ **1289 – 1293**

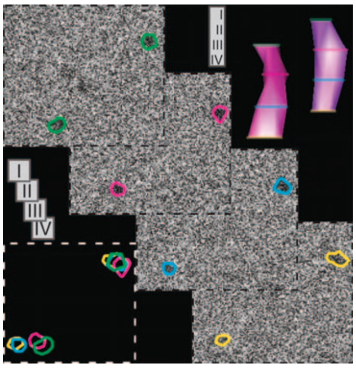
Synthesis of Metallophthalocyanine Covalent Organic Frameworks That Exhibit High Carrier Mobility and Photoconductivity

Molecular Sieves

L. Karwacki, D. A. M. de Winter,
L. R. Aramburo, M. N. Lebbink, J. A. Post,
M. R. Drury,
B. M. Weckhuysen* ______ **1294 – 1298**

Architecture-Dependent Distribution of Mesopores in Steamed Zeolite Crystals as Visualized by FIB-SEM Tomography

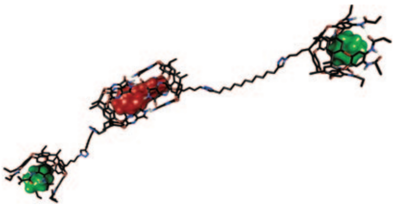
Break on through: Steaming-induced mesopores of individual ZSM-5 crystals were studied by a combination of focused ion beam (FIB) and scanning electron microscopy (SEM) tomography (see picture). In this manner, quantitative insight into the width, length, morphology, and distribution of mesopores generated within zeolite crystals has been obtained.



Host–Guest Compounds

A. Lledó, S. Kamioka, A. C. Sather,
J. Rebek, Jr.* ______ **1299 – 1301**

Supramolecular Architecture with a Cavitand–Capsule Chimera

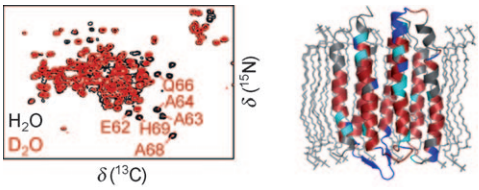


Molecule-within-molecule complexes are widely used in supramolecular chemistry for studies of molecular recognition and catalysis. Self-assembled hosts isolate their guests from the bulk media and reveal unique molecular behaviors. An assembly that features well-differentiated and non-interacting binding sites stabilized through hydrogen-bonding interactions is described (see picture).

Protein Structures

L. Shi, I. Kawamura, K.-H. Jung,
L. S. Brown,*
V. Ladizhansky* ______ **1302 – 1305**

Conformation of a Seven-Helical Transmembrane Photosensor in the Lipid Environment



Break on through: High-resolution multidimensional solid-state NMR spectroscopy was used to refine the molecular conformation of a seven-helical transmembrane photoreceptor in lipids (see picture, right). H/D exchange experiments (see picture, left; black spectrum: H_2O, red spectrum: D_2O) reveal the solvent-exposed surface of the protein, which is asymmetrically positioned in the bilayer.

Electronic Decay

N. V. Kryzhevoi,*
L. S. Cederbaum* ______ **1306 – 1309**

Using pH Value To Control Intermolecular Electronic Decay

pH deed: Intermolecular Coulombic decay (ICD) is an ultrafast relaxation pathway of a highly excited system. A theoretical investigation of ammonia dimers and trimers shows that the ICD efficiency is regulated by protonation or deprotonation. Varying the ICD rate by changing the environmental pH value provides a control over the relaxation dynamics (see scheme).

Frontiers in Silicon Chemistry 2011

1st Munich Forum on Functional Materials

April 14 – 15, 2011

Frontiers in Silicon Chemistry 2011 –
1st Munich Forum on Functional Materials

is an international symposium with special emphasis on new groundbreaking results in silicon-based materials (silicon, silicone, silica, and hybrid materials) with a potential for interesting new applications.

The Silicon Institute of the Technische Universität München (TUM) and Wacker Chemie AG are jointly hosting this new event to foster a scientific exchange of views on new topics in material-oriented silicon chemistry. The program will be rounded out by social evenings with renowned scientists and special guests. The first event of its kind, the forum will take place every two years at the TUM's Garching Campus, outside Munich, Germany.

Program

WED April 13, 2011
Registration
Welcome mixer (evening only)

THU April 14, 2011
Registration
Opening
Oral presentations
Poster session & social get-together

FRI April 15, 2011
Oral presentations
Closing ceremony

More information
www.makro.ch.tum.de/si-frontiers2011

Speakers

Florence Babonneau, France
Bhanu Chauhan, USA
Céline Croutxé Barghorn, France
Michael Fröba, Germany
Ferdinand Gonzaga, Canada
Nicola Hüsing, Austria
Tsuyoshi Kato, France
Guido Kickelbick, Germany
Paul Lickiss, United Kingdom
Norbert W. Mitzel, Germany
Aziz Muzafarov, Russia
Gerhard Sextl, Germany
James C. Sturm, USA
Jonathan G.C. Veinot, Canada
Ulrich Wiesner, USA
Michel Wong Chi Man, France

jointly hosted by Technische Universität München
and Wacker Chemie AG, Munich, Germany

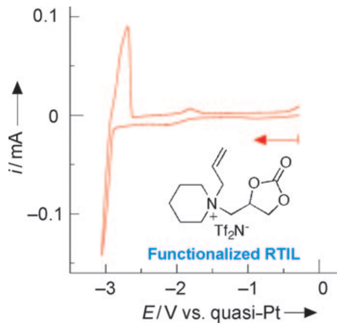
WACKER-Lehrstuhl - Institut für Siliciumchemie
Technische Universität München

Administration Franziska Graf antwort@makro.ch.tum.de +49 89 289 - 135 66

Ionic Liquids

T. Tsuda,* K. Kondo, T. Tomioka,*
Y. Takahashi, H. Matsumoto, S. Kuwabata,
C. L. Hussey ______ **1310 – 1313**

Design, Synthesis, and Electrochemistry of Room-Temperature Ionic Liquids Functionalized with Propylene Carbonate



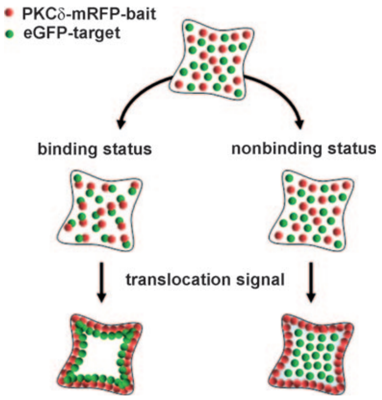
A PC organic salt: A series of piperidinium salts with a covalently attached propylene carbonate (PC) moiety provides a novel room-temperature ionic liquid (RTIL). This uniquely functionalized RTIL exhibits favorable electrochemical stability, leading to lithium metal deposition/stripping.

Protein–Protein Interactions

K.-B. Lee, J. M. Hwang, I. S. Choi, J. Rho,
J.-S. Choi, G.-H. Kim, S. I. Kim, S. Kim,*
Z.-W. Lee* ______ **1314 – 1317**

Direct Monitoring of the Inhibition of Protein–Protein Interactions in Cells by Translocation of PKCδ Fusion Proteins

Seeing is believing: When a bait protein is fused to protein kinase C (PKCδ), the proteins can interact and cotranslocate from the cytoplasm to the plasma membrane (see picture; imaging with red and green fluorescent proteins (RFP and GFP)). In contrast, when the bait–target interaction is inhibited, only the bait protein is translocated to the plasma membrane. This method was applied to several protein pairs.

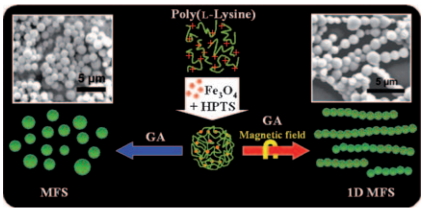


Anisotropic Nanohybrids

A. J. Amali, P. Saravanan,
R. K. Rana* ______ **1318 – 1321**

Tailored Anisotropic Magnetic Chain Structures Hierarchically Assembled from Magnetoresponsive and Fluorescent Components

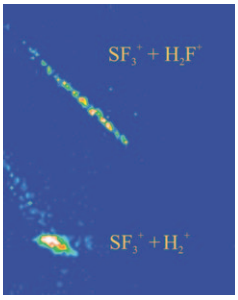
Chains for the better: A poly(L-lysine)-mediated self-assembly of citrate-functionalized Fe_3O_4 nanoparticles and hydroxy pyrene trisulfonate (HPTS) forms magnetoresponsive fluorescent spheres (MFS) in the presence of glutaric dialdehyde (GA). If the assembly is performed in the presence of a permanent magnet then 1D magnetic beaded-chain structures are formed (see scheme).



Reactivity of Dications

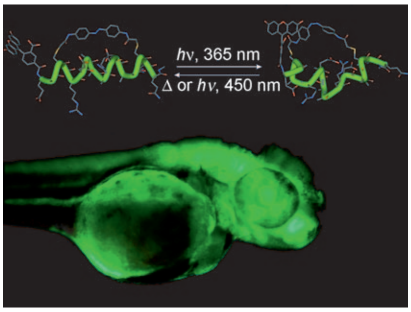
J. F. Lockyear, M. A. Parkes,
S. D. Price* ______ **1322 – 1324**

Fast and Efficient Fluorination of Small Molecules by SF_4^{2+}



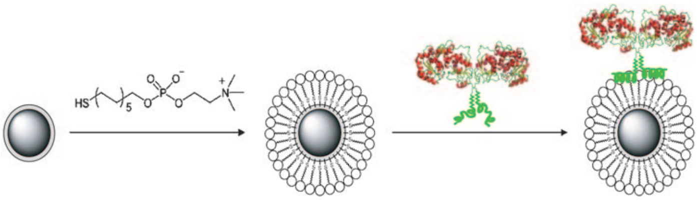
Doubly charged, highly efficient: The use of a mass spectrometric technique specifically designed to monitor the reactions of dications has revealed that gaseous SF_4^{2+} is a powerful fluorinating agent. The fluorination of different classes of compounds (Ar, CO, CH_4, C_2H_4, and H_2) has been efficiently achieved in the gas phase (see picture). Of particular note is the formation of C–F bonds in the reactions with organic compounds.

In Vivo Imaging



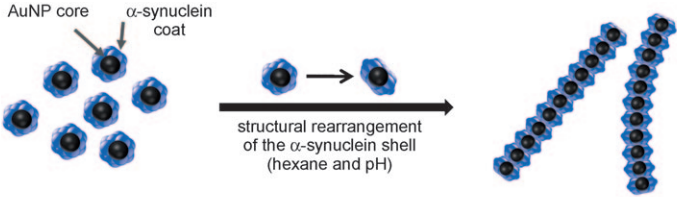
Switching zebrafish: A fluorescent reporter peptide permits imaging of azobenzene photoisomerization in vivo (see picture), which indicates that azobenzene-based photochemical switches may be generally useful for spatiotemporal control in living systems.

Protein Immobilization



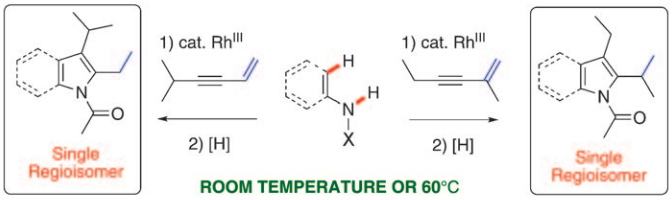
Turning tail: The specific functions of C-terminal cationic amphipathic peptide in the formation of bacterial membrane-bound glycosyltransferases have been demonstrated. This mechanism was applied to a general concept that allows highly oriented immobilization of enzymes on membrane-mimetic solid surfaces, such as recombinant full-length *H. pylori* α1,3-fucosyltransferase on a magnetic bead (see picture).

Nanotechnology



Nano bling: Pea-pod-type chains of gold nanoparticles were fabricated within a dielectric amyloid protein nanofibrillar matrix by the assembly of gold nanoparticles (AuNPs) coated with α-synuclein (see scheme). Instantaneous AuNP alignment into anisotropic chain structures was directed by either treatment with hexane or a pH change. The resulting AuNP-embedded dielectric protein matrix exhibits photoconductivity with visible light.

Heterocycles



Rho-Rho-Rho your boat: A rhodium catalyst effects the regioselective oxidative coupling of enynes with *N*-aryl ureas ($X = NR_2$) and *N*-vinylacetamides ($X = C(O)Me$), affording the corresponding 2-alkenylindoles and 2-alkenylpyrroles in good yield. Simple hydrogenation delivers the C2/C3-aliphatic-substituted indole or pyrrole (see scheme).

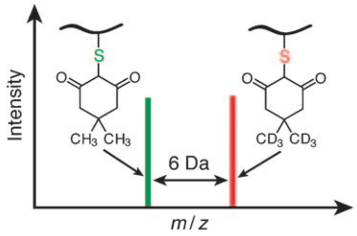
Contents

Redox Proteomics

Y. H. Seo, K. S. Carroll* 1342–1345

Quantification of Protein Sulfenic Acid Modifications Using Isotope-Coded Dimedone and Iododimedone

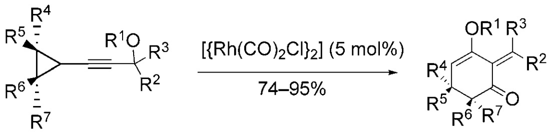
Quantitative proteomics: The new technique mentioned in the title—in short, ICDID—enables quantification of sulfenic acid modifications in proteins (see picture). The approach permits S-hydroxylation site occupancy to be monitored at individual cysteines within a single protein and is compatible with peptide-based proteomic strategies.



Rhodium Catalysis

D. Shu, X. Li, M. Zhang, P. J. Robichaux, W. Tang* 1346–1349

Synthesis of Highly Functionalized Cyclohexenone Rings: Rhodium-Catalyzed 1,3-Acyloxy Migration and Subsequent [5+1] Cycloaddition

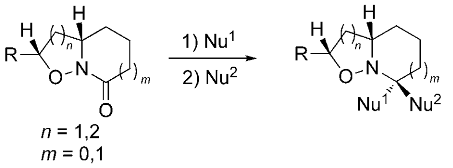


Lead Rh-ole: Highly substituted cyclohexenones were prepared from cyclopropyl-substituted propargyl esters by using a $[\{Rh(CO)_2Cl\}_2]$ catalyst. This metal catalyst promoted the 1,3-acyloxy migration of propargyl esters and a subsequent [5+1] cycloaddition of the resulting allenylcyclopropanes in the presence of CO with high regioselectivity.

Synthetic Methods

G. Vincent,* R. Guillot, C. Kouklovsky* 1350–1353

Stereodivergent Synthesis of Substituted N,O-Containing Bicyclic Compounds by Sequential Addition of Nucleophiles to *N*-Alkoxybicyclolactams

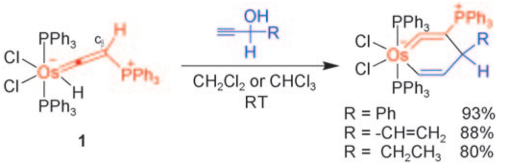


In control! *N*-alkoxybicyclolactams derived from the ring-rearrangement metathesis of nitroso Diels–Alder cycloadducts were subjected to the successive addition of two nucleophiles to yield substituted piperidine or pyrrolidine precursors with good to excellent stereoselectivity. The relative configuration of the newly formed stereocenter can be controlled by the order of addition of the two nucleophiles.

Cycloaddition

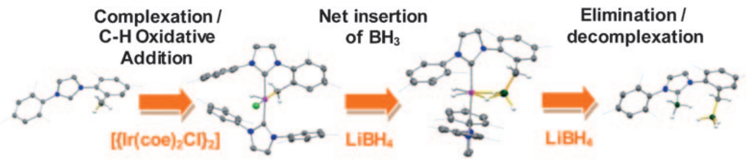
Q. Zhao, L. Gong, C. Xu, J. Zhu,* X. He, H. Xia* 1354–1358

Stable Iso-osmabenzenes from a Formal [3+3] Cycloaddition Reaction of Metal Vinylidene with Alkynols



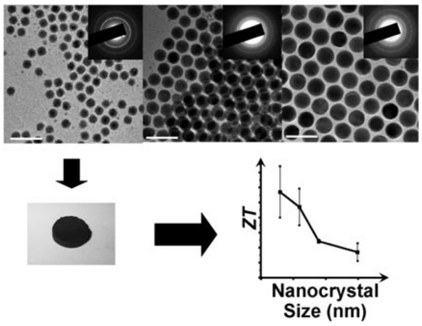
The magic of Os: An unprecedented formal [3+3] cycloaddition reaction of **1** with alkynols affords stable iso-osmabenzenes at room temperature (see scheme). The phosphonium substituent at the C_β position and the $18e^-$ nature of the compound play key roles in the origin of the high thermal stability of the products. Isomerization of iso-osmabenzenes into η^5-cyclopentadienyl complexes through metalated cyclopentadiene intermediates is also described.

C–H Borylation



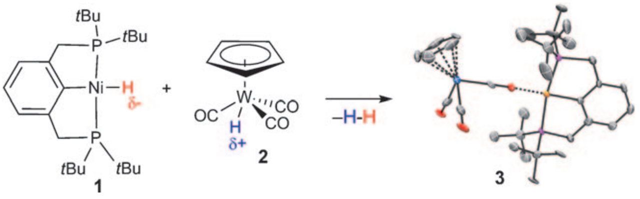
Simple source: An intramolecular iridium-mediated C–H borylation proceeds through transfer of a BH_3 fragment from borohydride to a benzylic carbon center (see scheme; coe = cyclooctene). Simple and inexpensive $LiBH_4$ is thus utilized as the boron source in C–H to C–B conversion.

Thermoelectric Nanocrystals



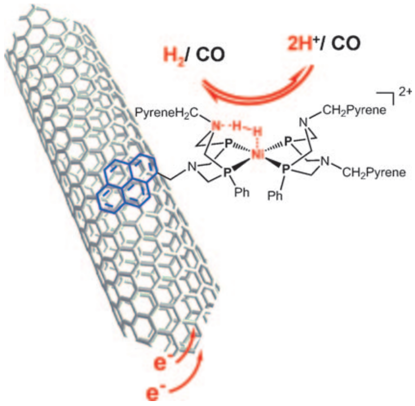
Pressed Bi nanocrystals synthesized by a simple colloidal method exhibited very high electrical conductivity of 10^4–10^5 S m^{-1} and extremely low thermal conductivity of 0.35 W m^{-1} K^{-1}. The synthetic method can be used for the inexpensive preparation of highly efficient thermoelectric materials by engineering the size of nanocrystals (see picture; scale bar 50 nm; *ZT* = figure of merit).

Transition-Metal Hydrides



Reaction of the acidic tungsten(II) hydride **2** with the nickel(II) pincer complex **1** in either THF or toluene after an initial dihydrogen bonding (DHB) interaction led to the formation of the Ni–W bimetallic species **3** (see picture). The first example of DHB between two metal hydrides with opposite polarity was analyzed by NMR and IR spectroscopy, X-ray crystallography, and DFT calculations.

Bioinspired Nanocatalysts



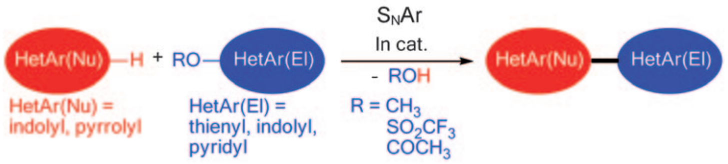
Go with the CO: The functionalization of multiwalled carbon nanotubes with molecular complexes through π–π stacking produces robust, noble-metal-free electrocatalytic nanomaterials for H_2 evolution and uptake. The catalysts are compatible with the conditions encountered in classical proton-exchange membrane devices and are tolerant of the common pollutant CO, thus offering significant advantages over traditional Pt-based catalysts.

Contents

Indium Catalysis

T. Tsuchimoto,* M. Iwabuchi, Y. Nagase, K. Oki, H. Takahashi ______ **1375 – 1379**

Indium-Catalyzed Heteroaryl–Heteroaryl Bond Formation through Nucleophilic Aromatic Substitution

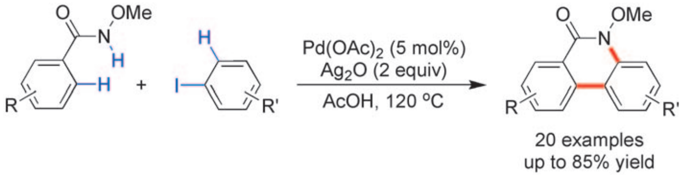


Unique performance: Bi-, ter-, and quater-heteroaryls have been prepared under indium catalysis by nucleophilic aromatic substitution (S_NAr). This is the first example of catalytic heteroaryl–heteroaryl bond formation based on S_NAr between two heteroaryl substrates without needing activating groups to enhance their reactivity (see scheme; El = electrophile, In = In(OTf)$_3$ or In(ONf)$_3$, Nu = nucleophile).

C–H Activation

G.-W. Wang,* T.-T. Yuan, D.-D. Li ______ **1380 – 1383**

One-Pot Formation of C–C and C–N Bonds through Palladium-Catalyzed Dual C–H Activation: Synthesis of Phenanthridinones

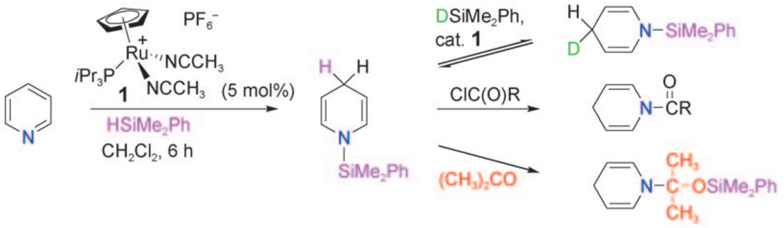


Two cycles in one pot! The synthesis of biologically important phenanthridinones has been achieved by the one-pot formation of C–C and C–N bonds through a palladium-catalyzed dual C–H activation, which involves four bond ruptures and two bond formations (see scheme). The conversion of phenanthridinones into natural product like derivatives further demonstrates the utility of this synthetic achievement.

Synthetic Methods

D. V. Gutsulyak, A. van der Est, G. I. Nikonov* ______ **1384 – 1387**

Facile Catalytic Hydrosilylation of Pyridines

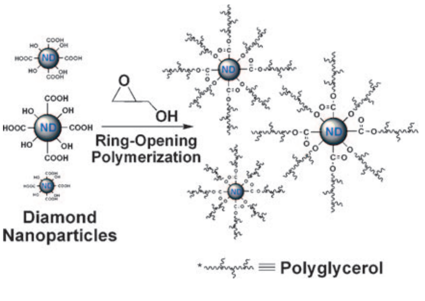


Not only surprisingly facile, a hydrosilylation of pyridines under the catalysis of [Cp(*i*Pr$_3$P)Ru(NCCH$_3$)$_2$]$^+$ has the advantages that it is 1,4-regioselective and reversible. The products can be transformed in a variety of ways (see scheme). The related complex [CpRu(NCCH$_3$)$_3$]$^+$ catalyzes the two-hydrogen-atom reduction of phenanthroline by HSiMe$_2$Ph/water.

Nanodiamonds

L. Zhao, T. Takimoto, M. Ito, N. Kitagawa, T. Kimura, N. Komatsu* ____ **1388 – 1392**

Chromatographic Separation of Highly Soluble Diamond Nanoparticles Prepared by Polyglycerol Grafting

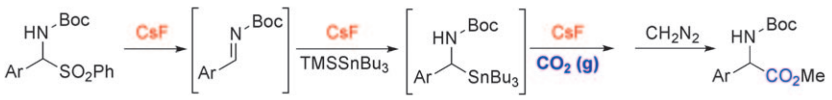


Making even tiny diamonds valuable: Nanodiamonds (NDs) were covalently functionalized with hyperbranched polyglycerol (PG) by ring-opening polymerization to improve their suitability for biomedical applications (see scheme). The PG-grafted NDs were highly soluble not only in pure water (> 20 mg mL^{-1}), but also in a buffer (> 16 mg mL^{-1}), and were separated according to size by size-exclusion chromatography.

Amino Acid Synthesis

T. Mita,* J. Chen, M. Sugawara,
Y. Sato* ________ **1393 – 1396**

One-Pot Synthesis of α-Amino Acids from Imines through CO_2 Incorporation: An Alternative Method for Strecker Synthesis



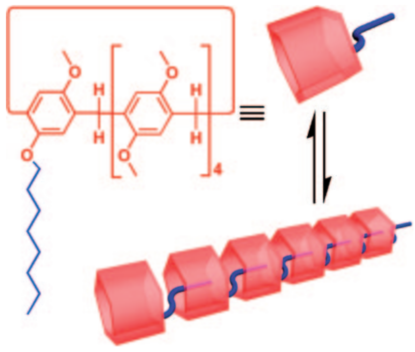
It's a gas: A novel one-pot process for the synthesis of α-amino acids from imine equivalents using CO_2 gas as a carbon source has been developed. This reaction was made possible by the reagent combination of $TMSSnBu_3$ and CsF (see scheme). Three successive reactions (imine formation, stannylation, and carboxylation) proceeded in the same flask under these conditions to give products in up to 79% yield. Boc = *tert*-butoxycarbonyl, TMS = trimethylsilyl.

Supramolecular Polymers

Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu,
Z. Ma, F. Huang* ________ **1397 – 1401**

Formation of Linear Supramolecular Polymers That Is Driven by C–H⋯π Interactions in Solution and in the Solid State

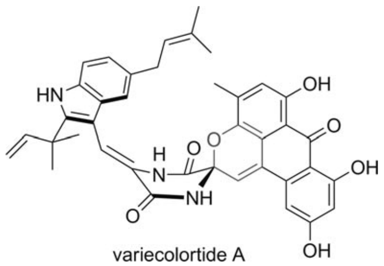
Copillararene convoy: A linear supramolecular polymer can be efficiently constructed in solution with a copillararene monomer (see picture). Single-crystal X-ray analysis and NMR spectroscopy revealed that aggregation was enthalpically driven by quadruple C–H⋯π interactions between the octyl tail (blue) and the aromatic cavity (red).



Natural Product Synthesis

C. A. Kuttruff, H. Zipse,*
D. Trauner* ________ **1402 – 1405**

Concise Total Syntheses of Variecolortides A and B through an Unusual Hetero-Diels–Alder Reaction



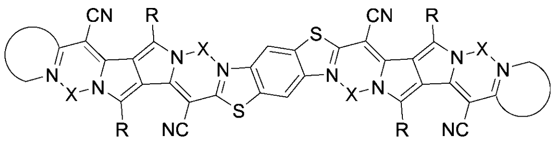
variecolortide A

A fusion of certain anthraquinones and diketopiperazines is an apt description of the variecolortides, a family of unusual fungal alkaloids. In a new, concise total synthesis of the variecolortides A and B, the natural racemates are obtained highly convergently and almost without protecting-group manipulations. The spirocyclic core is generated in a hetero-Diels–Alder reaction of a 1,4-anthraquinone with a didehydrodiketopiperazine.

NIR Dyes

G. M. Fischer, E. Daltrozzo,
A. Zumbusch* ________ **1406 – 1409**

Selective NIR chromophores: Bis(Pyrrolopyrrole) Cyanines

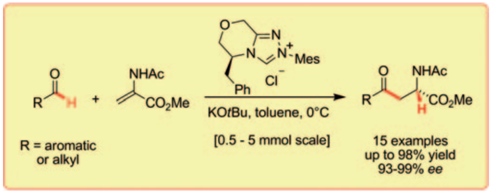


Very invisible: Bis(pyrrolopyrrole) cyanines are extended chromophores based on diketopyrrolopyrroles (general structure shown). The compounds are characterized by extremely high extinction coefficients, narrowband absorption in the near-IR range, and strong fluorescence around 1 μm. Since absorption in the visible region is negligible, they approach the ideal of selective NIR absorbers.

Asymmetric organocatalysis

T. Jousseaume, N. E. Wurz,
F. Glorius* ______________ 1410 – 1414

Highly Enantioselective Synthesis of α-Amino Acid Derivatives by an NHC-Catalyzed Intermolecular Stetter Reaction



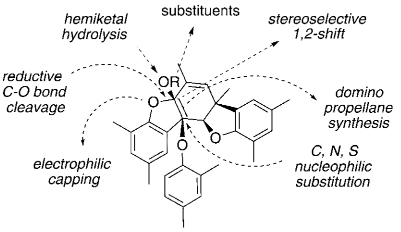
PROTONtype: An NHC-catalyzed (NHC = N-heterocyclic carbene), highly asymmetric intermolecular Stetter reaction allows the atom-economic and efficient formation of valuable α-amino acid derivatives (see scheme); the key step is an intramolecular stereoselective protonation. For the first time, a β-unsubstituted Michael acceptor was employed successfully in this kind of reaction, most importantly, with a broad range of different aldehydes.

Scaffold Diversity

J. Barjau, G. Schnakenburg,
S. R. Waldvogel* ______________ 1415 – 1419

Diversity-Oriented Synthesis of Polycyclic Scaffolds by Modification of an Anodic Product Derived from 2,4-Dimethylphenol

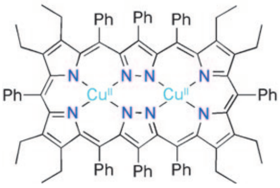
Like a Swiss army knife: The pentacycle shown, which results from the anodic oxidation of 2,4-dimethylphenol, displays a wealth of potential reactivity. Depending on the applied reaction conditions a variey of polycyclic architectures are obtained with impressive stereo-, regio-, and chemoselectivity.

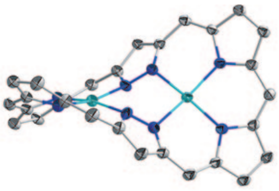


Expanded Porphyrins

L. K. Frensch, K. Pröpper, M. John,
S. Demeshko, C. Brückner,*
F. Meyer* ______________ 1420 – 1424

Siamese-Twin Porphyrin: A Pyrazole-Based Expanded Porphyrin Providing a Bimetallic Cavity



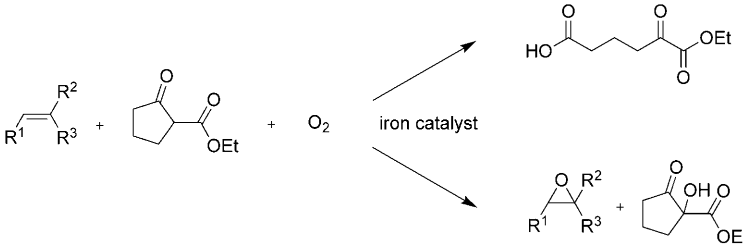


Porphyrins joined at the hip: A long-sought expanded porphyrin has been synthesized that contains two porphyrin-like {N$_4$} binding sites linked by two bridging pyrazole units. Structural and spectroscopic evidence indicates the absence of macrocyclic aromatic π conjugation. In its dicopper complex (see picture) the two magnetic Cu^{II} orbitals are nearly orthogonal, and consequently this represents the first ferromagnetically coupled doubly pyrazolato-bridged complex.

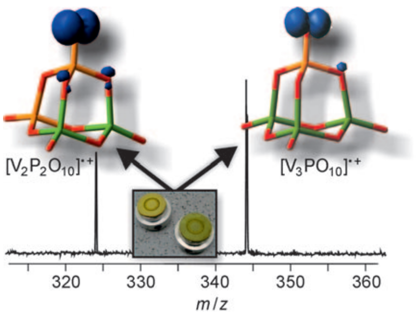
Catalytic Oxidation

K. Schröder, B. Join, A. J. Amali, K. Junge,
X. Ribas, M. Costas,*
M. Beller* ______________ 1425 – 1429

A Biomimetic Iron Catalyst for the Epoxidation of Olefins with Molecular Oxygen at Room Temperature



It's no sacrifice: A bio-inspired iron system, in which a β-keto ester serves as a sacrificial cosubstrate, readily epoxidizes olefins under ambient conditions with air. Aromatic olefins are oxidized in high yields with excellent chemoselectivity. Mechanistic investigations point out substantial differences to well-known radical-based autoxidations.



Composition counts! With a combination of inorganic synthesis as well as computational and mass spectrometry studies, the title cluster ions $[V_nP_{4-n}O_{10}]^{\bullet+}$ ($n=2, 3$; see picture) have been generated and their reactions with CH_4, C_2H_4, and C_2H_6 investigated. In addition to thermal C–H bond activation of methane, an unexpected reactivity towards the C_2-hydrocarbons has been uncovered.

C–H Activation

N. Dietl, R. F. Höckendorf, M. Schlangen,
M. Lerch, M. K. Beyer,
H. Schwarz* **1430–1434**

Generation, Reactivity Towards Hydrocarbons, and Electronic Structure of Heteronuclear Vanadium Phosphorous Oxygen Cluster Ions

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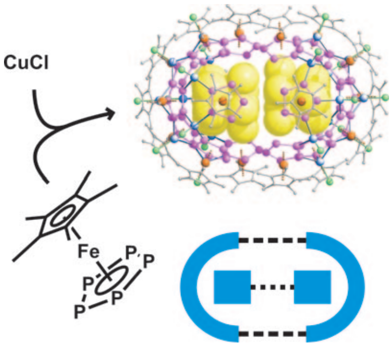

A giant organometallic molecule and a 2D coordination polymer are formed by template-assisted self-assembly between CuCl and the *cyclo*-P_5 complex $[Cp^*Fe(\eta^5-P_5)]$. The giant capsular molecule exhibits a skeleton of 110 inorganic core atoms and consists of two half-shells with threefold symmetry. Dipersion forces between two encapsulated $[Cp^*Fe(\eta^5-P_5)]$ guest complexes and half-shells are responsible for the cohesion of the capsule (see structure and model; $Cp^*=\eta^5-C_5Me_5$).

Organometallic Nanocapsules

S. Welsch, C. Gröger, M. Sierka,
M. Scheer* **1435–1438**

An Organometallic Nanosized Capsule Consisting of *cyclo*-P_5 Units and Copper(I) Ions

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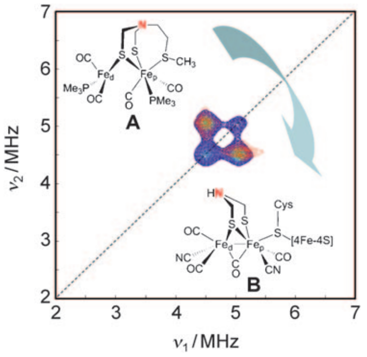

Convincing evidence for the presence of a nitrogen atom in the dithiolate bridge of the active site of native [FeFe] hydrogenases (**B**) is provided by a spectroscopic, electrochemical, and theoretical study of a well-characterized structural mimic of the [FeFe] hydrogenase subcluster (picture: ^{14}N matched-HYSCORE spectrum of the model compound **A**). This result should help to understand the mechanism of dihydrogen conversion and production.

Hydrogenase Models

Ö. F. Erdem,* L. Schwartz, M. Stein,
A. Silakov, S. Kaur-Ghumaan, P. Huang,
S. Ott,* E. J. Reijerse,
W. Lubitz* **1439–1443**

A Model of the [FeFe] Hydrogenase Active Site with a Biologically Relevant Azadithiolate Bridge: A Spectroscopic and Theoretical Investigation

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

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