



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

J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao*

Single Fused Gene Approach to Photoswitchable and Fluorescent Biliproteins

Y. Sohma,* Q. Hua, J. Whittaker, M. A. Weiss, S. B. H. Kent*
Design and Folding of [GluA4(O β ThrB30)]Insulin (Ester Insulin), a Minimal Proinsulin Surrogate Chemically Convertible into Human Insulin

S. Yang, X. Feng,* L. Wang, K. Tang, J. Maier, K. Müllen*
Graphene-Based Nanosheets with a 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 by Using Metalated Binuclear Rhodium Complexes

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

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

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

Qi Wang, M. Zhang, C. Chen, W. Ma, J. Zhao*
Photocatalytic Aerobic Oxidation of Alcohols on TiO₂: The Acceleration Effect of Bronsted Acids

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



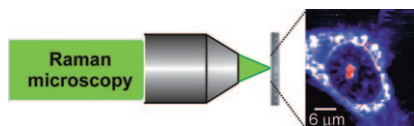
“When I was eighteen I wanted to be either a chemist or a paleontologist.

My favorite piece of research is the development of stereochemistry ...”

This and more about Gerhard Erker can be found on page 4536–4538.

Author Profile

Gerhard Erker _____ 4536–4538



A view of the room: A novel application of Raman microscopy takes advantage of a spectral window to map the uptake and distribution of metal-carbonyl-based drugs in single cells. The approach provides information on cell structure and molecular structure simultaneously and may have significant impact on drug screening and on the analysis of cellular processes in general.

Highlights

Raman Microscopy

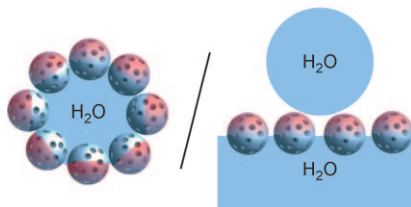
P. Hildebrandt* _____ 4540–4541

A Spectral Window to the Cell

Structure Hierarchy

U. Jonas,* M. Vamvakaki — 4542–4543

From Fluidic Self-Assembly to
Hierarchical Structures—
Superhydrophobic Flexible Interfaces



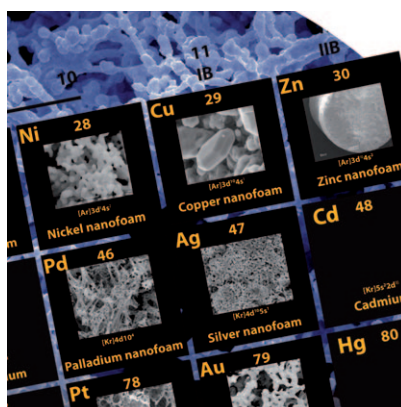
Two-faced: Through the combination of complex structural hierarchy and chemical diversity, amphiphilic Janus particles with a superhydrophobic and a hydrophilic hemisphere self-assemble at the air–water interface to form highly flexible and impregnable water-repelling layers. These layers of Janus particles have fascinating properties: for example, water droplets can rest on top of such a layer floating on water (see picture).

Reviews

Porous Materials

B. C. Tappan,* S. A. Steiner III,*
E. P. Luther — 4544–4565

Nanoporous Metal Foams

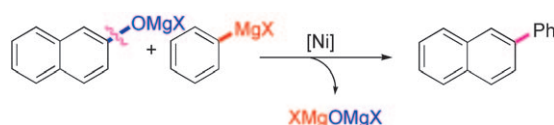


The holey grail of metallic materials: Synthetic pathways for preparing nanoporous metals foams have recently been demonstrated, opening a new frontier of high-surface-area catalysts and conductive materials. The scope and potential of techniques for preparing nanoporous metal foams are assessed with a focus on combustion synthesis employing metal bistetrazolamine complexes.

Communications

C–O Bond Activation

D.-G. Yu, B.-J. Li, S. F. Zheng, B.-T. Guan,
B.-Q. Wang, Z.-J. Shi* — 4566–4570



Direct Application of Phenolic Salts to
Nickel-Catalyzed Cross-Coupling
Reactions with Aryl Grignard Reagents

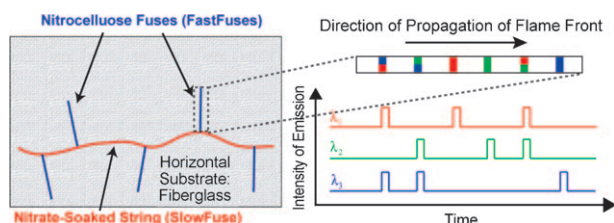
You're nickel'd pal! The first successful coupling reaction with the direct application of naphtholates as electrophiles (see scheme, X = halide) improves both the step economy and atom economy of

cross-coupling reactions whilst decreasing the cost of preparing complex scaffolds from readily available phenol derivatives.

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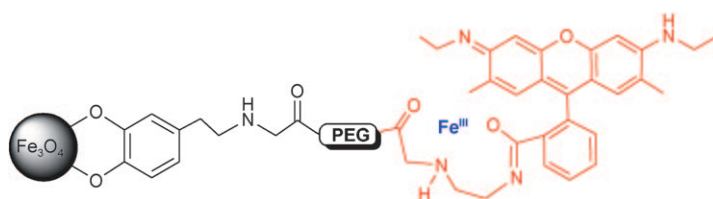
“Infuse” for long: “Infuses”—chemically based systems for non-electronic communication that can transmit alphanumeric information encoded as pulses of light (see picture)—can now operate for

hours without extinction. These characteristics improve their potential for a new approach to information technology that combines chemistry and information—“infochemistry”.

Infochemistry

C. Kim, S. W. Thomas III,
G. M. Whitesides* — 4571–4575

Long-Duration Transmission of
Information with Infuses



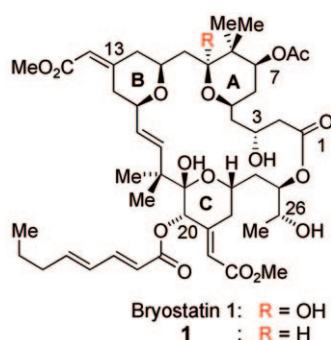
Rh-odin’s masterpiece: Coupling *N*-(rhodamine-6G)lactam-ethylenediamine to Fe_3O_4 nanoparticles through a polyethylene glycol chain renders the rhodamine unit more water soluble and useful for

sensitive and selective detection of Fe^{III} at the 2 ppb level in water. This sensitivity is also demonstrated in HeLa cells, thus indicating potential applications of this detection method in biological systems.

Cation Sensors

B. D. Wang, J. Hai, Z. C. Liu, Q. Wang,
Z. Y. Yang,* S. Sun* — 4576–4579

Selective Detection of Iron(III) by
Rhodamine-Modified Fe_3O_4
Nanoparticles

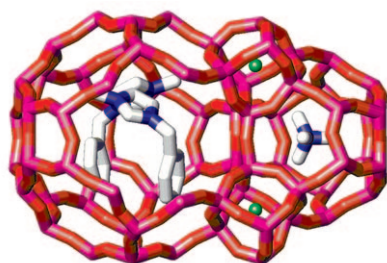


‘OH’ no you don’t: The title compound **1** has been synthesized and evaluated for biological function. Molecular modeling of bryostatin **1** with the C1 domain of protein kinase C δ indicates that the C9–OH of bryostatin **1** makes a hydrogen-bonding contact to the protein. Despite the absence of the hydrogen-bonding contact for **1**, it displays bryostatin-like biological effects in four assays using either U937 leukemia cells or prostate LNCaP cells.

Structure–Activity Relationship

G. E. Keck,* Y. B. Poudel, A. Rudra,
J. C. Stephens, N. Keddi, N. E. Lewin,
M. L. Peach,
P. M. Blumberg — 4580–4584

Molecular Modeling, Total Synthesis, and
Biological Evaluations of C9-Deoxy
Bryostatin **1**



Structurally sound: The synthesis of AlPO_4 -LTA zeolite in ionic liquids employs 1-benzyl-3-methylimidazolium, tetramethylammonium, and fluoride ions for structuring α cages, sodalite cages, and cubes (see picture; C gray, N blue, O red, Al and P purple, F green). Selective removal of 1-benzyl-3-methylimidazolium ions results in a stable AlPO_4 -LTA molecular sieve. The α cages of AlPO_4 -LTA framework can be evacuated while maintaining structural integrity.

Zeolites

E. J. Fayad, N. Bats,* C. E. A. Kirschhock,
B. Rebours, A.-A. Quoineaud,
J. A. Martens — 4585–4588

A Rational Approach to the Ionothermal
Synthesis of an AlPO_4 Molecular Sieve
with an LTA-Type Framework



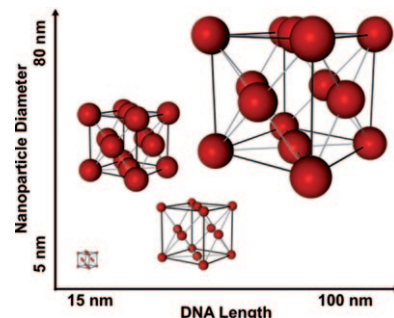
DNA-Programmed Assembly

R. J. Macfarlane, M. R. Jones, A. J. Senesi,
K. L. Young, B. Lee, J. Wu,
C. A. Mirkin* ————— 4589–4592



Establishing the Design Rules for DNA-Mediated Programmable Colloidal Crystallization

DNA-programmable colloidal crystals are assembled with 5–80 nm nanoparticles, and the lattice parameters of the resulting crystals vary from 25 to 225 nm. A predictable and mathematically definable relationship between particle size and DNA length dictates the assembly and crystallization processes, creating a set of design rules for DNA-based nanoscale assembly.

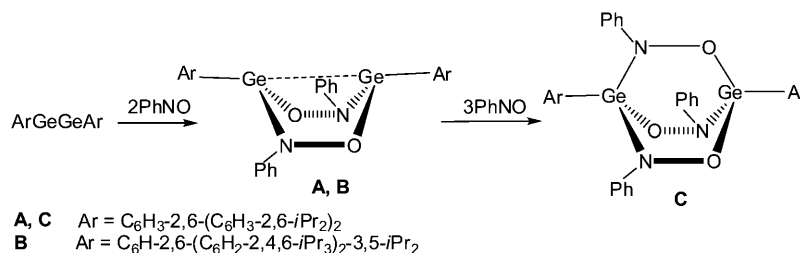


Germacyclic Compounds

X. Wang, Y. Peng, Z. Zhu, J. C. Fetting,
P. P. Power,* J. Guo,
S. Nagase ————— 4593–4597



Synthesis and Characterization of Two of the Three Isomers of a Germanium-Substituted Bicyclo[2.2.0]hexane Diradicaloid: Stretching the Ge–Ge Bond



Germane cycles: The inorganic bi- and tricyclohexane derivatives **A–C** provide novel coordination modes of a nitrosoarene to metals. DFT calculations show

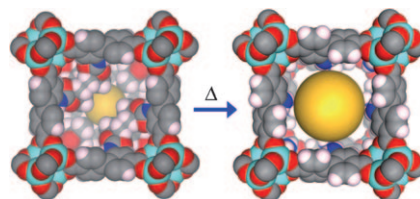
that **A** and **B** correspond to two of three possible stable isomers of the parent diradicaloid that have different Ge–Ge bond lengths.

Metal–Organic Frameworks

R. K. Deshpande, J. L. Minnaar,
S. G. Telfer* ————— 4598–4602



Thermolabile Groups in Metal–Organic Frameworks: Suppression of Network Interpenetration, Post-Synthetic Cavity Expansion, and Protection of Reactive Functional Groups



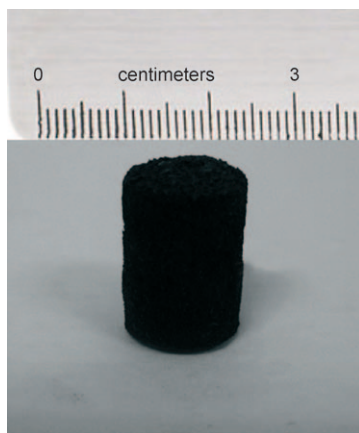
Creating nothing out of something: A bulky *tert*-butoxycarbonyl group on a biphenyl-4,4'-dicarboxylate ligand suppresses interpenetration to give an open, cubic metal–organic framework. Post-synthetic cleavage of this group by simple thermolysis (see picture) unmasks a potentially reactive amino functional group, increases the void space (yellow sphere), and widens the pore apertures.

Nanostructures

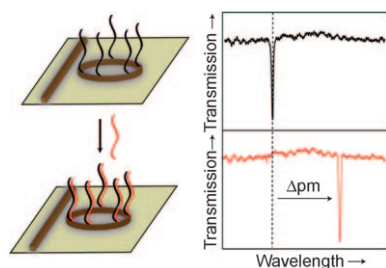
Z. H. Tang, S. L. Shen, J. Zhuang,
X. Wang* ————— 4603–4607



Noble-Metal-Promoted Three-Dimensional Macroassembly of Single-Layered Graphene Oxide



Barreling along: 3D macrostructures (cylinder; see picture) have been assembled from single-layered graphene oxide and noble-metal nanocrystals (Au, Ag, Pd, Ir, Rh, Pt, etc.). Although the density of the cylinders is very low (ca. 0.03 g cm^{−3}), they show excellent mechanical properties and have been utilized as a fixed-bed catalyst for the Heck reaction, which proceeded with nearly 100% selectivity and conversion.

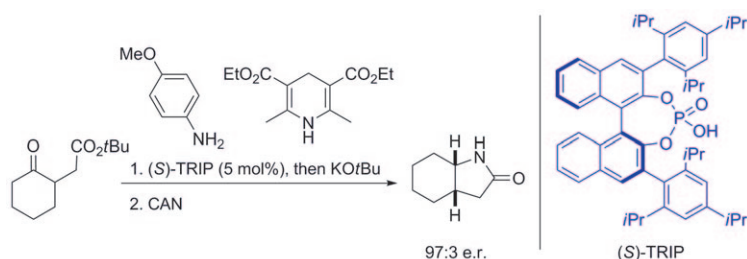


Microrings for microRNAs! A label-free method has been developed for the sensitive detection of microRNAs utilizing arrays of silicon photonic microring resonators. This simple and modularly multiplexable method for the direct profiling of microRNA within 10 minutes meets a number of challenges faced by current methodologies in this area.

Biosensors

A. J. Qavi, R. C. Bailey* — 4608–4611

Multiplexed Detection and Label-Free Quantitation of MicroRNAs Using Arrays of Silicon Photonic Microring Resonators



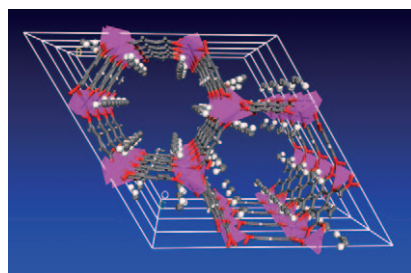
Branching out: An organocatalytic reductive amination of α -branched ketones using dynamic kinetic resolution is reported. The *cis*-2-substituted cyclohexyl

amines were obtained in high diastereoselectivity and enantioselectivity from the corresponding ketones.

Organocatalysis

V. N. Wakchaure, J. Zhou, S. Hoffmann, B. List* — 4612–4614

Catalytic Asymmetric Reductive Amination of α -Branched Ketones

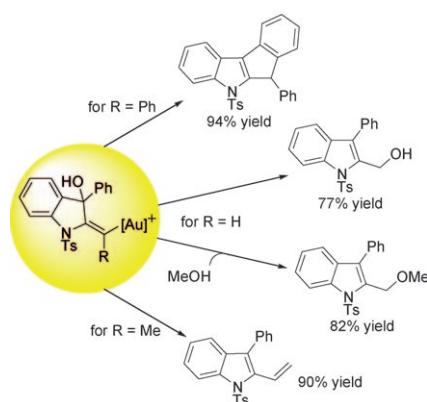


On the metal: Open metal sites within isostructural $[M_2(\text{DHTP})]$ metal–organic frameworks ($M = \text{Co}^{2+}$, Mn^{2+} , Mg^{2+} , and Zn^{2+} ; DHTP = 2,5-dihydroxyterephthalate) exhibit differential molecular recognition with acetylene. The extremely strong interaction of Co^{2+} with acetylene (see structure) makes $[\text{Co}_2(\text{DHTP})]$ the highest volumetric acetylene storage material with a capacity of $230 \text{ cm}^3 \text{ cm}^{-3}$ at 295 K and 1 atm.

Metal–Organic Frameworks

S.-C. Xiang, W. Zhou, Z.-J. Zhang, M. A. Green, Y. Liu,*
B. Chen* — 4615–4618

Open Metal Sites within Isostructural Metal–Organic Frameworks for Differential Recognition of Acetylene and Extraordinarily High Acetylene Storage Capacity at Room Temperature



A great combination: A putative indolyl-substituted vinyl gold species generated in situ from AuCl/AgOTf catalyzed the title transformation. Under these reaction conditions, indenyl-fused and 2,3-disubstituted indole derivatives were produced in good to excellent yields of up to 94% (see scheme).

Homogeneous Catalysis

P. Kothandaraman, W. Rao, S. J. Foo, P. W. H. Chan* — 4619–4623

Gold-Catalyzed Cycloisomerization Reactions of 2-Tosylaminophenylprop-1-yn-3-ols as a Versatile Approach for Indole Synthesis

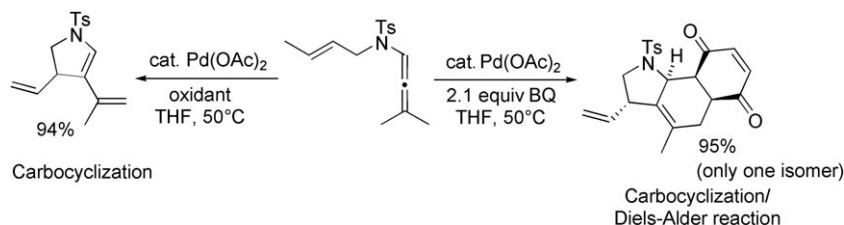


Carbocyclization

A. K. Å. Persson,
J.-E. Bäckvall* 4624–4627



Palladium(II)-Catalyzed Oxidative Carbocyclization of Aza-Enallenes



Live and let diene: A palladium(II)-catalyzed oxidative carbocyclization reaction of aza-enallenes provides access to potentially valuable heterocyclic dienes. In the presence of a dieneophile during the

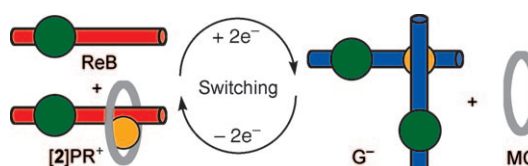
carbocyclization step, the products can react further in a one-pot cyclization/ Diels–Alder sequence to give polycyclic products. BQ = *para*-benzoquinone.

Switchable Architectures

K. Parimal, E. H. Witlicki,
A. H. Flood* 4628–4632



Interconverting Two Classes of Architectures by Reduction of a Self-Sorting Mixture



Two for the price of one: A Cu^I -based [2]pseudorotaxane ($[2]PR^+$) shows a complete switch in its architectural identity when it transforms into a “grid corner”

(G^-) and back again upon two-electron reduction (see picture; ReB: neutral (red) or reduced ligand (blue); Re: green; Cu: orange; MC: macrocycle).

Chiral indenenes

A. Martínez, P. García-García,
M. A. Fernández-Rodríguez, F. Rodríguez,
R. Sanz* 4633–4637



Gold(I)-Catalyzed Enantioselective Synthesis of Functionalized Indenes

Can you dig it? An asymmetric synthesis of functionalized 1*H*-indenenes from easily available *ortho*-(alkynyl)styrene derivatives under mild reaction conditions has been achieved. The reactions proceed through an unprecedented and selective 5-*endo-dig* gold(I)-catalyzed cycloisomerization or alkoxylation, if water or an alcohol is present (see scheme).

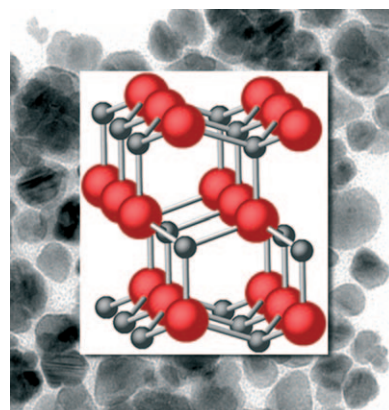


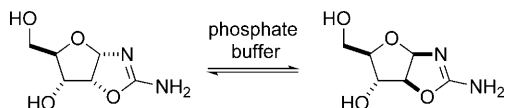
Nanoparticles

I. T. Sines, R. Misra, P. Schiffer,
R. E. Schaak* 4638–4640

Colloidal Synthesis of Non-Equilibrium Wurtzite-Type MnSe

Stabilizing an elusive phase: The wurtzite polymorph of the magnetic semiconductor MnSe, which is also the $x=1$ end member of the widely studied $Zn_{1-x}Mn_xSe$ solid solution, was synthesized in high yield for the first time as colloidal nanoparticles using a solution chemistry technique at low temperature (see pictures). Nanoparticles of wurtzite-type MnSe have an optical bandgap of approximately 3.5–3.8 eV and show evidence of antiferromagnetic ordering at 64 K.





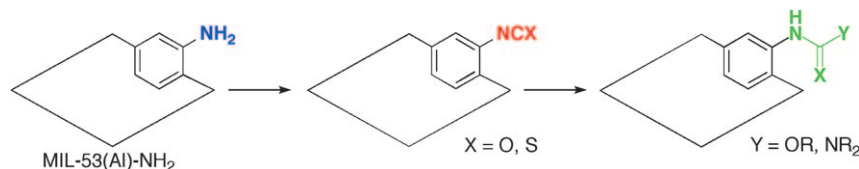
Flipping stereochemistry: Inorganic phosphate catalyzes the interconversion of ribose and arabinose aminooxazolines, suggesting that the prebiotic synthesis of

enantiopure pyrimidine ribonucleotides might have involved a single stereoinversion at C1' and a double stereoinversion at C2'.

Nucleotide Stereochemistry

M. W. Powner,
J. D. Sutherland* 4641–4643

Phosphate-Mediated Interconversion of *Ribo*- and *Arabino*-Configured Prebiotic Nucleotide Intermediates



MILs hold up: Robust aluminum-based metal–organic frameworks (MIL-53(Al)-NH₂) can undergo postsynthetic modification with phosgene reagents to produce

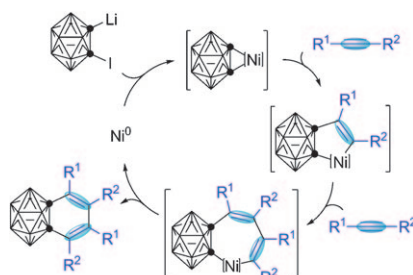
highly reactive, porous materials bearing isocyanate or isothiocyanate groups (see scheme).

Metal–Organic Frameworks

C. Volkringer, S. M. Cohen* 4644–4648

Generating Reactive MILs: Isocyanate- and Isothiocyanate-Bearing MILs through Postsynthetic Modification

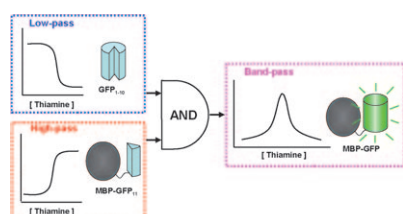
A View [2+2+2] a Kill: For the first time, nickel-catalyzed [2+2+2] cycloaddition reactions of alkynes or diynes with carbonyne using 1-iodo-2-lithiocarborane as a precursor have been achieved. The mechanism is proposed after the structural confirmation of the key intermediate, nickelacyclopentene.



Cycloaddition Reactions

Z. Qiu, S. R. Wang, Z. Xie* 4649–4652

Nickel-Catalyzed Regioselective [2+2+2] Cycloaddition of Carbonyne with Alkynes

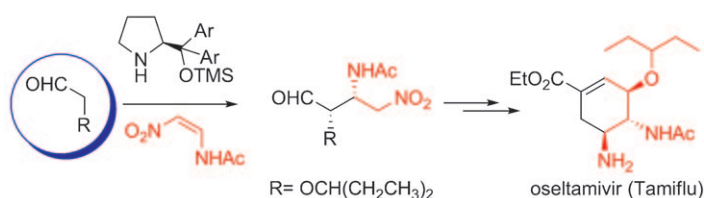


Light in the middle: A simple band-pass circuit has been designed using only posttranscriptional components in *Escherichia coli* (see figure). Two engineered riboswitches were used as the chemical sensor and to implement low-pass/high-pass functions. The two signals were integrated by protein complementation using split GFP fragments to achieve a band-pass response.

RNA Technology

N. Muranaka,
Y. Yokobayashi* 4653–4655

Posttranscriptional Signal Integration of Engineered Riboswitches Yields Band-Pass Output



Hey Mickey, you're so fine! Organocatalytic Michael additions of aldehydes with protected 2-amino-1-nitroethene could go through three different transition-states to afford adducts with usual and unusual

stereochemistry, thereby providing a facile entry to Tamiflu (see scheme) and substituted 3-aminopyrrolidines. TMS = trimethylsilyl, Ac = acetyl.

Organocatalysis

S. Zhu, S. Yu, Y. Wang,
D. Ma* 4656–4660

Organocatalytic Michael Addition of Aldehydes to Protected 2-Amino-1-Nitroethenes: The Practical Syntheses of Oseltamivir (Tamiflu) and Substituted 3-Aminopyrrolidines

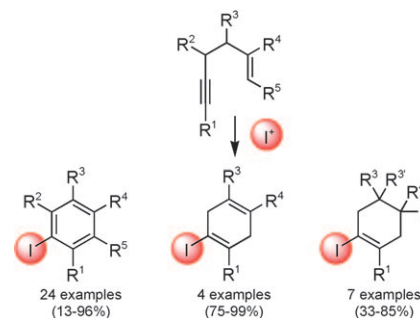
Carbocyclization

B. Crone, S. F. Kirsch,*
K.-D. Umland ————— 4661 – 4664



Electrophilic Cyclization of 1,5-Enynes

Valuable six-membered carbocycles including highly substituted benzenes, 1,4-cyclohexadienes, and 4-fluorocyclohexenes can be prepared from simple 1,5-enynes by iodonium-induced cyclization. This cyclization strategy was applied to the total synthesis of cybroadol, a sesquiterpenoid with a pentasubstituted aromatic core (see scheme).

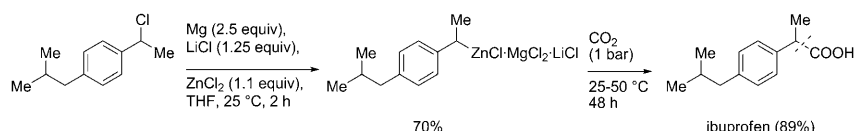


MgCl₂-Mediated Additions

A. Metzger, S. Bernhardt, G. Manolikakes,
P. Knochel* ————— 4665 – 4668



MgCl₂-Accelerated Addition of Functionalized Organozinc Reagents to Aldehydes, Ketones, and Carbon Dioxide



Pump it up! The sluggish reactivity of organozinc reagents in additions to aldehydes, ketones, and CO₂ can be increased by MgCl₂, which is usually generated in the preparation of the zinc reagent. The

direct reaction with CO₂, in particular, opens an expeditious route to phenylacetic acid derivatives, as demonstrated in a short synthesis of ibuprofen (see scheme).

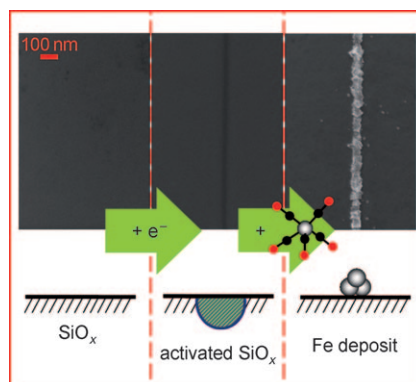


Nanotechnology

M.-M. Walz, M. Schirmer, F. Vollnhals,
T. Lukaszczuk H.-P. Steinrück,
H. Marbach* ————— 4669 – 4673



Electrons as “Invisible Ink”: Fabrication of Nanostructures by Local Electron Beam Induced Activation of SiO_x



Beam me up: A novel two-step process allows iron nanostructures to be generated locally on SiO_x/Si at 300 K. The surface is first locally activated by an electron beam. Then the activated structures are exposed to [Fe(CO)₅], which decomposes and grows autocatalytically to give pure Fe nanocrystals.

MicroRNA

C. E. Lünse, G. Michlewski, C. S. Hopp,
A. Rentmeister, J. F. Cáceres,
M. Famulok,* G. Mayer* — 4674 – 4677

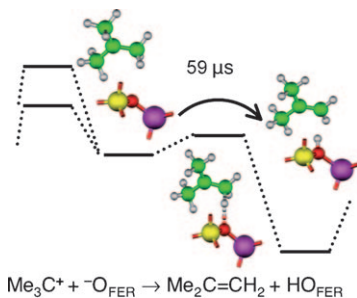


An Aptamer Targeting the Apical-Loop Domain Modulates pri-miRNA Processing

Gaining maturity: RNA aptamers can serve as specific targeting molecules to modulate the processing of pri-miRNAs. This approach can be used to selectively interfere with microRNA regulation and may open new routes for the development of novel therapies.



All experimental attempts to identify the *tert*-butyl carbenium ion in zeolites have been unsuccessful. Calculations with the hybrid MP2:DFT method predict that this ion is less stable than the isomeric surface species isobutene, isobutoxide, and *tert*-butoxide, but once it has been formed as an intermediate it will survive long enough (59 μ s) to be detected by laser spectroscopy (see picture; O red, Si yellow, Al magenta, C green).



Carbenium Ions

C. Tuma, T. Kerber, J. Sauer* 4678–4680

The *tert*-Butyl Cation in H-Zeolites: Deprotonation to Isobutene and Conversion into Surface Alkoxides



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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Authors 4683

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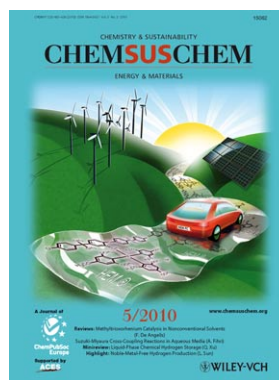
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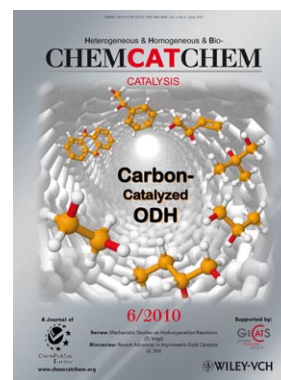
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