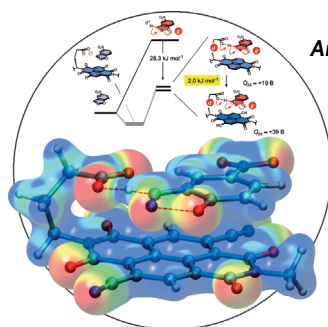
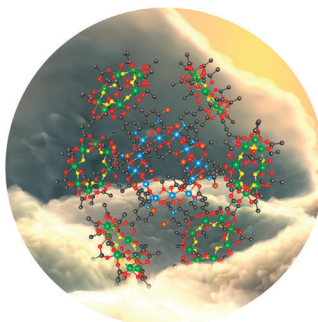


... is the first step of RNA structure determination by NMR spectroscopy. In their Communication on page 9996 ff., T. Carlomagno and co-workers present a suite of solid-state NMR experiments for RNA intranucleotide resonance assignment. These experiments open the way to structural studies of RNA by solid-state NMR spectroscopy.

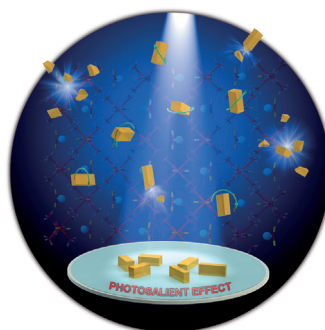
Nanoscale Assemblies

In their Communication on page 9932 ff., R. E. P. Winpenny et al. describe assemblies of polymetallic components that are linked together, such as six octametallic rings surround a dodecametallic central ring.



Anion- π Interactions

S. Matile et al. provide experimental evidence in their Communication on page 9940 ff. that anion- π interactions can contribute to catalysis. They also use simulations to show how the negative charge slides over the π -acidic surface of the catalyst.



Actuators

When subjected to a light stimulus, certain crystals jump to release the strain that accumulates in their interior as a result of a photochemical reaction, as P. Naumov, E. V. Boldyreva, et al. describe in their Communication on page 9990 ff.

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"... Given this explosion of 'sensor' research, one may ask the question why do we still have so few sensors for continuous monitoring of at least the most significant parameters in healthcare or the environment. Why do we still not have sensors to monitor Hg^{II} ions or other pollutants in groundwater, or glucose in the blood of diabetics for at least one month? ..."

Read more in the Editorial by Otto S. Wolfbeis.

Editorial

O. S. Wolfbeis* ————— 9864–9865

Probes, Sensors, and Labels:
Why is Real Progress Slow?

Spotlight on Angewandte's Sister Journals

Service

9882–9885



*"My motto is 'simple things first'.
My favorite composer is Johann Sebastian Bach. ..."*
This and more about Bernhard Breit can be found on page 9888.

Author Profile

Bernhard Breit ————— 9888–9889

News



A. Baldwin



J. F. Bower



A. Walsh



M. J. Gaunt

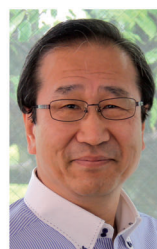


S. P. Armes

Royal Society of Chemistry
Prize Winners 2013 — 9890–9891



S. P. Nolan



S. Kitagawa



S. V. Ley



V. K. Aggarwal

Books

Design and Applications of Single-Site
Heterogeneous Catalysts

John Meurig Thomas

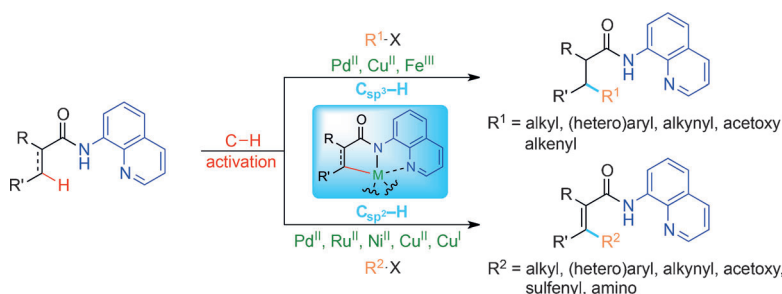
reviewed by J. Pérez-Ramírez — 9892

Highlights

C–H Activation

M. Corbet,* F. De Campo — 9896–9898

8-Aminoquinoline: A Powerful Directing
Group in Metal-Catalyzed Direct
Functionalization of C–H Bonds



Chelate me if you can: Over the last decade, strategies for the functionalization of both C_{sp^2} -H and C_{sp^3} -H bonds have witnessed an increasing use of a simple, yet powerful directing group,

8-aminoquinoline (in blue). This auxiliary is very efficient in a wide range of metal-mediated reactions, and can be readily removed to afford the desired carboxylic acids or corresponding derivatives.

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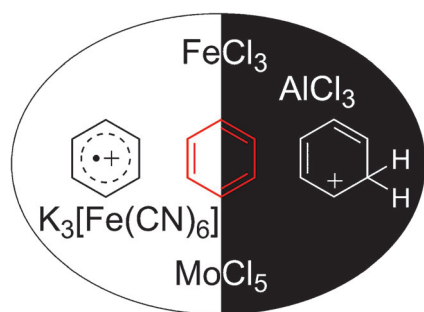
individuals who are personal members of
a national chemical society prices are available
on request. Postage and handling charges
included. All prices are subject to local VAT/
sales tax.

Reviews

Aromatic Dehydrogenation

M. Grzybowski, K. Skonieczny,
H. Butenschön,*
D. T. Gryko* _____ 9900–9930

Comparison of Oxidative Aromatic
Coupling and the Scholl Reaction



Where is the oxidant? Although the coupling of arenes in the presence of Lewis acids has been known for some time, the differentiation between reactions in the presence of a non-oxidizing Lewis acid (Scholl reaction) and in the presence of an oxidizing Lewis acid has been lost over the years. This Review highlights the similarities and differences between these reactions, which most probably proceed by two different mechanisms.

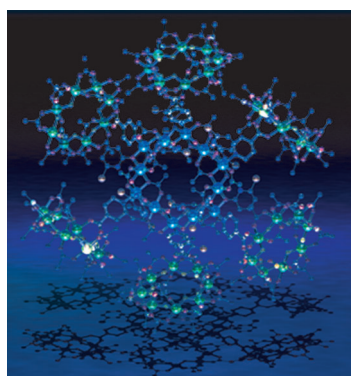
Communications

Nanoscale Polymetallic Assemblies

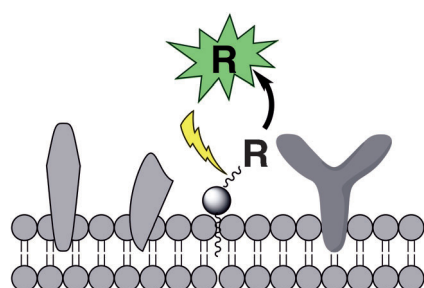
G. F. S. Whitehead, F. Moro, G. A. Timco,
W. Wernsdorfer, S. J. Teat,
R. E. P. Winpenny* _____ 9932–9935

A Ring of Rings and Other
Multicomponent Assemblies of Cages

Frontispiece



Ring a ring of roses: Spectacular nano-scale molecular assemblies have been created by design of individual polymetallic components that are then linked together through simple reactions. These include an assembly where six octametallic rings surround a dodecametallic central ring.

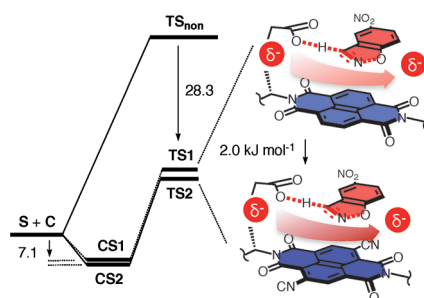


Inactive in the membrane: Lipidated light-responsive constructs that sequester bioagents (R, see scheme) to the membranes of organelles and cells have been constructed. When membrane-bound, the bioagent is not susceptible to processing by its biological target. Photolysis releases the bioagent from its membrane anchor and thereby renders it biologically active.

Fluorescent Probes

L. T. Nguyen, N. P. Oien, N. L. Allbritton,
D. S. Lawrence* _____ 9936–9939

Lipid Pools As Photolabile “Protecting
Groups”: Design of Light-Activatable
Bioagents



The conclusion is inevitable: Increasing stabilization of an anionic transition state with increasing π -acidity of the catalyst is observed; thus, anion– π interactions can contribute to catalysis.

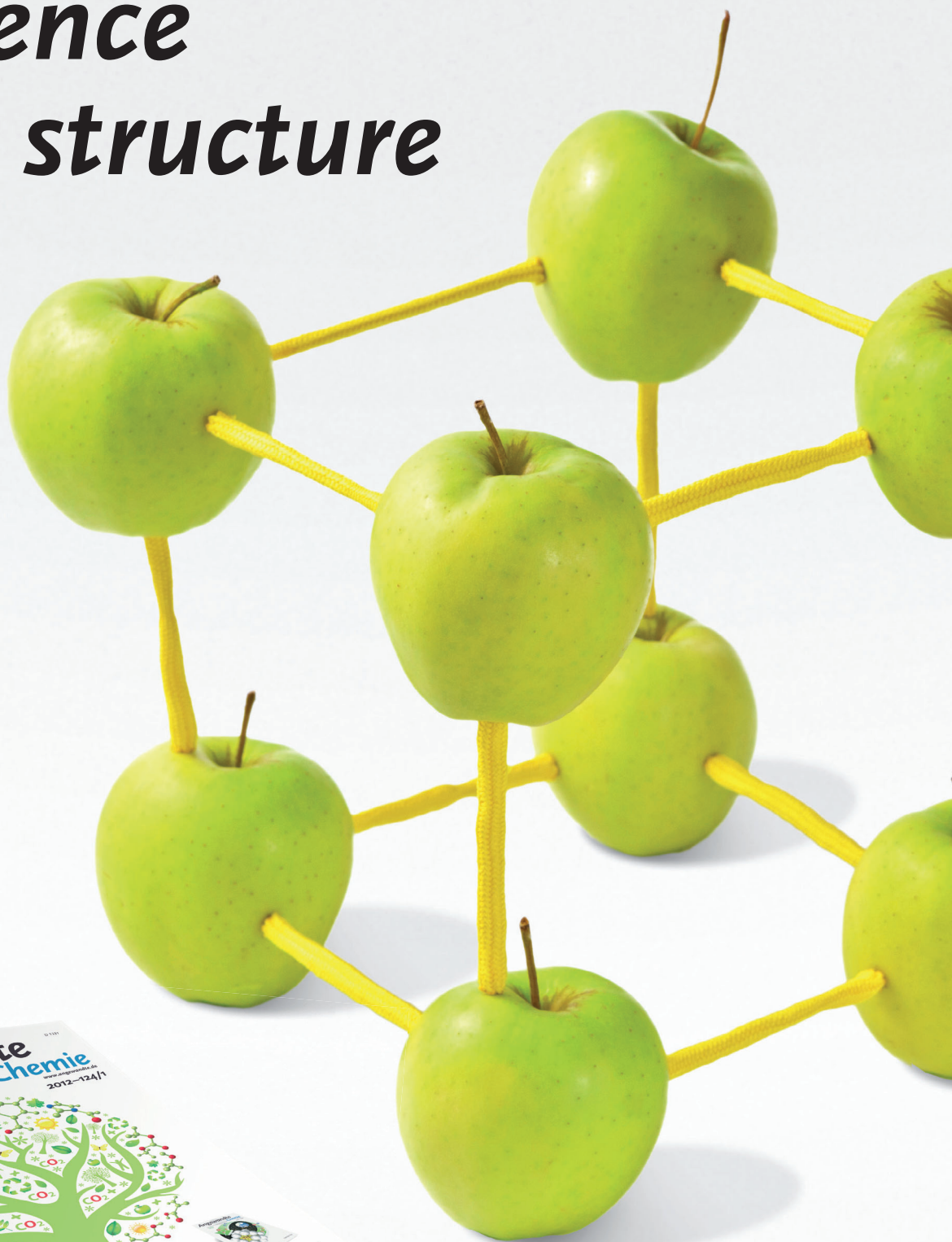
Anion– π Interactions

Y. Zhao, Y. Domoto, E. Orentas,
C. Beuchat, D. Emery, J. Mareda, N. Sakai,
S. Matile* _____ 9940–9943

Catalysis with Anion– π Interactions

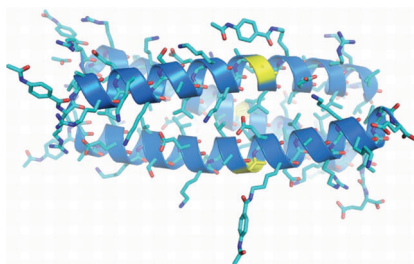
Inside Back Cover

Science with structure



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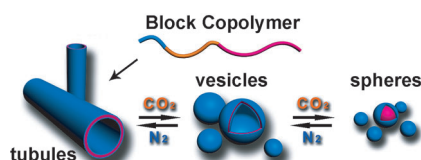


Stable and reactive: A crystal structure at 1.35 Å of a thioester coiled-coil protein reveals high similarity to all-peptide-bond proteins. In these assemblies, the thioester bonds are kept reactive towards thiol molecules in the mixture. This enables efficient domain exchange between proteins in response to changes in folding conditions or introduction of external templates.

Thiodepsipeptides

Z. Dadon, M. Samiappan, A. Shahar, R. Zarivach, G. Ashkenasy* **9944 – 9947**

A High-Resolution Structure that Provides Insight into Coiled-Coil Thiodepsipeptide Dynamic Chemistry

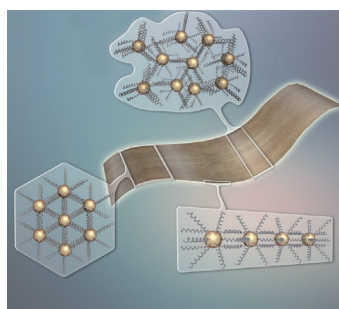


Tubular breathing motion: Polymer tubules self-assembled from a gas-sensitive triblock copolymer can undergo shape evolution. A sequence from microtubes through submicroscopic vesicles to nanosized spherical micelles is modulated by CO₂ stimulation levels.

Shape Transformation

Q. Yan, Y. Zhao* **9948 – 9951**

Polymeric Microtubules That Breathe: CO₂-Driven Polymer Controlled-Self-Assembly and Shape Transformation



Wet (nano)blanket: The self-assembly of Au nanoclusters into single-cluster-thick nanosheets is performed in two miscible high-boiling solvents with a slight polarity difference, which generates microphase separation and acts as a soft template to direct the self-assembly in a two-dimensional orientation.

Au Nanosheets

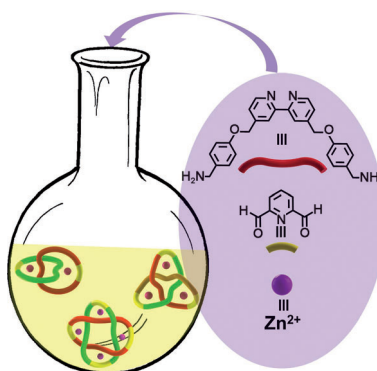
Z. N. Wu, C. W. Dong, Y. C. Li, H. X. Hao, H. Zhang,* Z. Y. Lu,*

B. Yang **9952 – 9955**

Self-Assembly of Au₁₅ into Single-Cluster-Thick Sheets at the Interface of Two Miscible High-Boiling Solvents



A topological triptych: Three molecular links, a [2]catenane, a trefoil knot, and a Solomon link, were obtained in one pot through the self-assembly of two simple ligands in the presence of Zn^{II} (see picture). The approach relied on dynamic covalent chemistry and metal templation.



Molecular Knots

T. Prakasam, M. Lusi, M. Elhabiri, C. Platas-Iglesias, J.-C. Olsen, Z. Asfari, S. Cianfèrari-Sanglier, F. Debaene, L. J. Charbonnière,* A. Trabolsi* **9956 – 9960**

Simultaneous Self-Assembly of a [2]Catenane, a Trefoil Knot, and a Solomon Link from a Simple Pair of Ligands

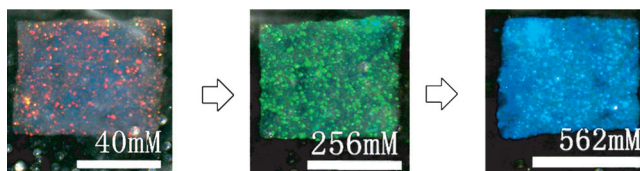


Inside Cover



Photonic Hydrogels

M. Chen, L. Zhou, Y. Guan,
Y. Zhang* — 9961 – 9965



Polymerized Microgel Colloidal Crystals:
Photonic Hydrogels with Tunable Band
Gaps and Fast Response Rates

Into and out of the blue: The highly ordered structure of a PNIPAM microgel colloidal crystal (MCC) is stabilized by photopolymerization of its surface-bound vinyl groups. The resulting polymerized MCCs can respond reversibly and quickly

to external stimuli, including temperature and ionic strength of the surrounding media, allowing the color (see picture) and band gap to be finely tuned in the whole visible range.

B,N Heterocycles

B. Neue, J. F. Araneda, W. E. Piers,*
M. Parvez — 9966 – 9969



BN-Dibenzo[*a,o*]picenes: Analogues of an
Unknown Polycyclic Aromatic
Hydrocarbon

Reflecting on synthetic pinnacles:

Whereas the parent hydrocarbon is not readily accessible, several examples of BN substituted-dibenzo[*a,o*]picenes can be prepared in two steps from known starting materials. These non-linear heptacene analogues are water-stable materials. Their preparation utilizes a potentially general method for preparing extended BN analogues of difficult-to-synthesize polycyclic aromatic hydrocarbon frameworks.

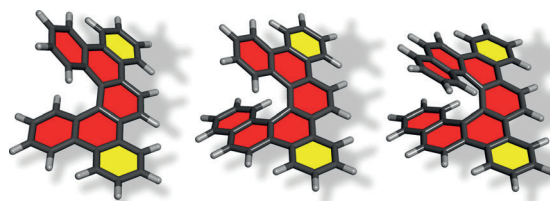


Helical Structures

A. Jančařík, J. Rybáček, K. Cocq,
J. Vacek Chocholoušová, J. Vacek, R. Pohl,
L. Bednářová, P. Fiedler, I. Císařová,
I. G. Stará,* I. Starý* — 9970 – 9975



Rapid Access to Dibenzohelicenes and
their Functionalized Derivatives



Spiraling up: Easy access to dibenzo[5]-, dibenzo[6]-, and dibenzo[7]helicenes (see picture) as well as their functionalized derivatives includes Sonogashira and Suzuki–Miyaura couplings, desilylation, and [2+2+2] alkyne cycloisomerization.

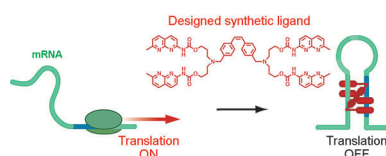
The simplicity of this non-photochemical approach combined with the potential for helicity control favors dibenzohelicenes over the parent helicenes for practical applications.

Synthetic Riboswitches

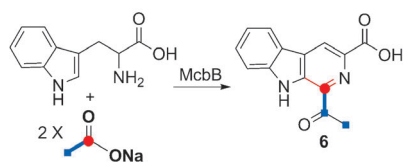
C. Dohno,* I. Kohyama, M. Kimura,
M. Hagihara, K. Nakatani* — 9976 – 9979



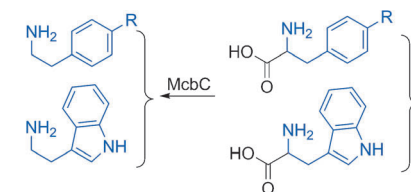
A Synthetic Riboswitch that Operates
using a Rationally Designed Ligand–RNA
Pair



The construction of an artificial riboswitch is based on a ligand–RNA pair without any molecular biology-based selection processes. The ligand selectively and significantly stabilized an RNA duplex containing an r(XGG)/r(XGG) sequence (X = U, A, G). The integration of the ligand-binding sequences into the 5′-untranslated region of mRNA provided an artificial riboswitch that was responsive to Z-NCTS.



Three genes, *mcbABC*, that drive the biosynthesis of marinacarboline, have been elucidated through genome mining, gene inactivation, heterologous expression, feeding, and site-directed mutagen-

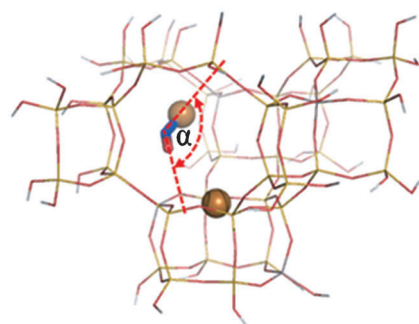


esis experiments. McbB is highlighted as a novel enzyme for the β -carboline core construction, which involves a Pictet–Spengler cyclization process and requiring E₉₇ for biochemical activity.

Alkaloid Biosynthesis

Q. Chen, C. Ji, Y. Song, H. Huang, J. Ma, X. Tian, J. Ju* **9980–9984**

Discovery of McbB, an Enzyme Catalyzing the β -Carboline Skeleton Construction in the Marinacarboline Biosynthetic Pathway



Side on! Combined FTIR and NMR studies revealed the presence of a side-on nitrosyl species in the zeolite Cu-SSZ-13. This intermediate is very similar to those found in nitrite reductase enzyme systems. The identification of this intermediate led to the proposal of a reaction mechanism that is fully consistent with the results of both kinetic and spectroscopic studies.

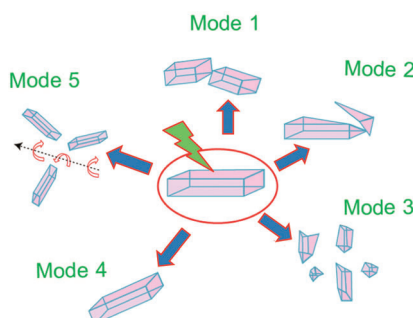
Zeolite Catalysis

J. H. Kwak,* J. H. Lee, S. D. Burton, A. S. Lipton, C. H. F. Peden, J. Szanyi* **9985–9989**

A Common Intermediate for N₂ Formation in Enzymes and Zeolites: Side-On Cu–Nitrosyl Complexes



Crystals on the move: If they are subjected to a strong light stimulus, crystals of the cobalt coordination compound [Co-(NH₃)₅(NO₂)]Cl(NO₃) undergo sudden jumps and leap over distances 10²–10⁵ times their own size to release the strain that accumulates in their interior. The first quantitative kinematic analysis of this phenomenon is reported. The observed effect could be employed for actuation on the macroscopic scale.



Actuators

P. Naumov,* S. C. Sahoo, B. A. Zakharov, E. V. Boldyreva* **9990–9995**

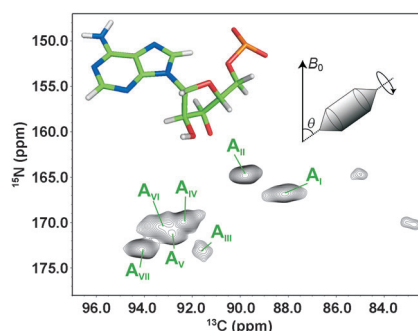
Dynamic Single Crystals: Kinematic Analysis of Photoinduced Crystal Jumping (The Photosolient Effect)



Back Cover



Intranucleotide resonance of the 26mer box C/D RNA in complex with the L7Ae protein were assigned by solid-state NMR (ssNMR; see picture) spectroscopy. This investigation opens the way for studying RNA in large protein–RNA complexes by ssNMR spectroscopy.



Protein–RNA Complexes

A. Marchanka, B. Simon, T. Carlomagno* **9996–10001**

A Suite of Solid-State NMR Experiments for RNA Intranucleotide Resonance Assignment in a 21 kDa Protein–RNA Complex



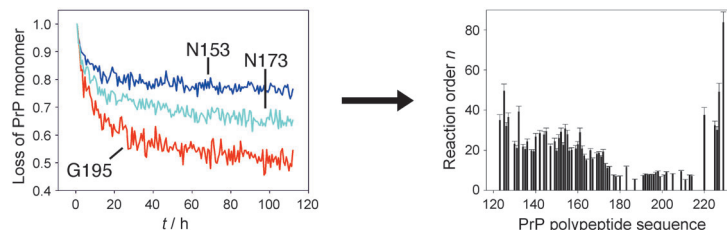
Front Cover



VIP NMR Spectroscopy

K. Schlepckow,
H. Schwalbe* 10002 – 10005

Molecular Mechanism of Prion Protein
Oligomerization at Atomic Resolution



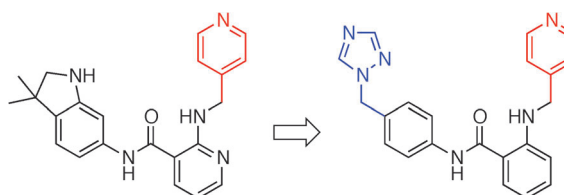
Prion protein oligomerization: Despite the crucial role of oligomers during prion protein (PrP) pathogenesis the molecular mechanism of their formation has remained largely elusive. A 2D time-

resolved NMR study which made it possible to characterize the oligomerization kinetics with unprecedented site-specificity is reported (see picture).

VIP Drug Discovery

T. Rodrigues, T. Kudoh, F. Roudnicky,
Y. F. Lim, Y.-C. Lin, C. P. Koch, M. Seno,
M. Detmar,
G. Schneider* 10006 – 10009

Steering Target Selectivity and Potency by
Fragment-Based De Novo Drug Design



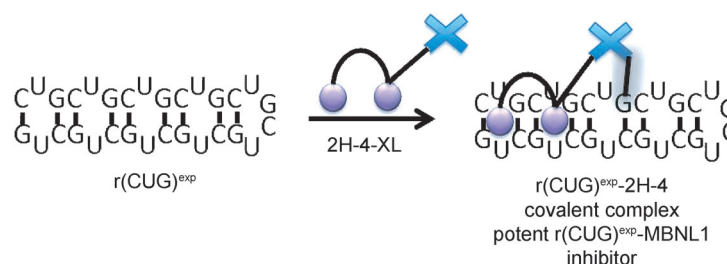
Kinase inhibitors: Ligand-based de novo design is validated as a viable technology for rapidly generating innovative compounds possessing the desired biochemical profile. The study discloses the dis-

covery of the most selective vascular endothelial growth factor receptor-2 (VEGFR-2) kinase inhibitor (right in scheme) known to date as prime lead for antiangiogenic drug development.

RNA Targeting

L. Guan, M. D. Disney* 10010 – 10013

Covalent Small-Molecule–RNA Complex
Formation Enables Cellular Profiling of
Small-Molecule–RNA Interactions



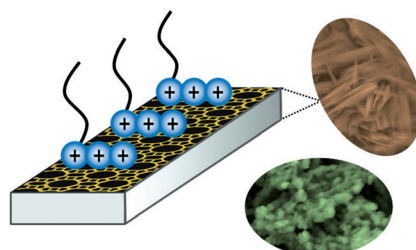
Won't let you go! A strategy is described to design small molecules that react with their cellular RNA targets. This approach not only improves the activity of com-

pounds targeting RNA in cell culture by a factor of about 2500 but also enables cell-wide profiling of its RNA targets.

Nanoparticles

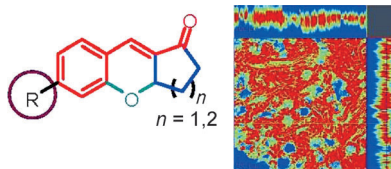
C. Jo, J. Jung, H. S. Shin, J. Kim,
R. Ryoo* 10014 – 10017

Capping with Multivalent Surfactants for
Zeolite Nanocrystal Synthesis



Multiammonium surfactants exhibited a remarkable capping effect for zeolite synthesis in the forms of nanoparticles, nanorods, and nanosponges in cases where common monovalent surfactants failed. A nanorod-shaped mordenite zeolite synthesized in this manner showed significantly enhanced catalytic lifetimes in acid-catalyzed cumene synthesis reactions.

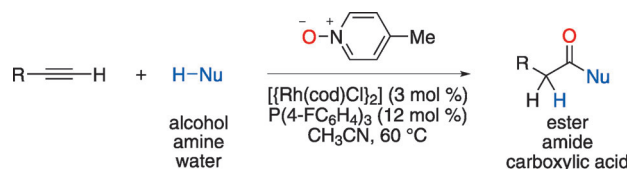
Conformationally restricted analogues of the GFP chromophore have been synthesized. The spectroscopic properties of GCTPOC, a unique family with tunable two-photon action cross-sections, were investigated. GCTPOC could be used as a robust two-photon platform for development of a two-photon fluorescent thiol sensor, which could stain endogenous thiols both in vitro and in vivo.



Fluorescent Probes

L. Yuan, W. Lin,* H. Chen, S. Zhu,
L. He ————— 10018 – 10022

A Unique Family of Rigid Analogues of the GFP Chromophore with Tunable Two-Photon Action Cross-Sections for Biological Imaging



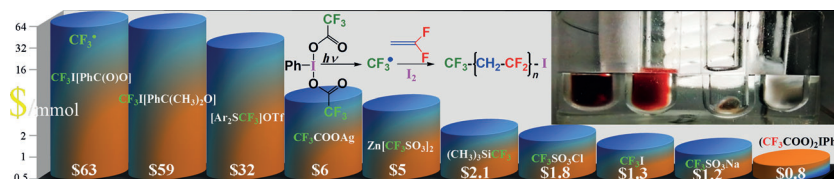
A gem of a couple: The title reaction of terminal alkynes with O and N nucleophiles proceeds in the presence of $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$, $\text{P}(4\text{-FC}_6\text{H}_4)_3$, and 4-picoline *N*-oxide. Alcohols, amines, and water

add to the terminal alkynes to give esters, amides, and carboxylic acids, respectively. The reaction involves formation of a rhodium vinylidene, oxidation to a ketene by oxygen transfer, and nucleophilic addition.

Synthetic Methods

I. Kim, C. Lee* ————— 10023 – 10026

Rhodium-Catalyzed Oxygenative Addition to Terminal Alkynes for the Synthesis of Esters, Amides, and Carboxylic Acids



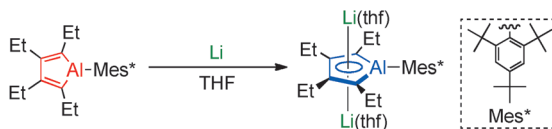
IFAB-ulous trifluoromethylation: $(\text{CX}_3\text{COO})_2\text{I}^{\text{III}}\text{Ph}$ ($\text{X} = \text{F}, \text{H}$) and $(\text{CH}_3\text{COO})_3\text{I}^{\text{IV}}(\text{C}_6\text{H}_4\text{COO})$ are introduced as $\text{CX}_3/\text{CX}_3\text{I}$ precursors for metal-free, visible-light, radical (trifluoro)-(iodo)methylations of alkenes, illustrated

by their use as photoinitiators for the controlled radical polymerization of vinylidene fluoride with external $(\text{I}(\text{CF}_2)_6\text{I})$ and in situ generated (CF_3I) iodine chain transfer agents, and for block copolymer synthesis.

Polymerization

A. D. Asandei,* O. I. Adebolu,
C. P. Simpson, J. S. Kim — 10027 – 10030

Visible-Light Hypervalent Iodide Carboxylate Photo(trifluoro)methylations and Controlled Radical Polymerization of Fluorinated Alkenes



Base free: An alumole was synthesized and treatment with lithium afforded the lithium salt of the alumole dianion. The structures of these two molecules were then investigated. The C–C bond lengths of the AlC_4 ring in the dianion are nearly

equal. DFT calculations revealed that the $3p(\text{Al})-\pi^*$ conjugation lowers the LUMO level of the alumole and that coordination of two lithium cations to the alumole dianion results in a planar AlC_4 ring.

Organoaluminum Compounds

T. Agou, T. Wasano, P. Jin, S. Nagase,
N. Tokitoh* ————— 10031 – 10034

Syntheses and Structures of an “Alumole” and Its Dianion

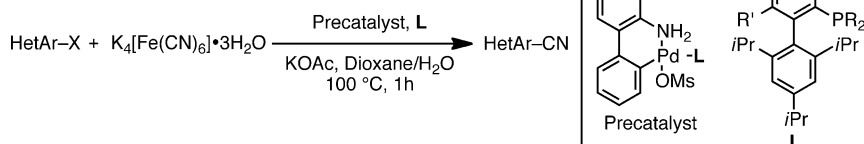


Cross-Coupling

T. D. Senecal, W. Shu,
S. L. Buchwald* 10035 – 10039



A General, Practical Palladium-Catalyzed Cyanation of (Hetero)Aryl Chlorides and Bromides



Playing it safe: The nontoxic cyanide source $K_4[Fe(CN)_6] \cdot 3H_2O$ can be used for the cyanation of (hetero)aryl halides. The application of palladacycle catalysts pre-

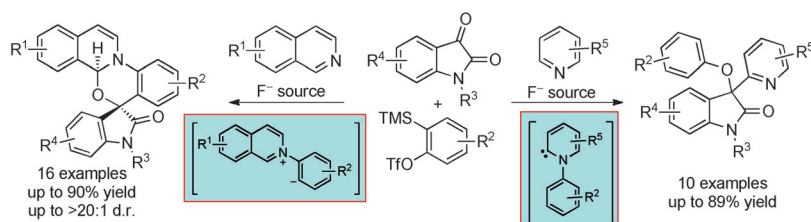
vents poisoning during catalyst formation, thereby allowing for low catalyst loadings, fast reaction times, and wide heterocyclic substrate scope.

Synthetic Methods

A. Bhunia, T. Roy, P. Pachfule,
P. R. Rajamohanan,
A. T. Biju* 10040 – 10043



Transition-Metal-Free Multicomponent Reactions Involving Arynes, N-Heterocycles, and Isatins



Mix and match: With isoquinoline as the nucleophilic trigger, multicomponent reactions afforded spirooxazino isoquinoline derivatives, proceeding through 1,4-dipolar intermediates. The use of pyridine

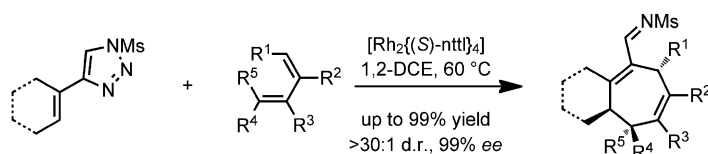
as a nucleophile furnished indolin-2-one derivatives, with the reaction likely proceeding through a pyridylidene intermediate.

Asymmetric Catalysis

B. T. Parr,
H. M. L. Davies* 10044 – 10047



Rhodium-Catalyzed Tandem Cyclopropanation/Cope Rearrangement of 4-Alkenyl-1-sulfonyl-1,2,3-triazoles with Dienes



Take your pick... A practical method for the synthesis of structurally diverse rhodium vinylcarbenes from stable 1-sulfonyl-1,2,3-triazole precursors has been developed. The reaction is general for a broad range

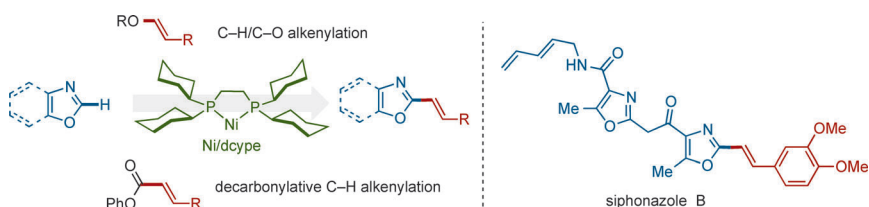
of 4-alkenyl triazoles and dienes, enabling the stereoselective synthesis of a variety of polycyclic imines, which are readily converted into amines or aldehydes in a one-pot process.

C–H Activation

L. Meng, Y. Kamada, K. Muto,
J. Yamaguchi,* K. Itami* 10048 – 10051

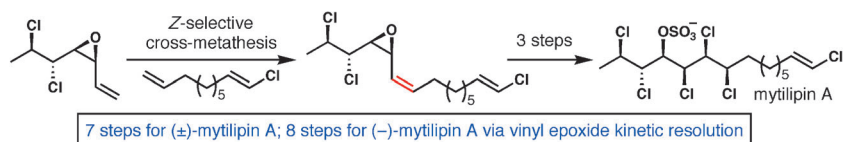


C–H Alkenylation of Azoles with Enols and Esters by Nickel Catalysis



Rather u(Ni)que: Two new C–H alkenylation reactions, that is C–H/C–O alkenylation and decarbonylative C–H alkenylation, of azoles are uniquely catalyzed by

Ni/dcype. These azole alkenylation reactions are successfully applied to the convergent formal synthesis of siphonazole B.



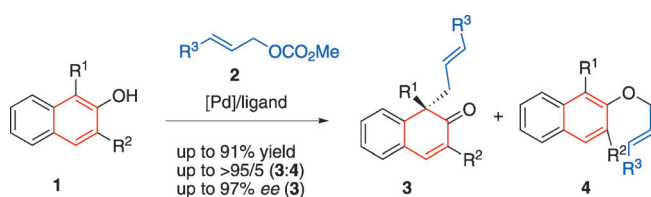
Magnificent seven: The chlorosulfolipid mytilipin A was synthesized in racemic form in seven steps and in enantioenriched form in eight steps. Key transformations include a highly diastereoselective bromoallylation of a sensitive α,β -

dichloroaldehyde, a kinetic resolution of a vinyl epoxide, a convergent and highly Z-selective alkene cross-metathesis, and a chemoselective and diastereoselective dichlorination of a complex diene.

Natural Product Synthesis

W.-j. Chung, J. S. Carlson, D. K. Bedke, C. D. Vanderwal* — 10052–10055

A Synthesis of the Chlorosulfolipid Mytilipin A via a Longest Linear Sequence of Seven Steps



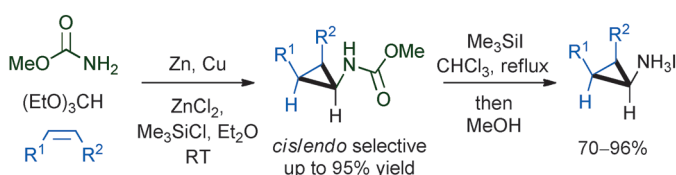
Baring all: The title reaction provides β -naphthalenones bearing an all-carbon quaternary center in good to excellent

yields, as well as excellent chemo- and enantioselectivity (see scheme).

Asymmetric Catalysis

C.-X. Zhuo, S.-L. You* — 10056–10059

Palladium-Catalyzed Intermolecular Asymmetric Allylic Dearomatization Reaction of Naphthol Derivatives



Easy as 1,2,3: Reaction of methyl carbamate, triethyl orthoformate, and readily available alkenes provides a highly practical preparation of protected aminocyclopropanes. The reaction proceeds with

preferential *cis* addition to alkenes, and cleavage of the methyl carbamate gives the free aminocyclopropanes as their HI salts (see scheme).

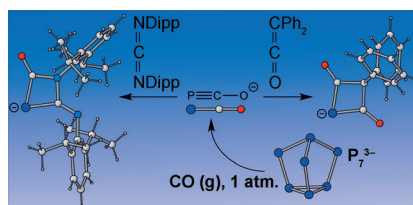
Synthetic Methods

S. Ishikawa, T. D. Sheppard, J. M. D'Oyley, A. Kamimura, W. B. Motherwell* — 10060–10063

A Rapid Route to Aminocyclopropanes via Carbamatoorganozinc Carbenoids



Hip to be square: Direct carbonylation of solutions of the heptaphosphide trianion (P_7^{3-}) afforded the phosphaeethynolate anion in moderate yields. This species undergoes [2+2] cycloaddition reactions with diphenylketene and bis(2,6-diisopropylphenyl)carbodiimide to yield the anionic four-membered heterocycles $P[C(O)]_2C(C_6H_5)_2^-$ and $PC(O)-(CNDipp)NDipp^-$.



Organophosphorus Compounds

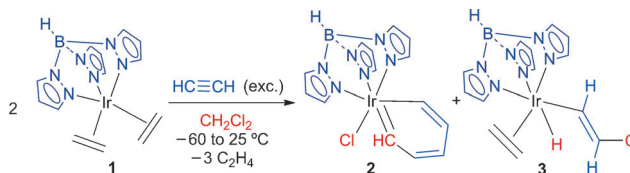
A. R. Jupp, J. M. Goicoechea* — 10064–10067

The 2-Phosphaeethynolate Anion: A Convenient Synthesis and [2+2] Cycloaddition Chemistry



Metallabenzenes

Á. Vivancos, M. Paneque,* M. L. Poveda,*
E. Álvarez — 10068 – 10071



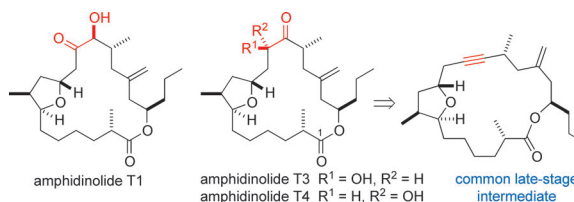
Building a Parent Iridabenzene Structure from Acetylene and Dichloromethane on an Iridium Center

Parenthood: The reaction of $[\text{TpIr}(\text{C}_2\text{H}_4)_2]$ (**1**) (Tp = hydrotris(pyrazolyl)borate) with acetylene in CH_2Cl_2 affords a 1:1 mixture of the “parent” metallabenzene **2** (that is, all the ring carbon centers are CH units) and the β -Cl substituted vinyl species **3**.

Generation of **2** is by the coupling of an iridacyclopentadiene (formed from two acetylene molecules at the Ir center) with the dichloromethane-derived chlorocarbene “ $\text{C}(\text{H})\text{Cl}$ ” and a subsequent α -Cl elimination event.

Natural Products

J. S. Clark,* F. Romiti — 10072 – 10075



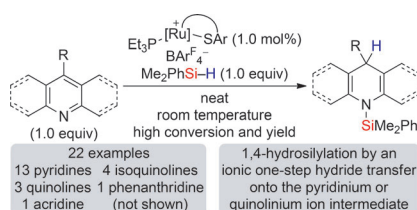
Total Syntheses of Amphidinolides **T1**, **T3**, and **T4**

Concise and high-yielding total syntheses of amphidinolides **T1**, **T3**, and **T4** have been completed using an alkynyl macro-lactone as a common late-stage intermediate. The required α -hydroxy ketone motif was installed by sequential alkyne

hydrosilylation, epoxidation, and Fleming–Tamao oxidation. An oxonium ylide rearrangement formed the trisubstituted tetrahydrofuran core found in the natural products.

Partial Reduction

C. D. F. Königs, H. F. T. Klare,
M. Oestreich* — 10076 – 10079



Catalytic 1,4-Selective Hydrosilylation of Pyridines and Benzannulated Congeners

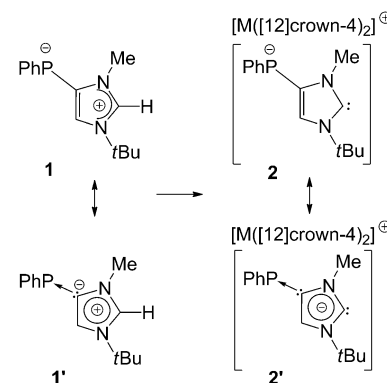
Radically different! The hydrosilylation of pyridines and quinolines is strictly 1,4-selective and likely involves an ionic one-step rather than the established radical two-step hydride transfer from a ruthenium(II) hydride complex onto the respective pyridinium and quinolinium ion intermediates (see scheme; $\text{Ar}^F = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$). Even 4-substituted substrates react highly regioselectively. Isoquinolines yield the 1,2-reduced heterocycles.

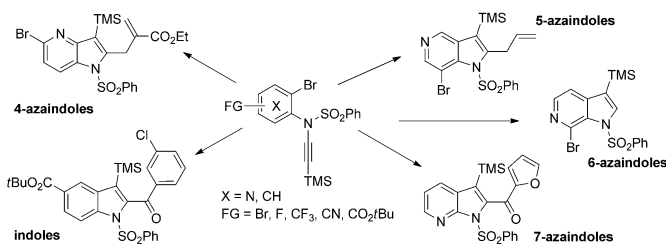
Abnormal N-Heterocyclic Carbenes

P. K. Majhi, G. Schnakenburg, Z. Kelemen,
L. Nyulaszi,* D. P. Gates,
R. Streubel* — 10080 – 10083

Synthesis of an Imidazolium Phosphanide Zwitterion and Its Conversion into Anionic Imidazol-2-ylidene Derivatives

Matter of opinion: The novel zwitterion **1** has been synthesized and studied theoretically and also converted into anionic NHCs **2**. The former can also be described as a phosphinidene adduct of an abnormal N-heterocyclic carbene (**1'**) and, in the same vein, the latter represents a phosphinidene adduct of an anionic N-heterocyclic dicarbene (**2'**).





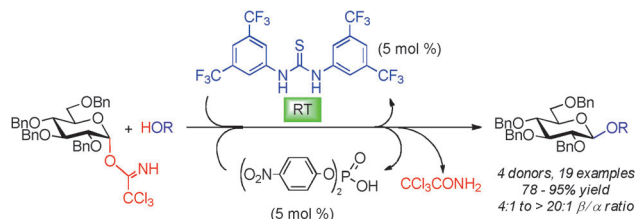
Variations on a theme: A mild and general intramolecular copper-mediated carbomagnesiation procedure for the synthesis of functionalized indoles as well as 4-, 5-,

6-, and 7-azaindoles starts from readily available ynamides. Subsequent reactions with various electrophiles provides polyfunctional N-heterocycles in good yields.

Azaindole Synthesis

A. Frischmuth,
P. Knochel* 10084–10088

Preparation of Functionalized Indoles and Azaindoles by the Intramolecular Copper-Mediated Carbomagnesiation of Ynamides



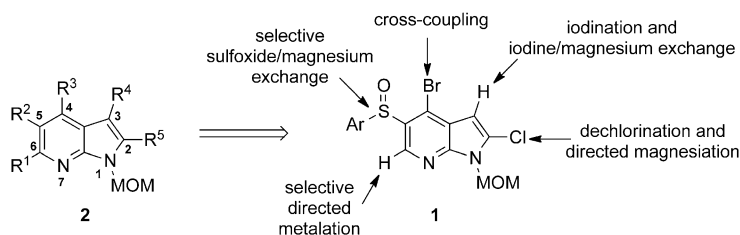
Thiourea mediates cooperative glycosidation through hydrogen bonding. *N,N'*-Diarylthiourea as cocatalyst enforces an S_N2 -type acid-catalyzed glycosidation even at room temperature (see scheme;

Bn = benzyl). From *O*-(α -glycosyl) trichloroacetimidates as glycosyl donors and various acceptors, β -glycosides are preferentially or exclusively obtained.

Glycosidation

Y. Geng, A. Kumar, H. M. Faidallah,
H. A. Albar, I. A. Mhkalid,
R. R. Schmidt* 10089–10092

Cooperative Catalysis in Glycosidation Reactions with *O*-Glycosyl Trichloroacetimidates as Glycosyl Donors



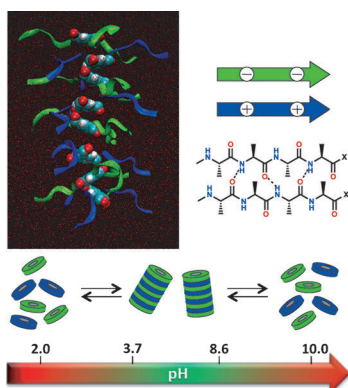
Filling positions: 7-Azaindoles are important targets in the pharmaceutical industry. All five carbon positions of the azaindole ring system can be functionalized in a predictable manner starting from the

appropriately substituted azaindole **1** by directed metalation and halogen/magnesium and sulfoxide/magnesium exchange. The products are fully substituted azaindoles of type **2**.

Synthetic Methods

N. M. Barl, E. Sansiaume-Dagousset,
K. Karaghiosoff,
P. Knochel* 10093–10096

Full Functionalization of the 7-Azaindole Scaffold by Selective Metalation and Sulfoxide/Magnesium Exchange



β -sheet-encoded anionic and cationic dendritic peptide amphiphiles form supramolecular copolymers when self-assembled in a 1:1 feed ratio of the monomers. These ampholytic materials have been designed for on-off polymerization in response to pH triggers. The cooperative supramolecular self-assembly process is switched on at a physiologically relevant pH value and can be switched off by increasing or decreasing the pH value.

Self-Assembly

H. Frisch, J. P. Unsleber, D. Lüdiker,
M. Peterlechner, G. Brunklaus, M. Waller,
P. Besenius* 10097–10101

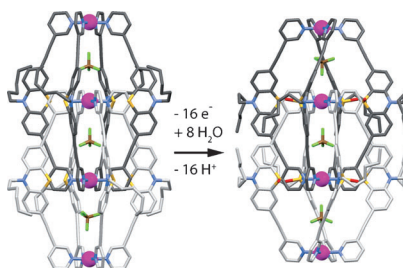
pH-Switchable Ampholytic Supramolecular Copolymers

Coordination Cages

M. Frank, J. Hey, I. Balcioglu, Y.-S. Chen,
D. Stalke, T. Suenobu, S. Fukuzumi,
H. Frauendorf,
G. H. Clever* 10102–10106



Assembly and Stepwise Oxidation of
Interpenetrated Coordination Cages
Based on Phenothiazine



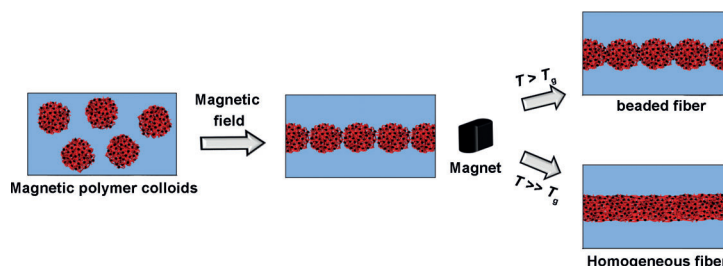
A breath of fresh air is sufficient for the eightfold S-monooxygenation of an interpenetrated double cage based on eight phenothiazine ligands and four square-planar-coordinated Pd^{II} cations. Besides these two cages, which were both characterized by X-ray crystallography, an eightfold S-dioxygenated double-cage was obtained under harsher oxidation conditions.

Hybrid Materials

M. B. Bannwarth,* S. W. Kazer, S. Ulrich,
G. Glasser, D. Crespy,
K. Landfester* 10107–10111



Well-Defined Nanofibers with Tunable
Morphology from Spherical Colloidal
Building Blocks



From particles to fibers: Nanofibers with different morphologies and periodicities can be fabricated by supraparticular assembly of magnetic spherical nanoparticles. A linear sintering process is used to

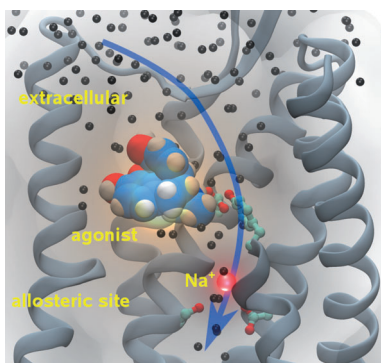
merge the assembled colloids together. The structure of the obtained fibers is controlled by the process parameters and the morphology of the spherical colloidal building blocks.

Structural Biology

S. Yuan,* H. Vogel,
S. Filipek* 10112–10115



The Role of Water and Sodium Ions in the
Activation of the μ -Opioid Receptor



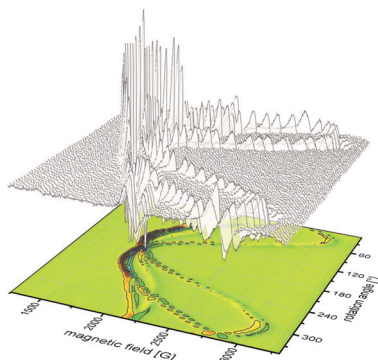
Dual effect of sodium ions: The activation of G-protein-coupled receptors depends on the presence of water molecules inside the receptor and also on allosteric interactions. The binding of sodium ions to the allosteric site of the μ opioid receptor was studied by microsecond molecular dynamics simulations and their seemingly contradictory roles in preventing ligand binding and facilitating receptor activation were explained.

Nitrogen Fixation

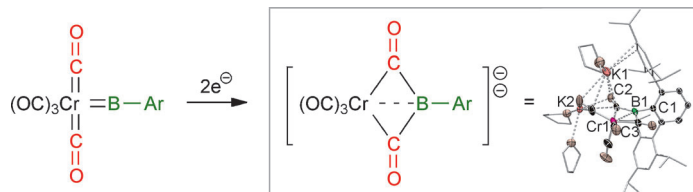
T. Spatzal, O. Einsle,*
S. L. A. Andrade* 10116–10119



Analysis of the Magnetic Properties of
Nitrogenase FeMo Cofactor by Single-
Crystal EPR Spectroscopy



The catalytic center of nitrogenase, the [Mo:7Fe:9S:C]:homocitrate FeMo cofactor, is a $S = 3/2$ system with a rhombic magnetic g tensor. Single-crystal EPR spectroscopy in combination with X-ray diffraction were used to determine the relative orientation of the g tensor with respect to the cluster structure. The protein environment influences the electronic structure of the FeMo cofactor, dictating preferred orientations of possible functional relevance.



Partial metal–boron bond cleavage and coupling of a borylene with two CO ligands was observed upon reduction of a new bulky arylborylene complex. Both the borylene precursor and dianionic product were structurally and spectro-

scopically characterized. In contrast, reduction of an aminoborylene complex led to complete loss of the borylene ligand and classical Hieber reduction. A rationale for these differences based on DFT methods is presented.

Borylene Reduction

H. Braunschweig,* R. D. Dewhurst, C. Hörl, K. Radacki, C. W. Tate, A. Vargas, Q. Ye **10120–10123**

Reductive Borylene–CO Coupling with a Bulky Arylborylene Complex



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



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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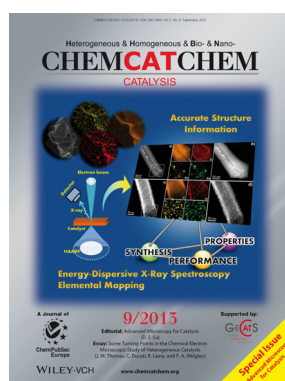


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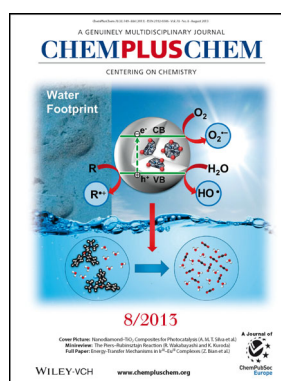
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In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and it should not mention graphical elements, tables, or references within the paper.