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:

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

*M. Griesser, D. Neshchadin, K. Dietliker, N. Moszner, R. Liska, G. Gescheidt**
Decisive Reaction Steps at Initial Stages of Photoinitiated Radical Polymerizations

*J.-G. Liu, T. Ohta, S. Yamaguchi, T. Ogura, S. Sakamoto, Y. Maeda, Y. Naruta**
Spectroscopic Characterization of a Hydroperoxo–Heme Intermediate of a Synthetic Model: Conversion of a Side-on Peroxy to an End-on Hydroperoxy Complex

*A. B. Chaplin, A. S. Weller**
B–H Activation at a Rhodium(I) Center: A Missing Link in the Transition-Metal-Catalyzed Dehydrocoupling of Amine–Boranes

M. Bandini, A. Eichholzer*
Enantioselective Gold-Catalyzed Allylic Alkylation of Indoles with Alcohols: Efficient Route to Functionalized Tetrahydrocarbazoles

*G. de Ruiter, E. Tartakovsky, N. Oded, M. E. van der Boom**
Sequential Logic Operations with Surface-Confined Polypyridyl Complexes Having Molecular Random Access Memory Features

*W. Li, P. H. C. Camargo, L. Au, Q. Zhang, M. Rycenga, Y. Xia**
Etching and Dimerization: A Simple and Versatile Route to Dimers of Silver Nanospheres with a Range of Sizes

*I. U. Khan, D. Zwanziger, I. Böhme, M. Javed, H. Naseer, S. W. Hyder, A. G. Beck-Sickinger**
Breast Cancer Diagnosis by Neuropeptide Y Analogues: From Synthesis to Clinical Application

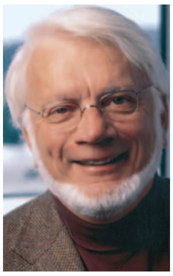
*K. Fesko, M. Uhl, J. Steinreiber, K. Gruber, H. Griengl**
Biocatalytic Access to α,α-Dialkyl-α-Amino Acids by a Mechanism-Based Approach

Author Profile

"The biggest challenge facing scientists is to solve the most urgent problems of humanity—the replacement of fossil fuels and supply of drinking water.
My biggest inspiration is listening to music in the great outdoors ..."
This and more about Christof M. Niemeyer can be found on page 9022.

News

V. Ramakrishnan



T. A. Steitz

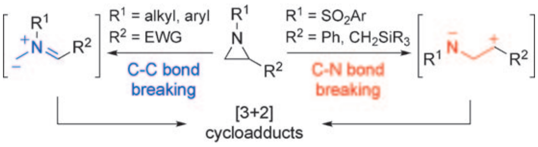
A. E. Yonath

Books

Contents

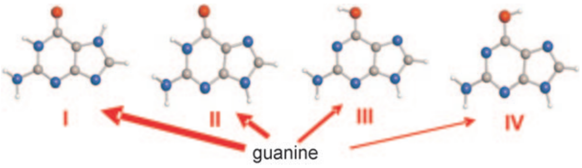
Highlights

Cycloaddition



Double agent: Switching the electronic nature of substituents on an aziridine ring induces the formation of the ring-opened zwitterionic 1,3-dipole through C–N bond cleavage instead of the usual C–C bond cleavage. This novel dipole reacts with alkenes, alkynes, nitriles, and carbonyl compounds to afford new types of [3 + 2] cycloadducts, thereby enhancing the diversity of nitrogen-containing heterocycles accessible through 1,3-dipolar cycloadditions. EWG = electron-withdrawing group.

Structure Determination



Laser ablation or desorption overcomes the problem of the thermal instability of some nucleobases upon vaporization for studies of their tautomeric/conformational equilibria. Laser-ablation supersonic jet Fourier transform microwave (FTMW) spectroscopy and ultrafast electron diffraction–laser desorption enabled the structural characterization of guanine. The thickness of the arrows in the picture represents the stability of the species.

Essays

History in the Making

The Wacker oxidation for the conversion of ethylene into acetaldehyde is one of the most important processes in the chemical industry. This year marks the 50th anniversary of the first publication on this process in *Angewandte Chemie*—an occasion for a retrospective from one of the original authors, Reinhard Jira.

For the USA and Canada:
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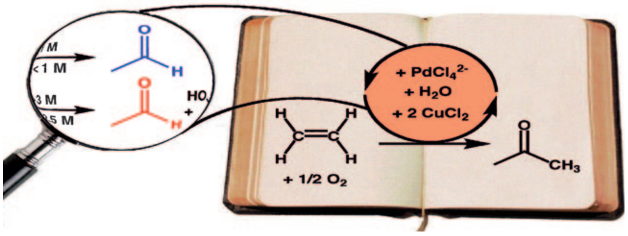
Minireviews

Wacker Oxidation



Still fascinating: Creative and elegant studies on the Wacker process, since its development 50 years ago, have led to apparently contradictory conclusions. A modern perspective shows an intricate and colorful picture of the "textbook" organometallic reaction dependent on reaction conditions.

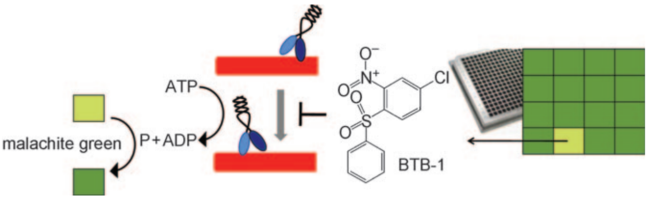
Reviews

Hypervalent Iodine

Iodine's got talent: Exciting developments have recently been made in the field of diaryliodonium salts. Facile and efficient one-pot synthetic routes have made these hypervalent iodine reagents easy to come by and as a result their applications are rapidly increasing, ranging from cross-couplings to benzyne generation and photoinitiation.

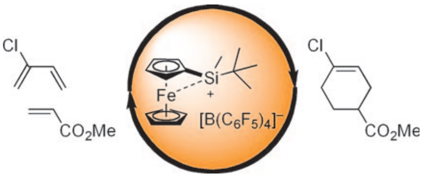
Communications

Chemical Biology

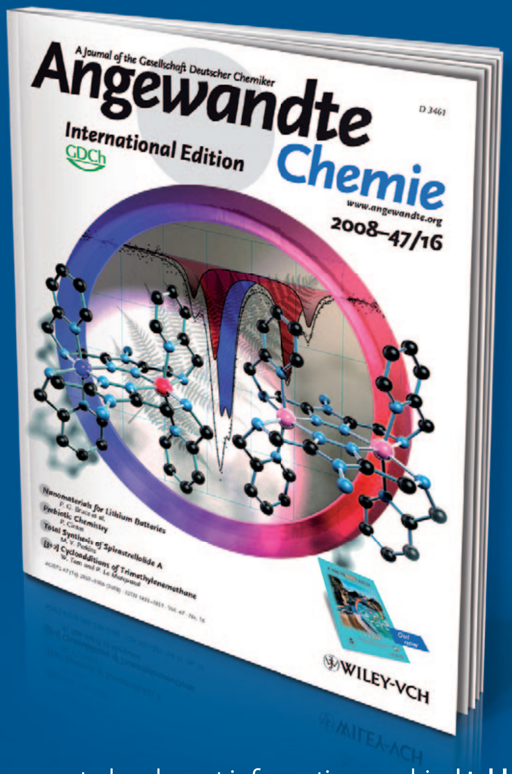


Turning the motor off: A malachite green based assay leads to the identification of BTB-1 (see picture), the first small-molecule inhibitor of the mitotic motor protein Kif18A. BTB-1 reversibly inhibits the ATPase activity of the recombinant motor domain of Kif18A in vitro (see picture; red microtubules, blue/black structure = Kif18A) and will be a valuable tool to dissect the mechanochemical properties of Kif18A.

Lewis Acid Catalysis



Some like it hot: A novel silicon-based Lewis acid having a trivalent silicon cation stabilized by an electron-rich transition metal as the "hot" Lewis acidic site catalyzes challenging Diels–Alder reactions at low temperatures with excellent reaction rates and selectivities (see scheme). In addition to the chemical stability of the silylium ion catalyst (in CH_2Cl_2), the potential of these reactive compounds is also discussed.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Angewandte Chemie
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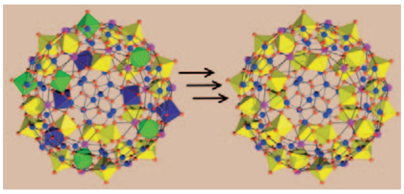
www.angewandte.org
2008–47/16
WILEY-VCH

Redox-controlled magnetism: The partial reduction of polyoxomolybdate building blocks in Keplerate cluster structures allows the magnetic superexchange mediated by these diamagnetic blocks to be altered. The isolation of a 16-fold reduced $\{Mo^{V/VI}{}_{72}Fe^{III}{}_{30}\}$ species illustrates how Raman-monitored synthesis can result in such clusters comprising a well-defined assembly of spin centers.



Polyoxometalate Molecular Magnets

B. Botar, A. Ellern, R. Hermann,
P. Kögerler* ______ **9080–9083**

Electronic Control of Spin Coupling in Keplerate-Type Polyoxomolybdates

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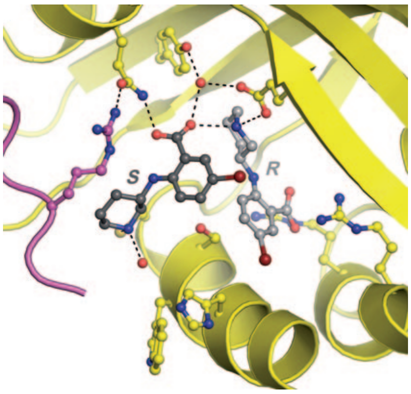
Two in one: Proteins usually bind only one enantiomer of a racemic ligand. Now a new binding mode for chiral drugs has been identified by protein crystallography. The homodimeric enzyme PhzA/B (in the picture the monomers are yellow and magenta) can host both enantiomers of a racemic ligand (light and dark gray) in its active site at the same time (dark red Br, blue N, light red O).



Chiral Drugs

M. Mentel, W. Blankenfeldt,*
R. Breinbauer* ______ **9084–9087**

The Active Site of an Enzyme Can Host Both Enantiomers of a Racemic Ligand Simultaneously

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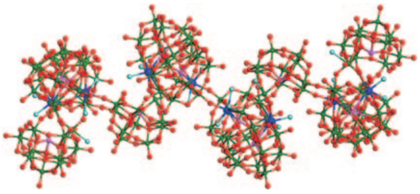
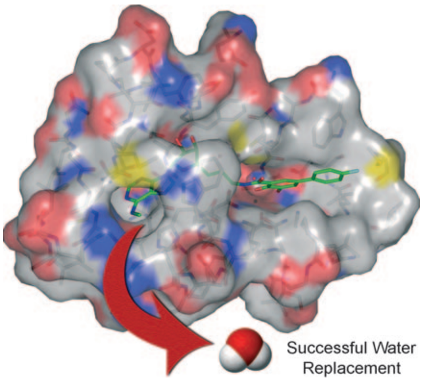
POMs de terre: The combination of tungsten-containing polyoxometalate (POM) fragments with gadolinium cations results in exceptionally long polyoxotungstates. The title anion (see structure; W green, As purple, Gd blue, O red, H_2O cyan) is almost 5 nm in length, resulting in a challenging solution chemistry and also new perspectives for POMs in nanochemistry.



Polyoxometalates

F. Hussain,* F. Conrad,
G. R. Patzke* ______ **9088–9091**

A Gadolinium-Bridged Polytungstoarsenate(III) Nanocluster: $[Gd_8As_{12}W_{124}O_{432}(H_2O)_{22}]^{60-}$



The import business: The binding mode of highly potent bisubstrate inhibitors of catechol-*O*-methyltransferase (COMT) has been elucidated by X-ray crystal structures of ternary complexes with COMT and a Mg^{2+} ion (see picture). A single ligand-imported water molecule is replaced, with a gain in binding free enthalpy of at least −1.8 kcal mol^{-1} compensating the costs of the energetically unfavorable conformation of the ligand in the bound state.

Inhibitors

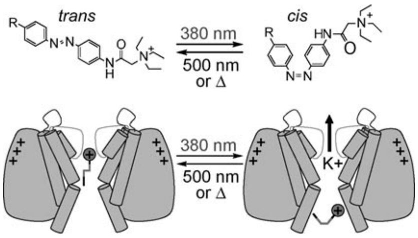
M. Ellermann, R. Jakob-Roetne, C. Lerner,
E. Borroni, D. Schlatter, D. Roth,
A. Ehler, M. G. Rudolph,*
F. Diederich* ______ **9092–9096**

Molecular Recognition at the Active Site of Catechol-*O*-Methyltransferase: Energetically Favorable Replacement of a Water Molecule Imported by a Bisubstrate Inhibitor

Photopharmacology

M. R. Banghart, A. Mourot, D. L. Fortin,
J. Z. Yao, R. H. Kramer,*
D. Trauner* ______ **9097 – 9101**

Photochromic Blockers of Voltage-Gated Potassium Channels



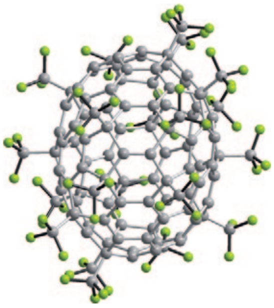
Light work: Studies into the mechanism of AAQ, a photoswitchable blocker of voltage-gated K^+ channels, led to the discovery and development of photochromic ligands that act at the internal tetraethylammonium binding site (see picture). These molecules can be applied from the extracellular side to impart long-lasting photosensitivity on K^+ channels in living cells and thereby afford photocontrol of action potential firing in neurons.

Higher Fullerenes

N. B. Tamm, L. N. Sidorov, E. Kemnitz,*
S. I. Troyanov* ______ **9102 – 9104**

Crystal Structures of $C_{94}(CF_3)_{20}$ and $C_{96}(C_2F_5)_{12}$ Reveal the Cage Connectivities in C_{94} (61) and C_{96} (145) Fullerenes

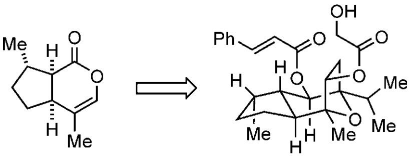
Perfluoroalkylation of a mixture of higher fullerenes has yielded the first direct proof of the cage connectivities in C_{94} (isomer 61) and C_{96} (isomer 145). The addition patterns of the R^F groups on these fullerene cages, the largest to be structurally investigated to date, were determined by X-ray structure analyses of $C_{94}(CF_3)_{20}$ (see structure; gray C, green F) and $C_{96}(C_2F_5)_{12}$.



Natural Product Synthesis

M. Willot, L. Radtke, D. Könning,
R. Fröhlich, V. H. Gessner, C. Strohmann,
M. Christmann* ______ **9105 – 9108**

Total Synthesis and Absolute Configuration of the Guaiane Sesquiterpene Englerin A



nepetalactone

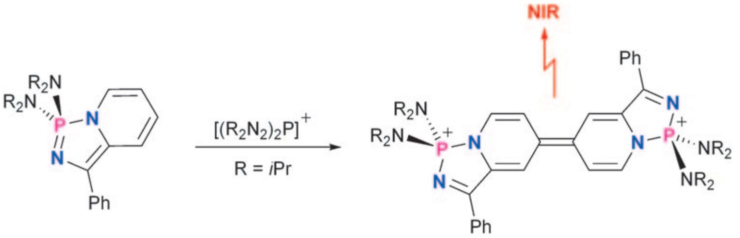
(+)-englerin A

Catnip craze: Nepetalactone, the psychoactive ingredient of catmint, was selected as starting material for the first enantioselective synthesis of englerin A. This cytotoxic guaiane sesquiterpene is a highly selective inhibitor (1–87 nM) of several renal cancer cell lines. The absolute configuration of this natural product was determined by total synthesis.

Phosphorus Heterocycles

D. A. Smith, A. S. Batsanov, M. A. Fox,
A. Beeby, D. C. Apperley, J. A. K. Howard,
P. W. Dyer* ______ **9109 – 9113**

From Cyclic Iminophosphoranes to π-Conjugated Materials

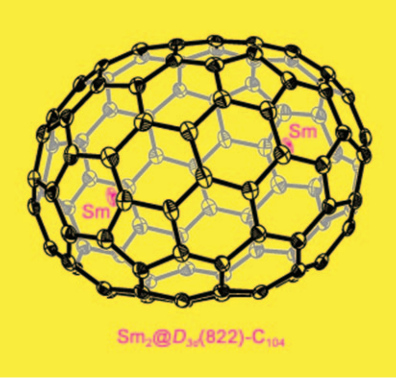


Join here! Phosphenium ion-mediated coupling of an annulated σ^4-1λ^5-[1,3,2]-diazaphosphole (or cyclic iminophosphorane) affords a pseudo-quinoidal dication with extended π-conjugation (see scheme), which emits in the near-infrared (NIR).

Endohedral Fullerenes

B. Q. Mercado, A. Jiang, H. Yang, Z. Wang, H. Jin, Z. Liu,* M. M. Olmstead,* A. L. Balch* ——— 9114 – 9116

Isolation and Structural Characterization of the Molecular Nanocapsule $Sm_2@D_{3d}(822)$-C_{104}

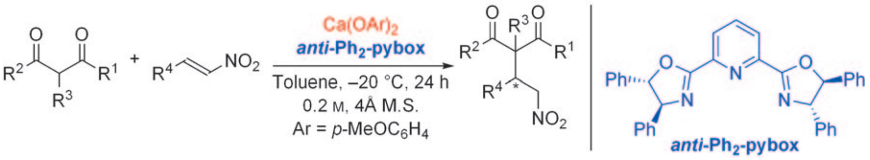


The bigger the more tubular? Structural characterization of $Sm_2@D_{3d}(822)$-C_{104} reveals that it is a member of a new class of nanocapsules with a carbon cage that resembles a small end-capped carbon nanotube. This remarkable molecule is the largest endohedral fullerene to be crystallographically characterized to date and is nearly twice the size of the prototypical C_{60}.

Asymmetric Catalysis

T. Tsubogo, Y. Yamashita, S. Kobayashi* ——— 9117 – 9120

Chiral Calcium Catalysts with Neutral Coordinative Ligands: Enantioselective 1,4-Addition Reactions of 1,3-Dicarbonyl Compounds to Nitroalkenes

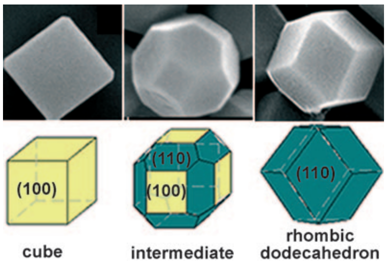


Salt of the earth: The first chiral, coordinative alkaline earth metal catalysts have been developed. These catalysts effectively promote catalytic asymmetric additions of β-dicarbonyl compounds to nitroalkenes in high yields with high enantioselectivities (up to 96 %).

Crystal Growth

X. J. Zhang,* C. Dong, J. A. Zapien, S. Ismathullakhan, Z. Kang, J. S. Jie, X. H. Zhang,* J. C. Chang, C. S. Lee, S. T. Lee* ——— 9121 – 9123

Polyhedral Organic Microcrystals: From Cubes to Rhombic Dodecahedra

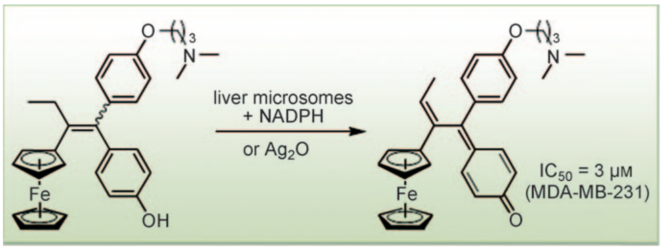


Many facets: A controlled synthesis results in high-symmetry small-molecular organic microcrystals with shapes that range from cubes through truncated cubes to rhombic dodecahedra (see picture). Morphological control was achieved by changes in solubility, which substantially alters the growth rate in the ⟨100⟩ direction relative to that in the ⟨110⟩ direction. Changes in morphology also lead to different optical properties of the crystals.

Antitumor Agents

D. Hamels, P. M. Dansette, E. A. Hillard, S. Top, A. Vessières, P. Herson, G. Jaouen,* D. Mansuy* ——— 9124 – 9126

Ferrocenyl Quinone Methides as Strong Antiproliferative Agents: Formation by Metabolic and Chemical Oxidation of Ferrocenyl Phenols



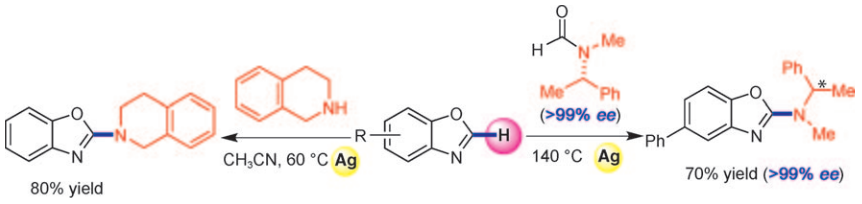
Hard on cancer cells: Ferrocenyl quinone methides, potentially cytotoxic species, are formed by metabolic and chemical oxidation of ferrocenyl phenols (see scheme). These species display strong antiproliferative properties.

Contents

C–N Bond Formation

S. H. Cho, J. Y. Kim, S. Yunmi Lee,
S. Chang* ________________ **9127 – 9130**

Silver-Mediated Direct Amination of Benzoxazoles: Tuning the Amino Group Source from Formamides to Parent Amines

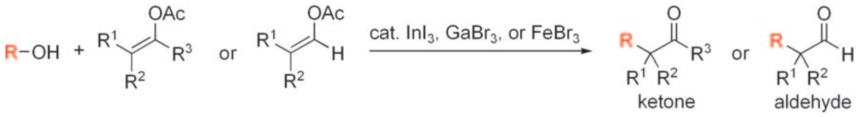


Going to the source: Formamides or parent amines were used as an amino group source for the silver-mediated amination of benzoxazoles. Although reactions with formamides proceeded at high temperatures, the direct amination with amines took place under much milder conditions (see scheme). Optically active amino groups could also be installed without racemization.

Carbonyl Chemistry

Y. Nishimoto, Y. Onishi, M. Yasuda,
A. Baba* ________________ **9131 – 9134**

α-Alkylation of Carbonyl Compounds by Direct Addition of Alcohols to Enol Acetates

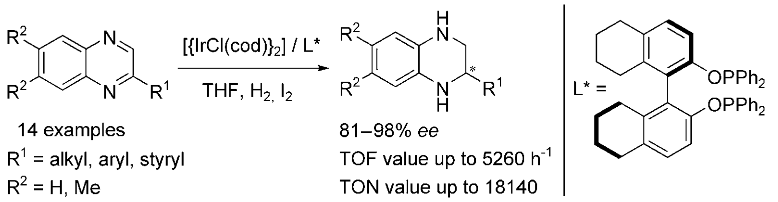


A practical α-alkylation of ketones and aldehydes has been achieved by the direct addition of alcohols to enol acetates. The moderate Lewis acidity of InI$_3$, GaBr$_3$, and FeBr$_3$ is a key factor in the catalytic cycle, and many different alcohols and enol acetates have been successfully used in this procedure.

Asymmetric Hydrogenation

W. Tang, L. Xu,* Q.-H. Fan,* J. Wang,
B. Fan, Z. Zhou, K.-h. Lam,
A. S. C. Chan* ________________ **9135 – 9138**

Asymmetric Hydrogenation of Quinoxalines with Diphosphinite Ligands: A Practical Synthesis of Enantioenriched, Substituted Tetrahydroquinoxalines

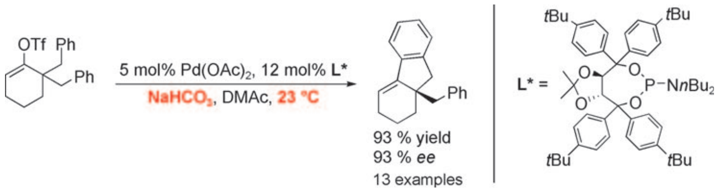


An easily accessible chiral Ir/H$_8$-binapo catalyst exhibits unprecedented reactivity and excellent enantioselectivity in the hydrogenation of quinoxalines at a high ratio of substrate to catalyst (from 100 to 20000). This new method provides a practical synthetic approach to give optically active chiral tetrahydroquinoxaline derivatives (see scheme; cod = 1,5-cyclooctadiene).

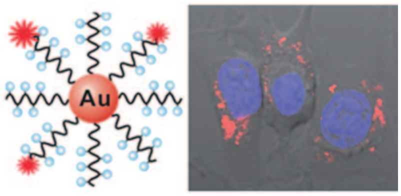
Asymmetric Catalysis

M. R. Albicker, N. Cramer* _ **9139 – 9142**

Enantioselective Palladium-Catalyzed Direct Arylations at Ambient Temperature: Access to Indanes with Quaternary Stereocenters



Ta daa: The title reaction proceeds under essentially neutral reaction conditions at ambient temperature with a taddol-based phosphoramidite ligand **L*** allowing the creation of indanes with quaternary stereogenic centers in high enantiomeric excess (see scheme; Tf = trifluoromethanesulfonyl, DMAc = dimethylacetamide).



Conjugate agent: A Gd^{III} enriched DNA-AuNP conjugate for intracellular magnetic resonance and fluorescence imaging is reported. The agent exhibits high relaxivity per particle and high cell uptake properties that provide a means to image and map small cell populations.

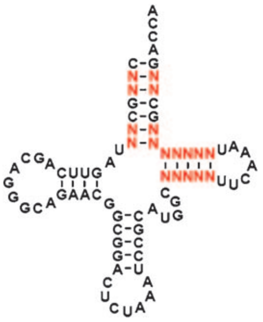
Magnetic Resonance Imaging

Y. Song, X. Xu, K. W. MacRenaris,
X.-Q. Zhang, C. A. Mirkin,*
T. J. Meade* ________ **9143–9147**

Multimodal Gadolinium-Enriched DNA–Gold Nanoparticle Conjugates for Cellular Imaging

---

Applied evolution: Regions of the *M. jannaschii* tyrosyl tRNA_{CUA} thought to interact with elongation factor Tu were randomized, and the resulting tRNA libraries were subjected to in vitro evolution. The tRNAs identified resulted in significantly improved yields of proteins containing nonnatural amino acids. In some cases, the degree of improvement varied in an amino acid dependent manner.



tRNA

J. Guo, C. E. Melançon, III, H. S. Lee,
D. Groff, P. G. Schultz* ____ **9148–9151**

Evolution of Amber Suppressor tRNAs for Efficient Bacterial Production of Proteins Containing Nonnatural Amino Acids

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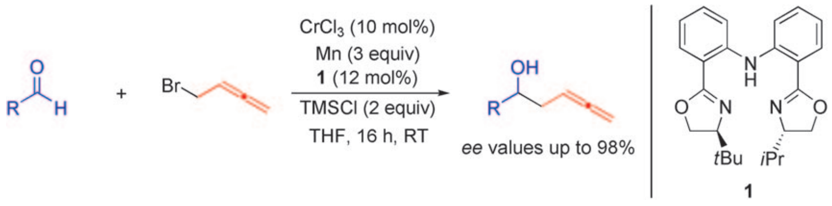

Game, set, and match: The first regio- and enantioselective version of the title reaction is described. The chiral catalyst prepared in situ from $CrCl_3$ and a non-C_2-symmetric bis(oxazoline) ligand **1** affords the valuable chiral β-allenols regioselectively in good yields with excellent *ee* values. R = aryl, alkyl.

Asymmetric Catalysis

V. Coeffard, M. Aylward,
P. J. Guiry* ________ **9152–9155**

First Regio- and Enantioselective Chromium-Catalyzed Homoallenylation of Aldehydes

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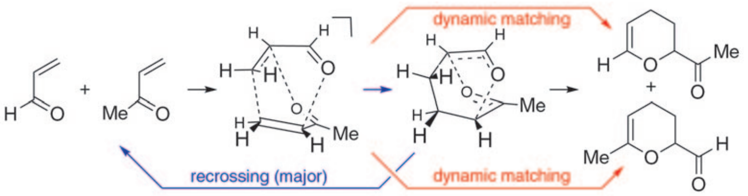


Up and down the hill: The products from the hetero-Diels–Alder reaction of acrolein with methyl vinyl ketone arise from a single transition state (see scheme) and trajectory studies accurately predict the selectivity. In an extension of the dynamic matching idea of Carpenter, the product formed is determined by the direction of motion passing through the transition state. Recrossing occurs extensively and decreases formation of the minor product.

Dynamic Effects

Z. Wang, J. S. Hirschi,*
D. A. Singleton* ________ **9156–9159**

Recrossing and Dynamic Matching Effects on Selectivity in a Diels–Alder Reaction

Biomimicry

S. H. Yang, K.-B. Lee, B. Kong, J.-H. Kim, H.-S. Kim, I. S. Choi* ______ 9160 – 9163

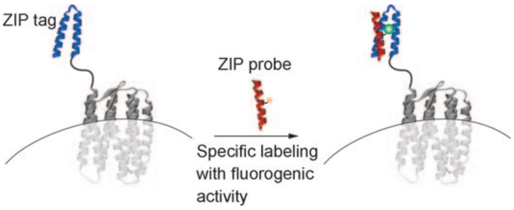
Biomimetic Encapsulation of Individual Cells with Silica

Yeast wears a silica coat: Various living cells were individually coated with silica using layer-by-layer self-assembly and biomimetic silicification (see picture). The viability of yeast cells was found to be enhanced threefold after silica encapsulation, and their cell division could be suppressed by encapsulation.

Protein Imaging

H. Tsutsumi, W. Nomura, S. Abe, T. Mino, A. Masuda, N. Ohashi, T. Tanaka, K. Ohba, N. Yamamoto, K. Akiyoshi, H. Tamamura* ______ 9164 – 9166

Fluorogenically Active Leucine Zipper Peptides as Tag–Probe Pairs for Protein Imaging in Living Cells

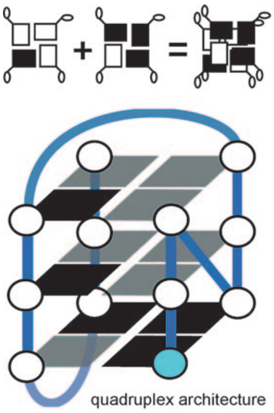


All zipped up: Pairs of leucine zipper peptides with a solvatochromic fluorescent dye show fluorogenic activity through formation of a 3α-helical bundle structure. Such peptides enable the in situ fluorescence imaging of proteins in the presence of excess fluorescent probe (see picture). Imaging of membrane-bound protein is demonstrated using these zipper peptides as functional tag–probe pairs.

Quadruplex Self-Assembly

M. Webba da Silva,* M. Trajkovski, Y. Sannohe, N. Ma'ani Hessari, H. Sugiyama, J. Plavec* ______ 9167 – 9170

Design of a G-Quadruplex Topology through Glycosidic Bond Angles

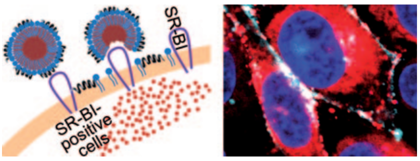


Building regulations: Thus far the discovery of novel DNA quadruplex topologies was either serendipitous or through coincidental emergence. Now a deductive system, based on the glycosidic bond angle of guanosines, can be used to derive a set of inference rules for the prediction of both known and theoretical quadruplex topologies. This formalism was used to design and control the self-assembly of a novel DNA quadruplex architecture.

Drug Delivery

Z. H. Zhang, W. G. Cao, H. L. Jin, J. F. Lovell, M. Yang, L. L. Ding, J. Chen, I. Corbin, Q. M. Luo, G. Zheng* ______ 9171 – 9175

Biomimetic Nanocarrier for Direct Cytosolic Drug Delivery

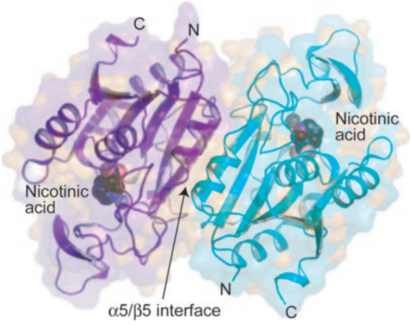


Getting straight to the point: A peptide–phospholipid-based biomimetic nanocarrier was developed that can transport cargo molecules directly into cytosolic compartments through a non-endocytotic uptake mechanism mediated by scavenger receptor class B type I (SR-BI; see schematic illustration). The fluorescent image shows the cytosolic localization of a dye (red) delivered by the nanocarrier to SR-BI-positive cells (nuclei: blue, membranes: cyan).

Enzyme Mechanisms

P. K. Fyfe, V. A. Rao, A. Zemla,
S. Cameron, W. N. Hunter* 9176 – 9179

Specificity and Mechanism of *Acinetobacter baumanii* Nicotinamidase: Implications for Activation of the Front-Line Tuberculosis Drug Pyrazinamide

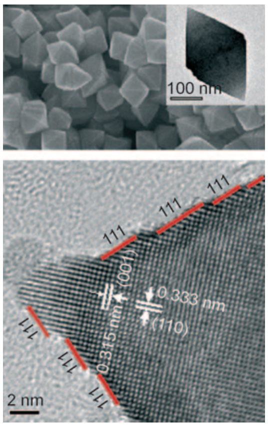


TB or not TB active: The high-resolution crystal structures (see picture) of the zinc-containing metalloenzyme nicotinamidase in complex with nicotinic acid and pyrazinoic acid reveal new aspects of enzyme mechanism that help to explain the activation of a front-line anti-tuberculosis (TB) drug.

Gas Sensors

X. G. Han, M. S. Jin, S. F. Xie, Q. Kuang,*
Z. Y. Jiang, Y. Q. Jiang, Z. X. Xie,*
L. S. Zheng 9180 – 9183

Synthesis of Tin Dioxide Octahedral Nanoparticles with Exposed High-Energy {221} Facets and Enhanced Gas-Sensing Properties

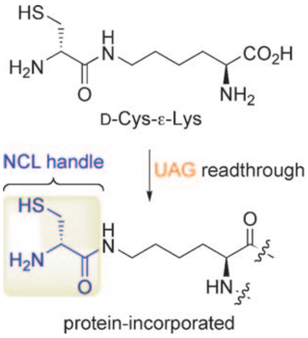


Selective exposure of high-energy {221} facets with many surface dangling bonds, (111) terraces, and (110) steps (bottom picture) at the surface of octahedral SnO_2 nanoparticles (top) through a simple hydrothermal synthesis route gives them enhanced gas-sensing performance over particles with other shapes, whereby the sensing activity is proportional to the fraction of {221} facets among the exposed surfaces.

Protein Engineering

X. Li, T. Fekner, J. J. Ottesen,
M. K. Chan* 9184 – 9187

A Pyrrolysine Analogue for Site-Specific Protein Ubiquitination

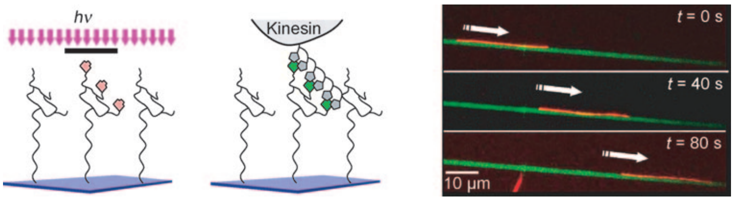


The art of stitching proteins: D-Cys-ε-Lys and its diastereomer L-Cys-ε-Lys read through the UAG codon (see scheme). As the resulting proteins can participate in native chemical ligation (NCL), this process provides a means to prepare proteins chemoselectively modified (e.g. ubiquitinated) through a peptidic side chain located at the ε position of a rationally selected lysine residue.

Surface Patterning

M. Bhagawati, S. Ghosh, A. Reichel,
K. Froehner, T. Surrey,
J. Piehler* 9188 – 9191

Organization of Motor Proteins into Functional Micropatterns Fabricated by a Photoinduced Fenton Reaction



Walking the line: Selective photodestruction of nitrilotriacetic acid moieties on a poly(ethylene glycol) polymer brush by a light-induced Fenton reaction enabled the functional organization of motor proteins into micropatterns (see schematic illustration). Microtubules were selectively captured on the structures, and adenosine triphosphate dependent transport along lines was observed.

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).

Service

Corrigendum

A DNA Nanostructure for the Functional Assembly of Chemical Groups with Tunable Stoichiometry and Defined Nanoscale Geometry

N. Mitchell, R. Schlapak, M. Kastner, D. Armitage, W. Chrzanowski, J. Riener, P. Hinterdorfer, A. Ebner, S. Howorka* **525–527**

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A corrected version of the Supporting Information is now available for this Communication. The labeling error in Table 3 on page S8 does not affect the interpretation of results reported in the original Communication. The authors apologize for this oversight.