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:

*K. Tedsree, A. T. Kong, S. C. Tsang**
Formate as a Surface Probe for Ru Nanoparticles in Liquid ^{13}C NMR Spectroscopy

*A. Asati, S. Santra, C. Kaittanis, S. Nath, J M. Perez**
Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles

*K. M. Gericke, D. I. Chai, N. Bieler, M. Lautens**
The Norbornene Shuttle: Multicomponent Domino Synthesis of Tetrasubstituted Helical Alkenes through Multiple C–H Functionalization

V. M. Hernández-Rocamora, B. Maestro, B. de Waal, M. Morales, P. García, E. W. Meijer, M. Merkx, J. M. Sanz**
Multivalent Choline Dendrimers as Potent Inhibitors of Pneumococcal Cell Wall Hydrolysis

*J.-Q. Wang, S. Stegmaier, T. F. Fässler**
$[Co@Ge_{10}]^{3?}$: An Intermetalloid Cluster with an Archimedean Pentagonal Prismatic Structure

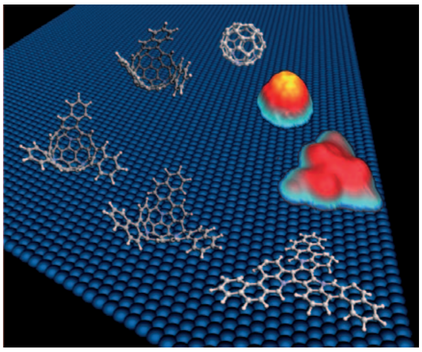
News

Author Profile

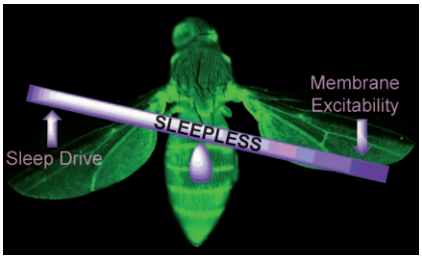
Books

Highlights

Fullerene Synthesis



Fullerenes made to order: The ability of catalytic surfaces to stitch together the arms of polycyclic aromatic hydrocarbons and heterocycles to form fullerenes and heterofullerenes has been demonstrated. This ability may provide wide-ranging access to tailor-made fullerenes, with the specific arrangements of rings and heteroatoms dictated by the design and synthesis of the precursors.



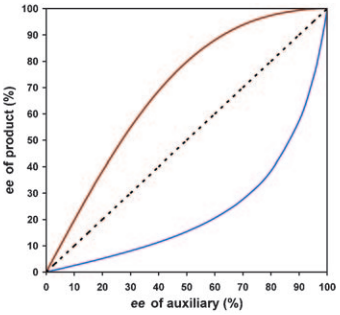
Lord of the flies: A gene, *sleepless*, has been identified in *Drosophila* that when mutagenized imparted an extreme short-sleeping phenotype. SLEEPLESS expression is independent of the circadian clock and was found to participate in the homeostatic regulation of sleep. Namely, SLEEPLESS appears to be a signaling molecule that couples sleep drive to changes in membrane excitability (see picture).

Minireviews

On and under water: Recent developments in aqueous olefin metathesis have followed two main strategies: 1) the use of water-insoluble commercially available ruthenium catalysts in aqueous mixtures and neat water, and 2) the design of special polar ruthenium catalysts that are active and stable in aqueous media. The general applicability of water as a solvent for olefin metathesis is shown.

Reviews

Informative deviation: The enantioselectivity (*ee*) of the reaction product arising from asymmetric catalysis with non-enantiopure chiral auxiliaries should be proportional to that of the chiral auxiliary or ligand (linearity). A deviation from linearity (nonlinear effects, see picture) can be rich in mechanistic information and can be synthetically useful (asymmetric amplification).



For the USA and Canada:
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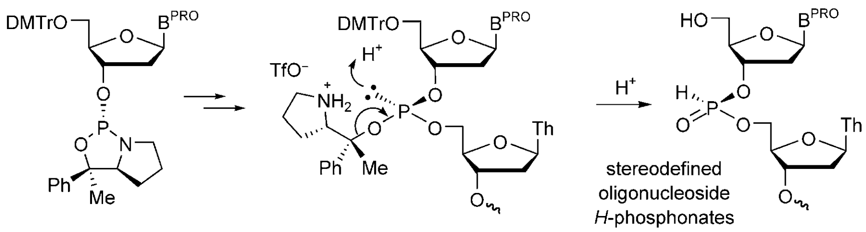
Asymmetric Synthesis

N. Iwamoto, N. Oka, T. Sato, T. Wada* ——— **496–499**

Stereocontrolled Solid-Phase Synthesis of Oligonucleoside *H*-Phosphonates by an Oxazaphospholidine Approach



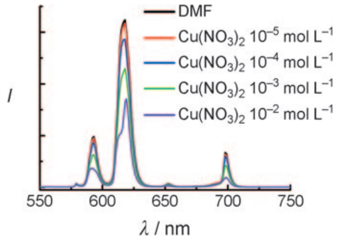
Stereodefined oligonucleoside *H*-phosphonates were synthesized on a solid support using diastereopure nucleoside 3′-*O*-oxazaphospholidine monomers. Several stereodefined backbone-modified analogues were obtained with the oligonucleoside *H*-phosphonates as precursors (see scheme; B^{PRO} = protected nucleobase, DMTr = 4,4′-dimethoxytrityl, Th = thymin-1-yl, TfO^- = triflate).

Metal–Organic Frameworks

B. Chen,* L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui, G. Qian* ——— **500–503**

A Luminescent Metal–Organic Framework with Lewis Basic Pyridyl Sites for the Sensing of Metal Ions

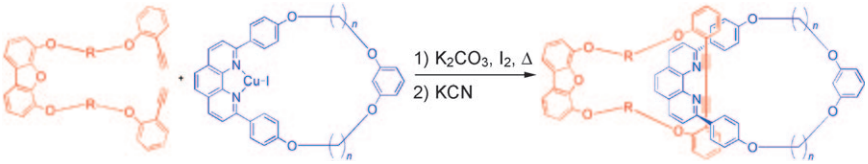
It all makes sense: A rationally developed europium metal–organic framework incorporating immobilized Lewis basic pyridyl sites oriented towards the center of one-dimensional channels is a rare example of a luminescent porous MOF. By comparison of the luminescence intensity quenching effects of various incorporated Lewis acidic metal cations, the MOF exhibits sensor capability.



Catenanes

Y. Sato, R. Yamasaki, S. Saito* **504–507**

Synthesis of [2]Catenanes by Oxidative Intramolecular Diyne Coupling Mediated by Macrocyclic Copper(I) Complexes

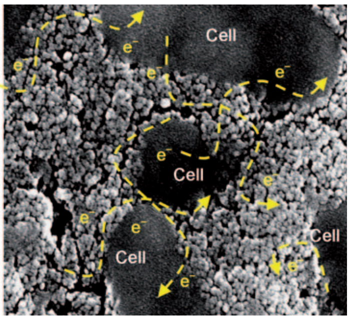


Right said thread: Oxidative intramolecular coupling reactions of α,ω-diynes in the presence of macrocyclic phenanthroline Cu^I complexes allows the synthesis of [2]catenanes in up to 64% yield (see scheme). The bond-forming reaction leads to concurrent threading of the diyne through the phenanthroline macrocycle.

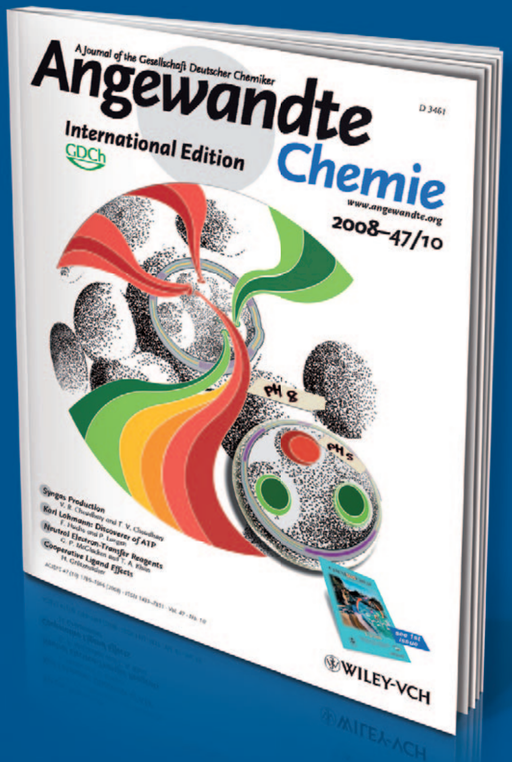
Bacterial Networks

R. Nakamura, F. Kai, A. Okamoto, G. J. Newton, K. Hashimoto* – **508–511**

Self-Constructed Electrically Conductive Bacterial Networks



Protein power grids: A metal-reducing bacterium, *Shewanella loihica* PV-4, has the ability to self-organize an electrically conductive network using outer-membrane proteins and semiconductive minerals as a long-distance electron transfer conduit.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Angewandte Chemie
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Coffee rings: Polymer solutions are confined in a simple geometry comprised of a curved surface placed upon a flat substrate. Simply by changing the shape of the upper surface of the imposed geometry, the controlled, evaporative self-assembly of polymer solutions yields a variety of complex, intriguing, and well-ordered structures over large areas (see picture).

Concentric Patterns

S. W. Hong, M. Byun, Z. Lin* **512–516**

Robust Self-Assembly of Highly Ordered Complex Structures by Controlled Evaporation of Confined Microfluids

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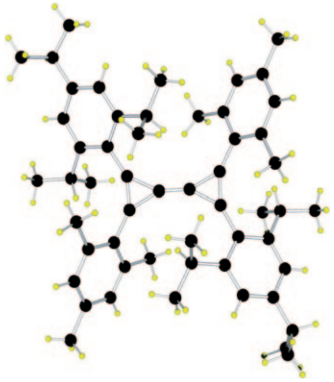

Small and stable: A triafulvalene derivative is indefinitely stable at room temperature both in solution and in the solid state under inert atmosphere. The triafulvalene is synthesized by the magnesium-catalyzed coupling of two bis(chlorocyclopropenyl) derivatives. The two unsaturated three-membered rings are linked together by a carbon–carbon double bond (1.303 Å, see structure), which is so reactive that spontaneous addition of water occurs at room temperature.

Highly Strained Molecules

R. Kinjo, Y. Ishida, B. Donnadieu, G. Bertrand* **517–520**

Isolation of Bicyclopropenylidenes: Derivatives of the Smallest Member of the Fulvalene Family

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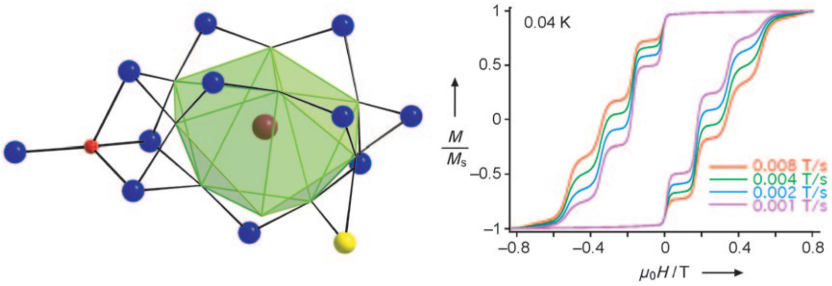


Quantum tunneling of magnetization (QTM) steps have been observed for a mixed 3d–4f single-molecule magnet for the first time in the hysteresis loops of $\{Mn_{12}Gd\}$. This phenomenon is assigned to larger than usual exchange coupling of the 4f atom with the $\{Mn_{12}\}$ shell. This improved quantum behavior for the important class of SMMs opens up the prospects for its detailed study using hysteresis methods. Gd purple, Mn(II) yellow, Mn(III) blue, O red, N green.

Single-Molecule Magnets

T. C. Stamatatos, S. J. Teat, W. Wernsdorfer, G. Christou* **521–524**

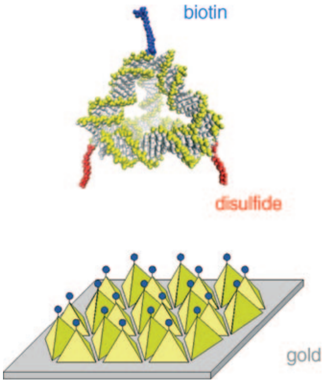
Enhancing the Quantum Properties of Manganese–Lanthanide Single-Molecule Magnets: Observation of Quantum Tunneling Steps in the Hysteresis Loops of a $\{Mn_{12}Gd\}$ Cluster

Contents

Nano-biotechnology

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

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



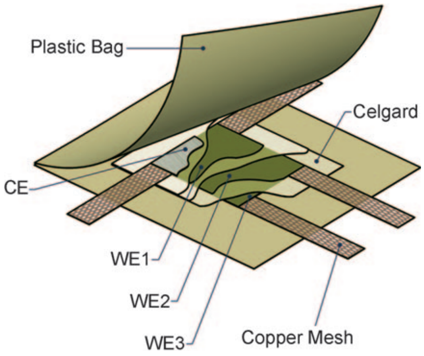
Many legs make light work: Tetrahedra are constructed with edges of double-stranded DNA and vertices tagged with biotin or disulfide units (see picture). They can act as supramolecular scaffolds to combine different chemical groups at defined nanoscale distances and with tunable stoichiometries. The disulfide groups bind to gold surfaces with high affinity, which leaves the biotin unit poised to capture streptavidin.

Electrochemical Cells

S.-H. Ng, F. La Mantia,
P. Novák* ____________ **528 – 532**

A Multiple Working Electrode for Electrochemical Cells: A Tool for Current Density Distribution Studies

Uneven distribution: The multiple working electrode for electrochemical cells (see image) is a unique tool for the quantitative study of current density distribution in lithium-ion batteries. During the cycling of the cell even at a low C-rate of C/37, an inhomogeneity in the average current density distribution of more than 8% is observed. WE = working electrode, CE = counter electrode.

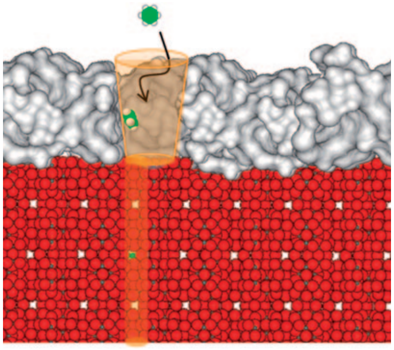


Sorption Enhancement

S. J. Reitmeier, O. C. Gobin, A. Jentys,
J. A. Lercher* ____________ **533 – 538**

Enhancement of Sorption Processes in the Zeolite H-ZSM5 by Postsynthetic Surface Modification

Catching molecules: When the surface of zeolite HZSM-5 (see picture, red) is modified by amorphous SiO_2 layers (gray), increased surface roughness results. The mesopores in the rough SiO_2 layer funnel benzene molecules into the micropores of the zeolite, thus increasing sorption rates for benzene at the acidic hydroxy groups by a factor of two. The size of the mesopores relative to the adsorbing molecules is critical for sorption-rate enhancement.

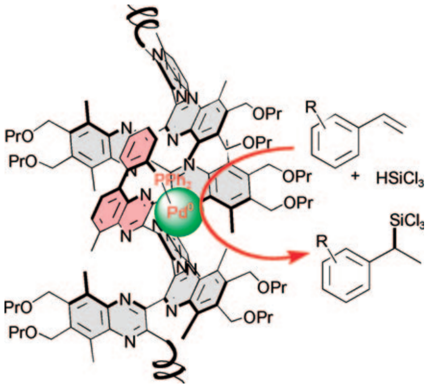


Chiral Catalysts

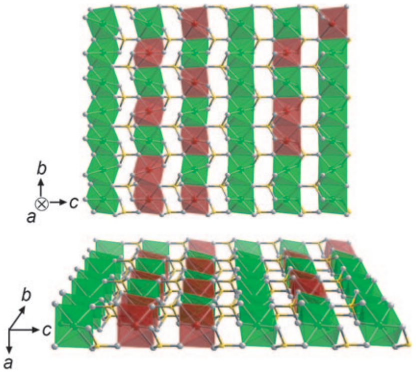
T. Yamamoto, M. Suginome* _ **539 – 542**

Helical Poly(quinoxaline-2,3-diyl)s Bearing Metal-Binding Sites as Polymer-Based Chiral Ligands for Asymmetric Catalysis

Living it up: Helical polyquinoxalines with single and multiple metal-binding sites, prepared by living polymerization of *o*-diisocyanobenzenes, are used in the asymmetric hydrosilylation of styrenes, resulting in comparable enantioselectivities to those obtained by low-molecular-weight catalyst systems (up to 87% *ee*, stereochemistry was determined by a chiral initiator) and a turnover number of almost 1000.

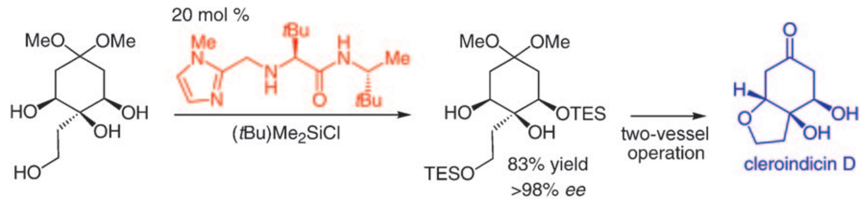


Defect Chemistry



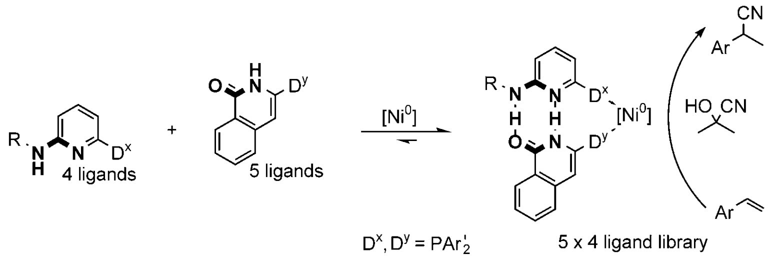
Aggregated antisite cations of iron (see picture, red) in the lithium sites of doped lithium iron phosphate ($LiFePO_4$) are arranged preferentially along the *b* axis. To probe the peculiar array of the defects, *Z*-contrast STEM with a spherical-aberration correction is utilized. The images obtained using *Z*-contrast STEM suggest that the distribution of antisite defects in $LiFePO_4$ can be adjusted for improved lithium ion transport.

Enantioselective Silylation



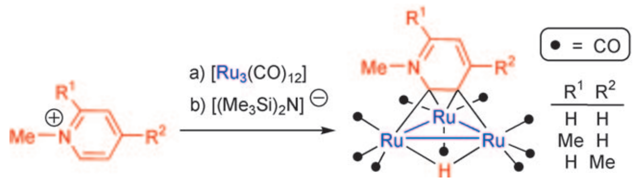
Pick one out of three: Acyclic and cyclic 1,2,3-triols are silylated with exceptional site- and enantioselectivity by a small-molecule catalyst to afford silyl ethers having a neighboring diol moiety. The new process is applied to the enantioselective total syntheses of three cleroindicins, natural products isolated from a plant used in China to battle malaria and rheumatism.

Homogeneous Catalysis



Well-stocked library: A catalyst with interesting activity, regioselectivity (rs), and functional-group tolerance could be identified from a 5×4 library of isoquinolone- or aminopyridine-derived self-assembled bidentate ligands. These ligands, which self-assemble through hydrogen bonding, form complexes with nickel(0) that appeared to be promising catalysts for the hydrocyanation of styrene (see scheme).

N-Heterocyclic Carbenes



Pyrid-2-ylidenes are trapped in solution by $[Ru_3(CO)_{12}]$ after being formed by deprotonation of N-substituted pyridinium cations. The great basicity of these NHC ligands and the polynuclear character of the ruthenium cluster trigger room temperature orthometalation of the initial κ^1-C^2-pyrid-2-ylidene ligands, leading to unprecedented face-capping κ^2-C^2,C^3-pyrid-3-yl-2-ylidene ligands.

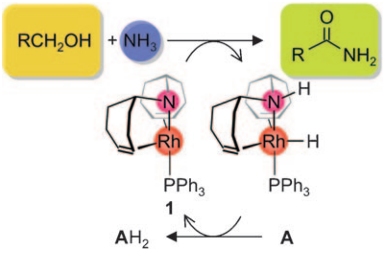
Contents

Synthetic Methods

T. Zweifel, J.-V. Naubron,
H. Grützmacher* ______ **559 – 563**

Catalyzed Dehydrogenative Coupling of Primary Alcohols with Water, Methanol, or Amines

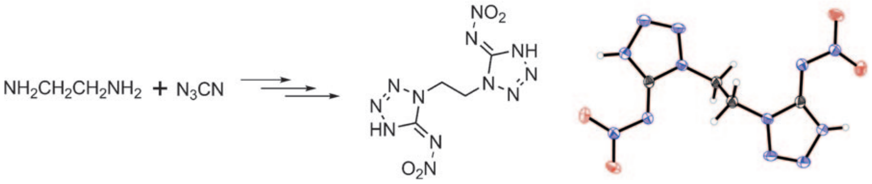
A working partnership: Metal–ligand cooperativity is responsible for the high activity of the rhodium amido complex **1** in the dehydrogenative coupling of primary alcohols with water, methanol, or amines, including ammonia (see scheme), to give carboxylic acids, methyl carboxylates, or amides, respectively. The catalysis proceeds under mild reaction conditions in the presence of a recyclable hydrogen acceptor **A**. The multistep mechanism was elucidated by computational methods.



Energetic Materials

Y.-H. Joo, J. M. Shreeve* ______ **564 – 567**

Energetic Mono-, Di-, and Trisubstituted Nitroiminotetrazoles

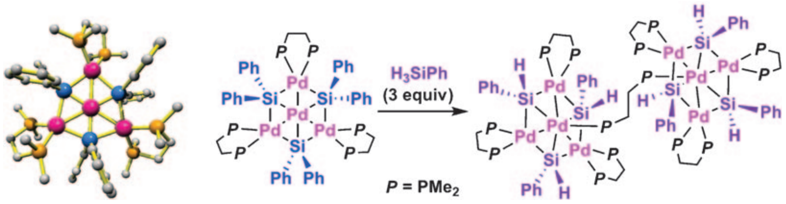


A bundle of energy: The title compounds were synthesized in good yield from aminotetrazoles (obtained from the reaction of cyanogen azide with primary amines) by treatment with 100% nitric acid and were fully characterized by spectroscopic methods, elemental analysis, and in some cases X-ray diffraction (see example; N blue, O red). The heats of formation of these energetic materials were calculated, as well as their detonation pressures and velocities.

Coordination Modes

T. Yamada, A. Mawatari, M. Tanabe,
K. Osakada,* T. Tanase ______ **568 – 571**

Planar Tetranuclear and Dumbbell-Shaped Octanuclear Palladium Complexes with Bridging Silylene Ligands

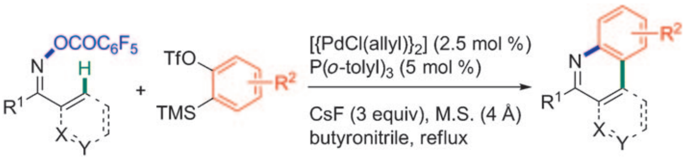


An uncommon structure: The novel title compounds (see scheme) were prepared and fully characterized. The tetranuclear complex contains a hexagonal Pd_4Si_3 core involving one central Pd atom, three outer Pd atoms, and three bridging Si atoms within the same plane, whereas the dumbbell-shaped octanuclear Pd complex is composed of two Pd_4Si_3 groups bridged by a diphosphine ligand.

Domino Reactions

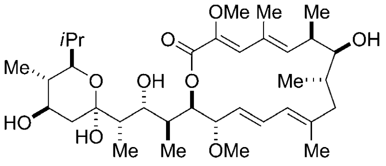
T. Gerfaud, L. Neuville,*
J. Zhu* ______ **572 – 577**

Palladium-Catalyzed Annulation of Acyloximes with Arynes (or Alkynes): Synthesis of Phenanthridines and Isoquinolines



Intermolecular insertion: A palladium-catalyzed domino aminopalladation/C–H functionalization sequence has been developed, and provides access to functionalized phenanthridines and isoquinolines (see scheme; Tf = triflate, TMS = trimethylsilyl, M.S. = molecular sieves). The use of butyronitrile as the solvent is determinant to the success of the domino process.

A convergent synthesis of bafilomycin A_1 (see structure) is presented, and relies on the $Zn(OTf)_2$-mediated diastereoselective addition of alkynes to aldehydes. The coupling of a complex enyne with a sensitive aldehyde in the key step, in combination with a novel strategy for a chemoselective *trans*-reduction of the enyne, establishes an alternative to standard palladium-catalyzed cross-coupling strategies for the formation of 1,3-dienes.

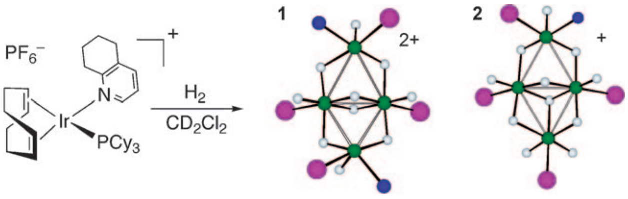


bafilomycin A_1

Natural Product Synthesis

F. Kleinbeck, E. M. Carreira* — **578 – 581**

Total Synthesis of Bafilomycin A_1



Butterfly clusters: Hydrogenation of a cationic iridium complex with the sterically bulky N-ligand tetrahydroquinoline (thq) leads to the formation of two distinct tetrameric polyhydrides (see scheme; Ir green, N blue, P purple), which differ by exchanging one thq ligand for hydride. Both complexes have butterfly structures, with similar core geometries, but markedly different hinge angles (40.8° for **1** and 9.1° for **2**).

Polyhydride Clusters

Y. Xu, M. A. Celik, A. L. Thompson, H. Cai, M. Yurtsever, B. Odell, J. C. Green, D. M. P. Mingos, J. M. Brown* **582 – 585**

Tetrameric Iridium Hydride-Rich Clusters Formed under Hydrogenation Conditions

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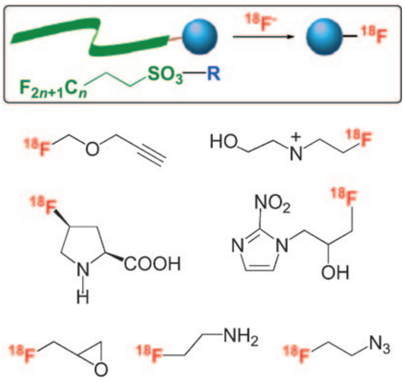
Tag team: The fluoro-detagging of fluorous sulfonates by the [^{18}F]fluoride ion was found to be an advantageous strategy for the preparation of various ^{18}F-labeled prosthetic groups and known radiotracers (see picture). Fluorous solid phase extraction (FSPE) was used to separate the excess fluorous precursor from the labeled material, which suggests that traditional purification protocols such as distillation or tedious separation can be avoided.



Radiochemistry

R. Bejot, T. Fowler, L. Carroll, S. Boldon, J. E. Moore, J. Declerck, V. Gouverneur* ———— **586 – 589**

Fluorous Synthesis of ^{18}F Radiotracers with the [^{18}F]Fluoride Ion: Nucleophilic Fluorination as the Detagging Process

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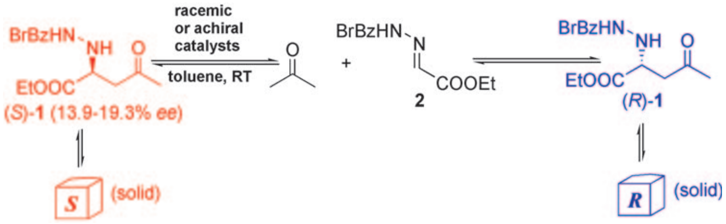


Backwards is better: By combining forward and backward reaction steps of a reversible chemical process (see scheme) with the physical processes of crystallization, crystal crushing, and dissolution, asymmetric amplification up to 100% *ee* can be achieved in the presence of racemic or achiral catalysts starting from a conglomerate of the reaction product **1** with a low enantiomeric excess.

Asymmetric Amplification

S. B. Tsogoeva,* S.-W. Wei, M. Freund, M. Mauksch* ———— **590 – 594**

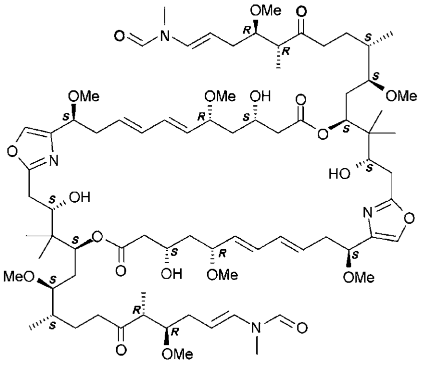
Generation of Highly Enantioenriched Crystalline Products in Reversible Asymmetric Reactions with Racemic or Achiral Catalysts

Protein–Inhibitor Complexes

G. Hagelueken, S. C. Albrecht,
H. Steinmetz, R. Jansen, D. W. Heinz,
M. Kalesse, W.-D. Schubert* **595 – 598**

The Absolute Configuration of Rhizopodin and Its Inhibition of Actin Polymerization by Dimerization

Three's company: Rhizopodin is a cytostatic macrolide and a potent actin depolymerizer produced by the myxobacterium *Myxococcus stipitatus*. A crystal structure analysis of the rhizopodin/actin complex reveals that rhizopodin is a C_2-symmetric bislactone (see formula). The ternary complex supports the mode of rhizopodin-induced actin dimerization and reveals the absolute configuration and biologically active conformation of this macrolide.

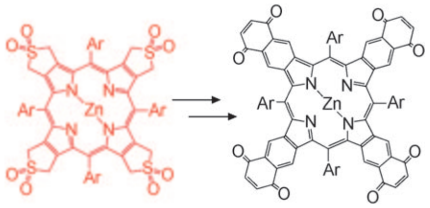


Black Porphyrins

S. Banala, T. Rühl, K. Wurst,
B. Kräutler* **599 – 603**

"Blackening" Porphyrins by Conjugation with Quinones

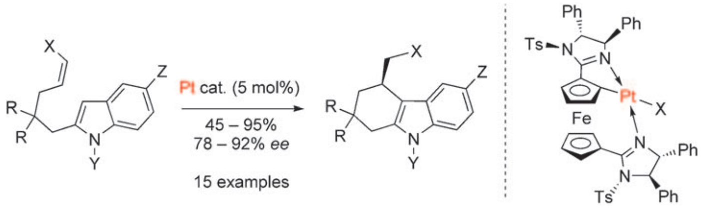
From red to black porphyrins: "Black" porphyrins absorb visible light effectively at all wavelengths and are available by conjugation of four benzoquinone units to a porphyrin core. These robust molecular components are likely to be useful in optoelectronic devices as they absorb a large fraction of the visible light.



Platinum Catalysis

H. Huang, R. Peters* **604 – 606**

A Highly Strained Planar-Chiral Platinacycle for Catalytic Activation of Internal Olefins in the Friedel–Crafts Alkylation of Indoles

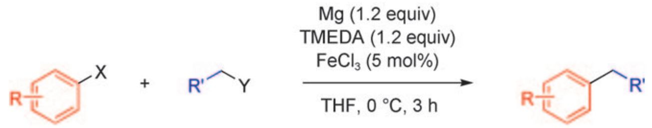


Activation by deformation: A planar-chiral platinacycle readily prepared by diastereoselective cycloplatination enables the enantioselective intramolecular hydroarylation of indoles having disubstituted *Z* olefins (see scheme; Ts = *p*-tolylsulfonyl). Sufficient activity is achieved by a combination of highly strained catalyst geometry and accelerated olefin coordination. This application represents the first highly enantioselective reaction catalyzed by a platinacycle.

VIP *Iron Catalysis*

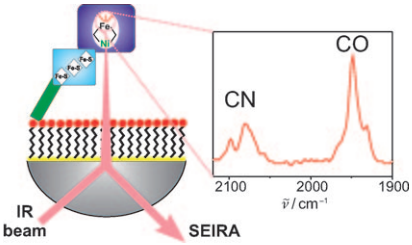
W. M. Czaplik, M. Mayer,
A. Jacobi von Wangelin* **607 – 610**

Domino Iron Catalysis: Direct Aryl–Alkyl Cross-Coupling



Striking while the iron is hot: Cheap $FeCl_3$ serves as the precatalyst for the direct cross-coupling of aryl and alkyl halides that is based on the sequence of Grignard formation and subsequent cross-coupling. This one-pot reaction obviates preformation of hazardous Grignard compounds and limits the amount of reactive organomagnesium intermediates to low quasi-stationary concentrations. TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

Immobilized biocatalyst: The oxygen-tolerant, membrane-bound hydrogenase of *Ralstonia eutropha* H16 is immobilized by a His-tag (see picture; green) onto a gold surface (yellow) modified with nickel–nitrilotriacetic acid (red/black). Catalytic activity towards hydrogen is investigated by surface-enhanced infrared absorption (SEIRA) spectroscopy. Switching redox states and related structural changes of the Ni–Fe active site are followed by the CO and CN⁻ ligand stretching modes.



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