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:

*R. Rose, S. Erdmann, S. Bovens, A. Wolf, M. Rose, S. Hennig, H. Waldmann, C. Ottmann**
Identification and Structure of Small-Molecule Stabilizers of 14-3-3 Protein–Protein Interactions

*A. Schlossbauer, S. Warncke, P. E. Gramlich, J. Kecht, A. Manetto, T. Carell, T. Bein**
A Programmable DNA-Based Molecular Valve for Colloidal Mesoporous Silica

*M. Walz, M. Schirmer, F. Vollnhals, T. Lukasczyk, H.-P. Steinrück, H. Marbach**
Electrons as "Invisible Ink"! Fabrication of Nanostructures by Local Electron Beam Induced Activation of SiO$_x$

*A. Takaoka, L. C. H. Gerber, J. C. Peters**
Access to Well-Defined Ruthenium(I) and Osmium(I) Metalloradicals

*J. Zhang, X.-J. Wu, Z. Wang, Yu Chen, X. Wang, M. Zhou, H. Scheer, K. Zhao**
Single Fused Gene Approach to Photo-Switchable and Fluorescent Biliproteins

D. Sišak, L. B. McCusker, G. Zandomeneghi, B. Meier,* D. Bläser, R. Boese,* W. B. Schweizer, R. Gilmour, J. D. Dunitz**
The Crystal Structure of Ribose – At Last!

Y. Sohma, Q. Hua, J. Whittaker, M. A. Weiss, S. B. H. Kent**
Design and Folding of [GluA4(OβThrB30)]Insulin (Ester Insulin), a Minimal Proinsulin Surrogate Chemically Convertible into Human Insulin

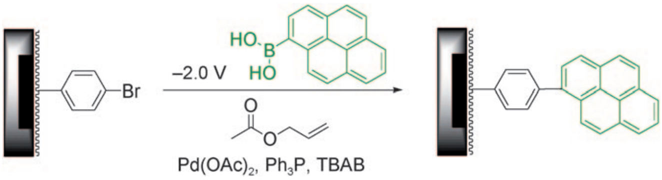
Author Profile

"The secret of being a successful scientist is curiosity and dedication.
A good work day begins with exciting new experimental results …"
This and more about Lutz Ackermann can be found on page 3716.

Books

Highlights

Electrochemistry



A well-stocked toolbox is available for the site-selective arrangement of molecules on microelectrode arrays to form addressable libraries thanks to a combination of electrochemistry with a variety of organometallic reactions, such as the Suzuki reaction (see scheme; TBAB = tetrabutylammonium bromide). A diblock copolymer formed an advantageous electrode coating in place of conventional agarose and sucrose.

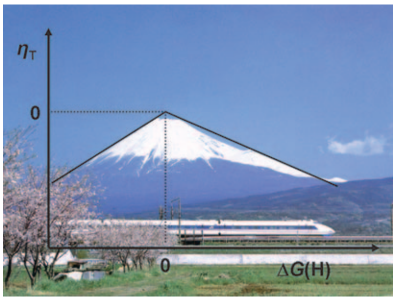
Contents

Hydrogen Production

M. T. M. Koper,*
E. Bouwman ———— **3723 – 3725**

Electrochemical Hydrogen Production: Bridging Homogeneous and Heterogeneous Catalysis

Beyond platinum: A recently reported nickel-based molecular catalyst stands out as one of the best non-platinum-based catalysts developed for the electrochemical evolution of hydrogen. These findings are discussed within the framework of a simple theory for this reaction that has evolved from the Sabatier principle (see volcano plot in the picture, η is the thermodynamic overpotential, ΔG(H) is the binding energy of H to the catalyst) and recent DFT calculations.



Essays

Plastic Banknotes

E. L. Prime,
D. H. Solomon* ———— **3726 – 3736**

Australia's Plastic Banknotes: Fighting Counterfeit Currency

More security: The world's first banknote printed on clear plastic film and using optically variable devices (OVDs) was issued in Australia in 1988 (see picture) after twenty years of research and development. In the course of this, a great deal of technical as well as logistic issues had to be solved. Shown is the Australian Bicentennial $10 note released in 1988.

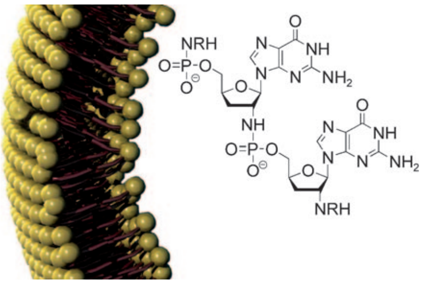
Reviews

The Origin of Life

U. J. Meierhenrich,* J.-J. Filippi,
C. Meinert, P. Vierling,
J. P. Dworkin ———— **3738 – 3750**

On the Origin of Primitive Cells: From Nutrient Intake to Elongation of Encapsulated Nucleotides

A primitive cell remodeled: Bilayer membrane vesicles (see picture) provide a multifaceted microenvironment in which protometabolic reactions could have been triggered. This Review summarizes experiments carried out to form vesicles by the aggregation of amphiphiles. The addition of nucleotides to the extravesicular medium results in them being taken up and their participation in non-enzymatic elongation of the DNA primer within the vesicular interior.



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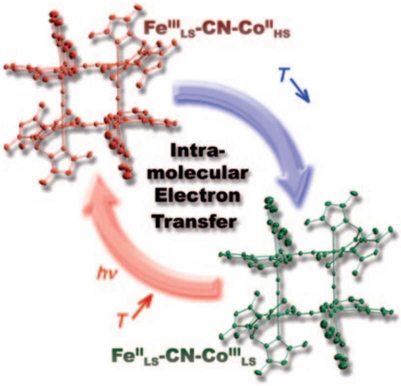
Communications

Flip to be square: Structural, spectroscopic, magnetic, and photomagnetic studies conclusively demonstrate that a tetranuclear cyanometalate $\{Fe_2Co_2\}$ complex undergoes reversible thermally and light-induced changes in its optical and magnetic properties. This bistability is induced by an intramolecular electron transfer, as observed in three-dimensional Co/Fe Prussian blue compounds (see picture).



Bistable Materials

Y. Zhang, D. Li, R. Clérac,* M. Kalisz, C. Mathonière,* S. M. Holmes* ______ **3752 – 3756**

Reversible Thermally and Photoinduced Electron Transfer in a Cyano-Bridged $\{Fe_2Co_2\}$ Square Complex

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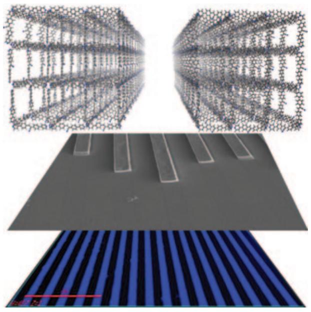

The fluorescent stripes: Coordination polymerization of pyridine-based ligands and zinc or silver ions was controlled by soft lithographic micromolding in capillaries. The polymer patterns (see picture) that are produced are highly fluorescent and supramolecularly structured.

Micropatterning

Y. You, H. Yang, J. W. Chung, J. H. Kim, Y. Jung, S. Y. Park* ______ **3757 – 3761**

Micromolding of a Highly Fluorescent Reticular Coordination Polymer: Solvent-Mediated Reconfigurable Polymerization in a Soft Lithographic Mold

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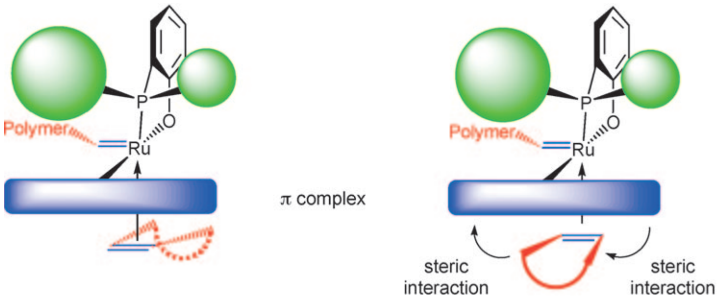


This way and that: Ruthenium complexes with asymmetric bidentate phosphine ligands bearing two substituents that differ in size (green spheres) produce a totally alternating copolymer of norbornene and cyclooctene by ring-opening metathesis polymerization (ROMP). The *E*/*Z* ratio can be influenced systematically by changing the bulkiness of the aryl sulfonate ligand (blue rectangles).

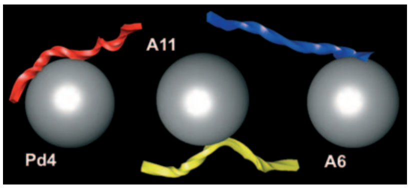
Designed Stereoselectivity

S. Torker, A. Müller, P. Chen* ______ **3762 – 3766**

Building Stereoselectivity into a Chemoselective Ring-Opening Metathesis Polymerization Catalyst for Alternating Copolymerization

---

A lot of pep: Simple changes to the sequence of peptide nanostructures were found to maintain stability and enhance the activity of peptide-based palladium nanocatalysts. A histidine to alanine substitution in the peptide chain afforded an increase in turnover frequency from 2234 to 5224, which suggests that the peptide modulates the functionality of bio-inspired nanomaterials.



Nanotechnology

R. Coppage, J. M. Slocik, M. Sethi, D. B. Pacardo, R. R. Naik, M. R. Knecht* ______ **3767 – 3770**

Elucidation of Peptide Effects that Control the Activity of Nanoparticles

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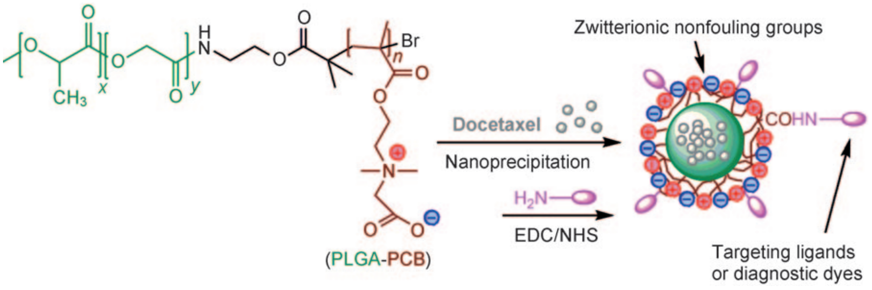
Nanoparticles

Z. Cao, Q. Yu, H. Xue, G. Cheng, S. Jiang* ———— 3771 – 3776

Nanoparticles for Drug Delivery Prepared from Amphiphilic PLGA Zwitterionic Block Copolymers with Sharp Contrast in Polarity between Two Blocks

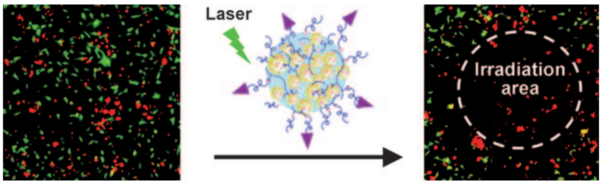


In sharp contrast: Poly(carboxybetaine) (PCB)–poly(lactic-co-glycolic acid) (PLGA) block copolymers were obtained by inclusion of *t*Bu groups onto the PCB monomers. The resulting self-assembled PLGA core/PCB shell nanoparticles have extraordinary stability and a high potential for functionalization because of the COO^- groups on the PCB shell (see picture; EDC = 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide; NHS = *N*-hydroxysuccinimide).

Nanotechnology

S. T. Wang,* K.-J. Chen, T.-H. Wu, H. Wang, W.-Y. Lin, M. Ohashi, P.-Y. Chiou,* H.-R. Tseng* —— 3777 – 3781

Photothermal Effects of Supramolecularly Assembled Gold Nanoparticles for the Targeted Treatment of Cancer Cells

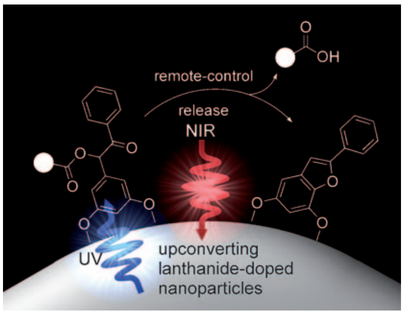


Laser-triggered nanobomb: Size-controlled gold supramolecular nanoparticles (Au-SNPs) were synthesized from 2 nm gold colloids by a supramolecular self-assembly approach. These Au-SNPs exhibited significantly enhanced photothermal effects and could be used in conjunction with laser irradiation for the selective destruction of cancer cells (see picture) after the incorporation of a target-specific ligand.

Photochemistry

C.-J. Carling, F. Nourmohammadian, J.-C. Boyer, N. R. Branda* —— 3782 – 3785

Remote-Control Photorelease of Caged Compounds Using Near-Infrared Light and Upconverting Nanoparticles

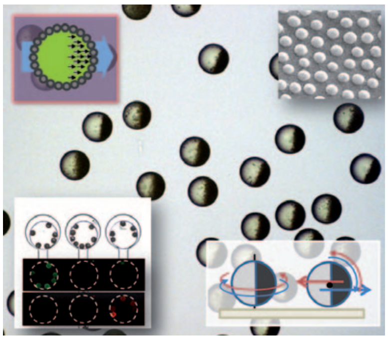


Cage fighter: Lanthanide-doped upconverting nanoparticles convert near-infrared light into ultraviolet light, which drives the photoinduced release of a "caged" species on the nanoparticle surface. This approach overcomes the problem that low-energy light is necessary for penetrating deeper into tissue without damage but cannot be used to directly trigger important organic photochemical reactions.

Magnetic Particles

S.-H. Kim,* J. Y. Sim, J.-M. Lim, S.-M. Yang* ———— 3786 – 3790

Magnetoresponsive Microparticles with Nanoscopic Surface Structures for Remote-Controlled Locomotion

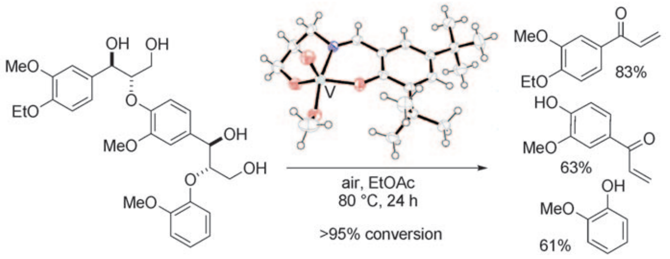


Rock and roll: The rotational and translational motion of magnetic Janus particles with nanoscopic surface structure can be controlled by an external magnetic field (see picture). The nanoscopic surface pattern enhances the microscopic motion of the microspheres by inducing strong coupling between rotation and translation. The separation of individual microspheres from the mixture in a microfluidic device is also demonstrated.

Selective C–O Cleavage

S. Son, F. D. Toste* ________ **3791 – 3794**

Non-Oxidative Vanadium-Catalyzed C–O Bond Cleavage: Application to Degradation of Lignin Model Compounds

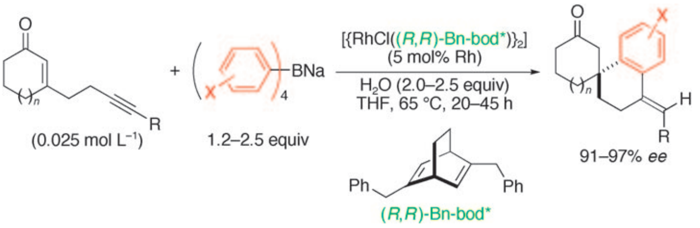


New direction: Changes in the ligand structure divert the reactivity of vanadium(V) oxo complexes from alcohol oxidation to a novel non-oxidative C–O bond cleavage. Thus, highly functionalized aryl enones can be selectively generated from lignin model compounds by vanadium-catalyzed cleavage of the β-O-4 linkage (see scheme; N blue, O red).

Asymmetric Catalysis

R. Shintani,* S. Isobe, M. Takeda, T. Hayashi* ________ **3795 – 3798**

Rhodium-Catalyzed Asymmetric Synthesis of Spirocarbocycles: Arylboron Reagents as Surrogates of 1,2-Dimetalloarenes

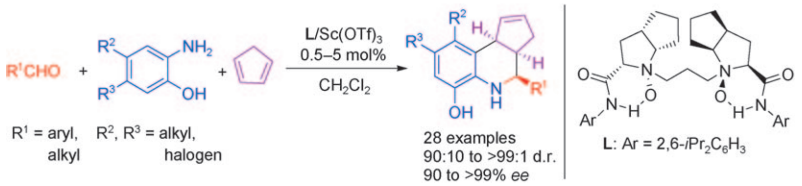


Revolutionary Rh-oad: A rhodium/diene-catalyzed addition of sodium tetraarylborates to alkyne-tethered 2-cycloalken-1-ones has been developed for the synthesis of spirocarbocycles. The tetraarylborates catalytically form two new carbon–carbon bonds. A chiral diene ligand also asymmetrically creates quaternary spirocarbon stereocenters with high enantiomeric purity.

Asymmetric Catalysis

M. S. Xie, X. H. Chen, Y. Zhu, B. Gao, L. L. Lin, X. H. Liu, X. M. Feng* ________ **3799 – 3802**

Asymmetric Three-Component Inverse Electron-Demand Aza-Diels–Alder Reaction: Efficient Synthesis of Ring-Fused Tetrahydroquinolines



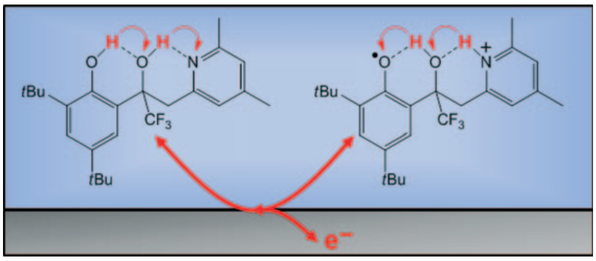
Diels or no Diels: The titled reaction of aldehydes, anilines, and cyclopentadiene, promoted by 0.5–5 mol% of an *N*,*N*′-dioxide scandium complex, afforded ring-fused tetrahydroquinolines that contained three contiguous stereocenters. The one-pot reaction delivers the products with good yields and excellent diastereo- and enantioselectivities.

VIP

Concerted Proton–Electron Transfer

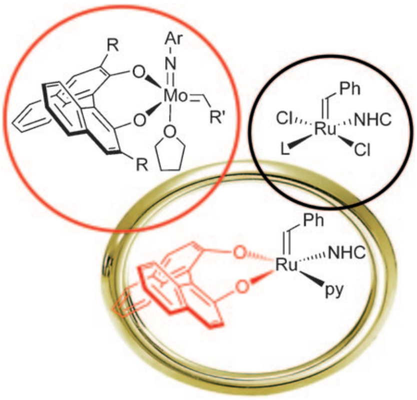
C. Costentin, M. Robert, J.-M. Savéant,* C. Tard ________ **3803 – 3806**

Inserting a Hydrogen-Bond Relay between Proton Exchanging Sites in Proton-Coupled Electron Transfers



Take the "H-bond" train: Introduction of a hydrogen-bond relay efficiently mediates the electron-transfer triggered exchange of protons between two sites over large distances (see picture). Thanks to this concerted proton–electron transfer mechanism, protonation of the relay group is avoided.

The best of both worlds: Direct incorporation of the atropisomeric binaphtholate ligand into the Grubbs class ruthenium metathesis catalysts is described. Chiral Ru–bino complexes are accessible in good to excellent yields by reaction of K_2(bino) with [$RuCl_2$(NHC)(py)$_2$(=CHPh)] in pyridine (see scheme; bino = 1,1′-binaphthyl-2,2′-diolate, py = pyridine, NHC = IMes, H_2IMes; IMes = *N*,*N*′-bis(mesityl)-imidazol-2-ylidene; L = PCy_3 or (py)$_2$).



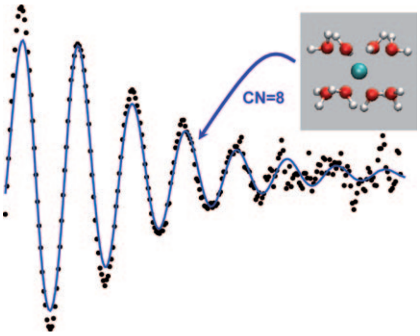
Chiral Catalysts

J. M. Blacquiere, R. McDonald,
D. E. Fogg* **3807–3810**

Integrating the Schrock and Grubbs Catalysts: Ruthenium–Binaphtholate Catalysts for Olefin Metathesis

---

Wish they all could be californium: X-ray absorption spectroscopy (black points) and Monte Carlo simulations (blue line) of Cf^{III} in aqueous solutions have been combined to determine the ligand distance and coordination number (CN) of the Cf^{III} aqua ion (see picture), the heaviest cation measured and simulated to date. The results confirm that a contraction takes place in the actinide series as in the lanthanide series.



Actinides

E. Galbis, J. Hernández-Cobos,
C. den Auwer,* C. Le Naour,
D. Guillaumont, E. Simoni,
R. R. Pappalardo,
E. Sánchez Marcos* **3811–3815**

Solving the Hydration Structure of the Heaviest Actinide Aqua Ion Known: The Californium(III) Case

---

Hitting the target: A combined computational and experimental approach defines optimal and suboptimal RNA motifs as targets for small molecules through two-dimensional combinatorial screening. The method, termed structure–activity relationships through sequencing (StARTS), uses information from the sequences of the RNA motifs selected to bind a ligand.

Cheminformatics

S. P. Velagapudi, S. J. Seedhouse,
M. D. Disney* **3816–3818**

Structure–Activity Relationships through Sequencing (StARTS) Defines Optimal and Suboptimal RNA Motif Targets for Small Molecules

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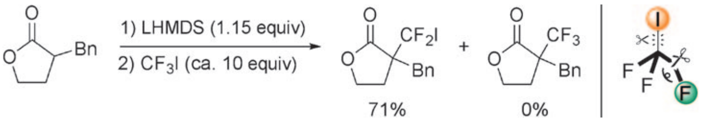


The I's have it: A conceptually new C–F activation/C–C formation and its mechanism are described. Surprisingly, a reaction with Li-enolates and trifluoromethyl iodide gave (alpha)-difluoromethyl product via C–F bond cleavage in preference to the weaker C–I bond of trifluoromethyliodide. This reaction proceeds without the use of any late transition-metal catalyst (see scheme; LHMDS = lithium hexamethyldisilaxide).

Fluorine Chemistry

K. Mikami,* Y. Tomita,
Y. Itoh **3819–3822**

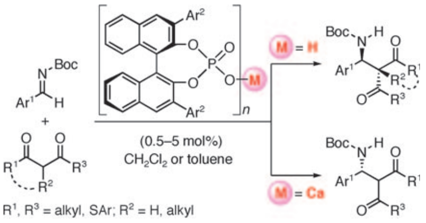
Activation of C–F Bonds in Preference to C–I Bonds: Difluoromethylation of Lithium Enolates with Trifluoromethyl Iodide

Contents

Asymmetric Catalysis

M. Hatano, K. Moriyama, T. Maki,
K. Ishihara* ______________ 3823 – 3826

Which Is the Actual Catalyst: Chiral Phosphoric Acid or Chiral Calcium Phosphate?

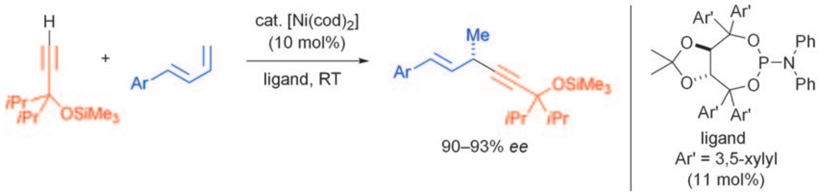


Both catalysts work: A highly enantioselective direct Mannich-type reaction of *N*-Boc-protected aldimines with 1,3-dicarbonyl compounds has been developed with the use of a chiral phosphoric acid in the presence or absence of Ca^{II}. The absolute stereoselectivity of the phosphoric acid catalysis was found to be opposite to that of the calcium phosphate catalysis (see scheme; Boc = *tert*-butoxycarbonyl).

Asymmetric C–H Addition

M. Shirakura,
M. Suginome* ______________ 3827 – 3829

Nickel-Catalyzed Asymmetric Addition of Alkyne C–H Bonds across 1,3-Dienes Using Taddol-Based Chiral Phosphoramidite Ligands

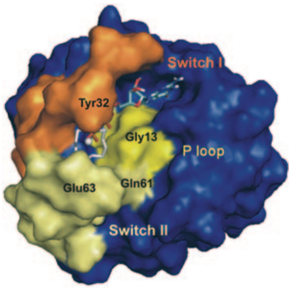


Enantioenriched 3-methyl-1,4-enynes are the products of the title reaction. The terminal α-siloxy-*sec*-alkyl groups were then converted into γ-oxoalkyl groups by rhodium-catalyzed conjugate alkynyl addition to α,β-unsaturated ketones through cleavage of the alkynyl C–C bond.

Inhibitors

I. C. Rosnizeck, T. Graf, M. Spoerner,
J. Tränkle, D. Filchtinski, C. Herrmann,
L. Gremer, I. R. Vetter, A. Wittinghofer,
B. König, H. R. Kalbitzer* __ 3830 – 3833

Stabilizing a Weak Binding State for Effectors in the Human Ras Protein by Cyclen Complexes



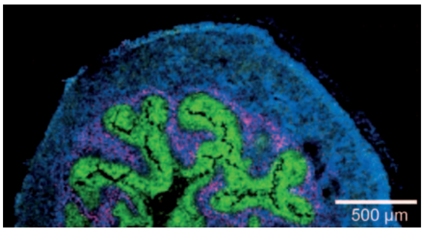
En route to new inhibitors: The binding of Zn^{2+} cyclen to the human Ras protein stabilizes a protein conformation that has a weak affinity for effectors. Consequently this complex is a lead structure for inhibition studies on the Ras–effector interaction. The picture shows the NMR structure of Ras·Mg^{2+}·GppNHp complexed to Zn^{2+} cyclen.

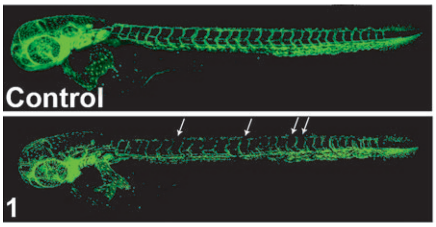
Mass-Spectrometry-Based Histology

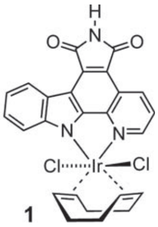
A. Römpp, S. Guenther, Y. Schober,
O. Schulz, Z. Takats, W. Kummer,
B. Spengler* ______________ 3834 – 3838

Histology by Mass Spectrometry: Label-Free Tissue Characterization Obtained from High-Accuracy Bioanalytical Imaging

Next-generation imaging mass spectrometry of biological tissue on the cellular level shows excellent agreement with histochemical evaluation whilst providing a much higher discrimination capacity based on label-free molecular information (see image of a mouse urinary bladder section).






1

Identified as nanomolar and selective inhibitor of receptor protein kinase VEGFR3 (Flt4), the nontoxic and octahedrally coordinated Ir^{III} complex **1** was synthesized by a stereoselective oxidative addition to a square-planar coordinated Ir^{I} precursor. The arrows in the image indicate positions at which the blood vessel formation in a zebrafish model of angiogenesis has been hampered by **1**.

Bioorganometallic Chemistry

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