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:

*C. Filser, D. Kowalczyk, C. Jones, M. Wild, U. Ipe, D. Vestweber, H. Kunz**
Synthetic Glycopeptides with Varied Sialyl Lewis^x Structures as Cell-Adhesion Ligands for E-Selectin

*J. Glöckler, S. Klützke, W. Meyer-Zaika, A. Reller, F. J. García-García, Hans-H. Strehblow, P. Keller, E. Rentschler, W. Kläui**
Towards Nanostructured Water-Soluble and Catalytically Active Rhodium Clusters

R. Fischer, M. Gärtner, H. Görls, L. Yu, M. Reiher, M. Westerhausen**
Synthesis and Properties of the THF Solvates of Extremely Soluble Bis(2,4,6-trimethylphenyl)calcium and Tris(2,6-dimethoxyphenyl)dicalcium Iodide

*J. Garcia-Álvarez, A. R. Kennedy, J. Klett, R. E Mulvey**
Alkali-Metal-Mediated Mangantion: A Method for Directly Attaching Manganese(II) Centers to Aromatic Frameworks

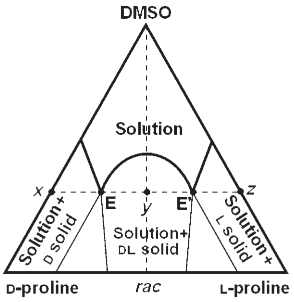
*M. R. Radowski, A. Shukla, H. v. Berlepsch, C. Böttcher, G. Pickaert, H. Rehage, R. Haag**
Supramolecular Aggregates of Dendritic Multishell Architectures as Universal Nanocarriers

C. Borek, K. Hanson, P. I. Djurovich, M. E. Thompson, K. Aznavour, R. Bau, Y. Sun, S. R. Forrest, J. Brooks, L. Michalski, J. Brown*
Highly Efficient, Near-Infrared Electrophosphorescence from a Pt Metalloporphyrin Complex

News

Books

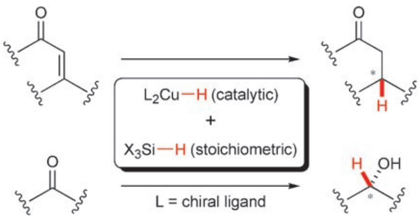
Highlights



What you have and what you get are not necessarily the same: for example, solid enantiomerically enriched proline provides solutions of constant *ee*, 99% in $CHCl_3$ and 50% in DMSO. The Highlight discusses recent papers that give insight into the behavior of enantioenriched proline under heterogeneous conditions which may provide an explanation for the nonlinear effects sometimes observed.

Enantioenriched Proline

Minireviews



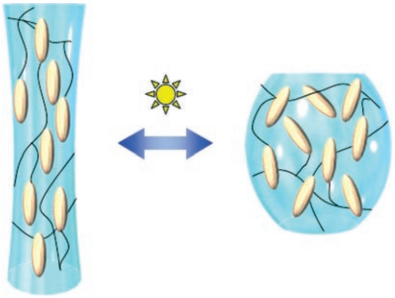
Copper hydride strikes back: The rediscovery of silanes as stoichiometric hydride sources for copper(I)-catalyzed reductions (see scheme) has triggered an avalanche of enantioselective procedures for 1,2- as well as 1,4-reductions and related tandem processes.

Asymmetric Catalysis

Contents

Reviews

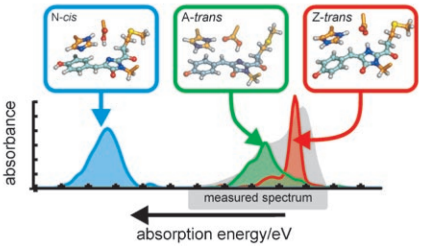
Artificial Muscles



Muscling in on the action: Liquid-crystalline elastomers are promising materials for artificial muscles driven by external stimuli. This Review describes the recent progress in the area of soft materials (liquid-crystalline elastomers and other polymers) that can effectively convert light into mechanical energy (photomechanical effect, see picture).

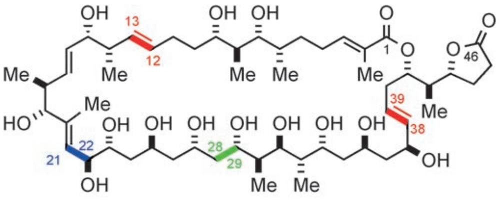
Communications

Photoswitching



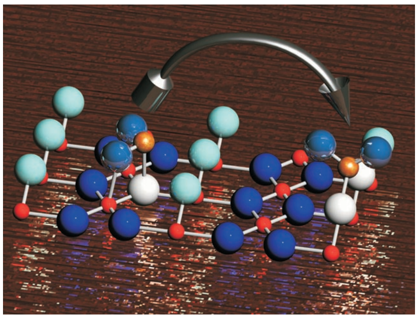
Molecular light-switch: Off–on switching of the fluorescence of the protein asFP595 involves a *trans–cis* isomerization. Mixed quantum/classical simulations elucidate the spectroscopic properties of asFP595 and give detailed insights into the photoswitching mechanism. The conformational *trans–cis* switching triggers a proton-transfer cascade between the chromophore and adjacent amino acids.

Natural Products Synthesis



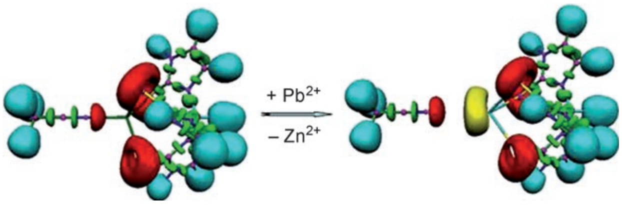
oasomycin A

Putting the pieces together: The total synthesis of the natural macrolide oasomycin A has been realized. Key fragment couplings include an *anti*-Felkin selective aldol addition (green), Kociensky–Julia olefinations (red), and competitive Weinreb amide acylation reaction (blue). The utility of the 4,5-diphenyloxazole as a carboxy surrogate and the late-stage macrolactonization affording the 42-membered macrocycle of oasomycin A are also described.



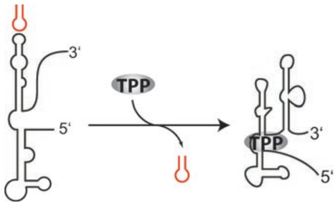
Oxygen vacancies are shown by STM to play a fundamental role in the stabilization of complex anions on an oxide surface at elevated temperatures. By increasing the temperature in the range 120–420 K, sulfite is transformed into sulfate on a $TiO_2(110)$ surface, and there is a change in the adsorption site which seems to be driven by stabilization of the adsorbate by an oxygen vacancy (see picture; Ti: red, O: blue, turquoise, and white, S: bronze).

Chemisorption



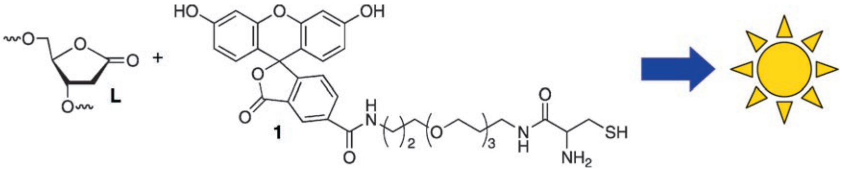
Chop and change: Upon substitution of native Zn^{2+} by exogenous Pb^{2+} ions in a model of δ-aminolevulinic acid dehydratase, a dramatic change occurs in the topology of the electron localization function at the active site of the protein. This effect is expected to disrupt the natural function of the metalated domain.

Saturnism



Molecular diversity meets RNA conformation: In vitro selected RNA hairpins (red) bind to the *thiM* riboswitch of *E. coli* and are released upon addition of thiamine pyrophosphate (TPP; see scheme). These hairpins guide the identification of nucleotides that are important for riboswitch function.

Riboswitches



Throwing light on lesions: DNA oxidation is a ubiquitous but potentially dangerous process that produces a variety of structural modifications in the biopolymer. One modified unit, 2-deoxyribonolactone (**L**), produces cross-links with DNA repair proteins and is mutagenic. Selective fluorescence sensors (e.g. **1**) show that **L** is the major alkali-labile deoxyribose lesion produced in DNA exposed to γ radiolysis.

DNA Damage

For the USA and Canada:
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Contents

Cascade Reactions

M. Movassaghi,* B. Chen —— **565 – 568**

Stereoselective Intermolecular Formal [3+3] Cycloaddition Reaction of Cyclic Enamines and Enones

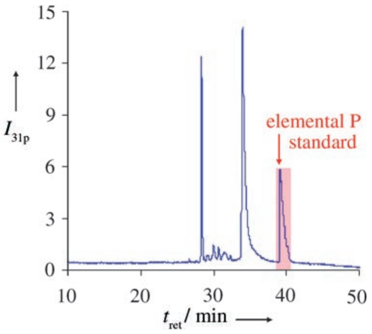
A convergent strategy for the synthesis of tricyclic imino alcohols was partly inspired by a postulated biosynthesis of galbulimima alkaloids. In this sequential α,α′ alkylation of unsymmetrical ketoimines, at least three stereocenters are created with a high level of diastereoselectivity. Organocatalytic and asymmetric variants of this methodology complement an organocuprate-based approach (see scheme).

Analytical Methods

A. Pereira Navaza, J. Ruiz Encinar,
A. Sanz-Medel* ———— **569 – 571**

Absolute and Accurate Quantification of Protein Phosphorylation by Using an Elemental Phosphorus Standard and Element Mass Spectrometry

The simpler the better: The combination of element mass spectrometry under optimized conditions and an elemental phosphorus standard provides a generic approach for absolute quantitative phosphoproteomics. This approach allows for simultaneous and reliable quantification of each individual phosphopeptide (corresponding to the different phosphorylation sites) present in a tryptic digest of a protein mixture.

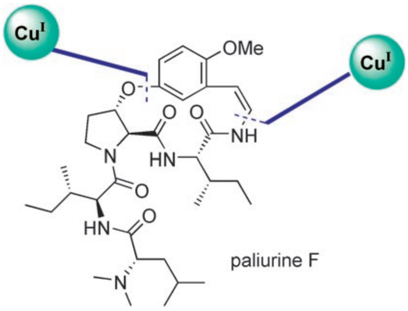


Natural Products Synthesis

M. Toumi, F. Couty, G. Evano* **572 – 575**

Total Synthesis of Paliurine F

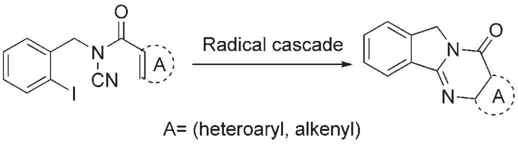
A couple of coppers: An efficient, asymmetric synthesis of the sedative cyclopeptide alkaloid paliurine F has been achieved. The strategy employs two copper(I)-mediated coupling reactions as key steps to install the aryl ether linkage as well as to form the enamide with a concomitant unprecedented macrocyclization.



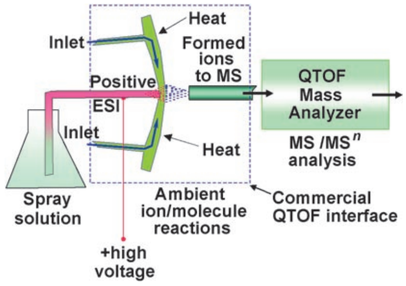
Polynitrogenated Heterocycles

A. Servais, M. Azzouz, D. Lopes,
C. Courillon,* M. Malacria* —— **576 – 579**

Radical Cyclization of *N*-Acylcyanamides: Total Synthesis of Luotonin A



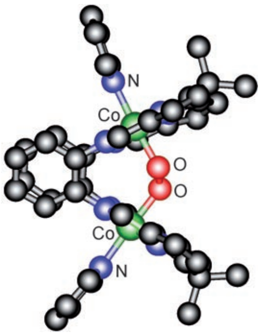
As radical chain cascade precursors, *N*-acylcyanamides give rise to amide–iminyl radicals which, when appropriately substituted, can finally yield pyrroloquinazolines. The versatility of these new radical acceptors is illustrated by the formation of N-heterocycles with wide structural variation and by the total synthesis of luotonin A.



A blow-by-blow account: Extractive electrospray ionization (EESI) quadrupole TOF (QTOF) mass spectrometry has been established with a commercial instrument without hardware modification for the rapid analysis of breath without sample pretreatment (see picture). Sulfur-containing compounds can be selectively detected by using silver cationization in the EESI source—a method of interest for in vivo metabolic studies and clinical diagnosis.

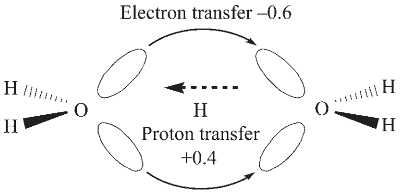
Analytical Methods

Fixed and reduced: Dicobalt complexes of a Schiff base calixpyrrole ligand adopt rigid, wedged "pacman" structures that can accommodate oxygen (see picture) and reduce it within the bimetallic molecular cleft.



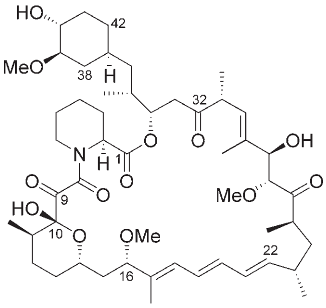
Oxygen Activation

The dynamics of the coupled transfer of electrons and protons were studied theoretically in the colliding system $H_2O + H_3O^+$. In the ground-state dynamics, the proton, tightly covered with electrons, carries a net charge of as much as about +0.4, and therefore about 0.6 electrons are carried back in the reverse direction through a different path (see scheme).



Molecular Dynamics

Rapamycin synthesis all wrapped up: A new convergent synthesis of rapamycin (**1**) is reported that involves a macroetherification/catechol tethering strategy for construction of the macrocyclic core of this intriguing natural product. Other studies on this commercialized potent immunosuppressant delineate new cell signaling pathways of relevance to cancer chemotherapy.



(−)-rapamycin **1**

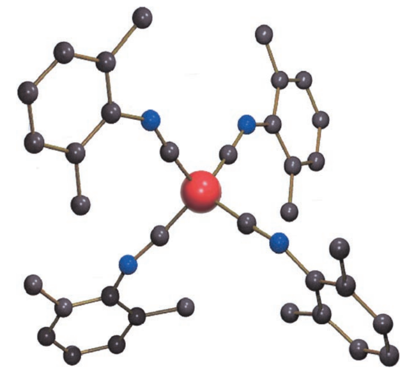
Natural Products Synthesis

Contents

Subvalent Compounds

W. W. Brennessel, J. E. Ellis* — **598 – 600**

$[Fe(CNXyl)_4]^{2-}$: An Isolable and Structurally Characterized Homoleptic Isocyanidemetalate Dianion



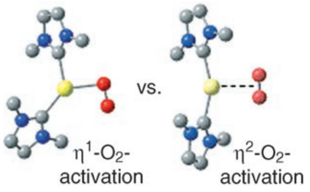
World's record: The first isolation and structural characterization of a homoleptic isocyanidemetalate dianion has been achieved with $[Fe(CNXyl)_4]^{2-}$ (Xyl = 2,6-dimethylphenyl; see structure, Fe red, N blue, C gray). Spectral and structural data indicate that metal-to-isocyanide back-bonding in this electron-rich species is the largest ever observed in a homoleptic isocyanide complex containing only terminally bound ligands.

Aerobic Oxidation

B. V. Popp, J. E. Wendlandt, C. R. Landis,* S. S. Stahl* ——— **601 – 604**

Reaction of Molecular Oxygen with an NHC-Coordinated Pd^0 Complex: Computational Insights and Experimental Implications

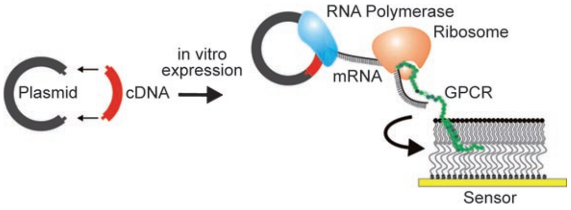
O_2 activation: Computational studies of the reaction of O_2 with an $[(NHC)_2Pd^0]$ (NHC = N-heterocyclic carbene) complex reveal an unexpectedly small driving force for formation of a $Pd^{II}(\eta^2\text{-}O_2)$ product. This result led to experimental demonstration of reversible O_2 coordination to the $(NHC)_2Pd$ center. Computational analysis of the reaction coordinate reveals that O_2 reacts with Pd^0 through a stepwise mechanism involving an $\eta^1\text{-}O_2$ transition state.



Artificial Membranes

R. Robelek, E. S. Lemker, B. Wiltschi, V. Kirste, R. Naumann, D. Oesterhelt, E.-K. Sinner* ——— **605 – 608**

Incorporation of In Vitro Synthesized GPCR into a Tethered Artificial Lipid Membrane System

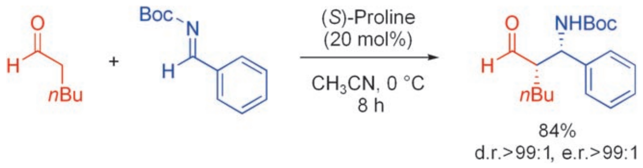


Controlling the context: A novel strategy for the in vitro expression and immediate post-translational membrane insertion of complex membrane proteins into an artificial membrane system is described. In this way problems are circumvented that arise when complex membrane proteins are overexpressed, detergent-solubilized, and subsequently reconstituted into suitable artificial membrane systems for biophysical characterization. GPCR = G-protein coupled receptor.

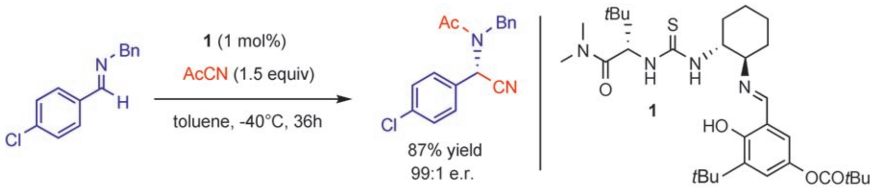
Organocatalysis

J. W. Yang, M. Stadler, B. List* **609 – 611**

Proline-Catalyzed Mannich Reaction of Aldehydes with *N*-Boc-Imines

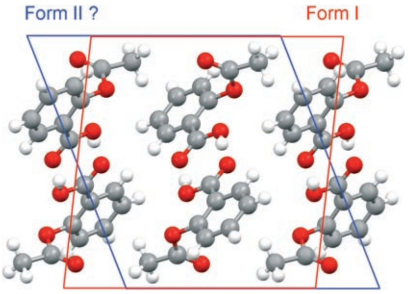


A curious cat.: The proline-catalyzed Mannich reaction between aldehydes and *N*-Boc-imines (Boc = *tert*-butoxycarbonyl) gives crystalline β-amino aldehydes with exceptionally high diastereoselectivities and enantioselectivities (see scheme). The products of this reaction typically precipitate from the reaction mixture and are useful intermediates in the synthesis of α- and β-substituted β-amino acids.



The less problematic acetyl cyanide can be used instead of toxic HCN for the highly enantioselective acyl-Strecker-type reaction. In the presence of an *N*-benzylimine and a catalytic amount of Jacobsen's catalyst **1**, the desired α-amidonitrile is obtained in excellent enantioselectivity and yield.

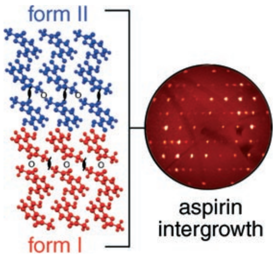
Organocatalysis



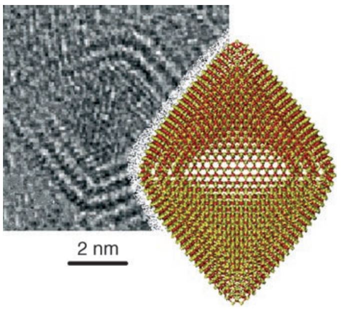
More headaches with aspirin: No new polymorph? Reduction and re-indexing of X-ray data collected on a crystal of the well-known form I of aspirin in a unit cell recently reported for the new form II results in a data set from which this so-called new form can be obtained and even refined isotropically! Form II, if it exists, needs to be identified with more rigorous experimentation and modeling.

Aspirin Polymorphism (1)

Aspirin: No end to the headaches? The two known crystalline arrangements of aspirin are so closely related that aspirin crystals form intergrowth structures containing domains of form I and domains of form II. The ratio and distribution of the domains is variable among aspirin samples, raising questions for the definition of the term polymorph in this case.



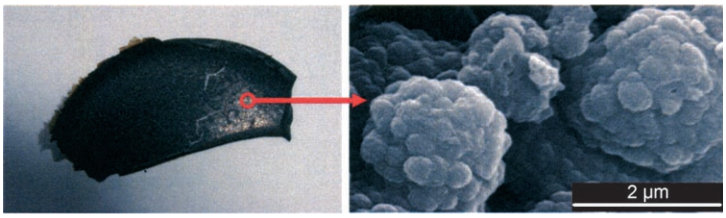
Aspirin Polymorphism (2)



Opening the window: Hollow multilayer nano-octahedra (see TEM image and structure) often appear in the laser-ablation products of layered transition-metal chalcogenides. Calculations on MoS_2 nanoparticles demonstrate that nano-octahedra exist in a window of stability between nanoplatelets and spherical fullerene-like nanoparticles.

Inorganic Fullerenes

Contents



A common source: In a novel twin polymerization, a single monomer is transformed into an organic–inorganic nanocomposite. For example, tetrafurfuryloxysilane polymerizes to form a dense interpenetrating network of poly(furfuryl alcohol) and SiO_2 (see picture). Nanoporous silicate, and potentially other metal oxides, can be obtained when the organic components are removed.

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

Service

Corrigendum

Solid-State Phase Transition of an Inclusion Complex of 5-Methyl-2-pyridone with 1,3,5-Benzenetricarboxylic Acid

S. Hirano, S. Toyota, F. Toda,* K. Fujii,
H. Uekusa* ——— **6013–6016**

Angew. Chem. Int. Ed. **2006**, *45*

DOI 10.1002/anie.200600845

The surname and E-mail address of one of the correspondence authors of this Communication appeared incorrectly in print. Professor Uekusa’s name should be spelt as it appears here, and his correct E-mail address is uekusa@cms.titech.ac.jp.