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:

H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama, H. Tokuyama**
Total Synthesis of (+)-Haplophytine

*K. Fuchibe, T. Kaneko, K. Mori, T. Akiyama**
Expedient Synthesis of N-Fused Indoles: A C–F Activation and C–H Insertion Approach

A. Giannis, P. Heretsch, V. Sarli, A. Stößel*
Synthesis of Cyclopamine Using a Biomimetic and Diastereoselective Approach

W. A. Chalifoux, R. McDonald, M. J. Ferguson, R. R. Tykwinski
***tert*-Butyl Endcapped Polyynes: Crystallographic Evidence of Reduced Bond-Length Alternation**

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

*D. C. K. Rathwell, S.-H. Yang, K. Y. Tsang, M. A. Brimble**
An Efficient Formal Synthesis of the Human Telomerase Inhibitor (±)-γ-Rubromycin

C. A. Strassert, M. Otter, R. Q. Albuquerque, A. Höne, Y. Vida, B. Maier, L. De Cola**
Photoactive Hybrid Nanomaterial for Targeting, Labeling, and Killing Antibiotic-Resistant Bacteria

*Y. Tanaka, Y. Hirana, Y. Niidome, K. Kato, S. Saito, N. Nakashima**
Experimentally Determined Redox Potentials of Individual (*n*,*m*)-Single-Walled Carbon Nanotubes

D. Loffreda, F. Delbecq, F. Vigné, P. Sautet*
Fast Prediction of Selectivity in Heterogeneous Catalysis from Extended Brønsted–Evans–Polanyi Relations: A Theoretical Insight

Author Profile

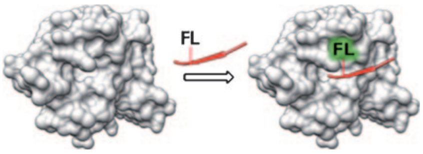
"The biggest challenge facing scientists is that every answer creates at least two new questions.
My favorite subject at school was history.. …"
This and more about Hans-Jörg Himmel can be found on page 7288.

Books

Highlights

Fluorescent Probes

To GFP and beyond: Green fluorescent protein and its array of wavelength variants have transformed cell biology. However, the next generation of fluorescent probes (FL) may emerge from the chemistry laboratory. Sensors have been described that display huge fluorescent changes upon binding to their protein targets (see picture). Nevertheless, a number of challenges must be overcome before these species find universal application in cells and beyond.

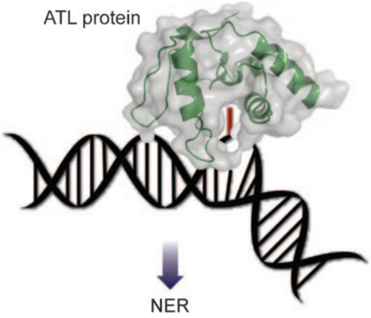


Contents

DNA Repair

T. Reißner, S. Schorr,
T. Carell* ______________ 7293 – 7295

Once Overlooked, Now Made Visible:
ATL Proteins and DNA Repair



Damage report: Alkyltransferase-like proteins (ATLs) flip DNA lesions out of the DNA duplex but have no catalytic function. They act as recognition proteins that mark DNA lesions and allow repair (see picture; NER = nucleotide excision repair).

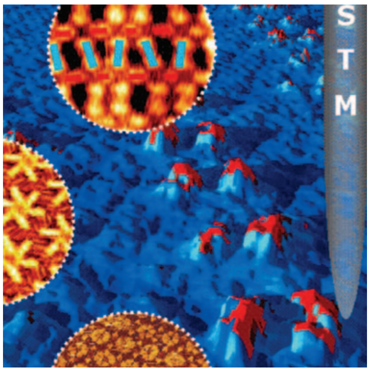
Reviews

Supramolecular Surface Chemistry

J. A. A. W. Elemans, S. Lei,
S. De Feyter* __________ 7298 – 7332

Molecular and Supramolecular Networks on Surfaces: From Two-Dimensional Crystal Engineering to Reactivity

Seeing is believing: Scanning tunneling microscopy (STM) allows the visualization of molecules in real space on atomically flat conductive substrates (see picture), and has formed the basis for the rapid development of supramolecular chemistry at surfaces. This Review highlights recent developments in the design and functionality of supramolecular surface patterns, with a focus on chirality, porosity, and reactivity.

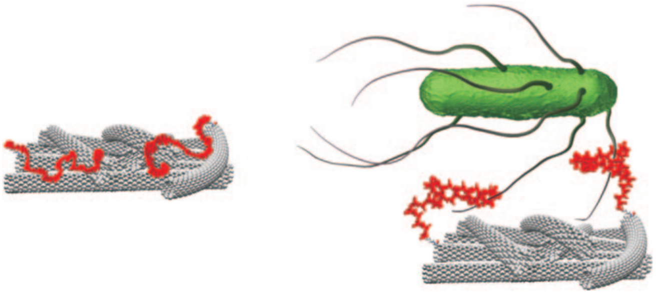


Communications

Biosensors

G. A. Zelada-Guillén, J. Riu,* A. Düzgün,
F. X. Rius* _____________ 7334 – 7337

Immediate Detection of Living Bacteria at Ultralow Concentrations Using a Carbon Nanotube Based Potentiometric Aptasensor



Keeping the doctor away: An aptamer attached to an electrode coated with single-walled carbon nanotubes interacts selectively with bacteria (see picture). The resulting electrochemical response is highly accurate and reproducible and starts at ultralow bacteria concentrations, thus providing a simple, selective method for pathogen detection.

For the USA and Canada:
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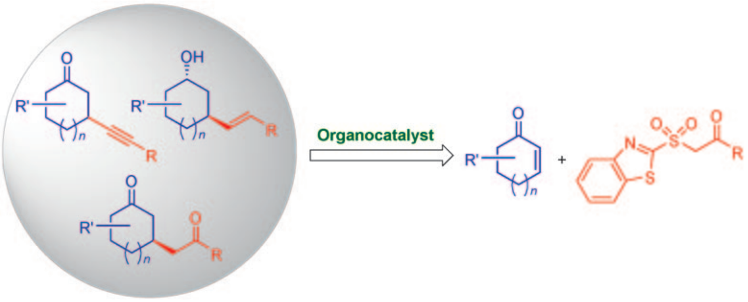
Organocatalysis

M. W. Paixão, N. Holub, C. Vila,
M. Nielsen,
K. A. Jørgensen* ________ **7338 – 7342**

Trends in Organocatalytic Conjugate Addition to Enones: An Efficient Approach to Optically Active Alkynyl, Alkenyl, and Ketone Products



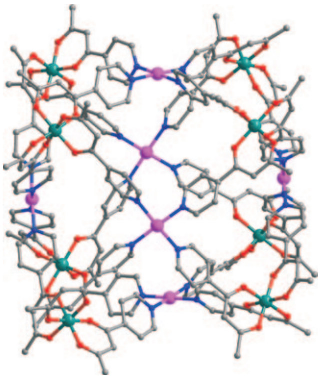
Three in one: Applying an organocatalytic tandem strategy to build a library of optically active alkynyl, alkenyl, and ketone products, starting from cyclic enones and β-keto sulfones, is shown to be rapid and efficient (see scheme; R = aryl, R′ = H or alkyl).

Cage Compounds

H.-B. Wu, Q.-M. Wang* ____ **7343 – 7345**

Construction of Heterometallic Cages with Tripodal Metalloligands

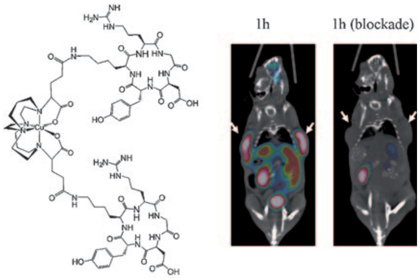
Changing cages: The coordination preferences of the incorporated metals dictates the geometry of the heterometallic cages that are assembled by using AlL_3 (HL = 1-(4-pyridyl)butane-1,3-dione) as a metalloligand. A trigonal bipyramid and a giant capped octahedron (see picture; green Al, red O, blue N, purple Pd) were isolated. The unprecedented spontaneous resolution of the chiral trigonal bipyramidal complex $M_2M'_3L_6$ with D_3 symmetry was observed.



Imaging Probes

W. Liu, G. Hao, M. A. Long, T. Anthony, J.-T. Hsieh, X. Sun* ________ **7346 – 7349**

Imparting Multivalency to a Bifunctional Chelator: A Scaffold Design for Targeted PET Imaging Probes

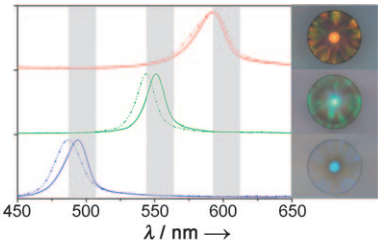


Two are better than one: Multivalent scaffolds for targeted PET imaging probes not only feature chelators that form stable and neutral complexes with a radiometal but also contain functional groups for presentation of multiple targeting molecules. A bivalent scaffold was synthesized and coupled with a targeting ligand to afford the probe, which was used to efficiently image tumors in vivo (see picture).

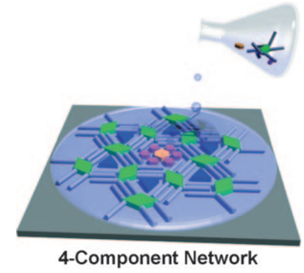
Biomolecule Detection

Y.-J. Zhao, X.-W. Zhao,* J. Hu, J. Li, W.-Y. Xu, Z.-Z. Gu* ________ **7350 – 7352**

Multiplex Label-Free Detection of Biomolecules with an Imprinted Suspension Array



Appearing in print: Polymer beads with a photonic crystal structure can be prepared that display the molecular imprint of a label-free biomolecule to be analyzed. A series of beads corresponding to a series of analytes could be used for multiplex detection of biomolecules with remarkable sensitivity and specificity (see picture).

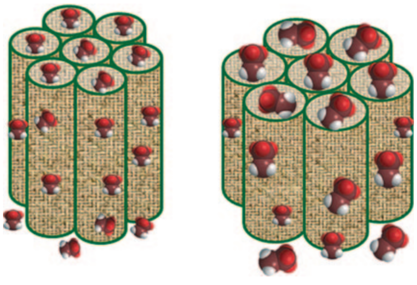


Get it together: A four-component 2D crystal has been formed at a liquid–solid interface and successfully visualized by scanning tunneling microscopy. Simply premixing the four components and applying the solution onto the graphite surface leads to the spontaneous self-assembly of the 2D crystal. Selected guest molecules induce a structural transformation of the host network from nonporous to porous by coadsorption inside the formed pores.

Supramolecular Chemistry

J. Adisoejoso, K. Tahara,* S. Okuhata,
S. Lei,* Y. Tobe,*
S. De Feyter* **7353 – 7357**

Two-Dimensional Crystal Engineering: A Four-Component Architecture at a Liquid–Solid Interface



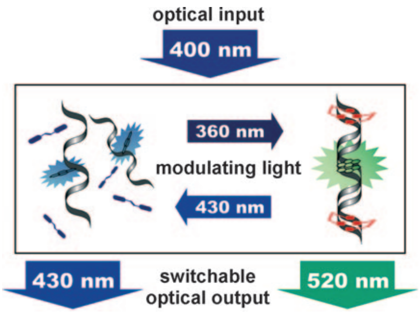
Fully loaded: A facile nanosieve approach for the preparation of Fe_2O_3 nanoparticles that have uniform and tunable sizes and are highly dispersed over a mesoporous support is achieved by the simple adjustment of the pore diameter of the template matrix (see picture). The nanoparticles are very small (6.5–9.0 nm) and show superior magnetic properties compared to pure Fe_2O_3 nanoparticles prepared without using a support.

Magnetic Nanoparticles

S. Alam, C. Anand, K. Ariga, T. Mori,
A. Vinu* **7358 – 7361**

Unusual Magnetic Properties of Size-Controlled Iron Oxide Nanoparticles Grown in a Nanoporous Matrix with Tunable Pores

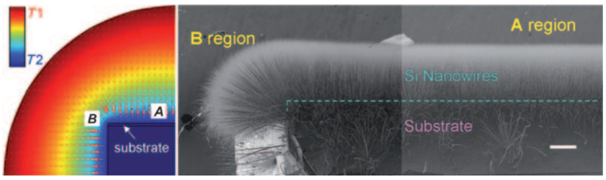
Switched on: The fluorescence emission of a DNA-based optical switch can be reversibly switched from blue to green using modulating light of different wavelengths (see picture). The device is based on the hybridization of two pyrene-functionalized DNA strands in the presence of a photochromic azobenzene-containing effector ligand. Hybridization occurs only with the *cis*-configured ligand, and results in pyrene excimer fluorescence.



DNA Hybridization

S.-n. Uno, C. Dohno, H. Bittermann,
V. L. Malinovskii, R. Häner,*
K. Nakatani* **7362 – 7365**

A Light-Driven Supramolecular Optical Switch



Going straight: A simple and robust mechanism coherently directs nanowire growth directions by introducing a local temperature gradient as the local kinetic variable during the conventional vapor–liquid–solid (VLS) growth (see picture, scale bar = 200 μm). The nanowires grow straight in the vertical direction, but possess kinks near the catalytic tips.

Silicon Nanowires

G. Lee, Y. S. Woo, J.-E. Yang, D. Lee,
C.-J. Kim, M.-H. Jo* **7366 – 7370**

Directionally Integrated VLS Nanowire Growth in a Local Temperature Gradient

Contents

Protein Design

A. F. A. Peacock, J. A. Stuckey,
V. L. Pecoraro* ———— 7371 – 7374

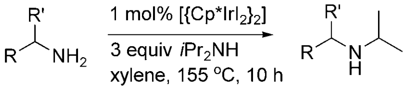
Switching the Chirality of the Metal Environment Alters the Coordination Mode in Designed Peptides

Outsiders make their presence felt: When the chirality of a single layer of amino acids was switched in a three-stranded coiled coil (see picture), X-ray crystallography revealed minimal perturbation of the α-helical backbone of the designed structure. In contrast, spectroscopic studies of cadmium binding showed that this switch in chirality dramatically altered the coordination environment and the position of binding.

Amine Exchange

O. Saidi, A. J. Blacker,
M. M. Farah, S. P. Marsden,
J. M. J. Williams* ———— 7375 – 7378

Selective Amine Cross-Coupling Using Iridium-Catalyzed "Borrowing Hydrogen" Methodology

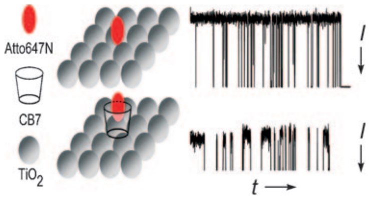


Something borrowed: Amine cross-coupling reactions are catalyzed using $[\{Cp^*IrI_2\}_2]$ ($Cp^* = C_5Me_5$) in the absence of a base. A range of anilines were converted into their *N*-isopropyl derivatives, and the same process was also effective for alkylation of benzylamines and other aliphatic primary amines.

Surface Processes

X. Wu, T. D. M. Bell,
E. K. L. Yeow* ———— 7379 – 7382

Electron Transport in the Long-Range Charge-Recombination Dynamics of Single Encapsulated Dye Molecules on TiO_2 Nanoparticle Films

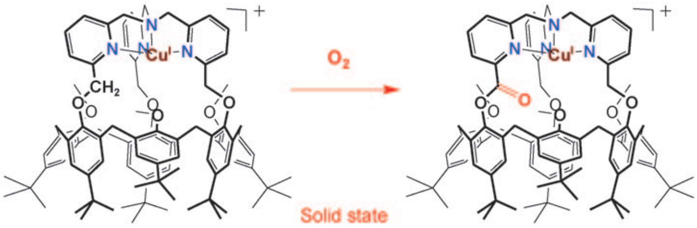


Hitching a slow ride: Long-lived dark charge-separated states arise from the transport of the injected electron on TiO_2 nanoparticles after it is transferred from single Atto647N dye molecules encapsulated in cucurbit[7]uril (CB7). These states are directly probed using the intermittency of the emission intensity trajectories (see spectra).

Dioxygen Activation

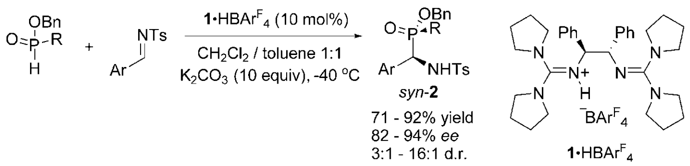
G. Thiabaud, G. Guillemot,
I. Schmitz-Afonso, B. Colasson,
O. Reinaud* ———— 7383 – 7386

Solid-State Chemistry at an Isolated Copper(I) Center with O_2



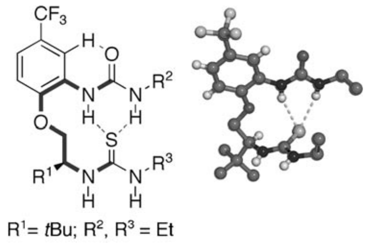
A solid performer: Chemo- and regioselective oxygenation of an organic moiety with O_2 in the solid state gives a Cu^I complex and a four-electron oxidized compound as final products (see scheme). A single Cu^I center in interaction with O_2 mediates an even-electron transfer process without the assistance of a redox cofactor and provides further support for a $[CuO_2]^+$ core as a reactive species allowing C–H bond cleavage.

Asymmetric Catalysis



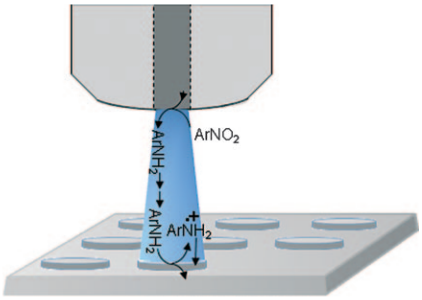
Zero, one, or two? Guanidinium catalyst $1\cdot HBAr^F_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$, Bn = benzyl, Ts = 4-toluenesulfonyl) was obtained in a single step from a commercially available diamine. By using this catalyst an asymmetric phospha-Mannich reaction has been developed, involving secondary phosphine oxides and H-phosphinates as the P nucleophile. A series of enantiomerically enriched α-amino phosphine oxides (**2**), α-amino phosphinate, and H-phosphinates containing a P-chiral center were prepared.

Cooperative Catalysis



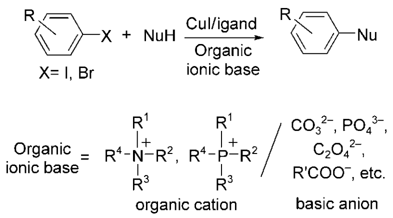
A new twist for a fold: Conformationally well-defined thiourea catalysts, like that shown, stabilized by intramolecular hydrogen bonds demonstrate cooperative ligand–receptor binding. This conformation leads to significantly enhanced catalytic efficiency, resulting in higher turnover rates and lower catalyst loading whilst maintaining high enantioselectivity in a model reaction.

Surface Derivatization



A micropatterning procedure based on the oxidation of an amine starts with the reduction of a nitro-containing compound at the scanning electrochemical microscope tip (see picture). After diffusion in the interelectrode gap, the amine is oxidized on a gold sample, thus resulting in a local derivatization. This procedure is expected to be suitable for extended microstructuring of surfaces.

Homogeneous Catalysis

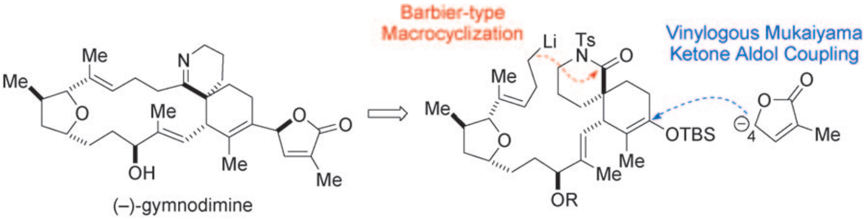


Good solubility alone does not explain the performance of organic ionic bases in the room-temperature coupling of aryl iodides and even bromides with aliphatic and aromatic amines and N-heterocycles (NuH; see scheme). Conductivity measurements show that these organic ionic bases, which contain tetraalkylammonium or -phosphonium cations, are readily ionized in organic solvents.

Natural Product Synthesis

K. Kong, D. Romo,* C. Lee **7402–7405**

Enantioselective Total Synthesis of the Marine Toxin (−)-Gymnodimine Employing a Barbier-Type Macrocyclization

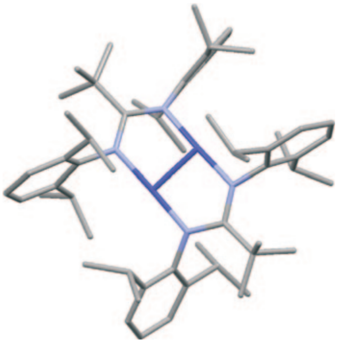


Sea the synthesis: At ambient temperature, *tert*-butyllithium promotes a Barbier-type macrocyclization in the first total synthesis of (−)-gymnodimine (Ts: toluene-4-sulfonyl; TBS: *tert*-butyldimethylsilyl), a member of the spirocyclic-imine family of marine toxins. The synthesis also features a vinylogous Mukaiyama aldol process to couple the labile butenolide moiety onto a macrocyclic ketone intermediate.

Metal–Metal Interactions

C. Jones,* C. Schulten, R. P. Rose,
A. Stasch, S. Aldridge, W. D. Woodul,
K. S. Murray, B. Moubaraki, M. Brynda,
G. La Macchia, L. Gagliardi **7406–7410**

Amidinato– and Guanidinato–Cobalt(I) Complexes: Characterization of Exceptionally Short Co–Co Interactions

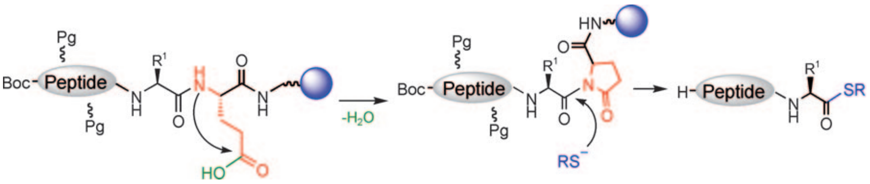


CoCo loco! Ligand-bridged dimers (see picture) with the shortest known Co–Co interactions are the first amidinato and guanidinato cobalt(I) complexes. The nature of the interactions has been probed by magnetic and theoretical investigations, and has been shown to be multiconfigurational. Preliminary reactivity studies of the complexes have also been carried out.

Amide Activation

A. P. Tofteng, K. K. Sørensen,
K. W. Conde-Frieboes, T. Hoeg-Jensen,*
K. J. Jensen* **7411–7414**

Fmoc Solid-Phase Synthesis of C-Terminal Peptide Thioesters by Formation of a Backbone Pyroglutamyl Imide Moiety

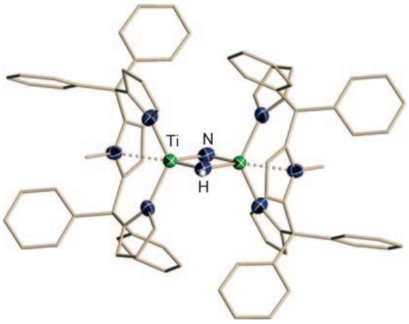


Activating an inactive bond: A new concept in synthetic peptide chemistry, backbone amide activation, proceeds through the selective conversion of a backbone amide into an imide, followed by nucleophilic acyl displacement (see scheme; Boc = *tert*-butoxycarbonyl, Pg = protecting group). This methodology represents a new approach to solid-phase synthesis of C-terminal peptide thioesters, and may become a general tool for the synthesis of peptide thioesters.

Dinitrogen Cleavage

G. B. Nikiforov, I. Vidyaratne,
S. Gambarotta,*
I. Korobkov **7415–7419**

Titanium-Promoted Dinitrogen Cleavage, Partial Hydrogenation, and Silylation

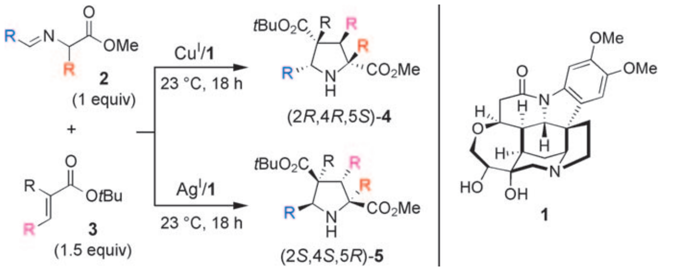


Breaking up: Reduction of a trivalent titanium complex afforded N–N cleavage with formation of Ti^{IV} nitride complexes (see structure), which can be converted into silylated derivatives.

Enantioselectivity

H. Y. Kim, H.-J. Shih, W. E. Knabe,
K. Oh* ———————— **7420 – 7423**

Reversal of Enantioselectivity between the Copper(I)- and Silver(I)-Catalyzed 1,3-Dipolar Cycloaddition Reactions Using a Brucine-Derived Amino Alcohol Ligand

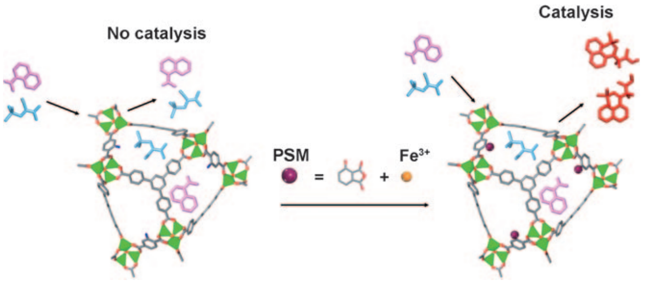


The old switcheroo: The switch in the enantioselectivity of a reaction by using a single chiral source has been achieved using different metal binding modes of the chiral amino alcohol **1** in the presence of Cu^{I} and Ag^{I} sources. Azomethine ylides were shown to undergo highly enantio- and diastereoselective 1,3-dipolar cycloadditions with substituted *tert*-butyl acrylates to provide both of the enantiomerically enriched pyrrolidines (see scheme).

MOF-Based Catalysts

K. K. Tanabe, S. M. Cohen* **7424 – 7427**

Engineering a Metal–Organic Framework Catalyst by Using Postsynthetic Modification

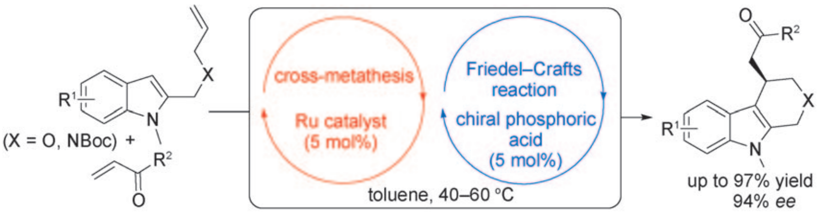


MOF + PSM = Cat: A highly porous metal–organic framework (MOF) is metalated and transformed into an active, robust, reusable catalyst (Cat.) using postsynthetic modification (PSM).

Asymmetric Catalysis

Q. Cai, Z.-A. Zhao,
S.-L. You* ———————— **7428 – 7431**

Asymmetric Construction of Polycyclic Indoles through Olefin Cross-Metathesis/Intramolecular Friedel–Crafts Alkylation under Sequential Catalysis

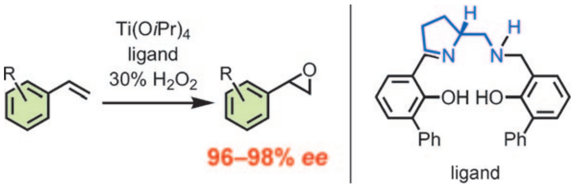


A synthetic shortcut: A highly efficient cascade reaction (see scheme) led to polycyclic indoles with excellent enantioselectivity. The combination of the two steps through sequential catalysis enables the use of more readily available starting materials and makes the synthesis more practical. Boc = *tert*-butoxycarbonyl.

Asymmetric Catalysis

K. Matsumoto, T. Oguma,
T. Katsuki* ———————— **7432 – 7435**

Highly Enantioselective Epoxidation of Styrenes Catalyzed by Proline-Derived C_1-Symmetric Titanium(Salan) Complexes



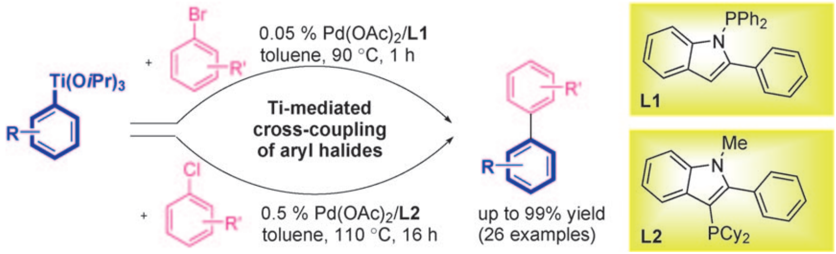
Titanium tough! Novel proline-derived C_1-symmetric titanium(salan) complexes have been used to catalyze the epoxidation of styrene derivatives with aqueous hydrogen peroxide as the oxidant (see scheme). High enantiomeric excesses ranging from 96 to 98% were obtained.

Contents

Cross-Coupling

H. W. Lee, F. L. Lam, C. M. So, C. P. Lau, A. S. C. Chan, F. Y. Kwong* **7436 – 7439**

Palladium-Catalyzed Cross-Coupling of Aryl Halides Using Organotitanium Nucleophiles

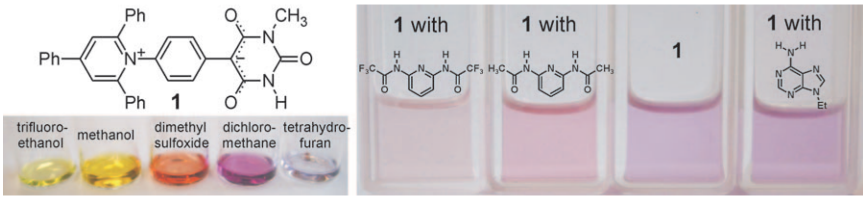


They make a good couple: Catalysts generated from Pd(OAc)$_2$ and indolylphosphine ligands are highly effective in the titanium-mediated coupling of aryl halides. Catalyst loadings as low as 0.05 mol% Pd can be used. The mild reaction conditions also allow the coupling of aryl sulfonyl chlorides with aryl titanium reagents to generate diaryl sulfones.

Molecular Recognition

I. Bolz, D. Schaarschmidt, T. Rüffer, H. Lang, S. Spange* **7440 – 7443**

A Pyridinium–Barbiturate–Betaine Dye with Pronounced Negative Solvatochromism: A New Approach for Molecular Recognition

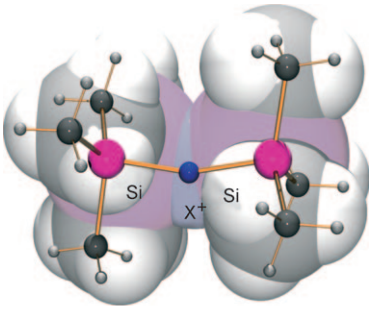


World record: The betaine dye **1** exhibits the highest negative solvatochromic range yet seen. Because of its pronounced push–pull system, **1** is suitable for the detection of polarity changes, acid–base reactions, and the formation of complexes with complementary hydrogen-bond sequences, which can even be followed by the naked eye.

Halonium Ions

M. Lehmann, A. Schulz,* A. Villinger* **7444 – 7447**

Bissilylated Halonium Ions: $[Me_3Si{-}X{-}SiMe_3][B(C_6F_5)_4]$ (X = F, Cl, Br, I)



Double duty: The series of salts containing the bissilylated halonium cation $[Me_3Si{-}X{-}SiMe_3]^+$ (X = F, Cl, Br, and I; see picture) has been generated and fully characterized in the super Lewis acidic silylating medium $Me_3Si{-}X$ (as solvent and reactant) and $[Me_3Si][B(C_6F_5)_4]$ (as silylating reagent).

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

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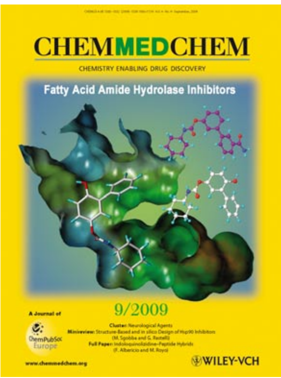

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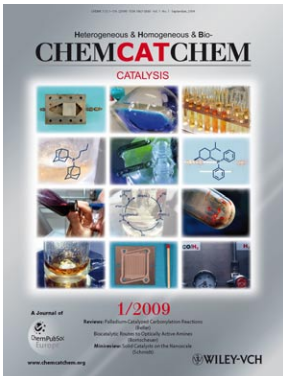

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