Editorial

"... We believe that there is a much wider role for medicinal chemists to play than they are currently permitted by industry to have ..."
Read more in the Editorial by T. Hoffmann and R. Metternich.

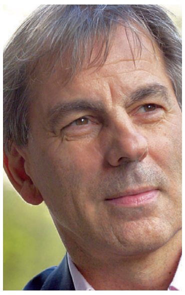
Service

Author Profile

"When I was eighteen I wanted to be a medical doctor. Looking back over my career, I am fortunate to be a chemist. ..."
This and more about Ayyappanpillai Ajayaghosh can be found on page 8692.

News


J.-Q. Yu


E. W. Meijer


T. F. Jamison

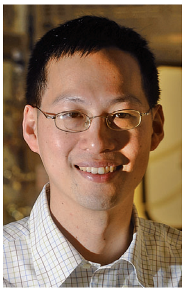

J. Aubé


M. R. Wasielewski


D. I. Schuster


S. A. Snyder


Y. Tang


C. J. Chang

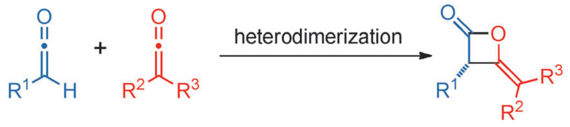
Books

Highlights

Lewis Base Catalysis

E. Marqués-López,*
M. Christmann* ______ 8696 – 8698

β-Lactones through Catalytic Asymmetric Heterodimerization of Ketenes



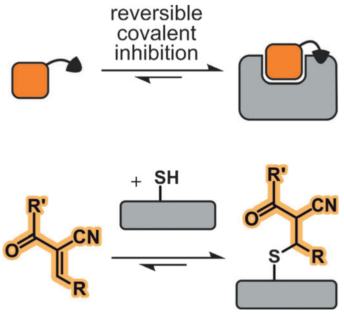
Simple, but effective: The asymmetric heterodimerization of two different ketenes (see scheme) has been developed 65 years after the first seminal studies on ketene dimerization. The key to sufficiently suppressing the competing homodimerization of the monosubstituted ketene donor (shown in blue) is its slow addition to the disubstituted acceptor (shown in red).

Inhibitors

C.-U. Lee,
T. N. Grossmann* ______ 8699 – 8700

Reversible Covalent Inhibition of a Protein Target

Electron-deficient Michael acceptors can be used in reversible addition/elimination reactions with thiols. These electrophiles were used to convert a known irreversible kinase inhibitor into a covalent and reversible inhibitor. Such an approach might provide high-affinity binders with increased selectivity without the toxicological risks associated with irreversible protein modifications.



Essays

Drug Discovery

B. Meunier* ______ 8702 – 8706

Does Chemistry Have a Future in Therapeutic Innovations?

A bright future for small molecules: Drugs based on molecules made by chemists are far from old-fashioned. Although biopharmaceuticals developed during the last two decades may have caught the public's imagination, traditional drugs remain a strong force in the pharmaceutical industry. Effective, inexpensive small-molecule drugs are crucial in fighting diseases and maintaining cost-effective health care.

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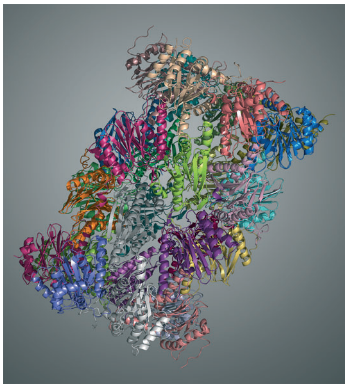
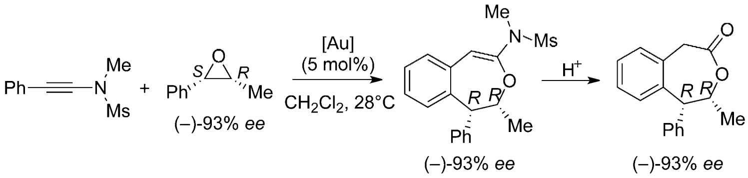
Reviews



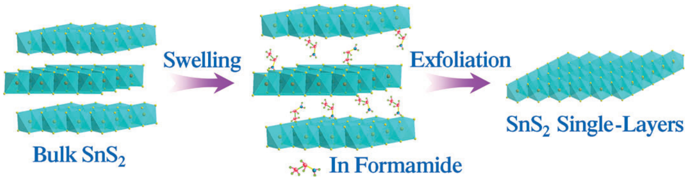
Under arrest: The first immunoproteasome-specific inhibitors were recently developed. The most potent one shows promise in the treatment of autoimmune diseases, thus opening the door for new clinical applications. Structure–affinity studies with the available immuno- and constitutive proteasome crystal structures will facilitate future drug development efforts.

Communications



Golden opportunity: [4+3] Cycloaddition reactions of arenynamides and epoxides are enabled under gold catalysis and have a broad substrate scope (see scheme; Ms = methanesulfonyl). An S_N2-type front-side attack of phenyl at the oxiranyl ring is expected to cause the retention of stereochemistry.

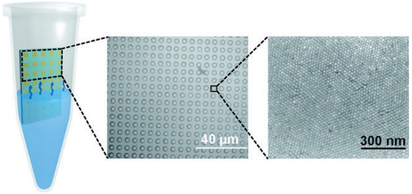
Frontispiece



Manipulation at the atomic level: Free-standing SnS_2 single-layers with three atom thickness were synthesized through an exfoliation strategy (see picture). The SnS_2 single-layers have an increased density of states at the valence band edge. A photoelectrode made from this material shows a visible-light conversion efficiency of 38.7% that is superior to most existing reports.

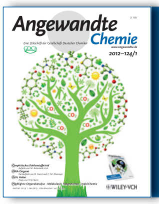
Inside Cover

Nanorods standing at attention! A self-assembly technique based on convective and capillary forces was used for the direct fabrication of standing arrays of gold nanorods on lithographically predefined areas (see picture). The hexagonal close-packed structure of gold nanorods creates an ideal substrate for surface-enhanced Raman spectroscopy.



Back Cover

The German Chemical Society (GDCh) invites you to:



Angewandte Anniversary Symposium

125 JAHRE

GDCh

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Tuesday, March 12, 2013

Henry Ford Building / FU Berlin

Speakers


Carolyn R. Bertozzi


François Diederich


Alois Fürstner


Roald Hoffmann (Nobel Prize 1981)


Susumu Kitagawa


Jean-Marie Lehn (Nobel Prize 1987)


E.W. “Bert” Meijer


Frank Schirrmacher (Publisher, *FAZ*)


Robert Schlögl


George M. Whitesides


Ahmed Zewail (Nobel Prize 1999)

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Freie Universität Berlin

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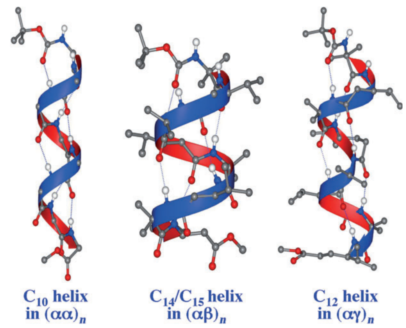


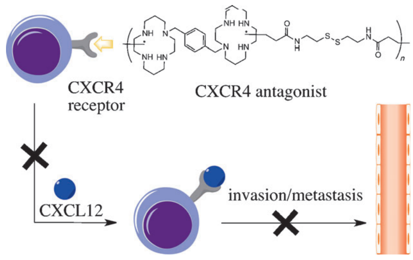
Learning your αβγ's: The diversity of hydrogen-bonding patterns in backbone-expanded hybrid helices is shown by crystal-structure determination of several oligomeric peptides (see scheme; C = gray; H = white; O = red; N = blue). C_{12} helices were observed in the αγ peptide series for $n = 2$–8. In comparison, the αα peptide and αβ peptide sequences show C_{10} and mixed C_{14}/C_{15} helices, respectively.

Hybrid Peptide Helices

K. Basuroy, B. Dinesh, N. Shamala,*
P. Balaram* ________ **8736 – 8739**

Structural Characterization of Backbone-Expanded Helices in Hybrid Peptides: $(\alpha\gamma)_n$ and $(\alpha\beta)_n$ Sequences with Unconstrained β and γ Homologues of L-Val

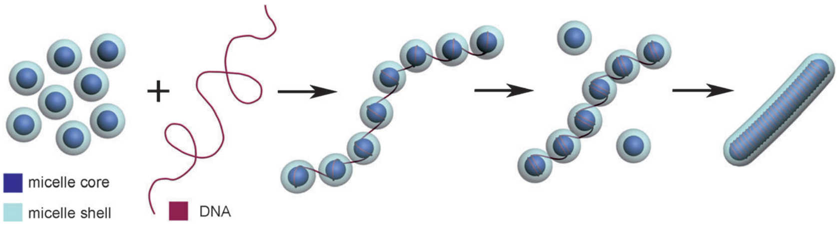
Giving a one-two punch: A bicyclam-based biodegradable polycation with CXCR4 antagonistic activity shows potential for combining cancer chemotherapy with gene therapy or siRNA therapy. This dual-function polycation prevents cancer cell invasion by inhibiting CXCL12-stimulated CXCR4 activation (see scheme), while at the same time efficiently and safely delivering therapeutic DNA into cancer cells.



Drug Delivery

J. Li, Y. Zhu, S. Hazeldine, C. Li,
D. Oupický* ________ **8740 – 8743**

Dual-Function CXCR4 Antagonist Polyplexes To Deliver Gene Therapy and Inhibit Cancer Cell Invasion



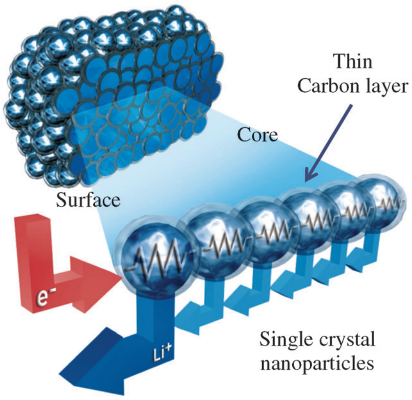
Get your daily (nano)fiber: Assemblies of DNA and polymeric core–shell micelles evolve from longer beads-on-a-string structures to shorter monodisperse solenoidal core–shell nanofibers (see picture). This self-assembly method allows for synthesis of one-dimensional nanomaterials with controlled dimensions and compositions, overcoming a limitation of existing nanomaterial synthesis.

Biomimetic Synthesis

K. Zhang, M. Jiang,
D. Chen* ________ **8744 – 8747**

DNA/Polymeric Micelle Self-Assembly Mimicking Chromatin Compaction

Electric results: The rate capability can be improved in lithium ion batteries (LIBs) by reducing the dimensions of the active material; however, the LIBs would then have insufficient electrode density. To overcome this problem, carbon-coated single-crystal $LiMn_2O_4$ nanoparticle clusters were synthesized as a cathode material for LIBs; this material can be densely packed on the current collector.

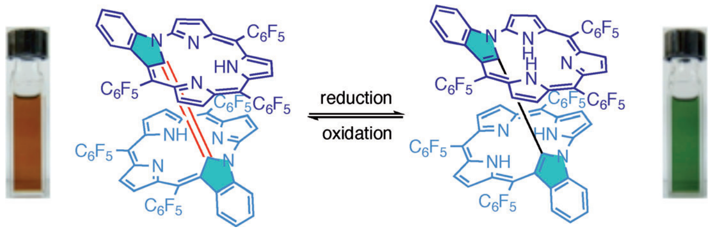


Nanoparticles

S. Lee, Y. Cho, H. K. Song, K. T. Lee,
J. Cho* ________ **8748 – 8752**

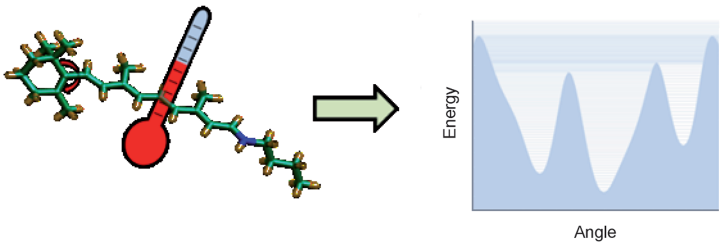
Carbon-Coated Single-Crystal $LiMn_2O_4$ Nanoparticle Clusters as Cathode Material for High-Energy and High-Power Lithium-Ion Batteries

Porphyrinoids



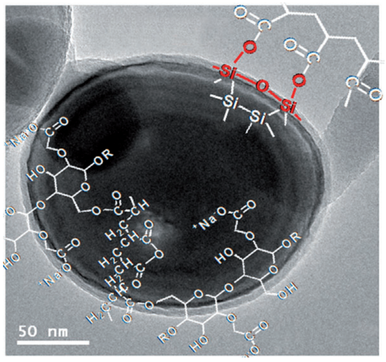
Direct link: Two directly linked benzonorrole dimers were prepared and characterized, and both have short interplane distances less than 3.5 Å. While a strong π–π interaction was recognized in the oxidized form (left), only a negligible π–π interaction was observed in the reduced form (right) in spite of its shorter π–π distance.

Photochemistry



Molecular ion calorimetry: A technique for measuring the heat capacity of an isolated gas-phase chromophore is presented and applied to the retinal protonated Schiff base (see picture). The potential use of this technique for studying barriers for internal rotations is discussed.

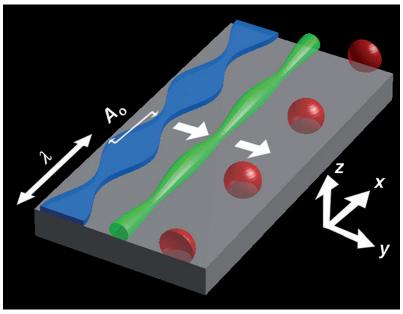
Anode Materials



A support bandage for electrodes: A cross-linked polymeric binder (see picture, red) inhibits mechanical fracture of silicon negative electrodes during cycling. Nanosized silicon powder with a 3D interconnected network of poly(acrylic acid) and sodium carboxymethylcellulose as binder exhibits high reversible capacity of over 2000 mAh g^{-1} after 100 cycles at 30 °C while maintaining a high capacity and high current density.

Directed Assembly

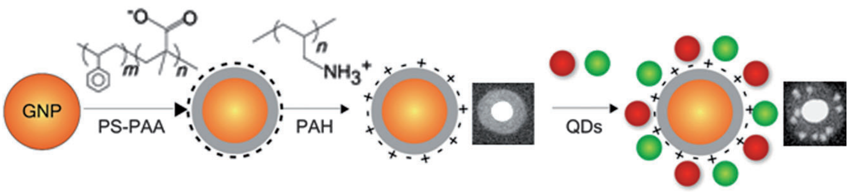
Multiscale patterning must be realized to harness the action of precisely arrayed nanoscale ensembles at practical meso- and microscales. Self- and directed assembly methods hold promise toward achieving arrays of nanoparticles with both precise interparticle spacing and tailored nanoparticle shape. Nanometer scale dewetting of 10 Å thick liquid copper films supported on graphite were investigated by molecular dynamics simulations.



Bio-Nanotechnology

F. Song, P. Tang, H. Durst, D. Cramb,
W. Chan* ________ **8773 – 8777**

Nonblinking Plasmonic Quantum Dot Assemblies for Multiplex Biological Detection

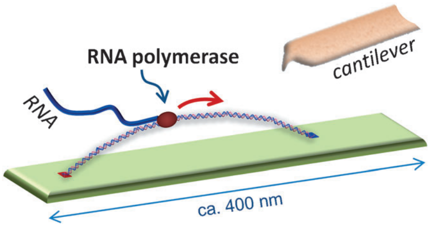


Nonblinking nanosystems are prepared by layer-by-layer polyelectrolyte deposition, which precisely controls the stoichiometry and the distance between quantum dots (QDs) and gold nanoparticles (GNPs). Conjugation of biorecognition molecules to these nanobarcodes enables cell targeting and entry with prolonged retention and minimal toxicity.

Atomic Force Microscopy

M. Endo,* K. Tatsumi, K. Terushima,
Y. Katsuda, K. Hidaka, Y. Harada,
H. Sugiyama* ________ **8778 – 8782**

Direct Visualization of the Movement of a Single T7 RNA Polymerase and Transcription on a DNA Nanostructure



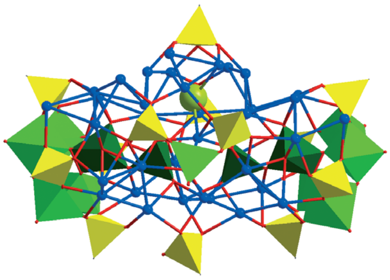
Snapshots of transcription: Movement of a single molecule of T7 RNA polymerase (RNAP) along a double-stranded DNA (dsDNA) template attached to a DNA origami platform (green, see scheme) was recorded using high-speed AFM. A one kilobase template dsDNA containing the T7 promoter was used to record AFM images of transcription of the template dsDNA by RNAP and the resulting biotinylated RNA product was detected by streptavidin-labeling.

Cluster Compounds

Y.-P. Xie, T. C. W. Mak* ________ **8783 – 8786**

High-Nuclearity Silver Ethynide Clusters Assembled with Phosphonate and Metavanadate Precursors

Giant mixed-metal clusters have been assembled with the multinuclear silver(I) *tert*-butylethynide supramolecular synthon and phosphonate-functionalized oxovanadate building blocks as surface components. Various anionic species can be used as their encapsulated templates. (Picture: Ag_{36} cluster anion encapsulating a chloride (sphere) and two $[(O_2)(V_2O_6)]^{4-}$ template anions (dark green); Ag blue, O red, P yellow, V green).

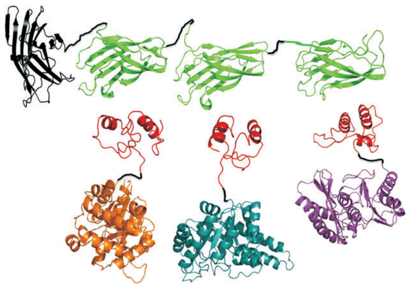


Biocatalysis

C. You, S. Myung,
Y.-H. P. Zhang* ________ **8787 – 8790**

Facilitated Substrate Channeling in a Self-Assembled Trifunctional Enzyme Complex

Three enzymes, triosephosphate isomerase (orange in picture), aldolase (cyan), and fructose 1,6-bisphosphatase (purple), which contained dockerins (red), self-assembled into a static trifunctional enzyme complex through interaction with a mini-scaffoldin protein consisting of three different cohesins (green). The synthetic enzyme complex exhibited an enhanced reaction rate compared to the noncomplexed three-enzyme mixture at the same enzyme concentration.

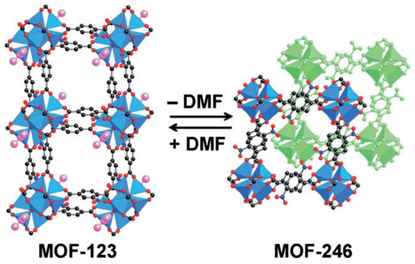


Metal–Organic Frameworks

S. B. Choi, H. Furukawa, H. J. Nam, D.-Y. Jung, Y. H. Jhon, A. Walton, D. Book, M. O'Keeffe, O. M. Yaghi, J. Kim* **8791 – 8795**

Reversible Interpenetration in a Metal–Organic Framework Triggered by Ligand Removal and Addition

Caging cages: Crystals of a metal-organic framework, MOF-123 [$Zn_7O_2(NBD)_5(DMF)_2$] have a three-dimensional porous structure in which DMF ligands (see picture, pink) protrude into small channels. Removal of these ligands triggers the transformation of this MOF to the doubly interpenetrating form, MOF-246 [$Zn_7O_2(NBD)_5$]. Moreover, addition of DMF into MOF-246 triggers reverse transformation to give MOF-123. NBD = 2-nitrobenzene-1,4-dicarboxylate.

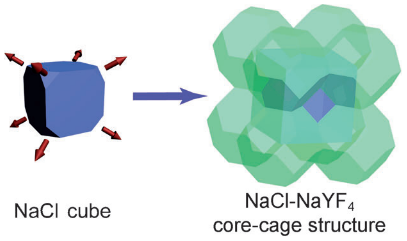


Selective Heteroepitaxy

F. Wang, L.-D. Sun,* J. Gu, Y.-F. Wang, W. Feng, Y. Yang, J. F. Wang,* C.-H. Yan* **8796 – 8799**

Selective Heteroepitaxial Nanocrystal Growth of Rare Earth Fluorides on Sodium Chloride: Synthesis and Density Functional Calculations

Selective growth: Instead of forming core–shell structures with NaCl, $NaYF_4$ was found to grow at the eight corners of the NaCl nanocubes, thereby forming an eight-in-one cage structure. Density functional calculations reveal that facet selectivity is determined by the interfacial energy, which is decided by anion compulsion and the coordination numbers of interfacial Y^{3+} ions.

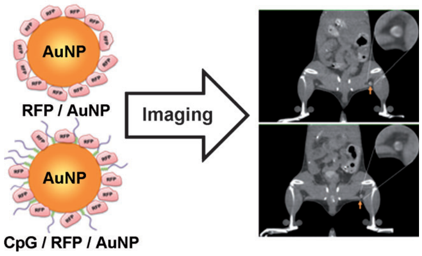


Functionalized Nanoparticles

I.-H. Lee, H. K. Kwon, S. An, D. Kim, S. Kim, M. K. Yu, J.-H. Lee, T.-S. Lee, S.-H. Im, S. Jon* **8800 – 8805**

Imageable Antigen-Presenting Gold Nanoparticle Vaccines for Effective Cancer Immunotherapy In Vivo

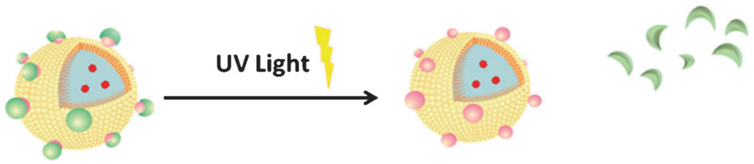
Delivery tracking: Goldnanoparticles (AuNPs) were functionalized with a red fluorescent protein (RFP, pink shapes in picture) as model antigen and an oligonucleotide (CpG) that stimulates the immune response. These functionalized AuNPs were used as cancer vaccines in a tumor model, where they enabled efficient delivery of an antigen to target sites, tracking of the vaccines using noninvasive clinical imaging, and cancer prevention and therapy.



Drug Delivery

N.-C. Fan, F.-Y. Cheng, J.-A. A. Ho,* C.-S. Yeh* **8806 – 8810**

Photocontrolled Targeted Drug Delivery: Photocaged Biologically Active Folic Acid as a Light-Responsive Tumor-Targeting Molecule

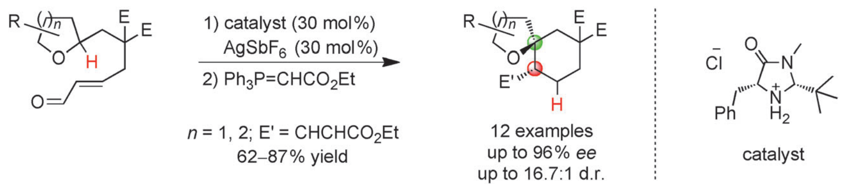


Light-controlled: Biodegradable nanoparticles encapsulating an anticancer drug (red dots in picture) have been synthesized that carry photocaged folate groups on the surface. Upon irradiation the photocaging group (green) is removed and the free folate group, a tumor-homing agent, binds to folate receptors on cell surfaces, thus leading to specific targeting and cellular uptake.

Asymmetric Catalysis

Z.-W. Jiao, S.-Y. Zhang, C. He, Y.-Q. Tu,* S.-H. Wang, F.-M. Zhang, Y.-Q. Zhang, H. Li ______ 8811–8815

Organocatalytic Asymmetric Direct C_{sp^3}–H Functionalization of Ethers: A Highly Efficient Approach to Chiral Spiroethers

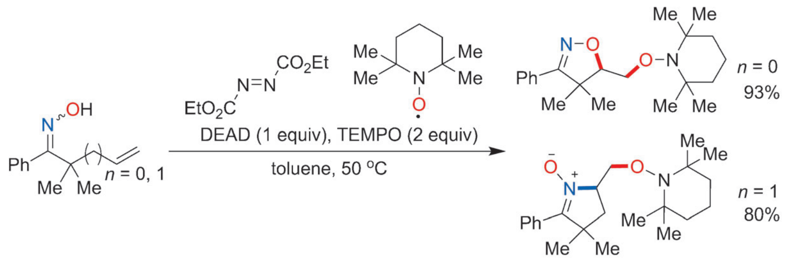


Spiro compounds: An organocatalytic asymmetric method for the C_{sp^3}–H functionalization of the α position of racemic cyclic ethers has been developed. The transformation, mediated by catalytic amounts of an imidazolidinone and strong acid, involves a tandem 1,5-hydride transfer/cyclization and provides access to a structurally diverse series of chiral spiroethers with high levels of enantioselectivity (see scheme).

Cyclization

B. Han,* X.-L. Yang, R. Fang, W. Yu, C. Wang, X.-Y. Duan, S. Liu ______ 8816–8820

Oxime Radical Promoted Dioxygenation, Oxyamination, and Diamination of Alkenes: Synthesis of Isoxazolines and Cyclic Nitrones

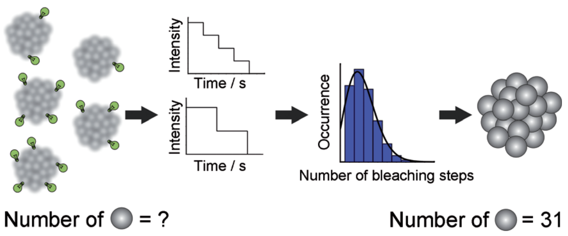


Up the tempo: The intramolecular addition of oxime radicals to C=C bonds was achieved by using DEAD and TEMPO to give 4,5-dihydroisoxazoles as a result of a C–O bond-forming, 5-*exo*-trig cyclization. γ,δ-Unsaturated ketoximes also reacted to afford cyclic nitrones through C–N bond formation. The reactions offer a metal-free approach for the vicinal difunctionalization of unactivated alkenes.

Single-Molecule Studies

N. Zijlstra, C. Blum, I. M. J. Segers-Nolten, M. M. A. E. Claessens, V. Subramaniam* ______ 8821–8824

Molecular Composition of Substoichiometrically Labeled α-Synuclein Oligomers Determined by Single-Molecule Photobleaching



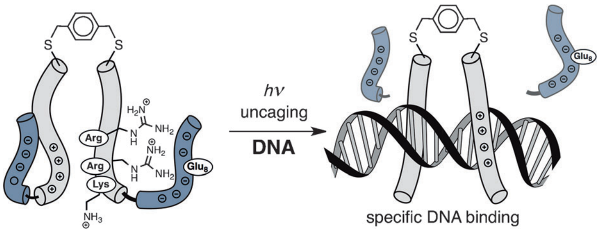
Bleaching proteins: Single-molecule photobleaching approaches and sub-stoichiometric labeling with fluorophores give insight into the number of monomers that form a specific α-synuclein oligomer. The results show that this α-synuclein oligomer is present as a single, well-defined species consisting of 31 monomers.

Front Cover

Electrostatic Caging

A. Jiménez-Balsa, E. Pazos,
B. Martínez-Albardonedo,
J. L. Mascareñas,*
M. E. Vázquez* ______ **8825 – 8829**

Temporary Electrostatic Impairment of DNA Recognition: Light-Driven DNA Binding of Peptide Dimers

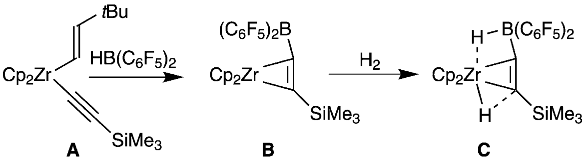


Appending negatively charged Glu_8 tails to a peptide dimer derived from the GCN4 transcription factor leads to an effective suppression of its DNA binding. The specific DNA recognition can be restored by irradiation with UV light by using a photolabile linker between the acidic tail and the DNA binding peptide.

H_2 Activation

S. K. Podiyanachari, R. Fröhlich,
C. G. Daniliuc, J. L. Petersen,
C. Mück-Lichtenfeld, G. Kehr,
G. Erker* ______ **8830 – 8833**

Hydrogen Activation by an Intramolecular Boron Lewis Acid/Zirconocene Pair

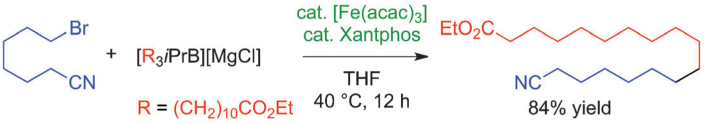


Let's split: Reaction of the zirconium complex **A** with Piers' borane [HB$(C_6F_5)_2$] yields the unusual borylalkyne zirconocene complex **B** which reacts with dihydrogen, activating it to give the doubly hydrido bridged alkyne zirconium complex **C**.

Cross-Coupling

T. Hatakeyama, T. Hashimoto,
K. K. A. D. S. Kathriarachchi, T. Zenmyo,
H. Seike, M. Nakamura* ___ **8834 – 8837**

Iron-Catalyzed Alkyl–Alkyl Suzuki–Miyaura Coupling

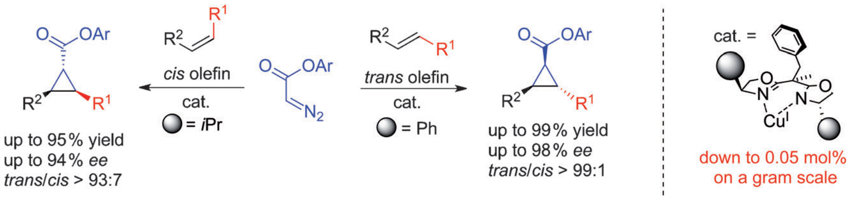


Chemoselective Suzuki–Miyaura coupling of primary and secondary alkyl halides is realized by using an iron/Xantphos catalyst. Primary and secondary alkyl bromides undergo the reaction to give the coupling products in good yields. Application to the synthesis of long-chain fatty acid derivatives is also described (see scheme).

Asymmetric Cyclopropanation

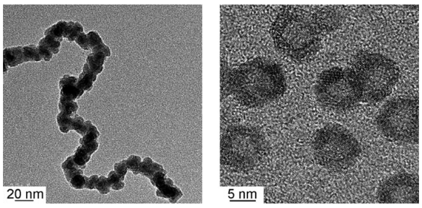
J. Li, S.-H. Liao, H. Xiong, Y.-Y. Zhou,
X.-L. Sun,* Y. Zhang, X.-G. Zhou,
Y. Tang* ______ **8838 – 8841**

Highly Diastereo- and Enantioselective Cyclopropanation of 1,2-Disubstituted Alkenes



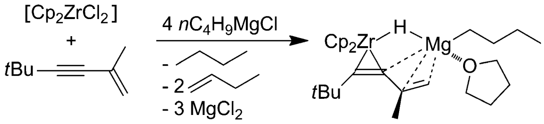
A helping hand: A series of bis(oxazoline) ligands, which contain pendant C_2-symmetry-breaking groups, for the Cu-catalyzed asymmetric cyclopropanation of 1,2-disubstituted alkenes has been developed. Under mild reaction conditions, both *cis*- and *trans*-1,2-substituted alkenes can be converted into the corresponding 1,2,3-trisubstituted cyclopropanes with high levels of diastereo- and enantioselectivity (see scheme).

Nanostructures



About phase: Ferromagnetic γ-Fe_2O_3 nanowires (left in the figure) with a saturation magnetization (M_s) of 54.0 emu g^{-1} and coercivity of 518 Oe at room temperature, and superparamagnetic hollow α-Fe_2O_3 nanoparticles (right) with a room-temperature M_s of 2.9 emu g^{-1} were synthesized by the thermal decomposition of $[Fe(CO)_5]$ but with the stabilizing action of maleic anhydride grafted polypropylene.

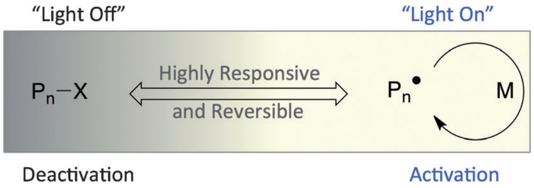
Organometallic Compounds



An enyne–zirconium complex stabilizes molecular magnesium hydride (MgH_2) and even a molecular hydride, nC_4H_9MgH. These systems feature magnesium olefin π complexation.

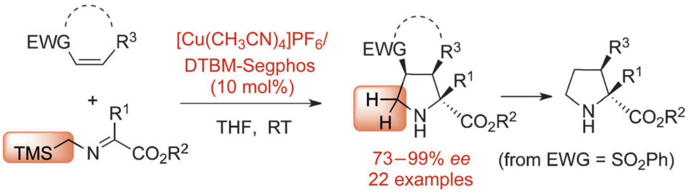
Polymerization

Inside Back Cover



On–off: A living radical polymerization procedure, which utilizes ppm levels of an iridium-based photoredox catalyst, affords control over chain growth through mediation by visible light (see scheme; P_n = polymer chain, X = halogen, M = monomer). This process can be activated and deactivated by light, enables control over the molecular weight and molecular weight distributions, and tolerates different functional groups.

Asymmetric Catalysis

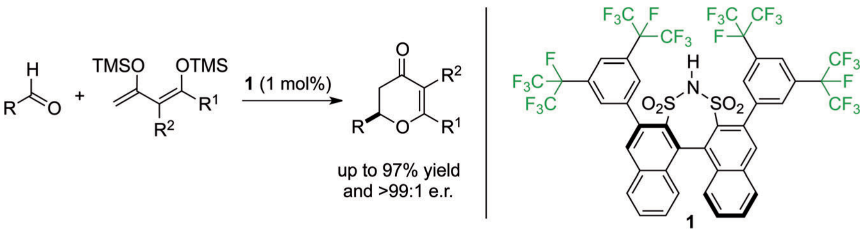


Going pro: The title reaction between α-silylimines and activated olefins proceeds in the presence of a Cu^I/DTBM-Segphos catalyst system with excellent diastereoselectivity and enantioselectivity. This process provides straightforward access to highly enantioenriched 5-unsubstituted α-quaternary proline derivatives. TMS = trimethylsilyl, DTBM-Segphos = 5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole.

Asymmetric Catalysis

J. Guin, C. Rabalakos,
B. List* ____ 8859 – 8863

Highly Enantioselective Hetero-Diels–Alder Reaction of 1,3-Bis(silyloxy)-1,3-dienes with Aldehydes Catalyzed by Chiral Disulfonimide

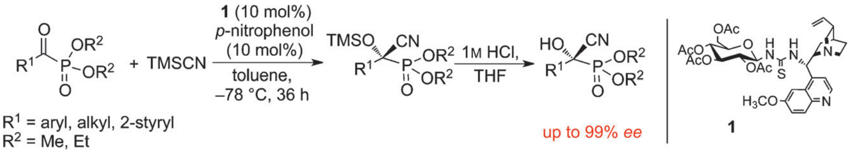


Bulking up with F: The title reaction proceeds using 1 mol % of the new perfluoroisopropyl chiral disulfonimide catalyst **1** to deliver several 2,6-disubstituted and 2,5,6-trisubstituted dihydropyrones in good yields and with excellent enantiomeric ratios. The utility of this methodology is illustrated with the first enantioselective synthesis of a potent aromatase inhibitor.

Organocatalysis

S. S. Kong, W. D. Fan, G. P. Wu,
Z. W. Miao* ____ 8864 – 8867

Enantioselective Synthesis of Tertiary α-Hydroxy Phosphonates Catalyzed by Carbohydrate/Cinchona Alkaloid Thiourea Organocatalysts



A pinch of sugar: The new bifunctional carbohydrate/cinchonine-based thiourea **1** has been designed for the asymmetric addition reaction of α-ketophosphonates and trimethylsilyl cyanide, the product of which can be hydrolyzed to afford tertiary α-hydroxy phosphonates with excellent enantioselectivities.

DOI: 10.1002/anie.201205472

50 Years Ago ...

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Heteroatom chemistry was “in vogue”: The reactions of alkylboron compounds were the subject of two Communications in Issue 9/1962. R. Köster and G. Benedikt reported how the exchange reaction of *B*-ethylboraindane or *B*-ethylboratetralin with aluminum trialkyl compounds resulted in aluminum heterocycles. The products exist as dimers in solution and as colorless crystals in the solid state. P. Binger and R. Köster reported on the preparation and properties of cyclopropylboranes, and described how 1,1-bis(dialkylboryl)-3-chloropropanes react with sodium tetraalkylboron compounds to form the desired products. Tricyclopropylborane was also prepared, and could undergo an exchange reaction with triethylaluminum to form cyclopropylaluminum species.

The reaction of pyrilium salts with triphenylphosphine derivatives was reported to lead to substituted aromatic compounds. As described by G. Märkl, the initial reaction resulted in a ring opening to form a vinylogous phosphineacylmethylene compound, which then underwent an intramolecular Wittig reaction to form a substituted benzene derivative.

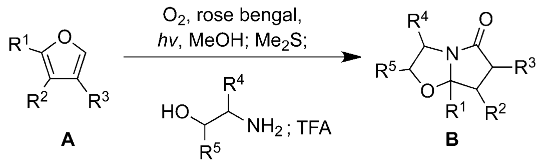
F. Hübenett et al. reported on a simple synthesis of isothiazole ring systems, which were formed by passing propylene, ammonia, and sulfur dioxide over catalysts such as activated aluminum oxide. This method contrasts that reported in Issue 6/1962 by F. Wille et al., who reacted sodium acrolein 3-thiosulfate or acrolein 3-thiocyanate derivatives with liquid ammonia to produce isothiazole rings.

Read more in Issue 9/1962

Synthetic Methods

D. Kalaitzakis, T. Montagnon, I. Alexopoulou, G. Vassilikogiannakis* ______ 8868 – 8871

A Versatile Synthesis of Meyers' Bicyclic Lactams from Furans: Singlet-Oxygen-Initiated Reaction Cascade

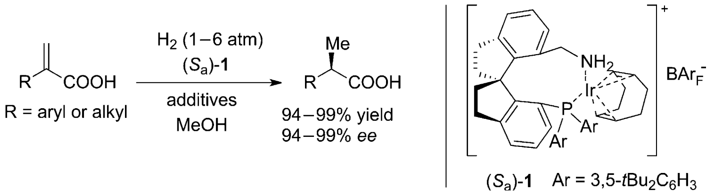


All in one: Meyers' bicyclic lactams were synthesized in high yield from furans using a new and powerful method that involves a one-pot singlet-oxygen-initiated reaction cascade (see scheme; TFA = trifluoroacetic acid). This method has broad synthetic potential because of the ease of access to a wide range of furans with a variety of substituents.

Homogeneous Catalysis

S.-F. Zhu, Y.-B. Yu, S. Li, L.-X. Wang, Q.-L. Zhou* ______ 8872 – 8875

Enantioselective Hydrogenation of α-Substituted Acrylic Acids Catalyzed by Iridium Complexes with Chiral Spiro Aminophosphine Ligands

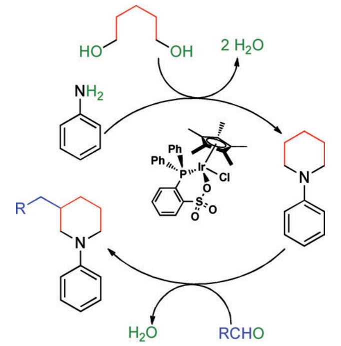


Highly active: Iridium complexes with chiral spiro aminophosphine ligands were synthesized and applied as catalysts for the asymmetric hydrogenation of α-substituted acrylic acids (see scheme). The complexes were highly active catalysts, showing turnover frequencies of up to 6000 h^{-1}, and catalyst loadings could be reduced to 0.01 mol%.

Synthetic Methods

K. Yuan, F. Jiang, Z. Sahli, M. Achard, T. Roisnel, C. Bruneau* ______ 8876 – 8880

Iridium-Catalyzed Oxidant-Free Dehydrogenative C–H Bond Functionalization: Selective Preparation of N-Arylpiperidines through Tandem Hydrogen Transfers

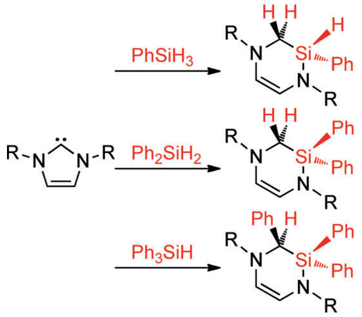


Relay to the finish: The atom-economical tandem hydrogen autotransfer catalyzed by iridium(III) has been efficiently applied for the preparation of N-arylpiperidines starting from easily accessible anilines, diols, and aldehydes (see scheme). This protocol is also compatible with the use of diethyl carbonate as an ecofriendly solvent.

N-Heterocyclic Carbenes

D. Schmidt, J. H. J. Berthel, S. Pietsch, U. Radius* ______ 8881 – 8885

C–N Bond Cleavage and Ring Expansion of N-Heterocyclic Carbenes using Hydrosilanes

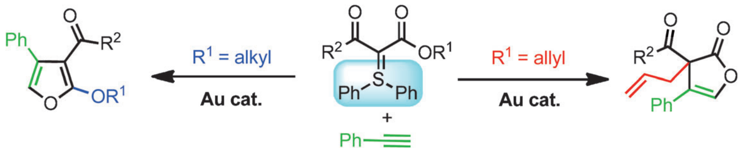


Ring expansion of NHCs! The reaction of N-heterocyclic carbenes (NHCs) with hydrosilanes Ph$_{4-n}$SiH$_n$ (n = 1, 2, 3) results in complete rupture of the heterocycle and silylene insertion into one of the C–N bonds of the carbene (see scheme; R = alkyl, aryl).

Gold Catalysis

X. Huang, B. Peng, M. Luparia,
L. F. R. Gomes, L. F. Veiros,
N. Maulide* ______________ 8886 – 8890

Gold-Catalyzed Synthesis of Furans and Furanones from Sulfur Ylides

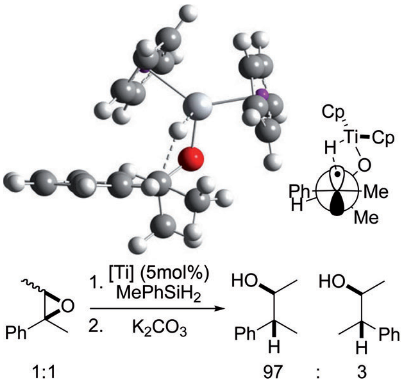


A golden switch: Doubly stabilized sulfonium ylides can be coupled with alkynes in a gold-catalyzed synthesis of heterocycles. This method hinges on a switch in the reactivity of the sulfur ylide resulting from the simple modification of the electron-withdrawing moieties and leads to either furans or furanones bearing a quaternary center (see scheme).

Radical Chemistry

A. Gansäuer,* M. Klatte, G. M. Brändle,
J. Friedrich* ______________ 8891 – 8894

Catalytic Hydrogen Atom Transfer (HAT) for Sustainable and Diastereoselective Radical Reduction



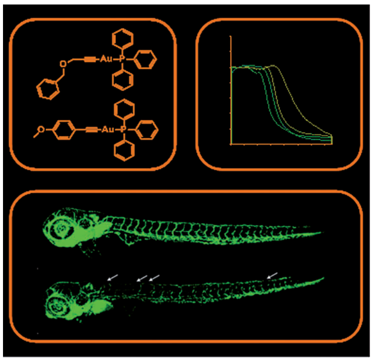
Going cyclic! A catalytic cycle and cyclic transition states enable a novel sustainable and catalytic hydrogen atom transfer (HAT) for highly diastereoselective radical reductions. Readily available nontoxic silanes are the terminal reductants for epoxides that are opened by bifunctional titanocene(III) hydride catalysts.

Bioorganometallic Chemistry

A. Meyer, C. P. Bagowski, M. Kokoschka,
M. Stefanopoulou, H. Alborzinia, S. Can,
D. H. Vlecken, W. S. Sheldrick, S. Wölfl,
I. Ott* ______________ 8895 – 8899

On the Biological Properties of Alkynyl Phosphine Gold(I) Complexes

Golden times for metal-based drugs? Alkynyl triphenylphosphine gold(I) complexes display interesting biological properties and show high potential for future drug development. They are strong inhibitors of the enzyme thioredoxin reductase, trigger antiproliferative effects in tumor cells, and influence tumor cell metabolism, mitochondrial respiration, and angiogenesis in zebrafish embryos.



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

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