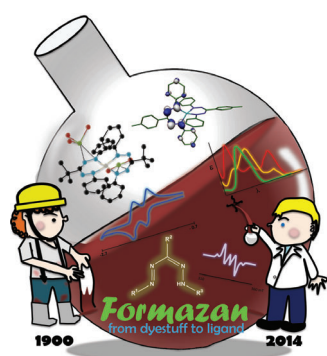
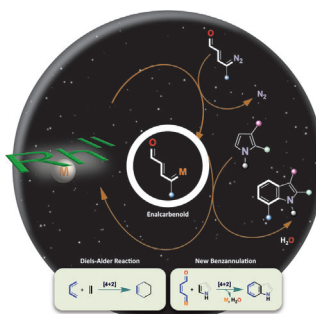


... a painting by Paul Klee, K. A. Jørgensen and co-workers present the organocatalytic asymmetric formation of steroids in their Communication on page 4137 ff. The picture applies mosaic shapes in analogy with the artistic elements of Paul Klee to illustrate the organocatalytic asymmetric formation of steroids. The A and B ring in the steroid (to the left) and the D ring (to the right) are merged by the green organocatalyst in the middle towards the blue sky.

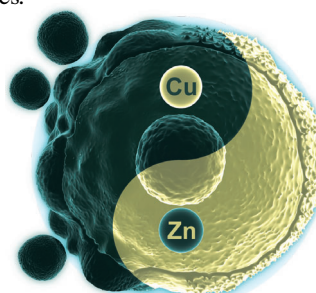
Annulation Methods

S. Katukojvala et al. describe in their Communication on page 4076 ff. the direct [4 + 2] benzannulation of pyrroles to indoles by using a rhodium enalcarbenoid generated by rhodium(II)-catalyzed decomposition of enal diazo compounds.



Redox-Non-Innocent Ligands

E. Otten and co-workers describe formazanate anions as unique ligands in coordination chemistry in their Communication on page 4118. The redox chemistry of these ligands allows the full characterization of bis(formazanate) zinc complexes in three oxidation states.



Enzyme Inhibition

In their Communication on page 4098 ff., N. P. Farrell and co-workers present evidence that zinc inhibits the pro-apoptotic protein caspase-3 through interacting with the active-site histidine residue rather than with the catalytic dyad.

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Spotlight on Angewandte's Sister Journals

Service

4028 – 4031



"My biggest inspiration is the Pacific Ocean. I advise my students to refresh their brains on Sundays ..."

This and more about Masaya Sawamura can be found on page 4032.

Author Profile

Masaya Sawamura _____ 4032



M. Albrecht



S. P. Cramer



M. W. Hosseini



J. Li



M. Murakami

News

Humboldt and Bessel Research
Awards _____ 4033

Photochemically-Generated
Intermediates in Synthesis

Angelo Albini, Maurizio Fagnoni

Books

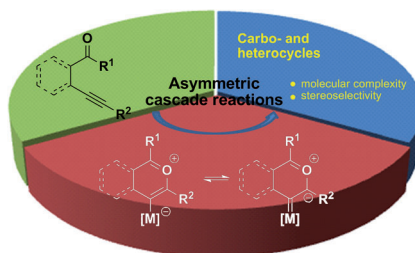
reviewed by A. G. Griesbeck _____ 4034

Highlights

Asymmetric Catalysis

J.-R. Chen,* X.-Q. Hu,
W.-J. Xiao* 4038–4040

Metal-Containing Carbonyl Ylides:
Versatile Reactants in Catalytic
Enantioselective Cascade Reactions

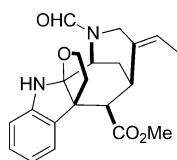


New players in town: In situ generated transition-metal-containing carbonyl ylides are a unique class of reagents which have found wide applications in catalytic asymmetric cascade reactions. Recent advances in reaction design are likely to lead to more novel developments with these reactive species.

Natural Products

E. Doris* 4041–4042

Total Syntheses of (±)-Aspidophylline A



Aspidophylline A

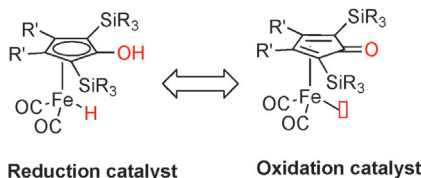
Yes they can! The groups of Zhu and Ma recently reinvestigated the synthetic route to aspidophylline A. These approaches are discussed in the context of the first total synthesis of the title alkaloid that was reported by Garg and co-workers in 2011.

Minireviews

Iron Catalysis

A. Quintard,* J. Rodriguez* 4044–4055

Iron Cyclopentadienone Complexes:
Discovery, Properties, and Catalytic
Reactivity



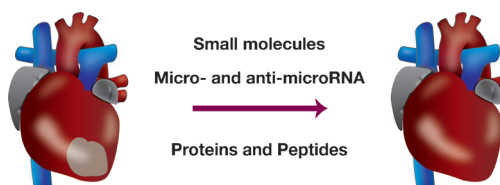
The new iron age? Iron cyclopentadienone complexes are easily synthesized from simple and cheap materials, are stable, and through the presence of a non-innocent ligand, have unique catalytic features. The properties of such complexes and their applications in original redox-neutral transformations in both racemic and enantioselective reactions are reviewed.

Reviews

Drug Discovery

A. T. Plowright,* O. Engkvist, A. Gill,
L. Knerr Q.-D. Wang 4056–4075

Heart Regeneration: Opportunities and
Challenges for Drug Discovery with Novel
Chemical and Therapeutic Methods or
Agents



Small molecules, RNA approaches, modified peptides, and proteins are promising candidates for the regeneration of heart tissue through differentiation of stem cells, proliferation of existing cardiomyocytes and cardiac progenitor cells,

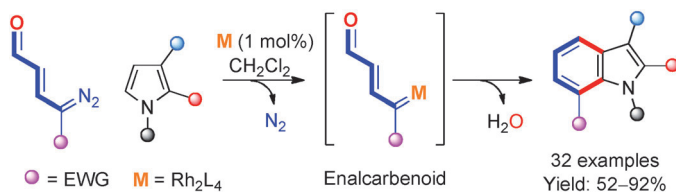
and cell reprogramming to cardiomyocytes. Recent advances, including novel screening strategies, and the upcoming challenges and opportunities to develop these hits into pharmaceuticals are summarized.

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Communications



Fat cat: A new class of enal diazo compounds resulted in the first transition-metal-catalyzed [4+2] benzannulation of pyrroles to deliver indoles. The benzannulation is proposed to involve an unpre-

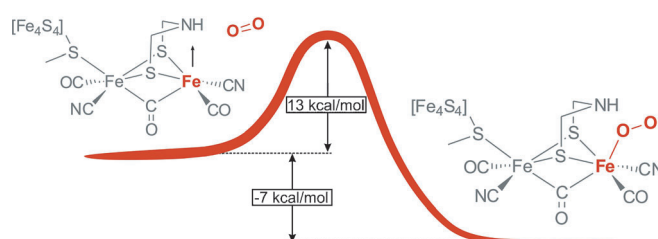
cedented diacceptor rhodium enalcarbenoid. The reaction was used in the highly efficient synthesis of the natural product leiocarpone and a potent adipocyte fatty-acid binding protein inhibitor.

Heterocycle Synthesis

S. G. Dawande, V. Kanchupalli, J. Kalepu, H. Chennamsetti, B. S. Lad, S. Katukojvala* 4076–4080

Rhodium Enalcarbenoids: Direct Synthesis of Indoles by Rhodium(II)-Catalyzed [4+2] Benzannulation of Pyrroles

Frontispiece



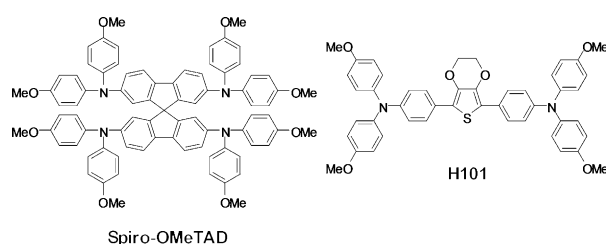
Clearing the air: The free energy profiles for the chemical attachment of O₂ to the active sites of [FeFe]-hydrogenases from *Clostridium pasteurianum* and *Desulfovibrio desulfuricans* were investigated. Based on

the results, possible target sites for future mutation studies were suggested that may reduce oxygen binding and thus the oxygen sensitivity of these enzymes.

Enzyme Models

A. Kubas, D. De Sancho, R. B. Best, J. Blumberger* 4081–4084

Aerobic Damage to [FeFe]-Hydrogenases: Activation Barriers for the Chemical Attachment of O₂



Heterocycle power! A power-conversion efficiency of 13.8% under AM 1.5G illumination was achieved in a perovskite-based solar cell with a new hole-transporting material based on 3,4-ethylenedioxythiophene (H101). This is the first

heterocycle-containing material with > 10% efficiency in such devices, and has great potential to replace the more expensive spiro-OMeTAD, given its much simpler and less expensive synthesis.

Hole Transport

H. Li, K. Fu, A. Hagfeldt, M. Grätzel, S. G. Mhaisalkar,* A. C. Grimsdale* 4085–4088

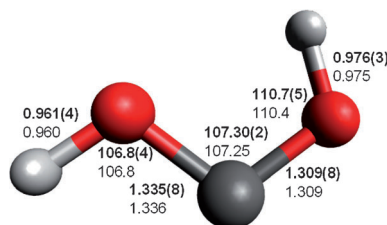
A Simple 3,4-Ethylenedioxythiophene Based Hole-Transporting Material for Perovskite Solar Cells

Reactive Intermediates

C. C. Womack, K. N. Crabtree,
L. McCaslin, O. Martinez, Jr., R. W. Field,
J. F. Stanton,
M. C. McCarthy* — 4089 – 4092



Gas-Phase Structure Determination of
Dihydroxycarbene, One of the Smallest
Stable Singlet Carbenes



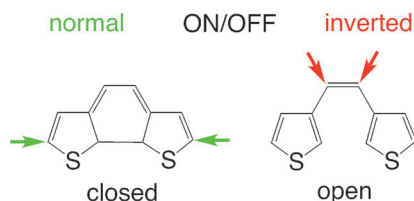
A small stable singlet carbene: The geometric structure of dihydroxycarbene ($\text{HO}-\ddot{\text{C}}-\text{OH}$) is experimentally determined using Fourier transform microwave spectroscopy. This carbene, a structural isomer of the simplest Criegee intermediate (CH_2OO) and formic acid (HCOOH), is found to be long-lived in the dilute gas phase because of the stabilizing effect of the two electron-donating hydroxy groups.

Molecular Switches

Y. Tsuji, R. Hoffmann* — 4093 – 4097



Frontier Orbital Control of Molecular
Conductance and its Switching



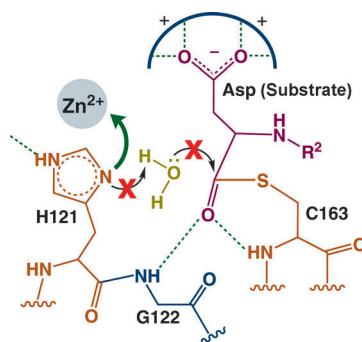
The phase and amplitude of the frontier molecular orbitals at the sites that are connected to electrodes play an essential role in determining transmission of electrons through a π system. When applied to two diarylethene switches, theory then predicts that for some specified sites the switching behavior will be inverted; that is, the “open” molecular form of the switch will be more conductive.

Enzyme Inhibition

A. G. Daniel, E. J. Peterson,
N. P. Farrell* — 4098 – 4101



The Bioinorganic Chemistry of Apoptosis:
Potential Inhibitory Zinc Binding Sites in
Caspase-3



Zinc site insight: Zinc inhibition of caspase-3 is largely uncompetitive. Substrate binding was shown to be unaffected by Zn^{2+} in the sub-micromolar range where most inhibition occurs. This rules out zinc binding to the catalytic dyad, the generally assumed inhibitory site. Based on a hypothesis that zinc inhibition occurs through interaction with the catalytic His residue, a new inhibitory zinc site was proposed and was shown to better fit the experimental observations.

Back Cover

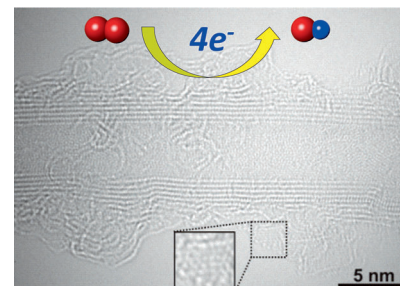
Electrocatalysts

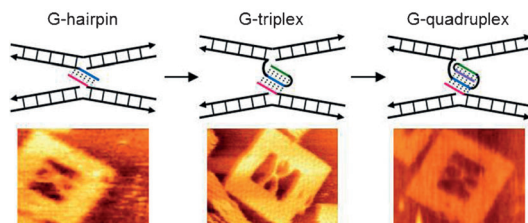
Y. J. Sa, C. Park, H. Y. Jeong, S.-H. Park,
Z. Lee, K. T. Kim, G.-G. Park,
S. H. Joo* — 4102 – 4106



Carbon Nanotubes/Heteroatom-Doped
Carbon Core-Sheath Nanostructures as
Highly Active, Metal-Free Oxygen
Reduction Electrocatalysts for Alkaline
Fuel Cells

A facile, scalable route for the synthesis of new nanocomposites that are based on carbon nanotubes/heteroatom-doped carbon (CNT/HDC) core-sheath nanostructures has been developed. The CNT/HDC nanostructures exhibit excellent electrocatalytic activity, kinetics, and durability for the oxygen reduction reaction, and they also performed well as the cathode catalysts in alkaline fuel cells.





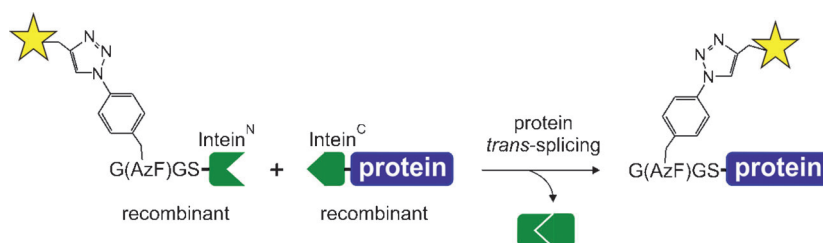
Back to the fold: Using a DNA origami frame as a nanoscaffold for the structural control, the unprecedented solution-state structures of a tetramolecular antiparallel and (3 + 1)-type G-quadruplex intermedi-

ates in the G-quadruplex folding, such as G-hairpin and G-triplex, can be visualized directly at the single-molecule level with nanometer resolution by AFM.

Single-Molecule Studies

A. Rajendran, M. Endo,* K. Hidaka, H. Sugiyama* — 4107–4112

Direct and Single-Molecule Visualization of the Solution-State Structures of G-Hairpin and G-Triplex Intermediates



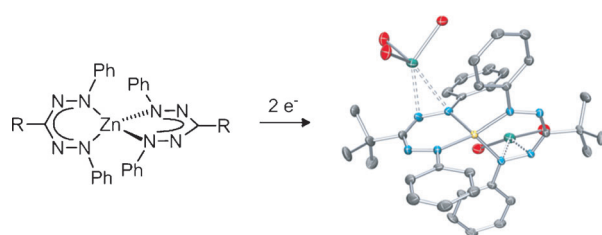
Click and splice: Short tags of only a few amino acids fused to a recombinantly produced split intein fragment were modified with synthetic moieties and then transferred to a protein of interest by protein *trans*-splicing. These two-step

procedures circumvent exposure of the protein of interest to copper ions for click chemistry and undesired modification of lysines, even though standard bioconjugation reagents are used.

Protein Chemistry

V. Schütz, H. D. Mootz* — 4113–4117

Click-Tag and Amine-Tag: Chemical Tag Approaches for Efficient Protein Labeling In Vitro and on Live Cells using the Naturally Split *Npu* DnaE Intein



N is better than C: Bis(formazanate) zinc complexes (see picture; Zn yellow, N blue, O red, Na green) show sequential and reversible redox chemistry in which the formazanate ligands are reduced to metallaverdazyl radicals. These ligands are

very similar to β -diketiminates, but the nitrogen-rich NNCNN backbone of formazanates opens the door to redox chemistry that is otherwise difficult to access.

Redox-Non-Innocent Ligands

M.-C. Chang, T. Dann, D. P. Day, M. Lutz, G. G. Wildgoose, E. Otten* — 4118–4122

The Formazanate Ligand as an Electron Reservoir: Bis(Formazanate) Zinc Complexes Isolated in Three Redox States



Inside Back Cover

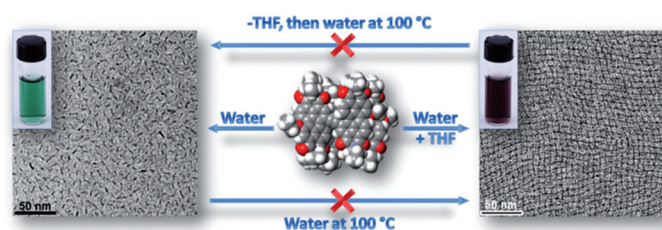


Supramolecular Chemistry

J. Baram, H. Weissman, Y. Tidhar,
I. Pinkas, B. Rybtchinski* — 4123–4126



Hydrophobic Self-Assembly Affords
Robust Noncovalent Polymer Isomers



A strong hold: Strong hydrophobic interactions result in stable noncovalent polymer isomers derived from a single covalent unit. These isomers have different

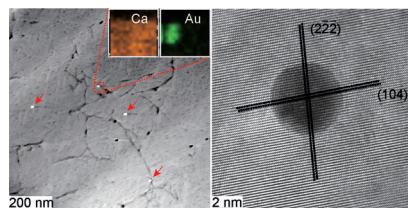
electronic and photonic properties and are stable in water, even upon prolonged heating to 100 °C.

Biomineralization

Y. J. Liu, W. T. Yuan, Y. Shi, X. Q. Chen,
Y. Wang, H. Z. Chen,
H. Y. Li* — 4127–4131



Functionalizing Single Crystals:
Incorporation of Nanoparticles Inside
Gel-Grown Calcite Crystals



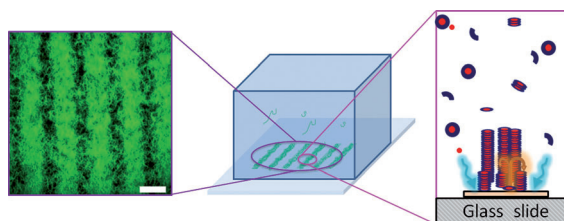
Functionalization of crystals: Biogenic single crystals incorporate biomacromolecules and form single-crystal composites. The abnormal composite structure led to the idea to obtain synthetic crystals with nonintrinsic properties by modifying their internal structure. Intrinsically colorless and diamagnetic calcite single crystals are turned into colored and paramagnetic solids through incorporation of gold and ferroferric oxide nanoparticles.

Surface Chemistry

A. G. L. Olive, N. H. Abdullah,
I. Ziemecka, E. Mendes, R. Eelkema,*
J. H. van Esch* — 4132–4136



Spatial and Directional Control over Self-
Assembly Using Catalytic Micropatterned
Surfaces



Following a pattern: Catalyst-assisted self-assembly is widespread in nature to achieve spatial control over structure formation. Reported herein is the formation of hydrogel micropatterns on catalytic surfaces. A unique mechanism of fiber

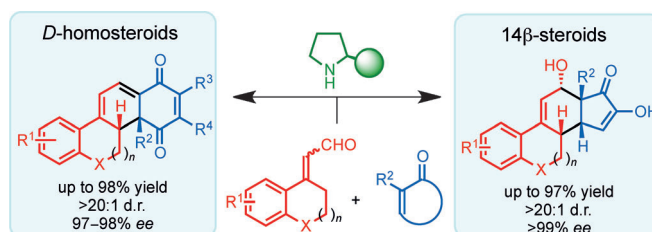
formation for a synthetic system, using building blocks added at the interface, leads to orientated structures. Therefore organization is attained at the micro- and nanoscale.

Synthetic Methods

K. S. Halskov, B. S. Donslund,
S. Barfüsser,
K. A. Jørgensen* — 4137–4141



Organocatalytic Asymmetric Formation of
Steroids

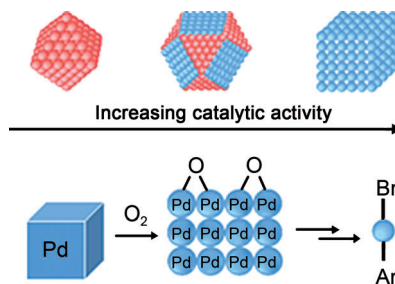


Organocatalysis made it possible: The reported methodology gives 14β-steroids, displaying a broad generality, in one step, and includes various substituents on the A ring, variations of the B ring, hydroxy or alkyl substituents in the 12-position of the

C ring, and different substituents in the angular position at C13. Furthermore, the developed reaction concept includes reactions with quinones to form D-homosteroids in excellent yields and stereoselectivities.

Front Cover

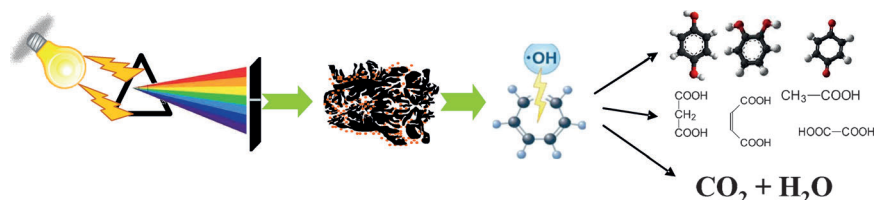
Tracking catalysis: The shape sensitivity of cubic, cuboctahedral, and octahedral Pd nanoparticle catalysts in Suzuki–Miyaura coupling reactions was studied. Superior catalytic reactivity is observed for Pd NCs with {100} surface facets compared to {111} facets. The origin of the enhanced reactivity associated with a cubic morphology is related to the leaching susceptibility of the nanocrystals.



Nanoparticle Catalysis

G. Collins, M. Schmidt, C. O'Dwyer, J. D. Holmes,*
G. P. McGlacken* — 4142–4145

The Origin of Shape Sensitivity in Palladium-Catalyzed Suzuki–Miyaura Cross Coupling Reactions



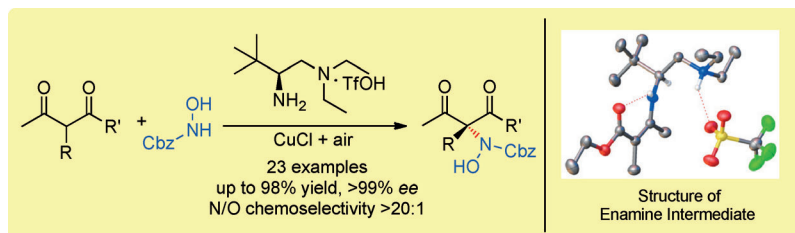
Scratching the surface: The ability of semiconductor-free nanoporous carbons to absorb low-energy photons from visible light and convert them into chemical reactions (i.e., phenol photooxidation) is demonstrated by using monochromatic

light. Data showed the strong dependence of the photochemical activity on the wavelength of the irradiation source and the chemical composition of the nanoporous carbon.

Nanoporous Carbon

L. F. Velasco, J. C. Lima, C. Ania* — 4146–4148

Visible-Light Photochemical Activity of Nanoporous Carbons under Monochromatic Light



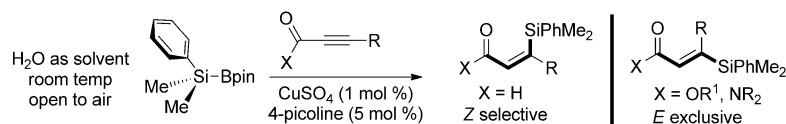
Merging O and N: Enantioselective α -amination of β -ketocarbonyl compounds has been achieved by merging enamine catalysis and Cu^I-catalyzed aerobic oxidation of hydroxycarbamates. Excellent che-

moselectivity and enantioselectivity are obtained with the aid of a simple primary/tertiary diamine catalyst. This presents a facile route for the asymmetric synthesis of unnatural amino acids.

α -Amination

C. Xu, L. Zhang, S. Luo* — 4149–4153

Merging Aerobic Oxidation and Enamine Catalysis in the Asymmetric α -Amination of β -Ketocarbonyls Using *N*-Hydroxycarbamates as Nitrogen Sources



Dial a diastereomer: The title reaction proceeds through the activation of Me₂PhSiBpin in water at room temperature and open atmosphere to produce high yields of vinylsilanes conjugated to carbonyl groups. A surprising diastereo-

divergent access to olefin geometry was discovered using this silyl conjugate addition strategy: aldehydes were Z selective while esters and amides exclusively delivered the E-configured products.

Synthetic Methods

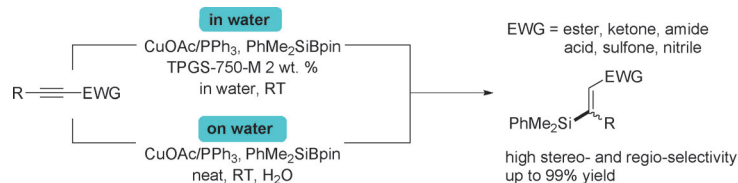
J. A. Calderone, W. L. Santos* — 4154–4158

Copper(II)-Catalyzed Silylation of Activated Alkynes in Water: Diastereodivergent Access to *E*- or *Z*- β -Silyl- α,β -Unsaturated Carbonyl and Carboxyl Compounds



Green Chemistry

R. T. H. Linstadt, C. A. Peterson,
D. J. Lippincott, C. I. Jette,
B. H. Lipshutz* — 4159–4163



Stereoselective Silylcupration of
Conjugated Alkynes in Water at Room
Temperature

Fast, cheap, and green: Micellar catalysis enables the selective construction of a variety β -silyl-substituted carbonyl derivatives under mild aqueous conditions. The reaction is catalyzed by low levels of Cu^I, is compatible with numerous

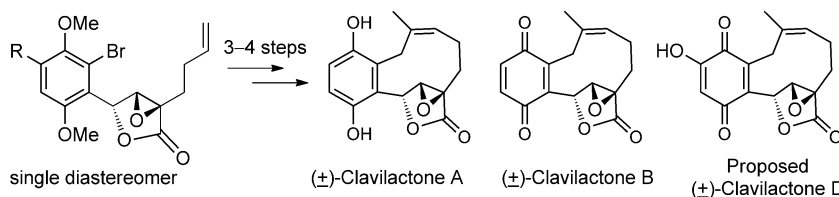
electron-withdrawing groups, affords high yields, and provides opportunities for scale-up and recycling of the reaction medium. The environmental impact, as measured by E Factors, is very low.

Natural Product Synthesis

L. Lv, B. Shen, Z. Li* — 4164–4167



Total Synthesis of (±)-Clavilactones A, B, and Proposed D through Iron-Catalyzed Carbonylation–Peroxidation of Olefin



A general, concise, and efficient approach for synthesis of clavilactones A, B, and D has been established. Three steps from aldehydes, 1,5-dienes, and *t*BuOOH build up α,β -epoxy- γ -butyrolactones (see

scheme, left) as the key building blocks for synthesis of clavilactone family and its derivatives. From these results, the previously proposed clavilactone D structure requires revision.

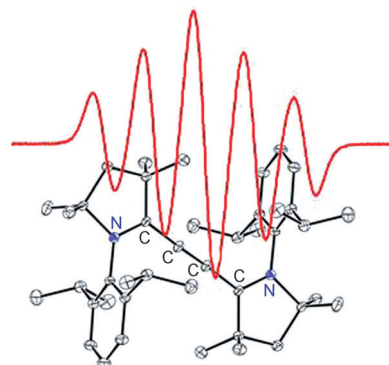
Cumulene Structures

Y. Li, K. C. Mondal, P. P. Samuel, H. Zhu,*
C. M. Orben, S. Panneerselvam,
B. Dittrich,* B. Schwederski, W. Kaim,*
T. Mondal, D. Koley,*
H. W. Roesky* — 4168–4172



C₄ Cumulene and the Corresponding Air-Stable Radical Cation and Dication

Carbons get excited! Commercially available CBr₄ is utilized as a source of dicarbon for the preparation of the C₄ cumulene that contains a cyclic alkyl-(amino) carbene (cAAC). Lithium or potassium is used as a reducing agent. The corresponding air-stable radical cation and dication of the C₄ cumulene were also synthesized and their interconversion was studied by cyclic voltammetry.



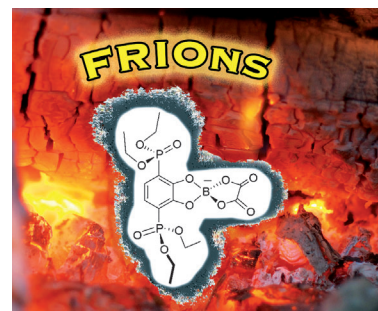
Functional Materials

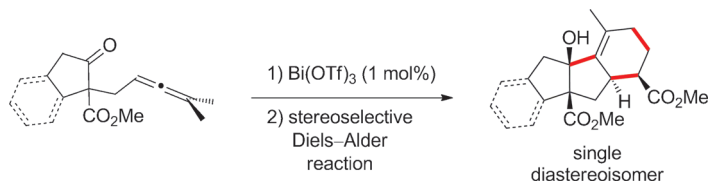
M. F. Rectenwald, J. R. Gaffen,
A. L. Rheingold, A. B. Morgan,
J. D. Protasiewicz* — 4173–4176



Phosphoryl-Rich Flame-Retardant Ions (FRIONS): Towards Safer Lithium-Ion Batteries

Playing with fire: A series of borate and phosphate anions (flame-retardant ions; FRIONS) have been produced in high yields and purity using a readily accessible diphosphinatocatechol. The phosphoryl-rich character of the anions imparts flame-retardant qualities and offers potential utility as lithium salts for safer lithium-ion batteries.





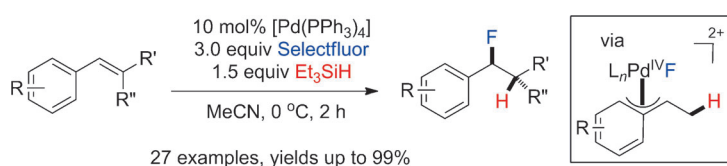
Simply complex: The described catalytic carbonyl-ene reaction is efficiently performed under mild reaction conditions by using only 1 mol % of bismuth(III) triflate, thus affording functionalized molecular

scaffolds. Complex polycyclic structures with a defined stereochemistry have been synthesized by using the carbonyl-ene products in a subsequent hydroxy-directed Diels-Alder reaction.

Synthetic Methods

I. Diaf, G. Lemi re,*
E. Du nach* 4177–4180

Metal-Triflate-Catalyzed Synthesis of Polycyclic Tertiary Alcohols by Cyclization of γ -Allenic Ketones



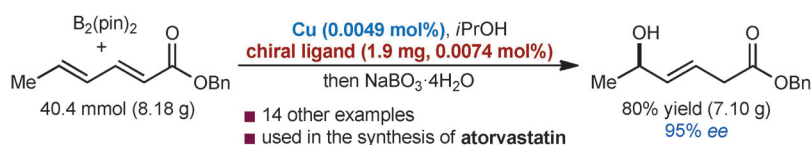
See attached PdF: A series of benzylic fluorides was prepared by hydrofluorination which proceeds through a $\text{Pd}^{\text{II/IV}}$ catalytic manifold. The method is mechanistically distinct from previously reported radical hydrofluorination, and is

characterized by its clean regioselectivity and unique *cis* stereospecificity. The first example of enantioselective net HF addition onto 2-vinylnaphthalene is also disclosed.

Homogeneous Catalysis

E. Emer, L. Pfeifer, J. M. Brown,
V. Gouverneur* 4181–4185

cis-Specific Hydrofluorination of Alkenylarenes under Palladium Catalysis through an Ionic Pathway



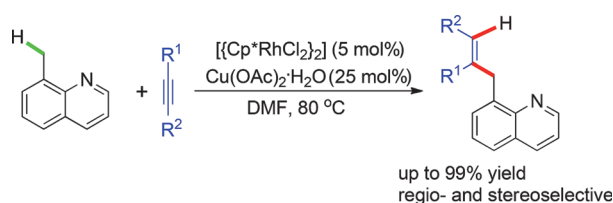
1,6-Borations of electron-deficient dienes with bis(pinacolato)diboron using copper catalyst loadings as low as 0.0049 mol % provided chiral allylboronates that, after oxidation, result in allylic alcohols in high

enantioselectivities and 1,6:1,4 ratios. The allylboronates can also be used in stereoselective allylations of aldehydes. This process was applied to a concise synthesis of atorvastatin.

Asymmetric Catalysis

Y. Luo, I. D. Roy, A. G. E. Madec,
H. W. Lam* 4186–4190

Enantioselective Synthesis of Allylboronates and Allylic Alcohols by Copper-Catalyzed 1,6-Boration



Highly regio- and stereoselective alkenylation reactions of 8-methylquinolines with alkynes give 8-allylquinolines in good

yields. These reactions are catalyzed by $[(\text{Cp}^*\text{RhCl}_2)_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) and proceed by $\text{C}(\text{sp}^3)\text{--H}$ bond activation.

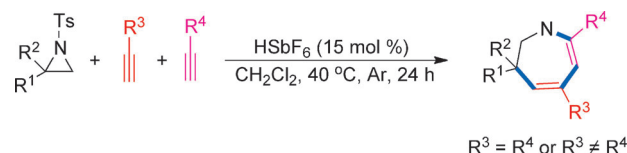
Homogeneous Catalysis

B. Liu, T. Zhou, B. Li, S. Xu, H. Song,
B. Wang* 4191–4195

Rhodium(III)-Catalyzed Alkenylation Reactions of 8-Methylquinolines with Alkynes by $\text{C}(\text{sp}^3)\text{--H}$ Activation

Heterocycles

M.-B. Zhou, R.-J. Song,
J.-H. Li* 4196–4199



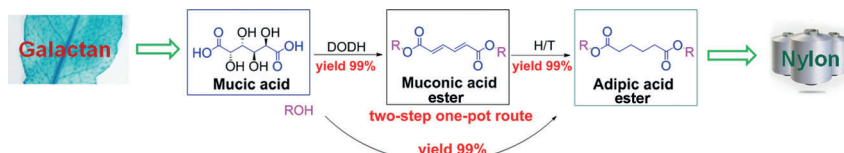
Hexafluoroantimonic Acid Catalysis:
Formal [3+2+2] Cycloaddition of
Aziridines with Two Alkynes

Superacid powers: The title reaction of unactivated aziridines with two of the same or different terminal alkyne components has been developed, thus opening a new access to seven-membered heterocyclic ring systems. This transformation is

experimentally simple while furnishing azepine derivatives in good yields (up to 78%) with good levels of chemo- and regioselectivity. Ts = 4-toluenesulfonyl.

Sustainable Chemistry

X. Li, D. Wu, T. Lu, G. Yi, H. Su,*
Y. G. Zhang* 4200–4204



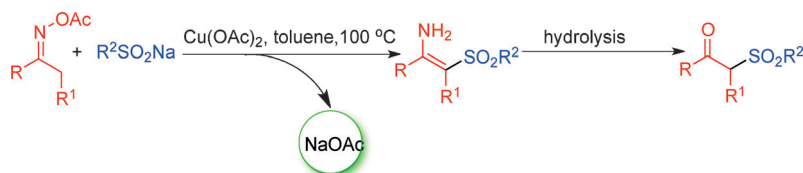
Highly Efficient Chemical Process To
Convert Mucic Acid into Adipic Acid and
DFT Studies of the Mechanism of the
Rhenium-Catalyzed Deoxydehydration

Taking a dip: A highly efficient synthetic protocol has been developed for the conversion of mucic acid into adipic acid by the oxorhenium-complex-catalyzed deoxydehydration reaction and subsequent Pt/C-catalyzed transfer hydrogenation.

Quantitative yields were achieved for the conversion of mucic acid into muconic acid and adipic acid esters either through separate sequences or through a one-pot process.

Synthetic Methods

X. Tang, L. Huang, Y. Xu, J. Yang, W. Wu,
H. Jiang* 4205–4208



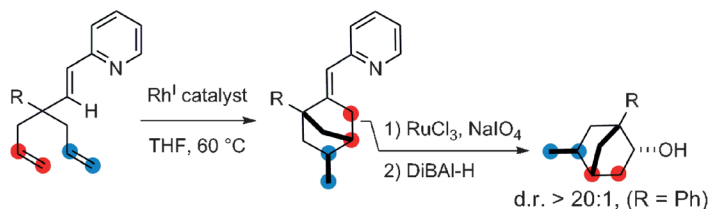
Copper-Catalyzed Coupling of Oxime
Acetates with Sodium Sulfonates: An
Efficient Synthesis of Sulfone Derivatives

Copper brings us together: The title reaction involves copper-catalyzed N–O bond cleavage, activation of a vinyl sp^2 C–H bond and C–S bond formation; it uses simple oxime acetates and sodium sulfonates to synthesize sulfonylvinylamine products without the need for additional oxidants or additives. Upon hydrolysis, useful β -ketosulfones are obtained.

Inside Cover

C–H Activation

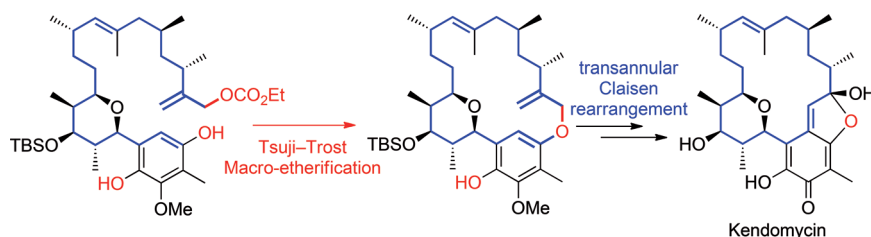
C. Aïssa,* K. Y. T. Ho, D. J. Tetlow,
M. Pin-Nó 4209–4212



Diastereoselective Carbocyclization of 1,6-
Heptadienes Triggered by Rhodium-
Catalyzed Activation of an Olefinic C–H
Bond

Folding alkenes: Described is the first example of a rhodium(I)-catalyzed functionalization of an olefinic C–H bond with a 1,6-heptadiene reagent. This carbocyclization is completely diastereoselective

and creates at least three stereogenic centers from simple prochiral substrates. The directing group can easily be converted into other functional groups.



A new construct: The asymmetric total synthesis of the antibiotic kendomycin was accomplished by using a highly stereocontrolled convergent route. The key feature of the synthetic strategy is the

construction of an 18-membered carbocycle based on an intramolecular Tsuji–Trost etherification/transannular Claisen rearrangement sequence. TBS = *tert*-butyldimethylsilyl.

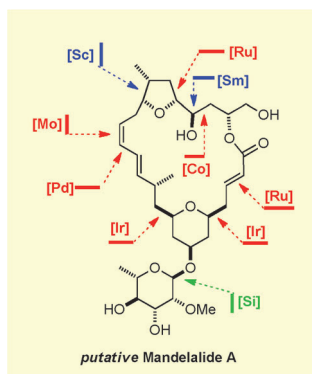
Natural Products

T. Sengoku, S. Xu, K. Ogura, Y. Emori, K. Kitada, D. Uemura, H. Arimoto* — 4213 – 4216

Total Synthesis of the Antibiotic Kendomycin: A Macrocyclization Using the Tsuji–Trost Etherification



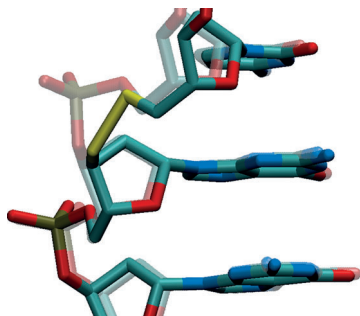
Bitter and sweet: The synthesis of the proposed structure of the cytotoxic macrolide mandelalide A reiterates the notion that structure elucidation of architecturally complex natural products is not always reliable. From the chemical viewpoint, the chosen route attests to the power of (transition) metals as catalysts for stereoselective synthesis. Most notable is the first application of terminal-acetylene metathesis to natural product chemistry.



Total Synthesis

J. Willwacher, A. Fürstner* — 4217 – 4221

Catalysis-Based Total Synthesis of Putative Mandelalide A



Thiolated oligonucleotides show unprecedented high reaction rates in chemical ligation experiments. The influence of temperature on the templated reaction is shown with a system designed for fluorescence monitoring. Side reactions and the nontemplated ligation reactions are efficiently suppressed by the choice of DNA modification and the activation site.

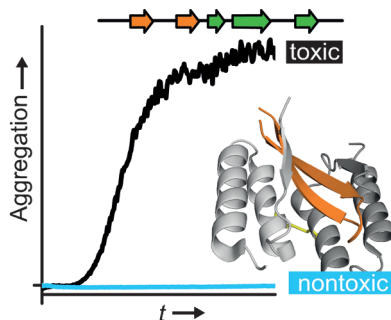
Chemical DNA Ligation

V. Patzke,* J. S. McCaskill, G. von Kiedrowski — 4222 – 4226

DNA with 3'-5'-Disulfide Links—Rapid Chemical Ligation through Isosteric Replacement



Wrapping the hairpin: NMR spectroscopy identifies a β -hairpin conformation of α -synuclein in complex with an engineered β -wrapin. The β -wrapin inhibits α -synuclein aggregation and toxicity at substoichiometric concentration. Sequestration of a β -hairpin is a novel approach to interfere with the initial steps of the aggregation reaction.



Protein Aggregation

E. A. Mirecka, H. Shaykhalishahi, A. Gauhar, Ş. Akgül, J. Lecher, D. Willbold, M. Stoldt, W. Hoyer* — 4227 – 4230

Sequestration of a β -Hairpin for Control of α -Synuclein Aggregation



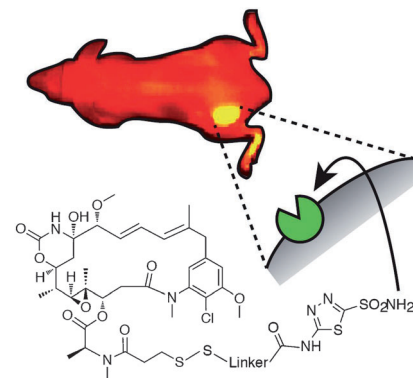
Cancer Therapy

N. Krall, F. Pretto, W. Decurtins,
G. J. L. Bernardes, C. T. Supuran,
D. Neri* 4231–4235



A Small-Molecule Drug Conjugate for the Treatment of Carbonic Anhydrase IX Expressing Tumors

Size advantage: Antibodies are currently the most widely used vehicles for drug-delivery applications. Small-molecule ligands, however, may have improved pharmacokinetics and better tissue penetration. Targeted small-molecule drug conjugates directed against the tumor marker carbonic anhydrase IX were synthesized, characterized in vitro, and tested in vivo.



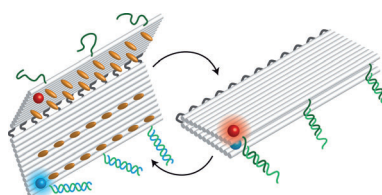
Bionanotechnology

J. List, M. Weber,
F. C. Simmel* 4236–4239



Hydrophobic Actuation of a DNA Origami Bilayer Structure

Hydrophobic interactions within cholesterol-modified DNA origami structures can induce large conformational changes, which can be used as the basis of a novel molecular switching mechanism. Intramolecularly folded DNA bilayer sheets are shown to unfold in the presence of surfactants and lipid membranes. Hydrophobic switching can be combined with a DNA-based lock and key mechanism, resulting in the conditional opening of the DNA bilayer structures.

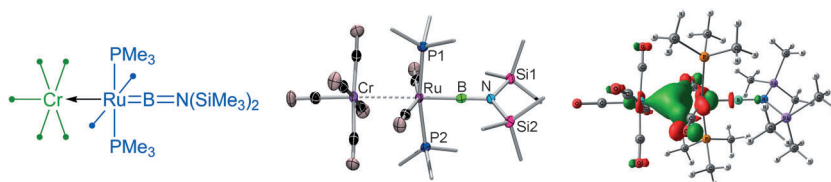


Borylene Exchange

S. Bertsch, R. Bertermann,
H. Braunschweig,* A. Damme,
R. D. Dewhurst, A. K. Phukan,
C. Saalfrank, A. Vargas, B. Wennemann,
Q. Ye 4240–4243



Metal-Only Lewis Pairs by Reversible Insertion of Ruthenium and Osmium Fragments into Metal–Boron Double Bonds



Separation anxiety: The insertion of a zerovalent ruthenium or osmium complex into the chromium–boron double bond of a borylene complex leads to new metal-only Lewis pairs (MOLPs: Ru→Cr and Os→Cr). The reaction creates new bor-

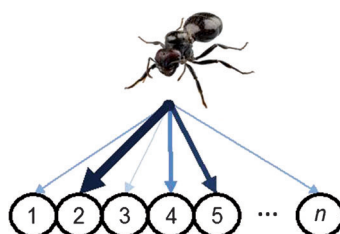
ylene complexes and is crystallization-controlled. A mechanism is proposed based on DFT calculations, along with a computational study of the unusual MOLPs.

Combinatorial Chemistry

M. Reutlinger, T. Rodrigues, P. Schneider,
G. Schneider* 4244–4248



Multi-Objective Molecular De Novo Design by Adaptive Fragment Prioritization



Finding the best way: A molecular design method inspired by ant colony optimization generated novel, highly potent, drug-like ligands for the sigma-1 and dopamine D₄ receptors. The computational approach is readily applicable to combinatorial chemistry and delivers focused compound libraries profiled for desired target-panel activities.

Angewandte Corrigendum

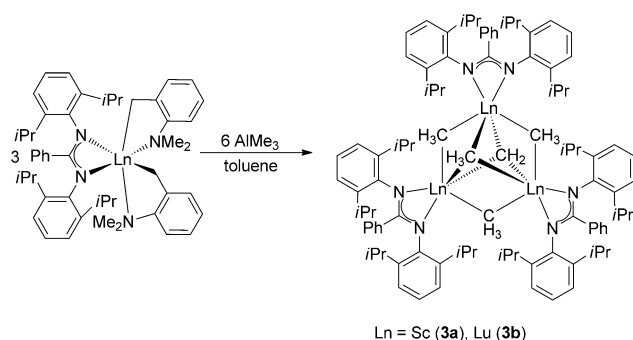
In this Minireview, trinuclear methylidene complexes by Zhou et al. (**3a**, **3b**) were described, but the ligand system was incorrectly reported. As supporting ligand *N,N'*-bis(diisopropylphenyl)benzamidinate was used. Schemes 3 and 14 also contain this error. The correct schemes are shown below.

Rare-Earth-Metal Methylidene Complexes

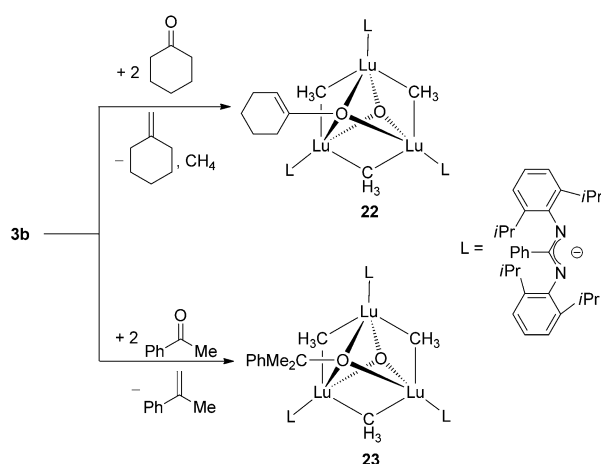
J. Kratsch, P. W. Roesky* — 376–383

Angew. Chem. Int. Ed. 2014, 53

DOI: 10.1002/anie.201303761



Scheme 3.



Scheme 14.



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).



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