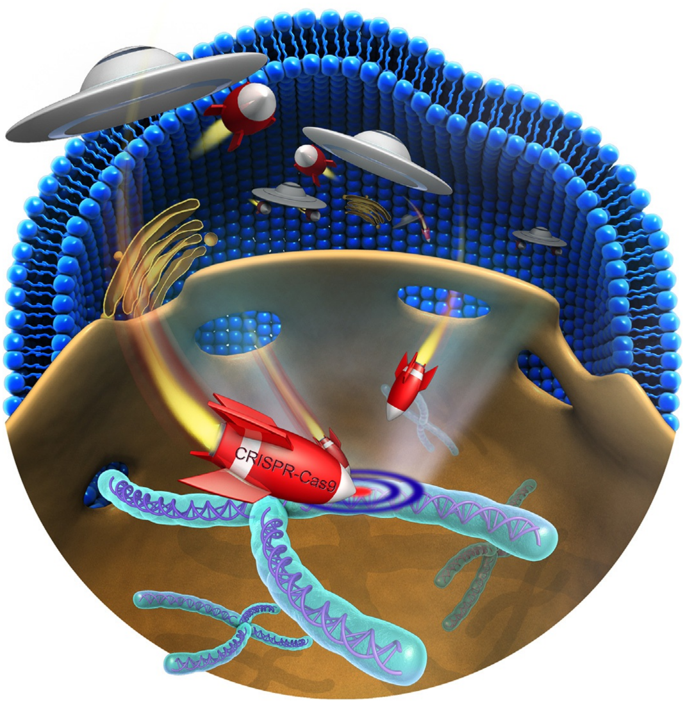
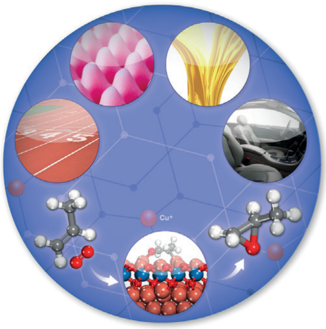
A biologically inspired carrier …

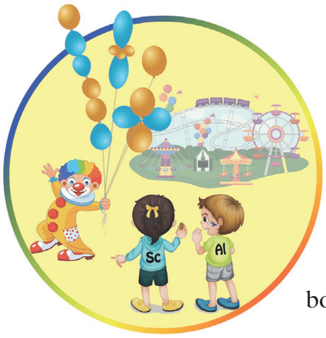


… for the delivery of CRISPR–Cas9 that is based on yarn-like DNA nanoparticles, so-called DNA nanoclews, is described by Z. Gu, C. L. Beisel, and co-workers in their Communication on page 12029 ff. DNA nanoclews (the flying saucers), partially complementary to the single guide RNA (sgRNA), were efficiently loaded with Cas9/sgRNA complexes (the missiles) and delivered the complexes into human cells for genome editing.

Propylene Epoxidation Catalysts

Cu$^+$ active sites on a Cu$_2$O surface are stabilized with TiO$_x$. J. G. Chen et al. show in their Communication on page 11946 ff. that the resulting mixed oxide helps form an oxametallacycle intermediate with propylene giving higher selectivity for propylene epoxidation.





Main Group Chemistry

In their Communication on page 12034 ff., F. M. Bickelhaupt, M. G. Goesten et al. report that the bonding in six-coordinate Group 13 complexes is best described in terms of 7-center-12-electron bonds.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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Service

Author Profile

"If I had one year of paid leave I would try a self-sufficient lifestyle.
My favorite drink is green tea …"
This and more about Donglin Jiang can be found on page 11902.

News


M. Neurock


C. Leumann


H. Braunschweig


P. R. Schreiner


K. Tatsumi

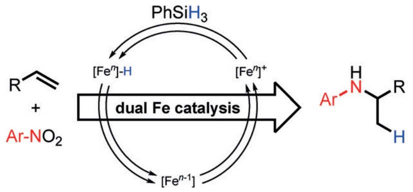
Highlights

Iron Catalysis

M. Villa,
A. Jacobi von Wangelin* ___ **11906 – 11908**

Hydroaminations of Alkenes: A Radical, Revised, and Expanded Version

Radical changes: The applicability of alkene hydroamination has recently been significantly expanded by the development of radical variants that are based on initial hydrogen atom transfer to the alkene. This Highlight assesses the current state of the art, focusing on an iron-catalyzed reaction that utilizes stable nitroarenes as the electrophilic N component and is based on the dual catalytic activation of both starting materials.



Essays

1915 Nobel Prize for Chemistry

D. Trauner* ___ **11910 – 11916**

Richard Willstätter and the 1915 Nobel Prize in Chemistry

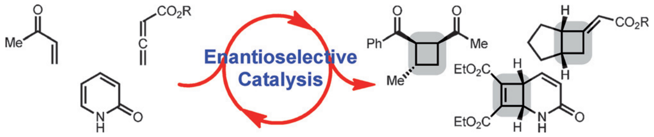
One hundred years after his Nobel Prize, Richard Willstätter's achievements and the fascinating role he played in 20th century chemistry are discussed in this Essay. Several of his discoveries, such as the anthocyanidins, cyclooctatetraene, the *ortho*-quinones, and the structure of cocaine, will forever be associated with his name.

Minireviews

Small-Ring Systems

Y. Xu, M. L. Conner,
M. K. Brown* ___ **11918 – 11928**

Cyclobutane and Cyclobutene Synthesis: Catalytic Enantioselective [2+2] Cycloadditions



Squared away: Cyclobutanes and cyclobutenes are important structural motifs found in numerous biologically significant molecules, and they are useful intermediates for chemical synthesis. Consequently, catalytic enantioselective [2+2] cycloadditions to access cyclobutanes and cyclobutenes have emerged as an attractive target for method development. The advances made in catalytic enantioselective [2+2] cycloadditions are described herein.

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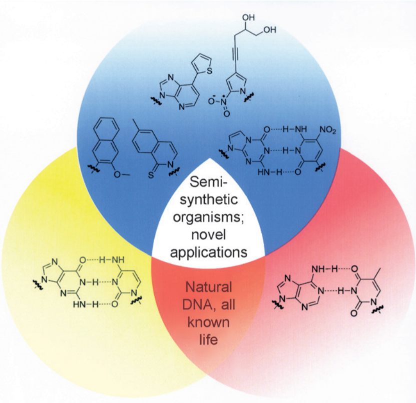
Reviews

Expanded Genetic Alphabet



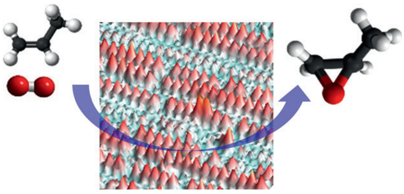
Rule of three: Natural nucleic acids and the genetic information they encode are limited by the use of only four nucleotides that form two base pairs, (d)G-(d)C and d(A)-dT/U. In the past decade, three classes of unnatural base pairs have been developed to a high level of proof-of-concept. This Review summarizes their development and the potentially revolutionary applications that they are now enabling.

D. A. Malyshev,
F. E. Romesberg* ______ **11930 – 11944**

The Expanded Genetic Alphabet

Communications

Epoxidation Catalysis



Ti-ed up: Cu^+ active sites on a Cu_2O surface can be stabilized with TiO_x by forming a mixed oxide, $TiCuO_x$. The basicity of the surface-bound oxygen atoms thus decreases which inhibits combustion and promotes the formation of an oxametallacycle intermediate with propylene leading to higher selectivity for propylene epoxidation.

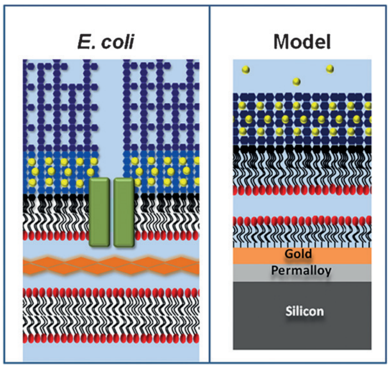
X. Yang, S. Kattel, K. Xiong,
K. Mudiyanselage, S. Rykov,
S. D. Senanayake, J. A. Rodriguez, P. Liu,
D. J. Stacchiola,
J. G. Chen* ______ **11946 – 11951**

Direct Epoxidation of Propylene over Stabilized Cu^+ Surface Sites on Titanium-Modified Cu_2O

Frontispiece

Antibiotics

Understanding the outer membranes of Gram-negative bacteria is important for the development of new antibacterial compounds. However, their structure and dynamics are poorly understood because of their small in vivo size and inaccurate in vitro models. A stable asymmetric model of the outer membrane that can be analyzed by a range of biophysical techniques and accurately imitates the in vivo behavior of natural outer membranes is presented herein.



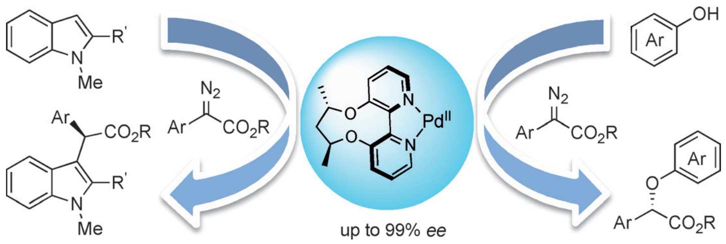
L. A. Clifton, S. A. Holt, A. V. Hughes,
E. L. Daulton, W. Arunmanee, F. Heinrich,
S. Khalid, D. Jefferies, T. R. Charlton,
J. R. P. Webster, C. J. Kinane,
J. H. Lakey* ______ **11952 – 11955**

An Accurate In Vitro Model of the *E. coli* Envelope

Ligand Design

X. Gao, B. Wu, W.-X. Huang, M.-W. Chen, Y.-G. Zhou* **11956 – 11960**

Enantioselective Palladium-Catalyzed C–H Functionalization of Indoles Using an Axially Chiral 2,2′-Bipyridine Ligand

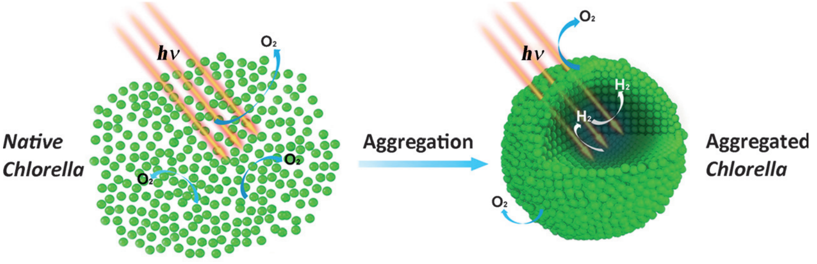


Get the axial: The title reaction involving diazo compounds was achieved with an axially chiral 2,2′-bipyridine ligand. Moreover, insertion into O–H bonds of phenols was also realized with up to 99 % *ee* by using this catalytic system.

Hydrogen Production

W. Xiong, X. Zhao, G. Zhu, C. Shao, Y. Li, W. Ma,* X. Xu,* R. Tang* **11961 – 11965**

Silicification-Induced Cell Aggregation for the Sustainable Production of H_2 under Aerobic Conditions

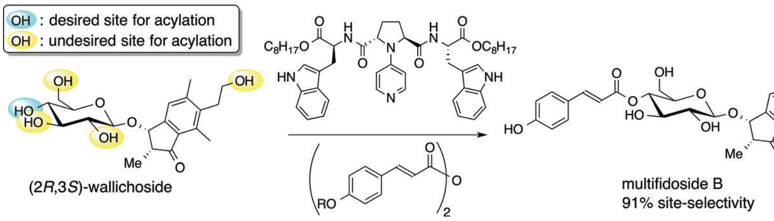


Green algae aggregates induced by biomineralization are a novel cell-material hybrid that can sustainably produce hydrogen even under natural aerobic conditions. Its evolution of photobiological hydrogen can be understood by the spatial–functional differentiation of the cells within the aggregate.

Unconventional Retrosynthesis

Y. Ueda, T. Furuta, T. Kawabata* **11966 – 11970**

Final-Stage Site-Selective Acylation for the Total Syntheses of Multifidosides A–C

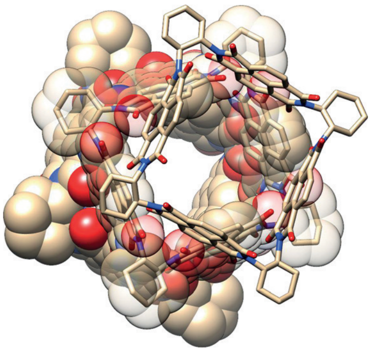


On “site”: A new retrosynthetic route to 4-O-acylated natural and unnatural glycosides is demonstrated. The title reaction of unprotected glycoside precursors, possessing multiple hydroxy groups, was performed successfully. The total syntheses of multifidosides A, B, and C were completed using this acylation strategy.

Organic Semiconductors

Y. Wu, S. K. M. Nalluri, R. M. Young, M. D. Krzyaniak, E. A. Margulies, J. F. Stoddart,* M. R. Wasielewski* **11971 – 11977**

Charge and Spin Transport in an Organic Molecular Square



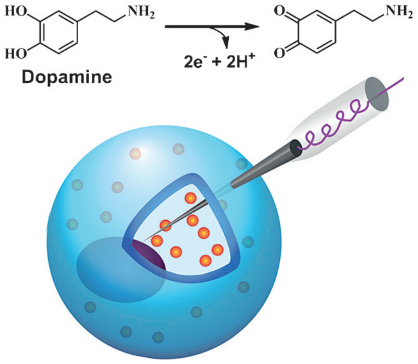
Square dance: A chiral shape-persistent macrocycle comprising four equivalent naphthalene diimide (NDI) subunits, which are almost perpendicular to each other (see figure), can be prepared in a stepwise fashion. EPR and ENDOR spectroscopy on the monoreduced state shows sharing of the unpaired electron over all four NDI subunits, despite the small overlap of the individual π systems.

Electrochemical Cytometry

X. Li, S. Majdi, J. Dunevall, H. Fathali,
A. G. Ewing* **11978 – 11982**

Quantitative Measurement of Transmitters in Individual Vesicles in the Cytoplasm of Single Cells with Nanotip Electrodes

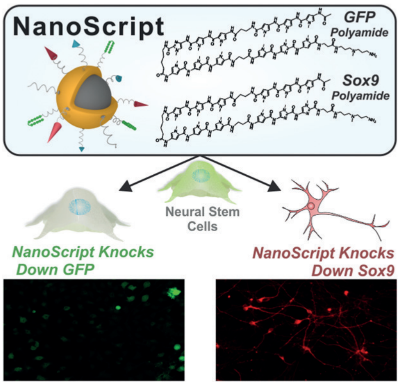
Tiny but tip-top: Nanotip conical carbon-fiber microelectrodes were used for the intracellular quantification of vesicular transmitter content in single cells by a method introduced as intracellular vesicle electrochemical cytometry. It was shown that vesicular levels of catecholamines, such as dopamine (see scheme), can be altered by pharmacological manipulation, and that only partial release of neurotransmitters occurs during normal exocytosis.



Neuronal Differentiation

S. Patel, S.-T. D. Chueng, P. T. Yin,
K. Dardir, Z. Song, N. Pasquale, K. Kwan,
H. Sugiyama, K.-B. Lee* **11983 – 11988**

Induction of Stem-Cell-Derived Functional Neurons by NanoScript-Based Gene Repression



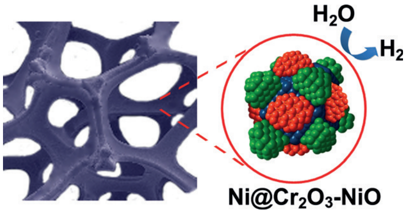
It will knock you down: A functionalized nanoparticle, termed “NanoScript”, is the key component in a platform designed to knock down transcriptional gene expression in stem cells. The tunable and non-viral NanoScript platform, which is functionalized with specific small molecules, effectively knocks down GFP in GFP-labeled neural stem cells (NSCs), and represses *Sox9* expression in NSCs to induce differentiation into functional neurons.

Electrocatalysis

M. Gong, W. Zhou, M. J. Kenney,
R. Kapusta, S. Cowley, Y. Wu, B. Lu, M. Lin,
D. Wang, J. Yang, B. Hwang,
H. Dai* **11989 – 11993**

Blending Cr_2O_3 into a NiO–Ni Electrocatalyst for Sustained Water Splitting

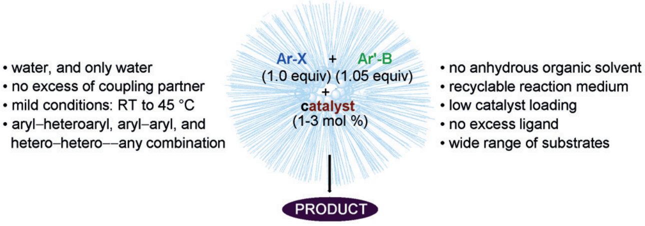
A triphase electrocatalyst composed of a Cr_2O_3-blended NiO coating on Ni nanocores (CrNN catalyst) synthesized on metal-foam substrates showed superior activity and stability for the hydrogen-evolution reaction in basic solutions. Using the CrNN catalyst, sustained electrolysis of water was achieved at a voltage lower than 1.5 V for at least 500 hours.



Green Chemistry

S. Handa, E. D. Slack,
B. H. Lipshutz* **11994 – 11998**

Nanonickel-Catalyzed Suzuki–Miyaura Cross-Couplings in Water

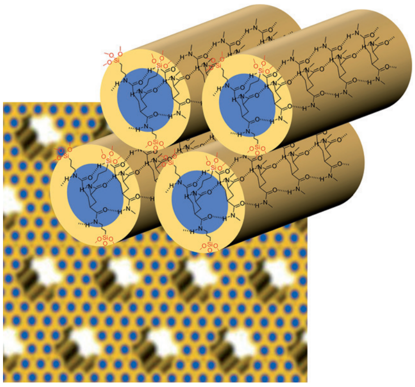


Under water: Nickel nanoparticles, formed in situ and used in combination with micellar catalysis, catalyze Suzuki–Miyaura cross-couplings in water under very mild reaction conditions. A wide range of substrates is tolerated and the reaction medium can be recycled.

Mesoporous Materials

N. Mizoshita,*
S. Inagaki* ______ 11999 – 12003

Periodic Mesoporous Organosilica with Molecular-Scale Ordering Self-Assembled by Hydrogen Bonds



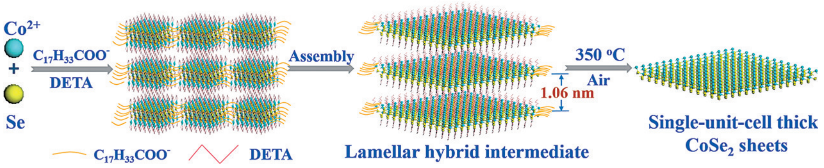
Host–guest systems: Self-assembly of an organosilane precursor by hydrogen bonding is the key to construction of a new class of crystal-like periodic mesoporous organosilicas (see picture). The present mesoporous materials can stably accomodate silane-free H-bonding guest molecules within the pore walls, which is applicable to non-covalent modification of organosilica hybrids.

Water Splitting

L. Liang, H. Cheng, F. Lei, J. Han, S. Gao, C. Wang, Y. Sun,* S. Qamar, S. Wei,*
Y. Xie* ______ 12004 – 12008

Metallic Single-Unit-Cell Orthorhombic Cobalt Diselenide Atomic Layers: Robust Water-Electrolysis Catalysts

Inside Cover



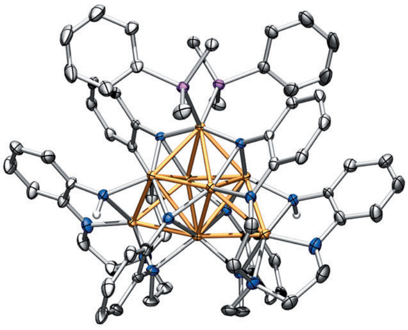
The shape of thins to come: Atomic layers bring better catalytic properties as shown by thermally exfoliating a lamellar $CoSe_2$–DETA hybrid to give single-unit-cell orthorhombic $CoSe_2$ sheets. The single-unit-cell thickness means that 66.7% of the Co^{2+} ions are exposed on the surface and are low coordinate leading to a lower Tafel slope and higher turnover frequency in water splitting.

Iron Clusters

R. H. Sánchez, A. M. Willis, S.-L. Zheng,
T. A. Betley* ______ 12009 – 12013

Synthesis of Well-Defined Bicapped Octahedral Iron Clusters $[(^{tren}L)_2Fe_8(PMe_2Ph)_2]^n$ ($n = 0, -1$)

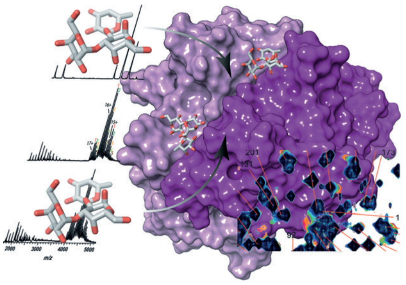
Expanding the nuclearity: Octairon clusters with a bicapped octahedral cluster core employing a polynucleating hepta-amine ligand have been synthesized and isolated. This cluster core geometry is unprecedented for first-row transition metals. The design principles used to obtain these clusters may be extended to other transition metals or generalized to synthesize even larger clusters. Atom colors: Fe = orange; N = blue; P = purple; C = gray.



Structural Virology

A. Mallagaray, J. Lockhauserbäumer,
G. Hansman, C. Uetrecht,
T. Peters* ______ 12014 – 12019

Attachment of Norovirus to Histo Blood Group Antigens: A Cooperative Multistep Process

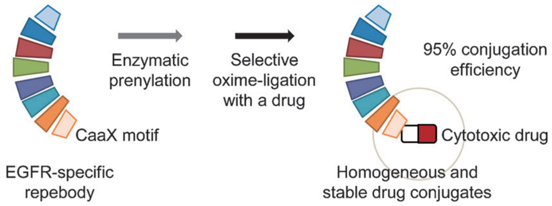


More than binding: Attachment of noroviruses to histo blood group antigens is a complex and cooperative process. This is in contrast to current perception conveying simple one-site binding. NMR spectroscopy and native mass spectrometry independently confirm this new paradigm of virus–carbohydrate interaction.

Drug Delivery

J.-j. Lee, H.-J. Choi, M. Yun, Y. Kang, J.-E. Jung, Y. Ryu, T. Y. Kim, Y.-j. Cha, H.-S. Cho,* J.-J. Min,* C.-W. Chung,* H.-S. Kim* ________ **12020 – 12024**

Enzymatic Prenylation and Oxime Ligation for the Synthesis of Stable and Homogeneous Protein–Drug Conjugates for Targeted Therapy

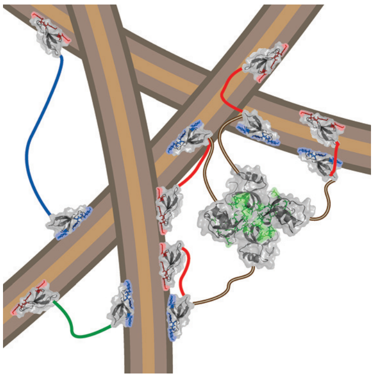


A chemoenzymatic conjugation method that is based on enzymatic prenylation and oxime ligation is a simple and efficient means for generating highly stable and homogeneous protein–drug conjugates in a site-specific manner. It can be generally applied to the conjugation of drugs to a wide range of protein binders, facilitating the development of targeted therapies with high efficacies and low off-target effects.

Molecular Biomimetics

J.-M. Malho, S. Arola, P. Laaksonen, G. R. Szilvay, O. Ikkala, M. B. Linder* ________ **12025 – 12028**

Modular Architecture of Protein Binding Units for Designing Properties of Cellulose Nanomaterials

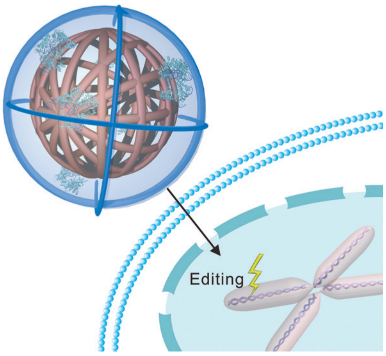


Better together: Engineered proteins were combined with nanofibrillated cellulose (NFC; gray/brown fibres) to show how a multimodular architecture leads to tuned properties. Two cellulose-binding modules (red and blue structures) were separated by 12-, 24-, or 48-mer linkers (red, green, and blue lines), with an optional multimerizing domain (green structure). The linkers significantly affect the interaction between protein and NFC in the wet colloidal and dry film states.

Drug Delivery

W. Sun, W. Ji, J. M. Hall, Q. Hu, C. Wang, C. L. Beisel,* Z. Gu* ________ **12029 – 12033**

Self-Assembled DNA Nanoclews for the Efficient Delivery of CRISPR–Cas9 for Genome Editing



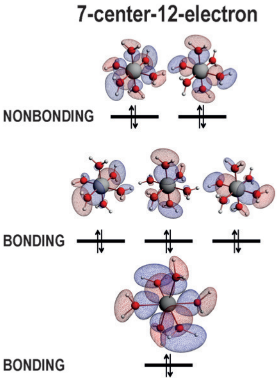
All rolled into one: A biologically inspired delivery vehicle for CRISPR–Cas9 is based on yarn-like DNA nanoparticles that are synthesized by rolling circle amplification. The DNA nanoclews were efficiently loaded with Cas9 protein/single guide RNA complexes and delivered them into human cells, enabling targeted gene disruption.

Front Cover

Main Group Chemistry

M. G. Goesten,* C. Fonseca Guerra, F. Kapteijn, J. Gascon, F. M. Bickelhaupt* ________ **12034 – 12038**

Six-Coordinate Group 13 Complexes: The Role of d Orbitals and Electron-Rich Multi-Center Bonding



According to molecular orbital theory and relativistic Kohn–Sham density functional theory, six-coordinate clusters based on Group 13 elements bind through an electron-rich 7-center-12-electron pattern instead of using d orbitals. Strongly polar bonding and an affinity towards small anions are thus predicted, properties that are indeed associated with materials and molecules based on such clusters.

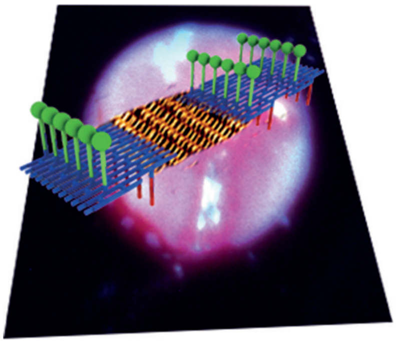
Inside Back Cover

Biosensors

R. Meyer, B. Saccà,
C. M. Niemeyer* ________ 12039 – 12043

Site-Directed, On-Surface Assembly of DNA Nanostructures

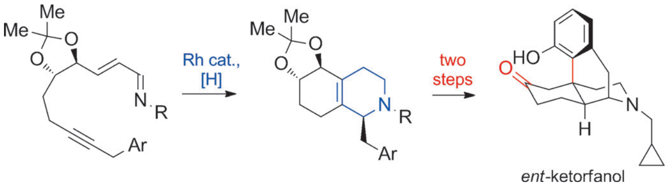
From micro to nano: Orthogonal topographic modification of planar DNA nanostructures combined with site-directed on-surface assembly provides a means to bridge top-down micropatterning with bottom-up nanotechnology.



Alkaloid Synthesis

E. M. Phillips, T. Mesganaw, A. Patel,
S. Duttwyler, B. Q. Mercado, K. N. Houk,*
J. A. Ellman* ________ 12044 – 12048

Synthesis of *ent*-Ketorfanol via a C–H Alkenylation/Torquoselective 6π Electrocyclization Cascade

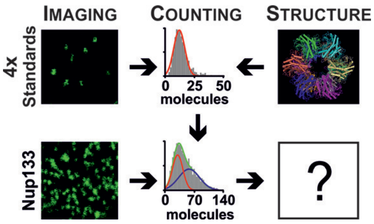


The asymmetric synthesis of *ent*-ketorfanol from simple and commercially available precursors is reported. A Rh^{I}-catalyzed intramolecular C–H alkenylation/torquoselective 6π electrocyclization cascade provides a fused bicyclic 1,2-dihydropyridine as a key intermediate. The ketone functionality and final ring are introduced in a single step through a redox-neutral acid-catalyzed rearrangement of a vicinal diol followed by intramolecular Friedel–Crafts alkylation.

Protein Counting

K. Finan,* A. Raulf,
M. Heilemann* ________ 12049 – 12052

A Set of Homo-Oligomeric Standards Allows Accurate Protein Counting

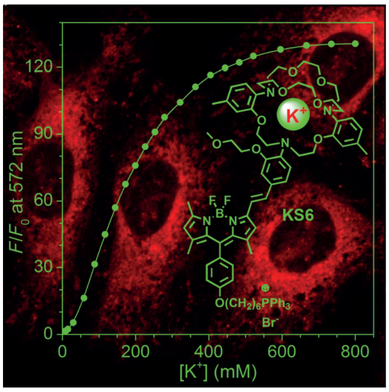


You can count on it: Quantitative fluorescence microscopy requires calibration standards. A set of four protein standards was developed that enables the robust quantification of unknown protein complexes. This versatile method is compatible with various microscopy techniques and was demonstrated with confocal microscopy and super-resolution imaging to quantify the number of Nup133-containing subunits in the nuclear-pore complex.

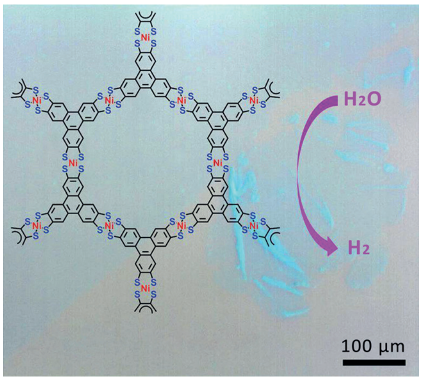
Fluorescent Probes

X. Kong, F. Su, L. Zhang, J. Yaron, F. Lee,
Z. Shi, Y. Tian,*
D. R. Meldrum* ________ 12053 – 12057

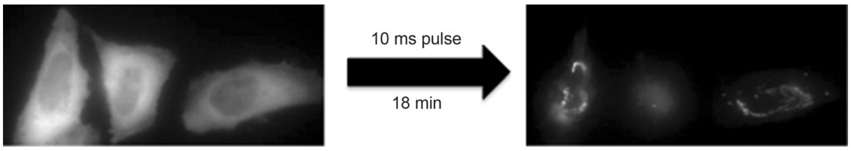
A Highly Selective Mitochondria-Targeting Fluorescent K^+ Sensor



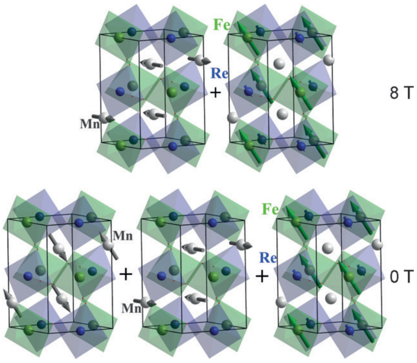
A lamp to light the K: An intracellular mitochondria-specific K^+ sensor, **KS6**, was developed. **KS6** shows a K^+ response range of 30–500 mM, sensitive fluorescence enhancement ($F_{max}/F_0 \approx 130$), high brightness ($\phi_f = 14.4\%$ at 150 mM of K^+), and insensitivity to both pH (in the range 5.5–9.0) and other metal ions under physiological conditions. **KS6** is thus the first sensor that can be used for monitoring K^+ ion flux in the mitochondria of live cells



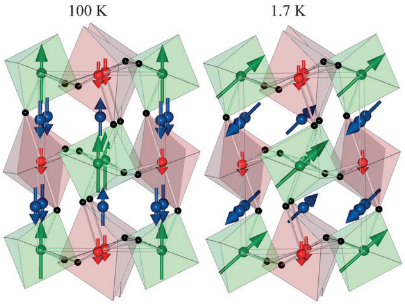
Standing up: The Langmuir–Blodgett method can be used to prepare two-dimensional supramolecular polymer (2DSP) sheets from nickel bis(dithiolene) complexes at the air–water interface (see figure). These free-standing single-layer sheets, which are 0.7–0.9 nm thick and square millimeters in area, showed excellent electrocatalytic activities in the hydrogen evolution reaction from water.



Optogenetic Apoptosis: An optogenetic design strategy is described that transforms the aberrant behavior of pro-apoptotic Bax mutants into light-responsive, genetically encoded constructs capable of triggering cell death in response to illumination.



The first transition-metal-only double perovskite, $Mn^{2+}{}_2Fe^{3+}Re^{5+}O_6$, displays ferrimagnetic ordering up to 520 K and a giant positive magnetoresistance of up to 220% at 5 K and 8 T. These properties result from the ferrimagnetically coupled Fe and Re sublattice and are affected by a two-to-one magnetic-structure transition of the Mn sublattice when a magnetic field is applied.

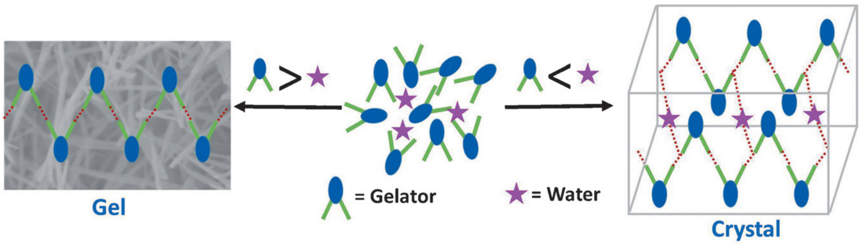


Double-perovskite magnetism: The double perovskite Mn_2FeReO_6 synthesized at high pressure has magnetic transition-metal cations at all sites. High-spin Mn^{2+} cations lead to record magnetizations for double-perovskite ferrimagnets and their frustrated magnetic order at 75 K switches magnetoresistance from negative to large positive values at low temperatures.

Gelation versus Crystallization

A. Vidyasagar,
K. M. Sureshan* ________ **12078 – 12082**

Stoichiometric Sensing to Opt between Gelation and Crystallization

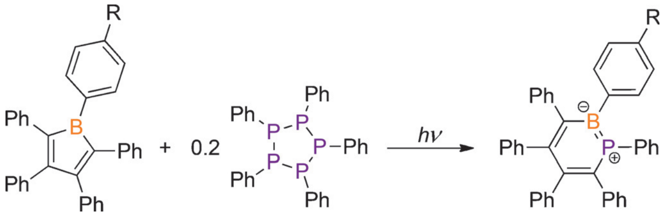


To gel or not to gel: A new class of organogelators having a cyclohexanediol motif uses molecular quorum sensing to make a definite choice between two competing modes of self-assembly: gelation or crystallization. When the concentration of gelator is less than that of adventitious water present in the system, the gelator molecules undergoes crystallization; when its concentration is more than water, it congeals the solvent to form a stable organogel.

Ring Expansion

J. H. Barnard, P. A. Brown, K. L. Shuford,
C. D. Martin* ________ **12083 – 12086**

1,2-Phosphaborines: Hybrid Inorganic/Organic P–B Analogues of Benzene

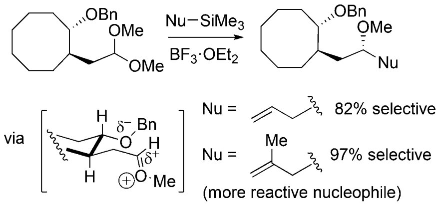


Jamming PB into benzene: 1,2-Phosphaborines were synthesized by the ring expansion reaction of boroles with the cyclic phosphine $[PPh]_5$ under UV irradiation. The products were structurally characterized revealing a planar central ring. The nature of the bonding was analyzed computationally and indicated that the heterocycle had appreciable aromatic character.

Nucleophilic Substitution

A. Garcia, J. R. Sanzone,
K. A. Woerpel* ________ **12087 – 12090**

Participation of Alkoxy Groups in Reactions of Acetals: Violation of the Reactivity/Selectivity Principle in a Curtin–Hammett Kinetic Scenario

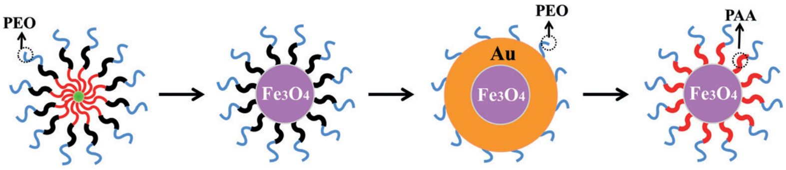


On principle: Nucleophilic substitution reactions of acetals having benzyloxy groups four carbon atoms away can be highly diastereoselective. The selectivity in several cases increased as the reactivity of the nucleophile increased, in violation of the reactivity/selectivity principle. The increase in selectivity with reactivity suggests that multiple conformational isomers of reactive intermediates can give rise to the products.

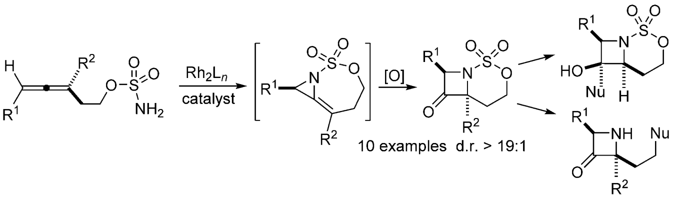
Core/Shell Nanoparticles

D. Yang, X. Pang, Y. He, Y. Wang, G. Chen,
W. Wang, Z. Lin* ________ **12091 – 12096**

Precisely Size-Tunable Magnetic/Plasmonic Core/Shell Nanoparticles with Controlled Optical Properties



Star-like amphiphilic triblock copolymers with narrow molecular weight distributions were synthesized by combining two sequential atom-transfer radical polymerizations with a click reaction. A family of uniform magnetic/plasmonic core/shell nanoparticles with precisely controllable core diameters and shell thicknesses were then obtained by capitalizing on these triblock copolymers as nanoreactors [PAA = poly(acrylic acid), PEO = poly(ethylene oxide)].



Regiocontrolled allene aziridination followed by diastereoselective epoxidation and rearrangement provides convenient access to densely functionalized azetidine scaffolds. The axial chirality of the allene can be transferred to the product to provide enantioenriched heterocycles.

Synthetic Methods

E. G. Burke,
J. M. Schomaker* ______ 12097 – 12101

Oxidative Allene Amination for the Synthesis of Azetidin-3-ones

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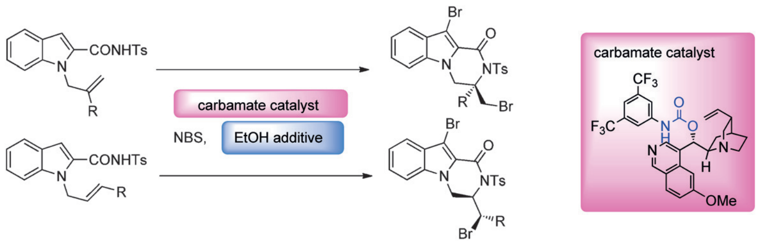
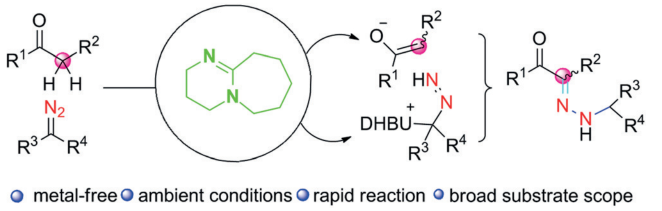


A splash of EtOH: A highly facile, efficient, and enantioselective bromolactamization of olefinic amides was effected by a carbamate catalyst and ethanol additive. The amide substrates undergo N-cyclization predominantly to give a diverse range of enantioenriched bromolactam products which contain up to two chiral centers. Ts = 4-toluenesulfonyl.

Asymmetric Catalysis

Y. A. Cheng, W. Z. Yu,
Y.-Y. Yeung* ______ 12102 – 12106

Carbamate-Catalyzed Enantioselective Bromolactamization



Active duty: 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) catalyzes the C–N bond-forming reactions of active methylenes, as C nucleophiles, with α-diazocarbonyls, as N-terminal electrophiles, under ambient reaction conditions. DBU activates both the active methylene and α-diazocarbonyl.

Diazo Compounds

L. Li, J.-J. Chen, Y.-J. Li, X.-B. Bu, Q. Liu,*
Y.-L. Zhao* ______ 12107 – 12111

Activation of α-Diazocarbonyls by Organic Catalysts: Diazo Group Acting as a Strong N-Terminal Electrophile

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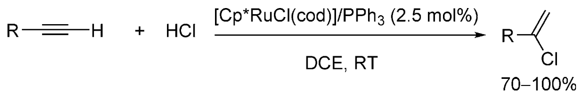


A new addition: An efficient and straightforward access to vinylchlorides is reported. This selective ruthenium-catalyzed alkyne hydrochlorination proceeds in excellent yields under mild reaction conditions by the *syn* addition of HCl. cod = 1,5-cyclooctadiene, Cp* = C_5Me_5, DCE = 1,2-dichloroethane.

Halogenation

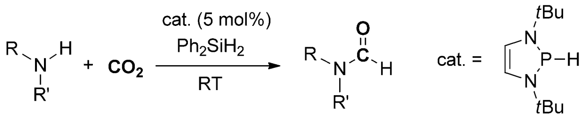
S. Dérien,* H. Klein,
C. Bruneau ______ 12112 – 12115

Selective Ruthenium-Catalyzed Hydrochlorination of Alkynes: One-Step Synthesis of Vinylchlorides

CO_2 Activation

C.-C. Chong, R. Kinjo* —— **12116–12120**

Hydrophosphination of CO_2 and Subsequent Formate Transfer in the 1,3,2-Diazaphospholene-Catalyzed N-Formylation of Amines

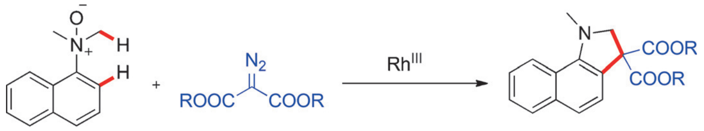


Formate formation: Hydrophosphination of CO_2 with 2-*H*-1,3,2-diazaphospholene afforded phosphorus formate, from which transfer of the formate to Ph_2SiH_2 produced $Ph_2Si(OCHO)_2$. These elementary reactions were applied to the metal-free catalytic N-formylation of various amine derivatives with CO_2 in a one-pot approach at room temperature.

C–H Activation

B. Zhou,* Z. Chen, Y. Yang,* W. Ai, H. Tang, Y. Wu, W. Zhu,* Y. Li —— **12121–12126**

Redox-Neutral Rhodium-Catalyzed C–H Functionalization of Arylamine *N*-Oxides with Diazo Compounds: Primary $C(sp^3)$–H/$C(sp^2)$–H Activation and Oxygen-Atom Transfer

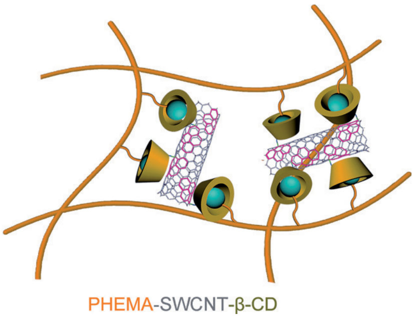


Untapped reactivity: The title reaction affords 1*H*-benzo[*g*]indolines under mild reaction conditions and external oxidants are not required. The only by-products are dinitrogen and water. This reaction represents the first example of dual functionalization of unactivated primary $C(sp^3)$–H and $C(sp^2)$–H bonds with diazocarbonyl compounds. Moreover, a method to access various amino-mandelic acid derivatives by an O-atom-transfer strategy is described.

Polymer Chemistry

K. Guo, D. Zhang, X. Zhang, J. Zhang, L. Ding, B. Li,* S. Zhang* **12127–12133**

Conductive Elastomers with Autonomic Self-Healing Properties

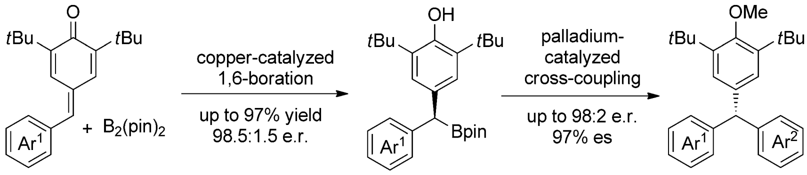


Candidates for smart robotics: Self-healing conductive composites were prepared by connecting single-walled carbon nanotubes (SWCNTs) to a polymer network through host–guest interactions (see picture). The poly(2-hydroxyethyl methacrylate)–SWCNT composite combines bulk electrical conductivity, proximity sensitivity, humidity sensitivity, and autonomic self-healing properties.

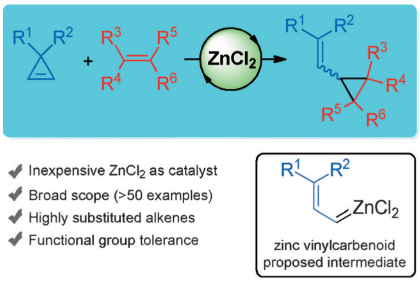
Asymmetric Catalysis

Y. Z. Lou, P. Cao, T. Jia, Y. Zhang, M. Wang, J. Liao* —— **12134–12138**

Copper-Catalyzed Enantioselective 1,6-Boration of *para*-Quinone Methides and Efficient Transformation of *gem*-Diarylmethine Boronates to Triarylmethanes



Quite a gem: The first enantioselective copper-catalyzed 1,6-conjugate addition of bis(pinacolato)diboron to *para*-quinone methides is presented. It proceeds with excellent yields and good to excellent enantioselectivities, and provides an attractive approach for the construction of optically active *gem*-diarylmethine boronic esters, which can be converted into triarylmethanes with highly enantiospecificity.



Open and close! The title reaction provides a convenient and general route to relevant vinylcyclopropane derivatives. Mechanistic studies support the participation of a zinc vinylcarbene intermediate, which may be subsequently involved in a concerted cyclopropanation reaction. This method represents a step towards identifying suitable precursors for the catalytic generation of zinc carbenoids.

Small-Ring Compounds

M. J. González, J. González, L. A. López,*
R. Vicente* ______ 12139 – 12143

Zinc-Catalyzed Alkene Cyclopropanation through Zinc Vinyl Carbenoids Generated from Cyclopropenes

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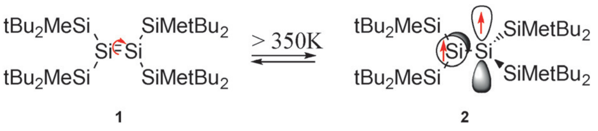

A triplet diradical that is formed in a thermally induced rotation around a main-group π bond, that is the Si=Si double bond of **1**, was directly observed by EPR spectroscopy. Both experiment and theory support a thermal equilibrium between singlet **1** and the perpendicular triplet diradical **2**.

Organodisilenes

A. Kostenko, B. Tumanskii, M. Karni,
S. Inoue, M. Ichinohe, A. Sekiguchi,*
Y. Apeloig* ______ 12144 – 12148

Observation of a Thermally Accessible Triplet State Resulting from Rotation around a Main-Group π Bond

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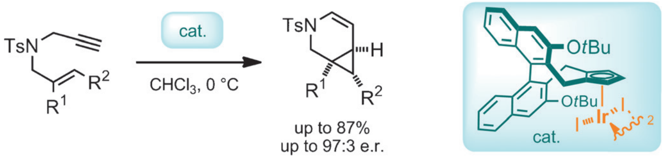

Be selective! A set of chiral Cp^{x}Ir^{III} complexes (Cp^x = chiral cyclopentadienyl) based on atropchiral cyclopentadienyl ligands are presented. The complexes, in particular the *tert*-butoxy-substituted derivative (see picture), are shown to promote the asymmetric cycloisomerization of enynes to form fused cyclopropanes with high enantioselectivities.

Asymmetric Catalysis

M. Dieckmann, Y.-S. Jang,
N. Cramer* ______ 12149 – 12152

Chiral Cyclopentadienyl Iridium(III) Complexes Promote Enantioselective Cycloisomerizations Giving Fused Cyclopropanes

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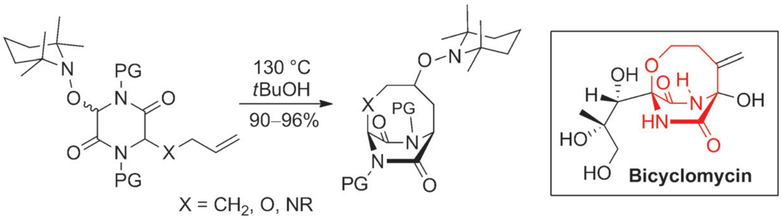


Persistent cyclization: A unified radical approach to diverse bridged diketopiperazines was developed by taking advantage of the persistent radical effect. The method allows rapid access to three-dimensional heterocyclic architectures and was applied to a formal synthesis of the antibiotic bicyclomycin.

Radical Cyclization

T. Amatov, R. Pohl, I. Císařová,
U. Jahn* ______ 12153 – 12157

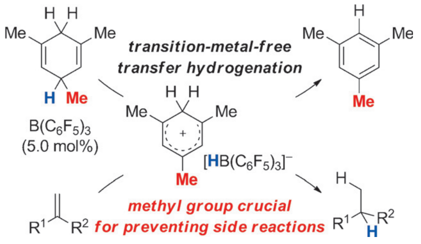
Synthesis of Bridged Diketopiperazines by Using the Persistent Radical Effect and a Formal Synthesis of Bicyclomycin

Transfer Hydrogenation

I. Chatterjee, Z.-W. Qu, S. Grimme,*
M. Oestreich* ________ 12158 – 12162

B(C_6F_5)$_3$-Catalyzed Transfer of Dihydrogen from One Unsaturated Hydrocarbon to Another

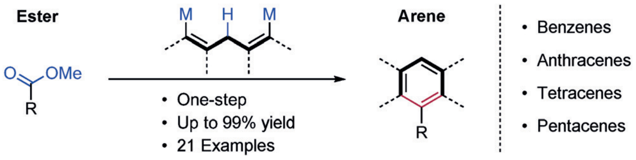
Well balanced: Wheland complexes that were generated by B(C_6F_5)$_3$-mediated hydride abstraction from cyclohexa-1,4-dienes engage in the transfer hydrogenation of alkenes. Problems arising from the involvement of carbenium ion intermediates, resulting in cationic hetero- or homodimerization, are overcome by sterically shielding the hydridic C3 position of the dihydrogen surrogate (see scheme). The mechanism was analyzed by quantum-chemical calculations.



Organomagnesium Reagents

A. Link, C. Fischer,
C. Sparr* ________ 12163 – 12166

Direct Transformation of Esters into Arenes with 1,5-Bifunctional Organomagnesium Reagents

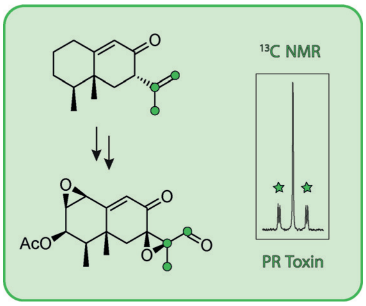


Almost replaced: A direct transformation of carboxylic acid esters into benzenes, anthracenes, tetracenes, and pentacenes is described. Utilizing 1,5-bifunctional organomagnesium reagents, the reaction integrates the ester carbon atom into the newly formed aromatic ring. The method enables the transformation of different esters into arenes in yields of up to 99%.

Terpene Biosynthesis

R. Riclea, J. S. Dickschat* 12167 – 12170

Identification of Intermediates in the Biosynthesis of PR Toxin by *Penicillium roqueforti*



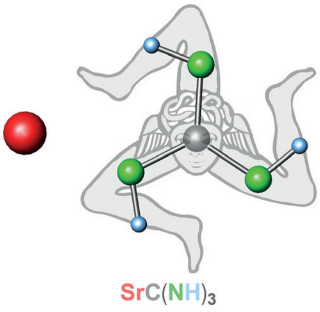
The sesquiterpenoid 7-*epi*-neopetasone was synthesized and shown to be identical to a previously tentatively identified headspace constituent of the fungus *Penicillium roqueforti*. Feeding with (11,12,13-$^{13}C_3$)-7-*epi*-neopetasone revealed that the compound is a pathway intermediate for PR toxin, while feeding with ^{13}C-labeled isotopomers of mevalonolactone gave additional insight into a double-bond isomerization/oxidation sequence along the pathway.

Strontium Guanidinate

R. Missong, J. George, A. Houben,
M. Hoelzel,
R. Dronskowski* ________ 12171 – 12175

Synthesis, Structure, and Properties of SrC(NH)$_3$, a Nitrogen-Based Carbonate Analogue with the Trinacria Motif

Keeping an ion guanidinate: Strontium guanidinate, SrC(NH)$_3$, the first compound with a doubly deprotonated guanidine unit, was synthesized, and its properties investigated using X-ray and neutron powder diffraction as well as IR spectroscopy. Combined with quantum-theoretical calculations, this allows a qualitative and quantitative discussion of some first insights into the structure of the anionic guanidine unit.



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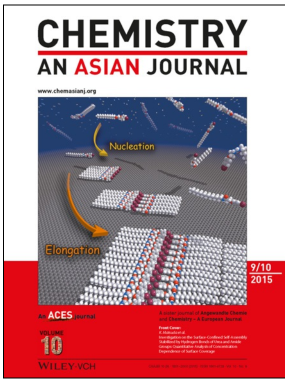

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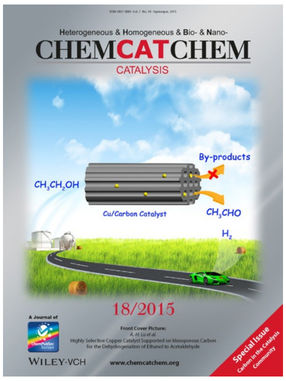

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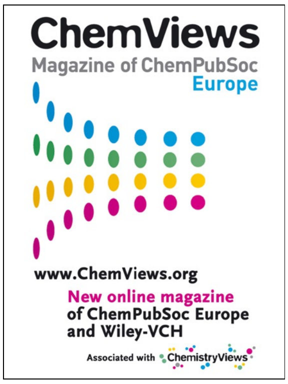

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