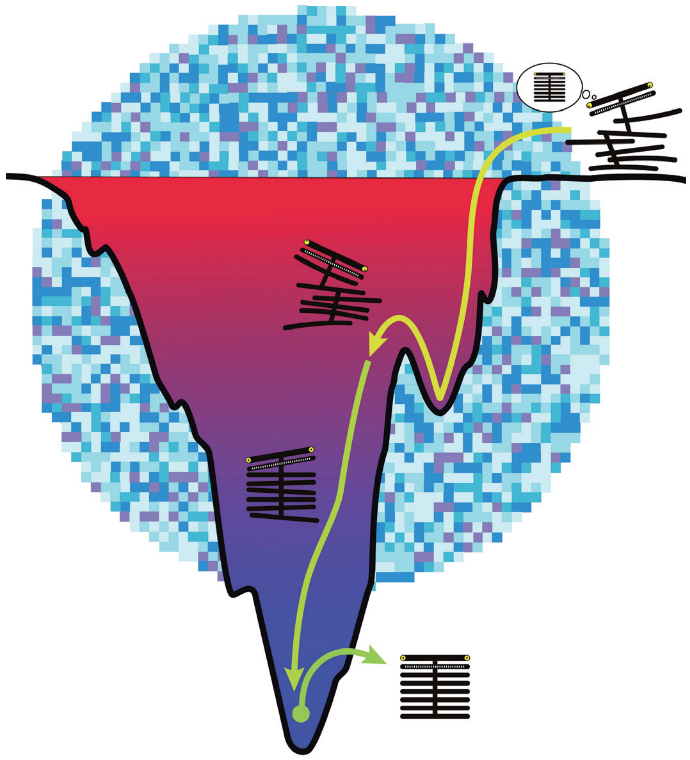
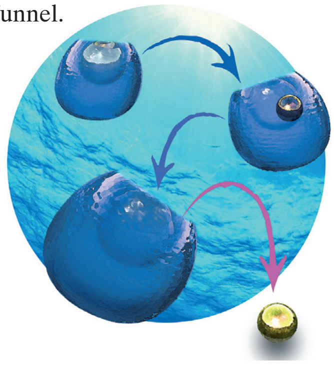
Complex DNA structures ...

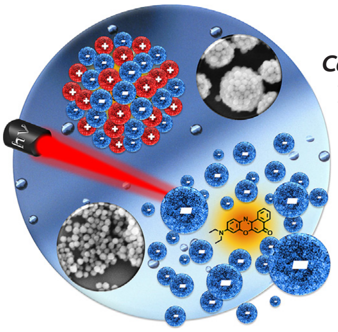


... can be folded in a deep-eutectic solvent composed of glycerol and choline chloride ("glycholine"). In their Communication on page 6765 ff., N. Hud et al. describe how the folding of DNA in glycholine alleviates kinetic traps that are typically encountered in aqueous buffer, allowing for isothermal folding at room temperature. The illustration represents the folding of the tall-rectangle DNA origami as it slides down a conceptualized folding funnel.

Host–Guest Systems

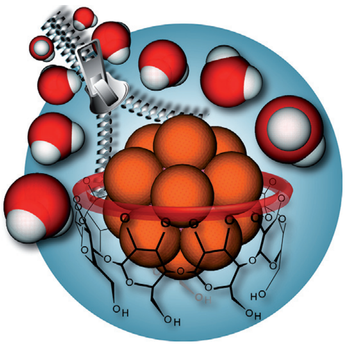
The fabrication of dynamic host–guest inclusion complexes of metal nanoparticles inside oxide nanocups via reactive double Janus nanoparticles is described by P. Fischer, T.-C. Lee, and M. Alarcón-Correa in their Communication on page 6730 ff.





Colloidosomes

In their Communication on page 6804 ff., N. Khashab et al. report colloidosomes that are composed of oppositely charged organosilica nanoparticles and are used as hollow carriers for large cargos.



Host–Guest Complexes

A supramolecular anchor motif that consists of dodecaborate dianions ($B_{12}X_{12}^{2-}$, X=H, Cl, Br, I) as purely inorganic guests and γ-cyclodextrin as a macrocyclic host are presented by K. Rissanen, D. Gabel, W. M. Nau et al. in their Communication on page 6852 ff.

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Service

Author Profile

"I lose track of time when I listen to music (especially live). My favorite saying is 'Starting is easy, but perseverance is an art' …"
This and more about Knut Rurack can be found on page 6678.

News

R. Herges

H. Kessler

R. B. Silverman

U. T. Bornscheuer

P. T. Anastas

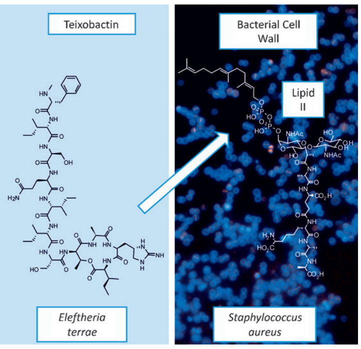
Books

Highlights

Antibiotics

F. von Nussbaum,*
R. D. Süssmuth* ______ **6684 – 6686**

Multiple Attack on Bacteria by the New Antibiotic Teixobactin



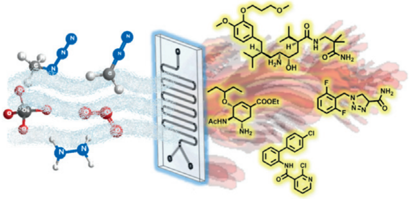
News from the antibiotics pipeline: The discovery of a depsipeptide-type lipid II binder, isolated from a previously unknown bacterium, raises hopes in the battle against multiresistant staphylococci.

Reviews

Flow Chemistry

B. Gutmann, D. Cantillo,
C. O. Kappe* ______ **6688 – 6728**

Continuous-Flow Technology—A Tool for the Safe Manufacturing of Active Pharmaceutical Ingredients



Go with the flow: Continuous-flow processing is becoming increasingly important in synthetic organic chemistry. The high heat and mass transfer, very fast mixing, and small reactor volumes allow reactions to be run safely under very harsh conditions also when hazardous intermediates are involved, as shown here with selected examples.

Communications

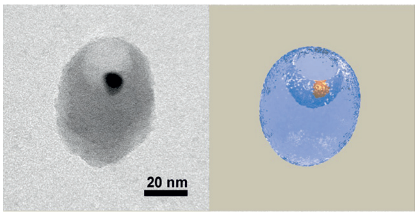
Host–Guest Systems

M. Alarcón-Correa, T.-C. Lee,*
P. Fischer* ______ **6730 – 6734**

Dynamic Inclusion Complexes of Metal Nanoparticles Inside Nanocups

Frontispiece

Nanocup with nanoparticle: Dynamic 1:1 host–guest inclusion complexes of metal nanoparticles inside oxide nanocups are fabricated by means of a reactive double Janus nanoparticle intermediate in a kinetically controlled process. Release of the nanoparticle guests from the nanocups can be efficiently triggered by an external stimulus.



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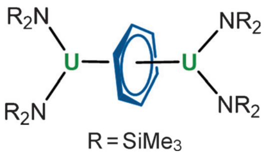


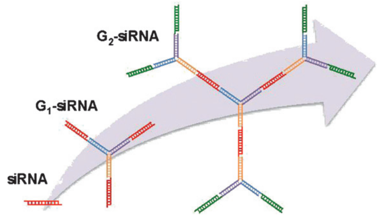
Under pressure: Computational analyses and high-pressure X-ray crystallography are combined to study the U^{III} compound $[UN''_2]_2(\mu\text{-}\eta^6{:}\eta^6\text{-}C_6H_6)$ $(N''=N(SiMe_3)_2)$. With increasing pressure, the U–U distances decrease and close contacts between the U and ligand C–H groups become significantly shorter. Calculations suggest that the greater U···H interaction at high pressure can be classified as agostic.

Agostic Interactions

P. L. Arnold,* A. Prescimone, J. H. Farnaby, S. M. Mansell, S. Parsons,* N. Kaltsoyannis* ______ **6735 – 6739**

Characterizing Pressure-Induced Uranium C–H Agostic Bonds

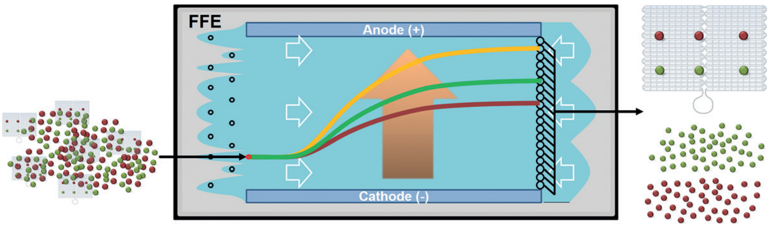
Self-assembly of siRNA molecules provides precisely controlled generation of dendrimeric siRNA nanostructures. The second-generation dendrimers can be complexed with a low-molecular-weight cationic polymer (PBAE) to generate stable nanostructures (ca. 160 nm diameter) by electrostatic interactions. Condensation and gene silencing efficiencies increase with increased generations of siRNA dendrimers owing to high charge density and structural flexibility.



Dendrimeric siRNA

C. A. Hong, A. A. Eltoukhy, H. Lee, R. Langer, D. G. Anderson,* Y. S. Nam* ______ **6740 – 6744**

Dendrimeric siRNA for Efficient Gene Silencing



A functional art form: The efficient separation of enzyme-decorated DNA origami structures from unbound proteins by free-flow electrophoresis (FFE; see picture) enabled a differentiated assessment of the activity of origami-tethered and non-DNA-bound enzymes. It was found that enzyme arranged on origami structures were more active than the free enzymes.

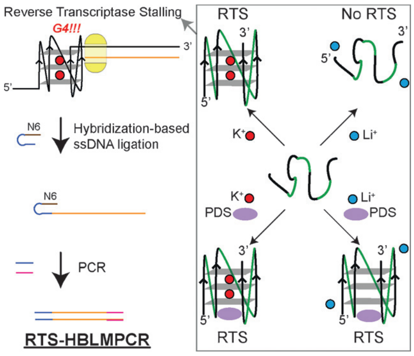
DNA Nanostructures

C. Timm, C. M. Niemeyer* _ **6745 – 6750**

Assembly and Purification of Enzyme-Functionalized DNA Origami Structures

---

Hunting G4s: This study describes a new approach for detecting and mapping RNA G-quadruplexes (G4) in low-abundance cellular transcripts by coupling reverse transcriptase stalling (RTS) and an amplification strategy (HBLMPCR). Rational control of RNA G4-mediated RTS can be achieved by exploiting RNA G4–cation and RNA G4–ligand interactions, as well as using a selective reverse transcriptase for monitoring purposes.



RNA Structures

C. K. Kwok, S. Balasubramanian* ______ **6751 – 6754**

Targeted Detection of G-Quadruplexes in Cellular RNAs

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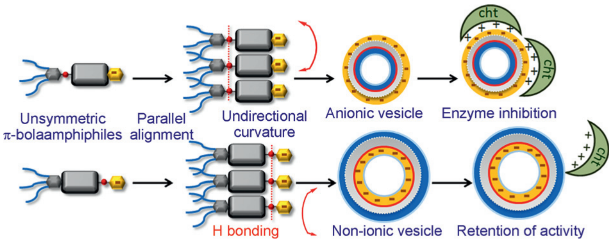
Bolaamphiphiles

A. Sikder, A. Das, S. Ghosh* **6755 – 6760**

Hydrogen-Bond-Regulated Distinct Functional-Group Display at the Inner and Outer Wall of Vesicles



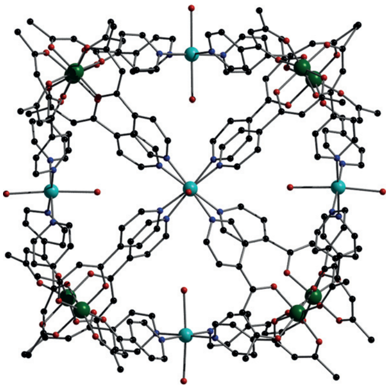
The unidirectional assembly of two bola-shaped unsymmetric π-amphiphiles that feature a naphthalene–diimide chromophore connected to non-ionic and anionic head groups on opposite arms is enabled by the formation of hydrogen bonds. These interactions fully compensate for electrostatic repulsion and induce the curvature of the bolaamphiphiles, which leads to monolayer vesicles with different surface functionalities and enzyme inhibition abilities.

Heterometallic Cages

S. Sanz, H. M. O'Connor, E. M. Pineda, K. S. Pedersen, G. S. Nichol, O. Mønsted, H. Weihe, S. Piligkos,* E. J. L. McInnes,* P. J. Lusby,* E. K. Brechin* **6761 – 6764**

$[Cr^{III}_8M^{II}_6]^{12+}$ Coordination Cubes (M^{II} = Cu, Co)

All about cubes: $[Cr^{III}_8M^{II}_6]^{12+}$ (M = Cu, Co) cubes were constructed from a simple $[Cr^{III}L_3]$ metalloligand and a "naked" M^{II} salt. The flexibility in the design proffers the potential to tune the physical properties, as all the constituent parts of the cage can be changed without structural alteration. Statistical and EPR spectroscopy were used to interpret the magnetic behavior.

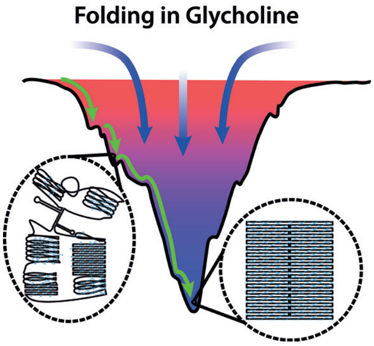


DNA Nanotechnology

I. Gállego, M. A. Grover, N. V. Hud* **6765 – 6769**

Folding and Imaging of DNA Nanostructures in Anhydrous and Hydrated Deep-Eutectic Solvents

Front Cover

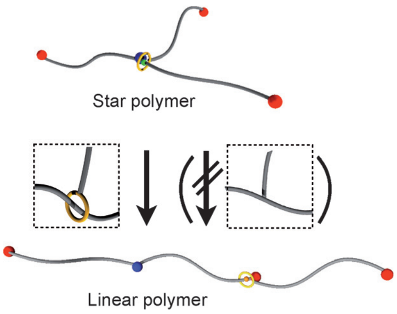


Who needs water? DNA structures, such as a two-dimensional DNA origami, can be folded in an anhydrous deep-eutectic solvent composed of glycerol and choline chloride ("glycholine"). In hydrated glycholine, folding is accelerated, and more complex nanostructures can be isothermally folded, demonstrating that DNA self-assembly kinetics can be tuned by changing solvent viscosity.

Topology Transformation

D. Aoki, S. Uchida, T. Takata* **6770 – 6774**

Star/Linear Polymer Topology Transformation Facilitated by Mechanical Linking of Polymer Chains



From star to linear: A rotaxane-linked arm-containing star polymer, formed by the attractive interaction of ammonium and crown ether groups, was transformed to a linear polymer by the removal of the attractive interaction by the *N*-acetylation of the ammonium moiety. The polymer component linked to the wheel component of the rotaxane linkage moves to the urethane terminal, thereby changing its shape.

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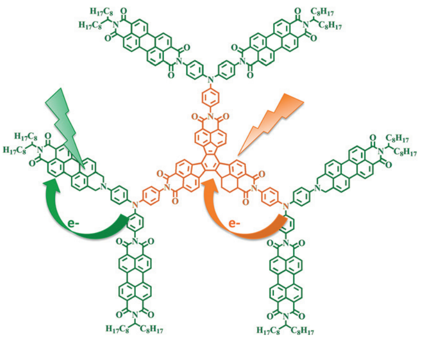

Quick as a flash: New polyimide dendrimers exhibiting rich photophysical properties have been synthesized. For example, in one of the new species, two different charge-separated states can be obtained on the femtosecond timescale. Such charge-separated states independently decay on the picosecond timescale.

Donor–Acceptor Systems

F. M. Toma, F. Puntoriero, T. V. Pho, M. La Rosa, Y.-S. Jun, B. J. Tremolet de Villers, J. Pavlovich, G. D. Stucky, S. Campagna,* F. Wudl* ______ **6775 – 6779**

Polyimide Dendrimers Containing Multiple Electron Donor–Acceptor Units and Their Unique Photophysical Properties

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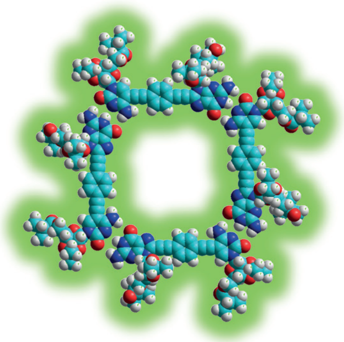
Fine design of a dinucleoside monomer leads to hydrogen-bonded macrocyclic tetramer assemblies with high effective molarities and remarkable thermodynamic and kinetic stability. The behavior of these assemblies in various solvents is discussed.



Supramolecular Chemistry

C. Montoro-García, J. Camacho-García, A. M. López-Pérez, N. Bilbao, S. Romero-Pérez, M. J. Mayoral, D. González-Rodríguez* ___ **6780 – 6784**

High-Fidelity Noncovalent Synthesis of Hydrogen-Bonded Macrocyclic Assemblies

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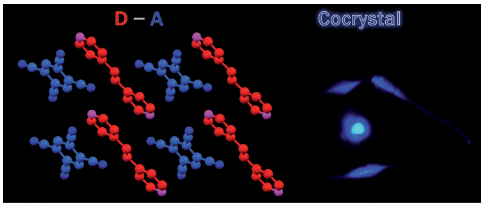

Crystal clear: A new crystal of a donor–acceptor (D–A) complex was prepared and it has a two-dimensional morphology. The charge-transfer interactions were fully investigated. This organic cocrystal has unique two-dimensional optical waveguide properties, and has potential applications in next-generation optoelectronic communications.

Donor–Acceptor Systems

W. G. Zhu, R. H. Zheng, X. L. Fu, H. B. Fu, Q. Shi, Y. G. Zhen, H. L. Dong, W. P. Hu* ______ **6785 – 6789**

Revealing the Charge-Transfer Interactions in Self-Assembled Organic Cocrystals: Two-Dimensional Photonic Applications

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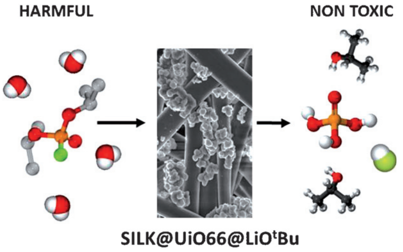

The silk of human kindness: Insertion of lithium alkoxides in zirconium metal–organic frameworks (MOF) which are then deposited on silk fibers gives rise to protective fabrics capable of self-detoxifying chemical-warfare agents. The fabrics combine the air-permeation properties of the textiles with the highly active phosphotriesterase catalytic activity of the MOF for the hydrolysis of P—F, P—O, and C—Cl bonds.

MOF Catalysts

E. López-Maya, C. Montoro, L. M. Rodríguez-Albelo, S. D. Aznar Cervantes, A. A. Lozano-Pérez, J. L. Cenís, E. Barea,* J. A. R. Navarro* ______ **6790 – 6794**

Textile/Metal–Organic-Framework Composites as Self-Detoxifying Filters for Chemical-Warfare Agents

Inside Cover

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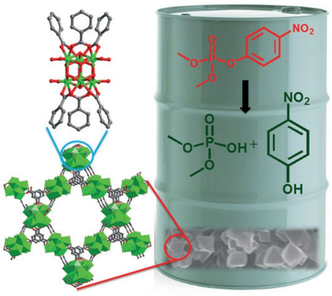
MOF Catalysts

S. Y. Moon, Y. Liu, J. T. Hupp,*
O. K. Farha* ______ 6795 – 6799

Instantaneous Hydrolysis of Nerve-Agent Simulants with a Six-Connected Zirconium-Based Metal–Organic Framework

Detox, faster than fast: Chemical-warfare agents, including nerve agents, are a threat to humans. A six-connected zirconium metal–organic framework (MOF) can hydrolyze a nerve-agent simulant within 30 s which is faster than any other catalyst reported. It is a promising material for protective equipment as well as the elimination of large stores of nerve agents.

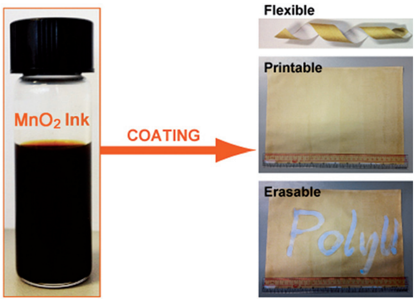


Energy-Storage Devices

J. Qian, H. Jin, B. Chen, M. Lin, W. Lu,
W. M. Tang, W. Xiong, L. W. H. Chan,
S. P. Lau, J. Yuan* ______ 6800 – 6803

Aqueous Manganese Dioxide Ink for Paper-Based Capacitive Energy Storage Devices

Printing the future: A simple chemical reduction method has been used to synthesize aqueous MnO_2 ink that exhibits long-term stability and can form continuous thin films on various substrates without the need for any binder. The as-prepared MnO_2 ink can also be coated onto conductive A4 paper to form capacitive energy storage devices.



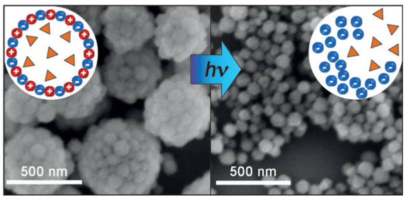
Colloidosomes

S. Li, B. A. Moosa, J. G. Croissant,
N. M. Khashab* ______ 6804 – 6808

Electrostatic Assembly/Disassembly of Nanoscaled Colloidosomes for Light-Triggered Cargo Release

Inside Back Cover

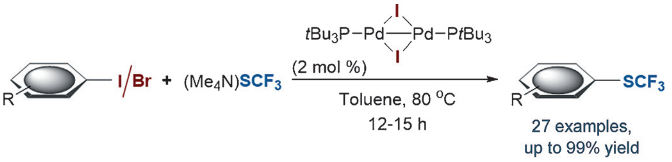
Nanocapsules for large cargos: Nanoscaled colloidosomes were designed by electrostatic assembly of organosilica nanoparticles (NPs) with oppositely charged surfaces, arising from different contents of a bridged nitrophenylene–alkoxysilane derivative in the silica. The positive charge was reversed by light irradiation because of the photoreaction of nitrophenylene moieties.



Cross-Coupling

G. Yin, I. Kalvet,
F. Schoenebeck* ______ 6809 – 6813

Trifluoromethylthiolation of Aryl Iodides and Bromides Enabled by a Bench-Stable and Easy-To-Recover Dinuclear Palladium(I) Catalyst



Pd double team: The cross-coupling enabled by an air-, moisture-, and thermally stable dinuclear Pd^I complex was explored. Highly efficient $C-SCF_3$ coupling of a range of aryl iodides and bromides was achieved and the catalyst was recovered by simple column chromatography, thus highlighting its robustness and the possibility for catalyst recycling. Kinetic and computational data support the feasibility of dinuclear Pd^I catalysis.

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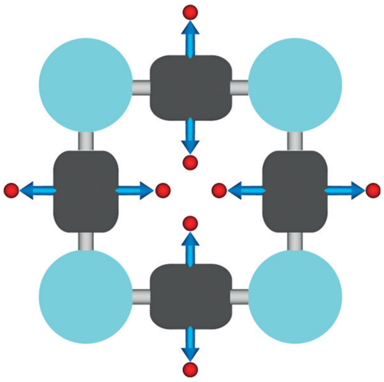
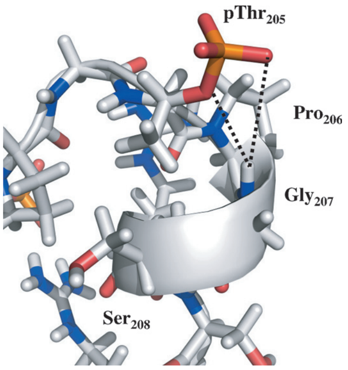


Efficient energy storage: A facile strategy for converting a conventional covalent organic framework (COF) into outstanding energy storage materials is described. The channel walls are provided with organic radicals in a controlled manner to achieve immobilized openly accessible polyradicals, leading to the development of a new, facile, and general way to design COFs for high-performance electrochemical energy storage.

Radical Frameworks

F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu,
H. Liu, C. Gu, R. Fu,
D. Jiang* ______________ **6814 – 6818**

Radical Covalent Organic Frameworks: A General Strategy to Immobilize Open-Accessible Polyradicals for High-Performance Capacitive Energy Storage



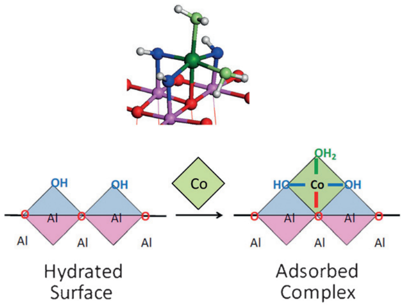
The AT8 epitope of the phosphorylated tau protein was mapped by NMR spectroscopy, and its defining structural features were derived by a combination of NMR analyses and molecular dynamics. A particular turn conformation is stabilized by a hydrogen bond of the phosphorylated Thr_{205} residue ($pThr_{205}$) to the amide proton of Gly_{207}.

Epitope Mapping

N. S. Gandhi, I. Landrieu, C. Byrne,
P. Kukic, L. Amniai, J.-F. Cantrelle,
J.-M. Wieruszeski, R. L. Mancera,
Y. Jacquot, G. Lippens* ______ **6819 – 6823**

A Phosphorylation-Induced Turn Defines the Alzheimer's Disease AT8 Antibody Epitope on the Tau Protein

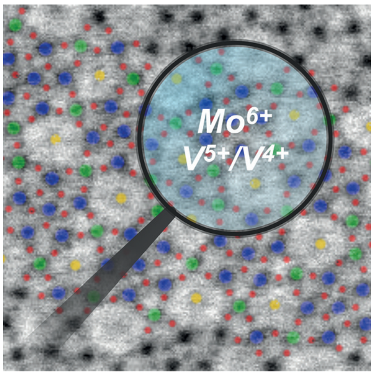
The interaction of cobalt-based catalyst precursors with γ-alumina and amorphous silica–alumina surfaces was investigated by means of DFT calculations. A structural recognition between the surface and the precursor could be evidenced. A model for the growth of the experimentally observed β-$Co(OH)_2$ on the surface could be proposed from those calculations.



Interfacial Chemistry

K. Larmier, C. Chizallet,*
P. Raybaud ______________ **6824 – 6827**

Tuning the Metal–Support Interaction by Structural Recognition of Cobalt-Based Catalyst Precursors



ABF-STEM (annular bright field scanning transmission electron microscopy) was used to study a beam-sensitive Mo/V mixed oxide. The recorded micrographs show the oxygen sublattice and directly reveal the local distortion in the metal–oxygen octahedra. From the observed distortion, conclusions on the oxidation state of each metal site can be drawn just by looking at the atomic arrangement.

Electron Microscopy

T. Lunkenbein, F. Girgsdies,
A. Wernbacher, J. Noack, G. Auffermann,
A. Yasuhara, A. Klein-Hoffmann, W. Ueda,
M. Eichelbaum, A. Trunschke, R. Schlögl,
M. G. Willinger* ___________ **6828 – 6831**

Direct Imaging of Octahedral Distortion in a Complex Molybdenum Vanadium Mixed Oxide

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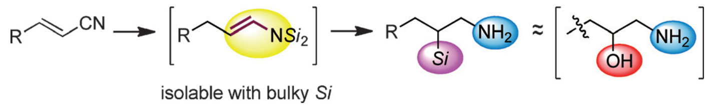
Hydrosilylation

N. Gandhamsetty, J. Park, J. Jeong,
S.-W. Park, S. Park,
S. Chang* ______ **6832 – 6836**

Chemoselective Silylative Reduction of Conjugated Nitriles under Metal-Free Catalytic Conditions: β-Silyl Amines and Enamines

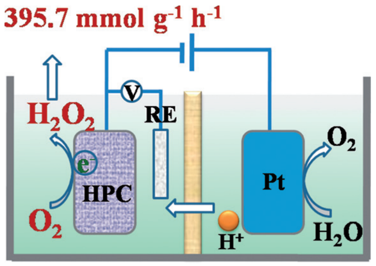


Triple whammy: The $B(C_6F_5)_3$-catalyzed silylative reduction of conjugated nitriles has been developed to afford synthetically valuable β-silyl amines. Based on the mechanistic understanding, a preparative route to enamines was also established using bulky silanes. The reaction is chemoselective, has a broad scope, and proceeds under mild reaction conditions. The mechanism of the triple hydrosilylation is discussed.

Electrochemistry

Y. M. Liu, X. Quan,* X. F. Fan, H. Wang,
S. Chen ______ **6837 – 6841**

High-Yield Electrosynthesis of Hydrogen Peroxide from Oxygen Reduction by Hierarchically Porous Carbon

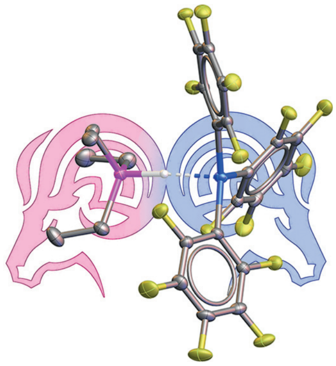


The electroreduction of O_2 is achieved with hierarchically porous carbon (HPC) to give H_2O_2. It exhibits good selectivity, a high production rate, and current efficiency for the electrosynthesis of H_2O_2 at a wide range of pH values. The correlation between H_2O_2 production rate and sp^3-C atoms and defects was explored. This provides an effective method for tuning the activity of carbon materials for the selective electrosynthesis of H_2O_2. RE = reference electrode.

Lewis Pairs

J. Chen, E. Y.-X. Chen* ______ **6842 – 6846**

Elusive Silane–Alane Complex [Si–H⋯Al]: Isolation, Characterization, and Multifaceted Frustrated Lewis Pair Type Catalysis



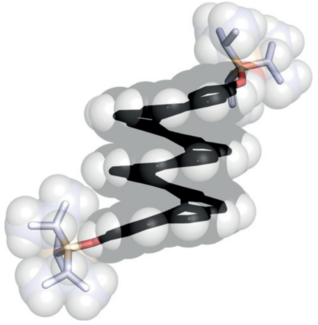
Al does it all: The elusive silane–alane complex [Si–H⋯Al] was isolated and structurally characterized by spectroscopic and X-ray diffraction methods. The Janus-like nature of this adduct, coupled with strong silane activation, effects multifaceted frustrated-Lewis-pair-type catalysis. Its use in four different reactions is described.

VIP

Helical Structures

K. Mori, T. Murase,*
M. Fujita* ______ **6847 – 6851**

One-Step Synthesis of [16]Helicene



An aromatic spiral layer: A [16]helicene core was prepared in a single step by sextuple photocyclization from a single-strand arylene–vinylene precursor containing four phenylene and three naphthylene units linked by six vinylene spacers. X-ray crystallographic analysis revealed the triple-layered structure. A new guideline for the design of precursor olefins resulted in the longest helicene synthesized to date.

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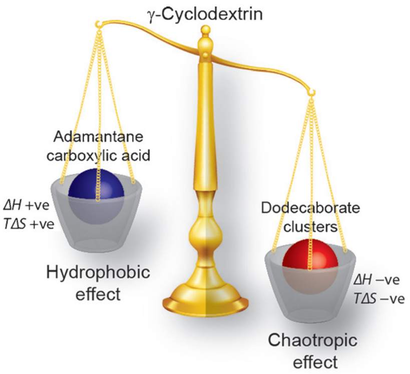
A supramolecular anchor motif has been found, which consists of dodecaborate dianions ($B_{12}X_{12}^{2-}$; X = H, Cl, Br, I) as purely inorganic guests and γ-cyclodextrin as the macrocyclic host. The high micromolar affinity of this hybrid organic–inorganic host–guest complex is traced back to the chaotropic (water structure-breaking) nature of the globular clusters, their shape complementarity, and their high polarizabilities.

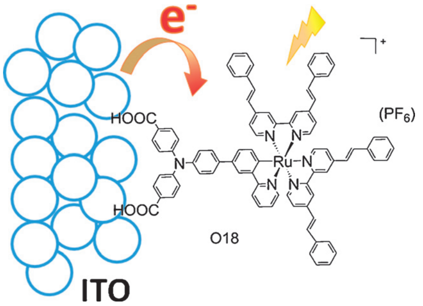


Host–Guest Complexes

K. I. Assaf, M. S. Ural, F. Pan, T. Georgiev, S. Simova, K. Rissanen,* D. Gabel,* W. M. Nau* ______ **6852 – 6856**

Water Structure Recovery in Chaotropic Anion Recognition: High-Affinity Binding of Dodecaborate Clusters to γ-Cyclodextrin

Back Cover



ITO as a photocathode: The scarcity of optimal p-type semiconductors has hindered the development of efficient photocathodes for dye-sensitized solar cells and photoelectrosynthesis cells. Mesoporous indium tin oxide (ITO), an n-type degenerated semiconductor, can generate remarkably high cathodic currents after sensitization by energy-aligned cyclometalated Ru^{II} complexes. Studies into the mechanism indicate hole injection from the excited dye.

Energy Conversion

Z. Huang, M. He, M. Yu, K. Click, D. Beauchamp, Y. Wu* ______ **6857 – 6861**

Dye-Controlled Interfacial Electron Transfer for High-Current Indium Tin Oxide Photocathodes

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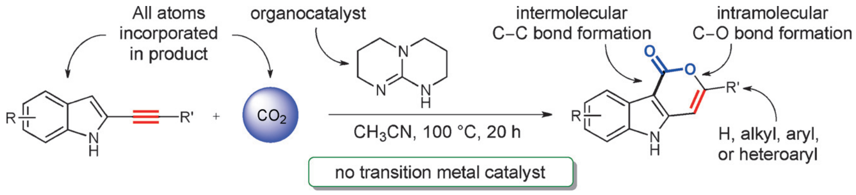
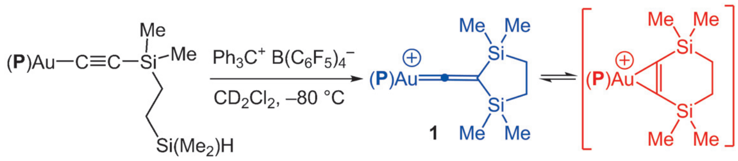


Caught in a trap: The first trapping of CO_2 through organocatalyzed C–C and C–O bond formation is reported. By using alkynyl indoles, this method generates novel indole lactone derivatives by using as little as 5 mol% of the simple organic base 1,5,7-triazabicyclo-[4.4.0]dec-5-ene as an organocatalyst. The transformation shows excellent atom economy and a broad substrate scope, including aromatic, heteroaromatic, and aliphatic 2-alkynyl indoles.

Heterocycles

Z. Xin, C. Lescot, S. D. Friis, K. Daasbjerg, T. Skrydstrup* ______ **6862 – 6866**

Organocatalyzed CO_2 Trapping Using Alkynyl Indoles



Good as gold: Cationic gold (β,β-disilyl)-vinylidene complex **1** was generated by addition of a pendant silylium ion to the C≡C bond of a gold acetylide complex (see scheme, **P** = $PtBu_2$(*o*-biphenyl)). The vinylidene C1 and C2 atoms of **1** undergo facile interconversion, presumably via a π-disilacyclohexyne intermediate. ^{29}Si NMR analysis of **1** indicates delocalization of positive charge onto both the β-silyl groups and the (**P**)Au fragment.

Gold Complexes

R. J. Harris, R. A. Widenhoefer* ______ **6867 – 6869**

Synthesis and Characterization of a Gold Vinylidene Complex Lacking π-Conjugated Heteroatoms

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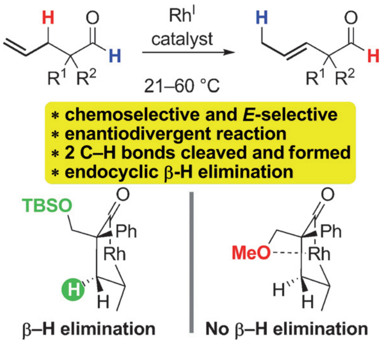
C–H Activation

S. Y. Y. Yip, C. Aïssa* ______ 6870 – 6873

Isomerization of Olefins Triggered by Rhodium-Catalyzed C–H Bond Activation: Control of Endocyclic β-Hydrogen Elimination

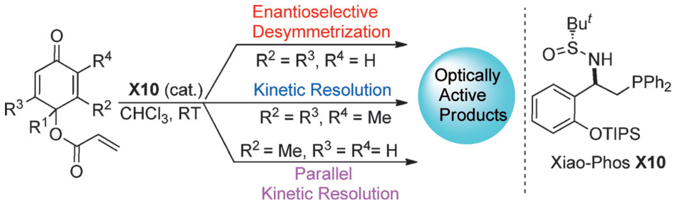


Control of endocyclic β-H elimination of a pivotal five-membered metallacycle enables the rhodium-catalyzed isomerization of 4-pentenals into 3-pentenals without decarbonylation and leads to *trans* olefins with exquisite selectivity. Other sensitive olefins, even if prone to isomerization, remain intact. Endocyclic β-H elimination can also be prevented, in which case an enantiodivergent reaction on the racemic substrate was observed.

Organocatalysis

X. Su, W. Zhou, Y. Li, J. Zhang* ______ 6874 – 6877

Design, Synthesis, and Application of a Chiral Sulfinamide Phosphine Catalyst for the Enantioselective Intramolecular Rauhut–Currier Reaction



Xiao-Phos: A new class of chiral sulfinamide phosphine catalyst was developed. These Xiao-Phos catalysts can be prepared from inexpensive commercially available starting materials and show good performance in the enantioselective intramolecular Rauhut–Currier reaction under mild conditions. Moreover, kinetic resolution was also observed with the use of two different substituted racemic precursors.

DOI: 10.1002/anie.201582314

Flashback: 50 Years Ago . . .

Ivar Ugi is today best known for the multicomponent reaction that bears his name. In a Review, he summarized various routes for the synthesis of isonitriles (now known as isocyanides according to the IUPAC rules); the most efficient method for the preparation of large quantities of isonitriles was the reaction of phosgene with tertiary amines. In another Review, Hans Bock discussed the synthesis and spectroscopic characterization of azo compounds in order to establish the relationship between the color and constitution of the derivatives. It was found that varying the substituents caused shifts in the $n\rightarrow\pi^*$ transition. Interestingly, this was one of the first articles in *Angewandte Chemie* to contain color figures.

Hellmut Bredereck et al. published two Communications on the subject of acetals. The first report addressed the reactions of dimethylformamide acetals with isothiocyanates. Depending on the substituents, either 1,3-disubstituted 2,4-dithioxoparabanic O,N-acetals or α-substituted imino-α-(ethylthio)dimethylacetamides were formed. In the second Communication, the reactions of amide acetals with hydrocyanic acid were reported; O,N-acetals of α-ketonitriles were produced in good yields. Bredereck was President of the Gesellschaft Deutscher Chemiker (GDCh; German Chemical Society) in 1968/1969.

Christian Reichardt reported on the synthesis and spectroscopic properties of γ-phenylazopentamethinecyanine dyes. Introduction of the phenylazo group led to a hypsochromic shift of the long-wavelength bands. Reichardt is the author of *Solvent Effects in Organic Chemistry*, which was first published by Verlag Chemie in 1969, and the fourth edition of this truly classic text (published by Wiley-VCH and with Thomas Welton as co-author) appeared in 2011.

Read more in Issue 6/1965.

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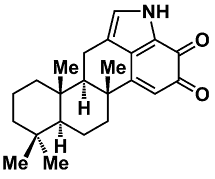
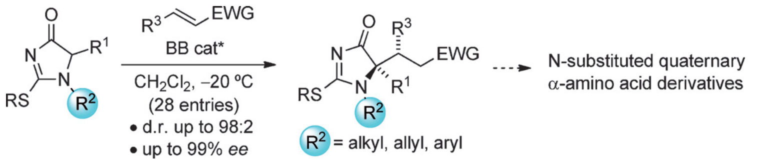
The first and enantioselective total synthesis of mycoleptodiscin A (see picture), a structurally unusual indolosesquiterpenoid, is accomplished by using iridium-catalyzed polyene cyclization and copper-mediated C–N bond forming reactions as key steps.



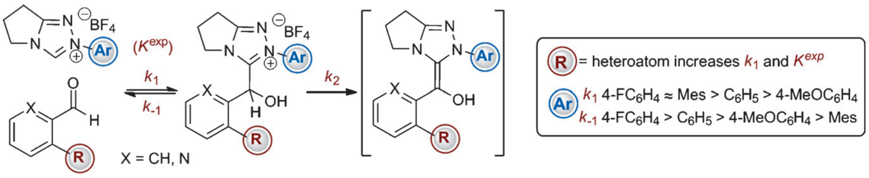
mycoleptodiscin A

Natural Product Synthesis



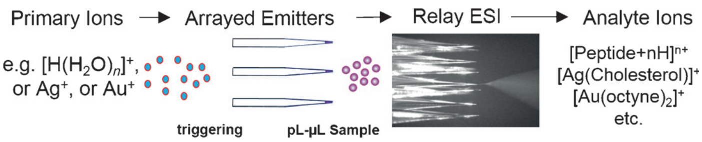
A BB method: 1*H*-imidazol-4(5*H*)-ones serve as effective and easily available α-amino acid surrogates for the catalytic and highly diastereo- and enantioselective direct construction of N-substituted quaternary α-amino acid derivatives. The reaction is catalyzed by a Brønsted base (BB) and proceeds with different Michael acceptors. EWG = electron-withdrawing group.

Asymmetric Catalysis



It takes 2-: Measurement of rate and equilibrium constants for the reaction between *N*-aryl triazolium NHC precatalysts and substituted benzaldehydes under catalytic and stoichiometric conditions demonstrate the remarkable kinetic and thermodynamic effect of the benzaldehyde 2-substituent in these reactions, potentially providing insight into the chemoselectivity of cross-benzoin reactions.

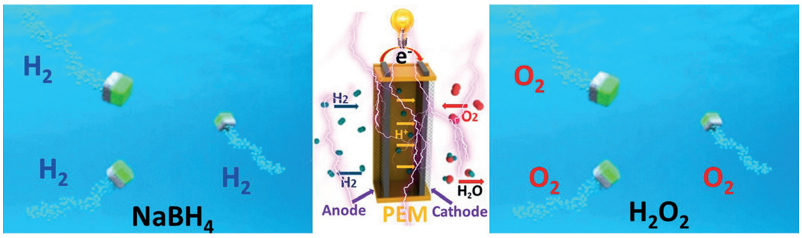
Reaction Mechanisms



Relay electrospray ionization (rESI) from a capillary containing a sample solution (or from an array of such capillaries) is triggered by charge deposition onto the capillary. With no requirement for physical contact, high-throughput sample screening is enabled by rapidly addressing individual secondary (sample) capillaries. Subpicoliter sample volumes can be loaded and sprayed.

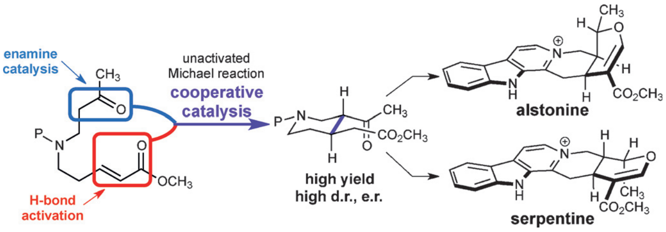
Mass Spectrometry

Hydrogen Production



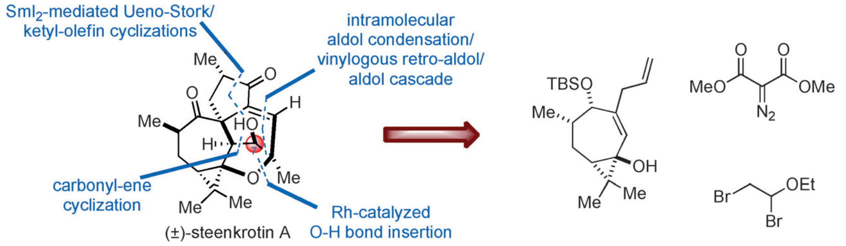
Fuel metal jacket: Micromotors give enhanced energy generation by the movement of Pt-black/Ti Janus microparticles in a liquid-phase chemical fuel. The autonomous motion of these micromotors leads to enhanced mixing and transport of $NaBH_4$ fuel compared to static microparticles or films, and hence to a substantially faster hydrogen-generation rate. The practical utility is illustrated by powering a hydrogen–oxygen fuel cell car. PEM = proton-exchange membrane.

Cooperative Catalysis



The enantioselective total syntheses of the natural products alstonine and serpentine are presented. They proceed through a sequence with a cooperative hydrogen bonding/enamine-catalyzed Michael addition as the key step.

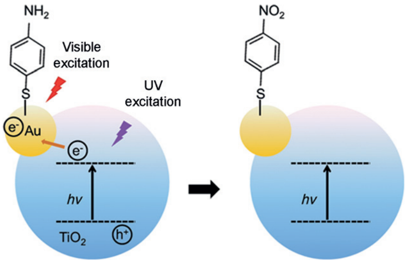
Natural Products



Work of steen: A concise and diastereoselective total synthesis of the diterpenoid (±)-steenkrotin A is reported for the first time. The key features of the strategy are based on a rhodium-catalyzed O–H bond insertion, an intramolecular carbonyl-ene reaction, sequential SmI_2-mediated Ueno–Stork and ketyl–olefin cyclizations, and a cascade intramolecular aldol condensation/vinylogous retro-aldol/aldol process.

Photocatalysis

Controlling selectivity: The selectivity of the surface plasmon resonance (SPR) mediated oxidation of *p*-aminothiophenol was controlled by the choice of catalysts (Au or TiO_2–Au nanoparticles; NPs) and by the modulation of the charge transfer from UV-excited TiO_2 to Au. While *p*,*p*-dimercaptobenzene was obtained using Au NPs as catalyst, the use of TiO_2–Au NPs under both UV illumination and SPR excitation led to the formation of *p*-nitrophenol.



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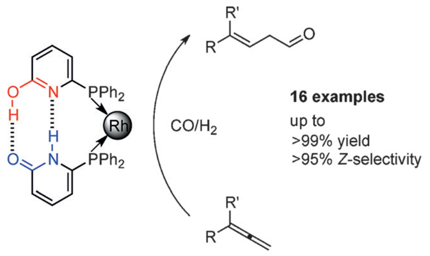
Synthetic Methods

A. Köpfer, B. Breit* ———— 6913 – 6917

Rhodium-Catalyzed Hydroformylation of 1,1-Disubstituted Allenes Employing the Self-Assembling 6-DPPon System

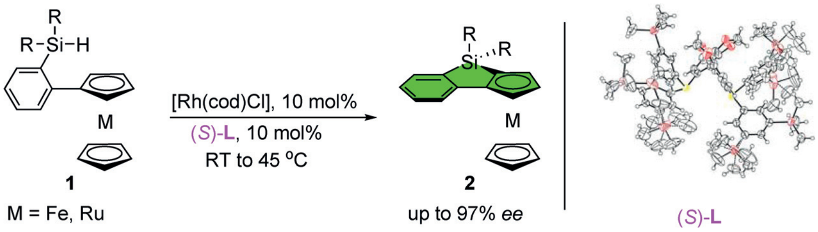


β,γ-Unsaturated aldehydes are obtained by a rhodium-catalyzed hydroformylation of 1,1-disubstituted allenes. For unsymmetrically 1,1-disubstituted allenes the *Z*-configured product is formed in up to about 95 % selectivity. This is the first time that these building blocks are accessible by hydroformylation of allenes. The utility of this methodology is demonstrated by further transformations of one of the obtained products.

C–H Activation

Q.-W. Zhang, K. An, L.-C. Liu, Y. Yue, W. He* ———— 6918 – 6921

Rhodium-Catalyzed Enantioselective Intramolecular C–H Silylation for the Syntheses of Planar-Chiral Metallocene Siloles



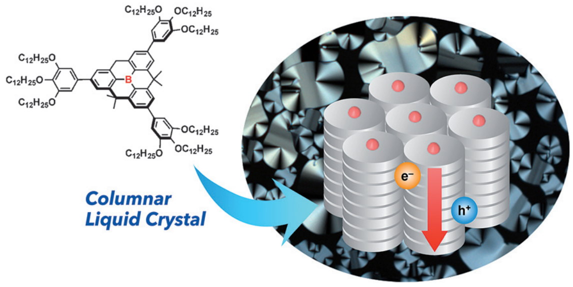
New on the (metallo)cene: The title reaction of cyclopentadiene (Cp) rings in Fe and Ru metallocenes is reported. Fine-tuning the steric hindrance of diphosphine ligands led to the identification of (*S*)-TMS-Segphos [(*S*)-**L**], which enabled efficient, enantioselective C–H silylation of the Cp rings in metallocenes under mild reaction conditions. cod = 1,5-cyclooctadiene, TMS = trimethylsilyl.

Liquid Crystals

VIP

T. Kushida, A. Shuto, M. Yoshio,* T. Kato, S. Yamaguchi* ———— 6922 – 6925

A Planarized Triphenylborane Mesogen: Discotic Liquid Crystals with Ambipolar Charge-Carrier Transport Properties

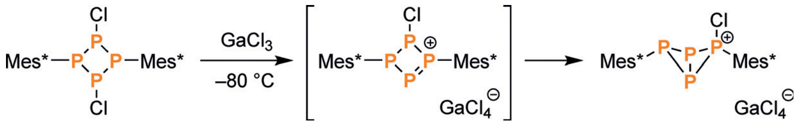


B planar, B aligned: A planarized triphenylborane, bearing three 3,4,5-tridodecyloxyphenyl groups, forms a hexagonal columnar liquid-crystalline phase at ambient temperature. It has a columnar π-stacked structure and ambipolar carrier-transport properties with hole- and electron-mobility values of $3\times10^{-5}\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$ and approximately $10^{-3}\,\text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1}$, respectively.

Phosphorus Ring Systems

J. Bresien, K. Faust, A. Schulz,* A. Villinger ———— 6926 – 6930

Low-Temperature Isolation of the Bicyclic Phosphinophosphonium Salt $[\text{Mes*}_2\text{P}_4\text{Cl}][\text{GaCl}_4]$



Bicycle ride: The first bicyclic triphosphinophosphonium cation was synthesized from dichlorocyclotetraphosphane $[\text{ClP}(\mu\text{-PMes*})]_2$ and Lewis acid GaCl_3 at low temperatures (see scheme). The reaction proceeds via a highly reactive tetraphosphenium intermediate, which was trapped by reaction with dimethylbutadiene (dmb).

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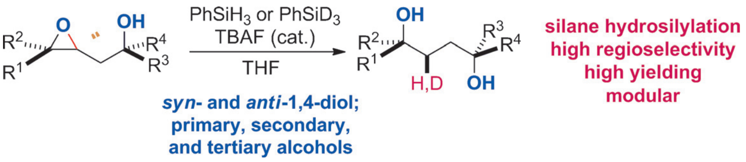
Synthetic Methods

Y.-Q. Zhang, N. Funken, P. Winterscheid, A. Gansäuer* ______________ **6931 – 6934**

Hydroxy-Directed, Fluoride-Catalyzed Epoxide Hydrosilylation for the Synthesis of 1,4-Diols

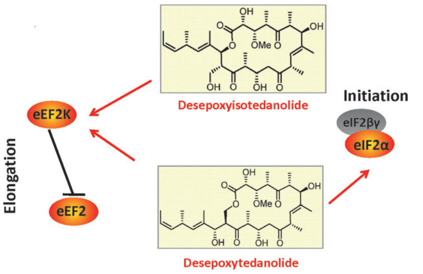


A modular, convergent, and stereoselective synthesis of 1,4-diols by epoxide hydrosilylation has been developed (see scheme). The reaction occurs under fluoride catalysis, is high yielding, highly regioselective, and can be carried out on a large scale.

Natural Products

A. Naini, Y. Muthukumar, A. Raja, R. Franke, I. Harrier, A. B. Smith, III, D. Lee, R. E. Taylor, F. Sasse, M. Kalesse* ______________ **6935 – 6939**

The Synthesis and Biological Evaluation of Desepoxyisotedanolide and a Comparison with Desepoxytedanolide



A step in the right direction: Desepoxyisotedanolide, a hypothetical biosynthetic precursor of the tedanolide desepoxytedanolide, was synthesized. Biological studies of the two macrolactones revealed an additional cellular target for desepoxytedanolide, as well as evidence that the proposed isomerization of the precursor provides a survival advantage for the producing microorganism.

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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The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

Polymerization of Ethylene by Silica-Supported Dinuclear Cr^{III} Sites through an Initiation Step Involving C–H Bond Activation

M. P. Conley, M. F. Delley, G. Siddiqi, G. Lapadula, S. Norsic, V. Monteil, O. V. Safonova, C. Copéret* **1872–1876**

Angew. Chem. Int. Ed. **2014**, *53*

DOI: 10.1002/anie.201308983

On page 1875 in this Communication the bands at ca. 3600 cm^{-1} in the IR spectrum of [($\equiv$SiO)$_6$Cr$_2$] contacted with ethylene were assigned to a silanol interacting with a Cr^{III} site, referred to as Si–(μ-OH)–Cr in the manuscript. However, such bands also appear in polyethylene and are associated with combination bands from C–H vibrations, making the unequivocal observation of Si–(μ-OH)–Cr species impossible in these samples using IR spectroscopy.

The authors would like to thank a reviewer who directed them to literature references about the FTIR spectrum of polyethylene during the review process for Ref. [1].

---

[1] M. P. Conley, M. F. Delley, F. Nunez-Zarur, A. Comas-Vives, C. Copéret, *Inorg. Chem.* **2015**, *Article ASAP*, DOI: 10.1021/ic502696n.

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Angewandte Corrigendum

In this Communication, an incorrect address for the authors affiliation was given. The correct address is College of Pharmaceutical Sciences, Zhejiang University, 866 Yuhangtang Road, Hangzhou 310058 (China).

Antitumor Drug Delivery Modulated by A Polymeric Micelle Having Upper Critical Solution Temperature

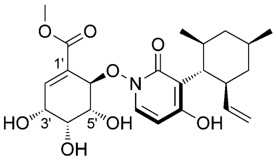
W. S. Li, L. W. Huang, X. Ying, J. You,
H. Yuan, F. Q. Hu, Y. Z. Du* **3126–3131**

Angew. Chem. Int. Ed. **2015**, *54*

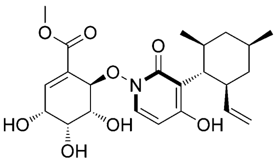
DOI: 10.1002/anie.201411524

Angewandte Corrigendum

The absolute configuration of maximiscin (**1**) has been revised as shown. The authors determined an isomeric product was formed when **1** was held in [D$_6$]DMSO under the experimental conditions employed for VCD spectroscopy. In this instance, the resulting artifact led to a misinterpretation of the experimental VCD data and an incorrect assignment of the absolute configuration of **1**. The revised assignment is supported based on a reconsideration of ^{1}H NMR $^3J_{H-H}$ data, tracking the fate and disposition of several selectively labeled (^{13}C) positions in the shikimate-derived portion of **1**, and by comparing the experimental ECD spectrum of **1** with DFT-calculated data prepared for several of its diastereomers.



(*P*)-**1**



(*M*)-**1**

Crowdsourcing Natural Products Discovery to Access Uncharted Dimensions of Fungal Metabolite Diversity

L. Du, A. J. Robles, J. B. King,
D. R. Powell, A. N. Miller,
S. L. Mooberry,*
R. H. Cichewicz* **804–809**

Angew. Chem. **2014**, *53*

DOI: 10.1002/anie.201306549

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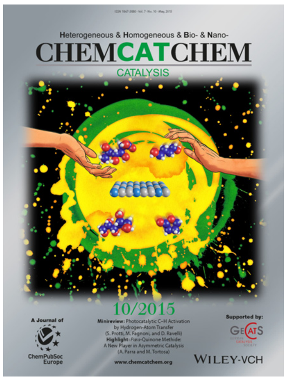

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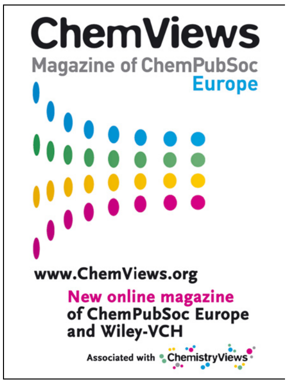

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