



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

B. L. Merner, L. N. Dawe, G. J. Bodwell*

1,1,8,8-Tetramethyl[8](2,11)teropyrenophane: Half of an Aromatic Belt and a Segment of an (8,8) Single-walled Carbon Nanotube

B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia*

Osmapyridine and Osmapyridinium from a Formal [4+2] Cycloaddition Reaction

J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich*

An Enantiomerically Pure Alleno-Acetylenic Macrocycle: Synthesis and Rationalization of Its Outstanding Chiroptical Response

P. García-García, M. A. Fernández-Rodríguez, E. Aguilar*

Gold-Catalyzed Cycloaromatization of 2,4-Dien-6-yne Carboxylic Acids: Synthesis of 2,3-Disubstituted Phenols and Unsymmetrical Bi- and Terphenyls

H. Jiang, P. Elsner, K. L. Jensen, A. Falcicchio, V. Marcos, K. A. Jørgensen*

Achieving Molecular Complexity by Organocatalytic One-Pot Strategies: A Fast Entry for the De Novo Synthesis of Sphingoids, Amino Sugars, and Polyhydroxylated α -Amino Acids

T. J. Kucharski, Z. Huang, Q.-Z. Yang, Y. Tian, N. C. Rubin, C. D. Concepcion, R. Boulatov*

Kinetics of Thiol/Disulfide Exchange Correlates Weakly with the Restoring Force in the Disulfide Moiety



“My favorite subject at school was chemistry!
The most significant scientific advance of the last 100 years
has been the discovery of how DNA works. ...”
This and more about Uwe T. Bornscheuer can be found
on page 5236.

Author Profile

Uwe T. Bornscheuer — 5236

Structural Crystallography of Inorganic
Oxysalts

Sergey V. Krivovichev

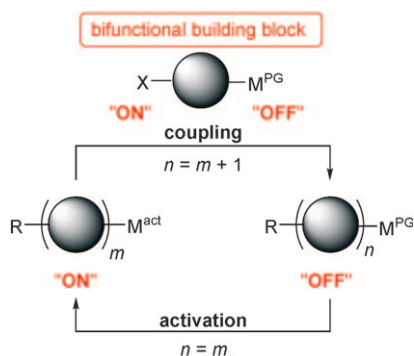
Reviving the Living

Yair Neuman

Books

reviewed by T. Albrecht-Schmitt — 5237

reviewed by R. Prinz — 5237



Repetition does not hurt! New strategies for the modulation of the reactivity of difunctional building blocks are discussed, allowing the palladium-catalyzed controlled iterative cross-coupling and, thus, the efficient formation of complex molecules of defined size and structure (see scheme). As in peptide synthesis, this development will enable the automation of these reactions. M^{PG} = protected metal, M^{act} = metal.

Highlights

Cross-Coupling

C. Wang, F. Glorius* — 5240–5244

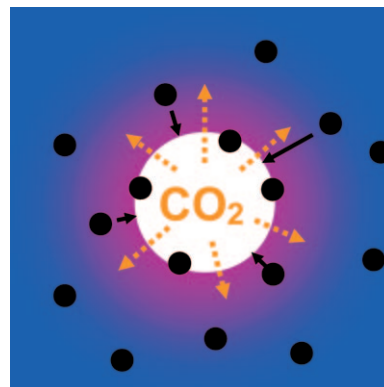
Controlled Iterative Cross-Coupling: On the Way to the Automation of Organic Synthesis

Gas Bubbles

W. Drenckhan* — 5245 – 5247

Generation of Superstable, Monodisperse Microbubbles Using a pH-Driven Assembly of Surface-Active Particles

Bubbling to the surface: Microscale gas bubbles can be generated in a microfluidic device by simultaneously injecting CO₂ and a dispersion of particles whose hydrophobicity increases as the pH value decreases. The CO₂ dissolves rapidly out of the bubbles, which shrink, and render the dispersion increasingly acidic. This drives the particles to the bubble surface where they form a type of “armor” against further dissolution (see picture).

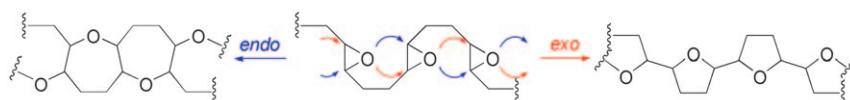


Reviews

Cascade Reactions

I. Vilotijevic,*
T. F. Jamison* — 5250 – 5281

Epoxide-Opening Cascades in the Synthesis of Polycyclic Polyether Natural Products



The structural features of polycyclic polyether natural products can, in some cases, be traced to their biosynthetic origin. However in case that are less well understood, only biosynthetic pathways that feature dramatic, yet speculative, epoxide-

opening cascades are proposed. We summarize how such epoxide-opening cascade reactions have been used in the synthesis of polycyclic polyethers (see scheme) and related natural products.

Communications

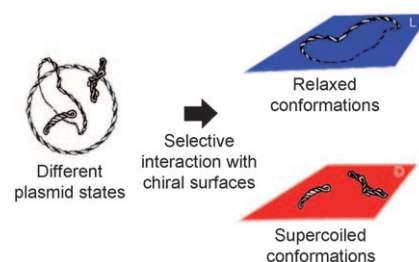
DNA on Chiral Surfaces

H. Gan, K. Tang, T. Sun,* M. Hirtz, Y. Li,
L. Chi,* S. Butz, H. Fuchs — 5282 – 5286



Selective Adsorption of DNA on Chiral Surfaces: Supercoiled or Relaxed Conformation

The right fit: Plasmid DNA molecules show chirality-dependent interaction with gold surfaces modified by L and D N-isobutyrylcysteine. Relaxed DNA molecules have a stronger interaction and adsorption on the L surface, while their counterparts on the D surface maintain a supercoiled conformation, indicating a weak interaction (see picture).

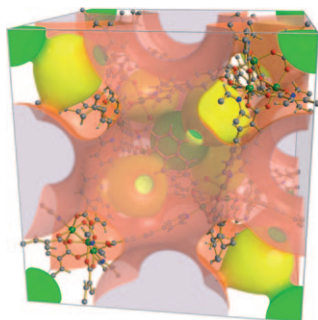


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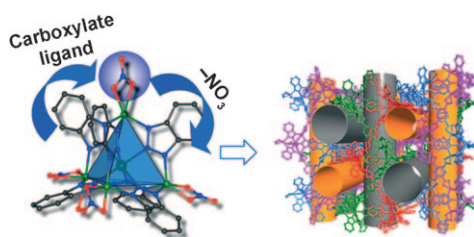


Making connections: A hydroxy-centered trinuclear nickel cluster has been employed to construct a highly connected, highly symmetric framework with a uninodal nine-connected topology. An array of triakis tetrahedra leads to a biporous intersecting-channel system (see picture).

Porous Materials

Y.-B. Zhang, W.-X. Zhang, F.-Y. Feng, J.-P. Zhang,* X.-M. Chen* — **5287 – 5290**

A Highly Connected Porous Coordination Polymer with Unusual Channel Structure and Sorption Properties



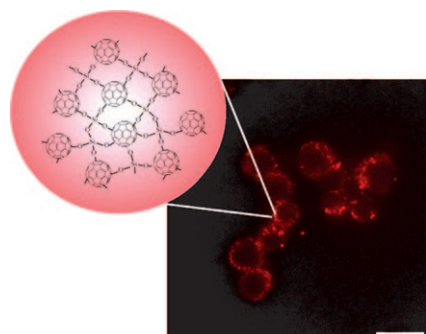
Top down goes bottom up: A family of microporous interpenetrating diamond frameworks can be constructed from a pentanuclear tetrahedral complex with nitrate groups at the apical positions as an inorganic precursor. A “bottom-up”

methodology was used for substitution of the nitrate groups by linear ditopic carboxylate ligands (see picture). The Langmuir surface area of the resulting frameworks is higher than that of classical zeolites.

Microporous Frameworks

X.-L. Wang, C. Qin, S.-X. Wu, K.-Z. Shao, Y.-Q. Lan, S. Wang, D.-X. Zhu, Z.-M. Su,* E.-B. Wang* — **5291 – 5295**

Bottom-Up Synthesis of Porous Coordination Frameworks: Apical Substitution of a Pentanuclear Tetrahedral Precursor

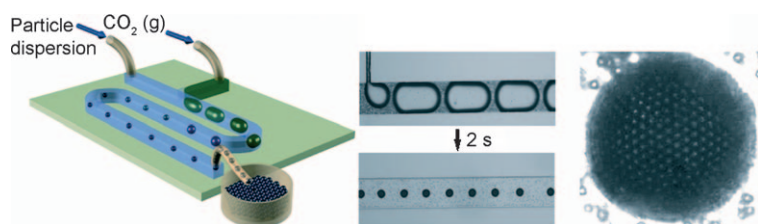


Bright lights: Fullerene–silica hybrid nanoparticles have bright photoluminescence, high photostability, and low cytotoxicity, which are assets for bioimaging agents. The origin of the photoluminescence of the nanoparticle is the C–O–Si bond (see picture).

Photoluminescent Nanoparticles

J. Jeong, M. Cho, Y. T. Lim, N. W. Song,* B. H. Chung* — **5296 – 5299**

Synthesis and Characterization of a Photoluminescent Nanoparticle Based on Fullerene–Silica Hybridization



Bubbling up: Dissolution of CO₂ bubbles in a suspension of colloidal particles chemically induces the assembly of particles on the surface of shrunken bubbles, and thus yields rapid continuous forma-

tion of a colloidal armor. This approach maintains the high colloidal stability of particles in bulk, has increased productivity, and allows the formation of bubbles with precisely controlled dimensions.

Colloidal Assembly

J. I. Park, Z. H. Nie, A. Kumachev, A. I. Abdelrahman, B. P. Binks, H. A. Stone, E. Kumacheva* — **5300 – 5304**

A Microfluidic Approach to Chemically Driven Assembly of Colloidal Particles at Gas–Liquid Interfaces



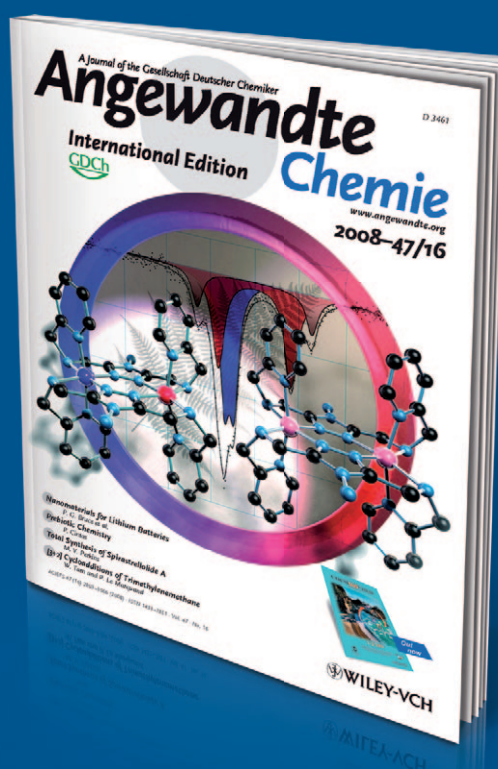
Incredibly

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R F R I

E N D

L Y



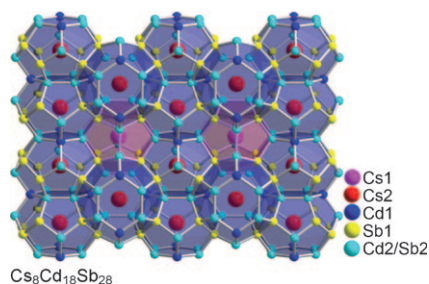
An aesthetically attractive **cover picture** that arouses curiosity, a well-presented and most informative graphical **table of contents**, and carefully selected articles that are professionally edited give *Angewandte Chemie* its distinctive character, which allows both easy browsing and further in-depth reading. Nearly 20 well-trained chemists, as well as eight further associates, work week in and week out to assemble reader-friendly issues and daily Early View articles online.



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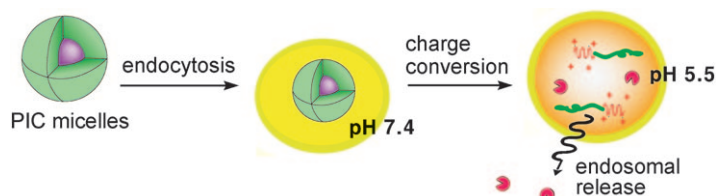


In phase: The title compounds lie in a new region of phase space for such a structure, and have stoichiometries in accord with a classical Zintl phase formulation. The small semiconductor gaps indicated by DFT calculations are also supported by their diamagnetic susceptibilities.

Clathrates

Y. Liu, L.-M. Wu, L.-H. Li, S.-W. Du, J. D. Corbett, L. Chen* — 5305–5308

The Antimony-Based Type I Clathrate Compounds $\text{Cs}_8\text{Cd}_{18}\text{Sb}_{28}$ and $\text{Cs}_8\text{Zn}_{18}\text{Sb}_{28}$



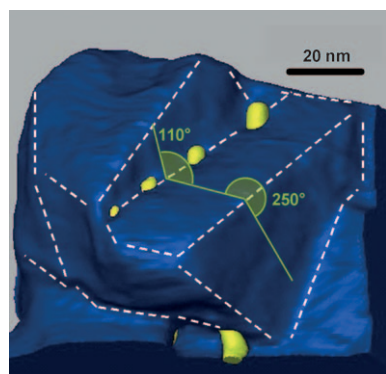
Special delivery! Polyionic complex (PIC) micelles that contain the charge-conversional moieties citraconic amide or *cis*-aconitic amide were developed for cytoplasmic protein delivery. The increase of the charge density on the protein cargo

helped the stability of the PIC micelles without cross-linking, and the charge-conversion in endosomes induced the dissociation of the PIC micelles to result in efficient endosomal release (see picture).

Protein Delivery

Y. Lee, T. Ishii, H. Cabral, H. J. Kim, J. Seo, N. Nishiyama, H. Oshima, K. Osada, K. Kataoka* — 5309–5312

Charge-Conversional Polyionic Complex Micelles—Efficient Nanocarriers for Protein Delivery into Cytoplasm



Living on the edge: Three-dimensional reconstructions from electron tomography data recorded from $\text{Au}/\text{Ce}_{0.50}\text{Tb}_{0.12}\text{Zr}_{0.38}\text{O}_{2-x}$ catalysts show that gold nanoparticles (see picture; yellow) are preferentially located on stepped facets and nanocrystal boundaries. An epitaxial relationship between the metal and support plays a key role in the structural stabilization of the gold nanoparticles.

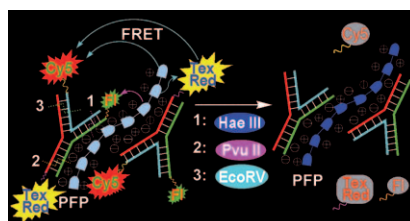
Supported-Catalyst Tomography

J. C. González, J. C. Hernández, M. López-Haro, E. del Río, J. J. Delgado, A. B. Hungria, S. Trasobares, S. Bernal, P. A. Midgley, J. J. Calvino* — 5313–5315

3 D Characterization of Gold Nanoparticles Supported on Heavy Metal Oxide Catalysts by HAADF-STEM Electron Tomography



An energy-transfer cascade is generated from a cationic conjugated polymer (PFP) and negatively charged, Y-shaped DNA labeled with three dyes at its termini (fluorescein (Fl), Tex Red, and Cy5). Multistep fluorescence resonance energy transfer regulates the fluorescence intensities of PFP and the dyes. Different types of logic gates can be operated by observing the emission wavelengths of different dyes with multiplex nucleases as inputs.



Biosensors

X. Feng, X. Duan, L. Liu, F. Feng, S. Wang,* Y. Li, D. Zhu — 5316–5321

Fluorescence Logic-Signal-Based Multiplex Detection of Nucleases with the Assembly of a Cationic Conjugated Polymer and Branched DNA

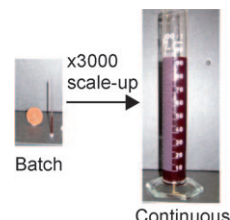


Clean Oxidation

R. A. Bourne, X. Han, M. Poliakoff,*
M. W. George* 5322–5325

Cleaner Continuous Photo-Oxidation
Using Singlet Oxygen in Supercritical
Carbon Dioxide

High pressure under the spotlight: A new milliliter-scale reactor is developed for using supercritical CO₂ to perform continuous photo-oxidation reactions. Changing from a traditional microliter-scale batch reaction to 8 hours of reaction using the new reactor gives a 3000-fold scale-up of the oxidation of α -terpinene (see picture).

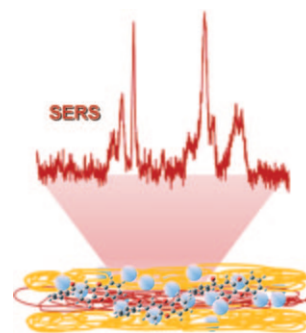


Raman Spectroscopy

S. Abalde-Cela, S. Ho,
B. Rodríguez-González,
M. A. Correa-Duarte,
R. A. Álvarez-Puebla,* L. M. Liz-Marzán,
N. A. Kotov* 5326–5329

Loading of Exponentially Grown LBL
Films with Silver Nanoparticles and Their
Application to Generalized SERS
Detection

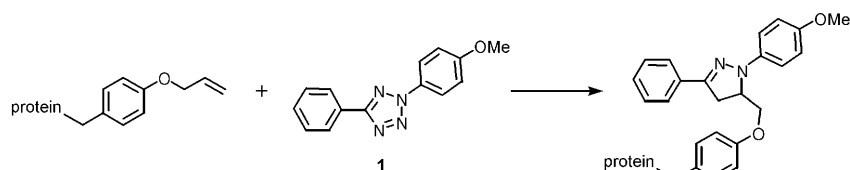
Feature film: Thin films made by exponential layer-by-layer growth display high diffusivity and can be readily infiltrated with inorganic nanoparticles. They can sequester molecular systems from solution as a function of the composition of their layers, while providing intense surface-enhanced Raman scattering (SERS) signals (see picture).



Bioorthogonal Chemistry

Y. Wang, W. Song, W. J. Hu,
Q. Lin* 5330–5333

Fast Alkene Functionalization In Vivo by
Photoclick Chemistry: HOMO Lifting of
Nitrile Imine Dipoles



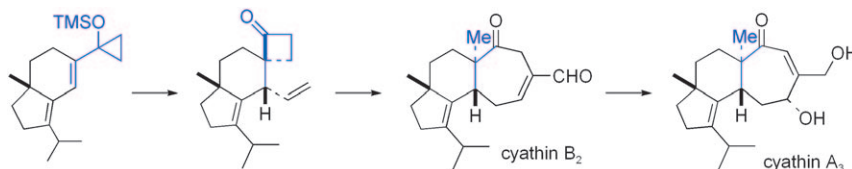
Extremely fast fluorescence labeling
(< 1 min) of a recombinant alkene-
encoded protein in living *Escherichia coli*
cells was observed with tetrazole **1**. The
electron-donating methoxy substituent
raises the energy of the highest occupied

molecular orbital of the nitrile-imine
intermediate derived from **1**. This strategy
greatly accelerates the functionalization of
alkenes by 1,3-dipolar cycloaddition in
living systems.

Natural Product Synthesis

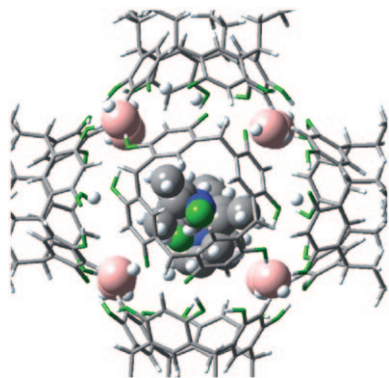
K. Kim, J. K. Cha* 5334–5336

Total Synthesis of Cyathin A₃ and
Cyathin B₂



A stereoselective synthesis of cyathin A₃
and cyathin B₂ has been achieved by a
Prins-type reaction of a cycloalkenyl
cyclopropanol. Particularly noteworthy is
the use of a spirocyclobutanone moiety as

a convenient scaffold for an efficient ring-
closing metathesis to stereoselectively
construct a suitably functionalized seven-
membered ring (see scheme).

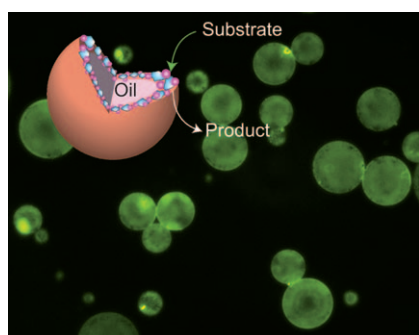


In quarantine: Nitroxide spin probes are encapsulated by hexameric resorcinarene molecular capsules in dichloromethane solutions (see picture). A substantial reduction in the tumbling rates occurs upon encapsulation of two cationic probes and one neutral probe. As the molecular volume of the probe increases, the tumbling rate of the probe reflects the overall tumbling rate of the entire supramolecular assembly.

Supramolecular Chemistry

E. Mileo, S. Yi, P. Bhattacharya, A. E. Kaifer* 5337–5340

Probing the Inner Space of Resorcinarene Molecular Capsules with Nitroxide Guests



Involuntary association: Anionic β -galactosidase enzymes associate with positively charged Au nanoparticles to produce reduced-charge conjugates, which assemble at oil–water interfaces to result in stable microcapsules (see picture). The microcapsules were formed quickly and showed high enzymatic activity, which makes them promising materials for biotechnology applications.

Enzyme Immobilization

B. Samanta, X.-C. Yang, Y. Ofir, M.-H. Park, D. Patra, S. S. Agasti, O. R. Miranda, Z.-H. Mo, V. M. Rotello* 5341–5344

Catalytic Microcapsules Assembled from Enzyme–Nanoparticle Conjugates at Oil–Water Interfaces



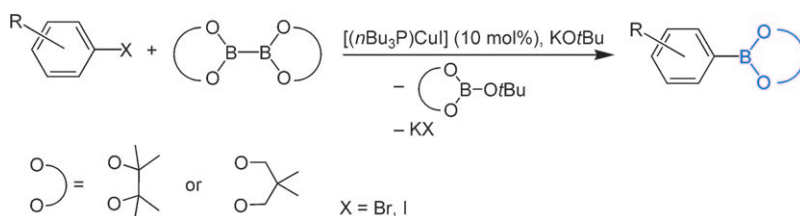
From imines to amines through catalysis by Ir complexes of a new type of P,N ligand (see scheme): This reaction affords the corresponding optically active amines

with up to 98% *ee* and has also been used with perfect stereoselectivity in the asymmetric synthesis of sertraline (**1**), an important antidepressant chiral drug.

Asymmetric Catalysis

Z. Han, Z. Wang, X. Zhang, K. Ding* 5345–5349

Spiro[4,4]-1,6-nonadiene-Based Phosphine–Oxazoline Ligands for Iridium-Catalyzed Enantioselective Hydrogenation of Ketimines



A simple but effective copper-catalyzed borylation of aryl halides, including electron-rich and sterically hindered aryl bromides, with alkoxy diboron reagents occurs under mild conditions (see

scheme). Preliminary DFT studies of the mechanism suggest that σ -bond metathesis between a copper–boryl intermediate and the aryl halide generates the aryl boronate product.

Borylation

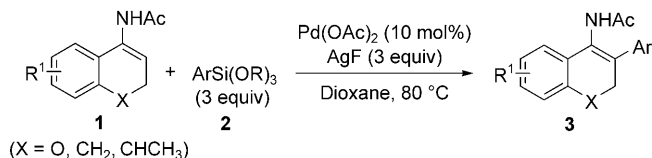
C. Kleeberg, L. Dang, Z. Lin,* T. B. Marder* 5350–5354

A Facile Route to Aryl Boronates: Room-Temperature, Copper-Catalyzed Borylation of Aryl Halides with Alkoxy Diboron Reagents



C–H Activation

H. Zhou, Y. H. Xu, W. J. Chung,
T. P. Loh* 5355–5357

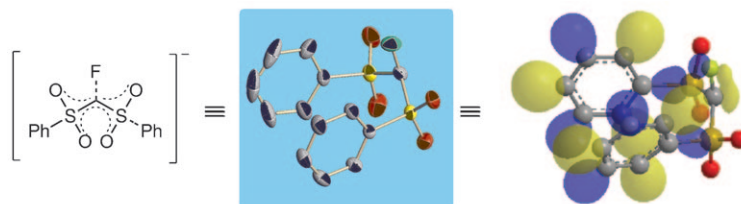


Palladium-Catalyzed Direct Arylation of Cyclic Enamides with Aryl Silanes by sp² C–H Activation

It does get in! A fluoride-assisted direct cross-coupling of cyclic enamides with trialkoxy aryl silanes by a palladium-catalyzed C–H activation leads to a wide range of enamides in yields of up to 95%.

Carbanions

G. K. S. Prakash,* F. Wang, N. Shao,
T. Mathew, G. Rasul, R. Haiges, T. Stewart,
G. A. Olah* 5358–5362



A Persistent α -Fluorocarbanion and Its Analogues: Preparation, Characterization, and Computational Study

Fluoro power: In agreement with theoretical studies on α -fluorocarbanions an X-ray crystal structure shows the α -fluorobis(phenylsulfonyl)methide anion adopts a pyramidal configuration (see picture).

High-level calculations and NMR spectroscopy studies demonstrate that electron-withdrawing substituents play a crucial role in modulating the properties of bis(phenylsulfonyl)methide anions.

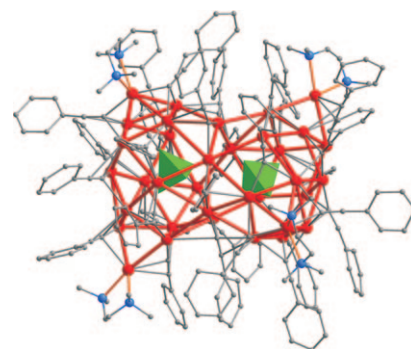
Template Synthesis

S.-D. Bian, H.-B. Wu,
Q.-M. Wang* 5363–5365



A Facile Template Approach to High-Nuclearity Silver(I) Alkynyl Clusters

Peanut clusters: Anion templates are used in a facile approach for the synthesis of high-nuclearity silver clusters. The cluster nuclearity can be controlled by adjusting the size of the templating anions and by using different alkynyl ligands. The largest silver alkynyl cluster, which consists of 35 silver(I) centers in the shape of a peanut, has been prepared by using chromate anions as templates (see picture).

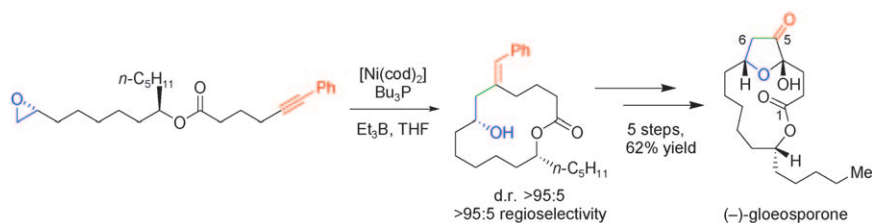


Total Synthesis

J. D. Trenkle,
T. F. Jamison* 5366–5368

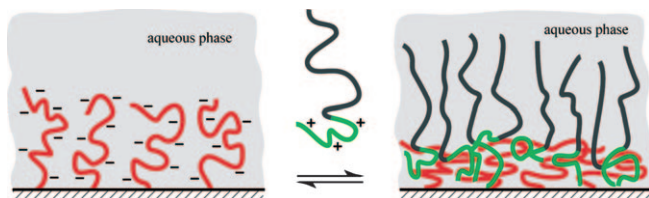


Macrocyclization by Nickel-Catalyzed, Ester-Promoted, Epoxide–Alkyne Reductive Coupling: Total Synthesis of (–)-Gloeosporone



Ring the changes: The total synthesis of the title compound centers around a novel strategy that employs a nickel(0)–phosphine complex and triethyl borane in an efficient closure of a 14-membered ring

through C–C bond formation (see scheme; cod = cyclooctadiene). The synthesis was accomplished in 10 steps and in approximately 9% overall yield.



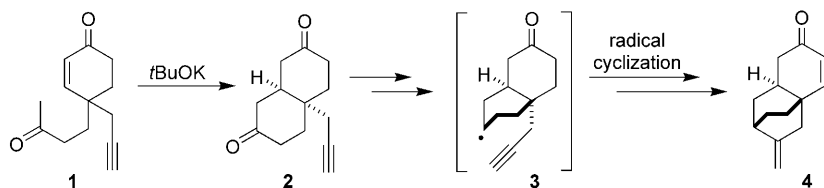
Standing room only: Dense polymer brushes can be prepared by adsorbing a diblock copolymer comprising a neutral block and a polyelectrolyte block to an oppositely charged polyelectrolyte brush (see picture). The density of the resulting

neutral brush is determined by charge compensation, leading to brush densities well over 1 nm^{-2} . The diblock copolymer can be desorbed by changing the solution conditions.

Polymer Brushes

W. M. de Vos,* J. M. Kleijn, A. de Keizer,
M. A. Cohen Stuart — 5369–5371

Ultradense Polymer Brushes by Adsorption



Quick access: A concise and efficient formal synthesis of platencin has been accomplished in nine steps from a commercially available starting material. The synthesis utilized only one protecting

group. The base-catalyzed Michael cyclization of precursor **1** afforded the key diketone **2**, which was converted into the desired core structure **4** via the radical intermediate **3**.

Antibiotic Synthesis

A. K. Ghosh,* K. Xi — 5372–5375

A Symmetry-Based Concise Formal Synthesis of Platencin, a Novel Lead against “Superbugs”



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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Preview — 5379

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