



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:

T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg,
D. M. Heinekey*

Preparation of a Dihydrogen Complex of Cobalt

M. Mastalerz,* M. W. Schneider, I. M. Opper, O. Presly

**A Salicylbisimine Cage Compound with a High Surface Area and
Selective CO₂/CH₄ Adsorption**

F. Lockyear, M. A. Parkes, S. D. Price*

Fast and efficient fluorination of small molecules by SF₄²⁺

X. Zeng, H. Beckers,* H. Willner,* J. F. Stanton

Elusive Diazirine, N₂CO

J. H. Schrittwieser, V. Resch, J. Sattler, W.-D. Lienhart,
K. Durchschein, A. Winkler, K. Gruber, P. Macheroux, W. Kroutil*

**Biocatalytic Enantioselective Oxidative C–C Coupling by Aerobic
C–H Activation**

D. V. Gutsulyak, A. van der Est, G. I. Nikonov*

Facile Catalytic Hydrosilylation of Pyridines

D. T. Cohen, B. Cardinal-David, K. A. Scheidt*

**Lewis Acid Activated Synthesis of Highly Substituted
Cyclopentanes by the N-Heterocyclic-Carbene-Catalyzed
Addition of Homoenoate Equivalents to Unsaturated Ketoesters**

T. Reiner, E. J. Keliher, S. Earley, B. Marinelli, R. Weissleder*
**Synthesis and In Vivo Imaging of an ¹⁸F-Labeled PARP1 Inhibitor
by a Chemically Orthogonal Scavenger-Assisted
High-Performance Method**

Z. Zhao, E. L. Jacovetty, Y. Liu,* H. Yan*

Encapsulation of Gold Nanoparticles in a DNA-Origami Cage

M. Barsukova-Stuckart, N. V. Izarova, G. B. Jameson,
V. Ramachandran, Z. Wang, J. v. Tol, N. S. Dalal,* R. N. Biboum,
B. Keita, L. Nadjo, U. Kortz*

**The Dicopper(II)-Containing 22-Palladate(II)
[Cu^{II}₂Pd^{II}₂₂P^V₁₂O₆₀(OH)₈]²⁰⁻**

Author Profile



“My science “heroes” are my co-workers in my group.
The biggest problem that scientists face is to keep an open
and prepared mind ...”

This and more about Annie Powell can be found on
page 800.

Annie Powell _____ 800

News



C. Nájera



M. S. Sanford



V. M. Dong

Franco-Spanish Prize:
C. Nájera _____ 801

ACS Pure Chemistry Award:
M. S. Sanford _____ 801

AstraZeneca Award in Chemistry:
V. M. Dong _____ 801

Books

Protein Misfolding Diseases

Marina Ramirez-Alvarado, Jeffery W. Kelly,
Christopher M. Dobson

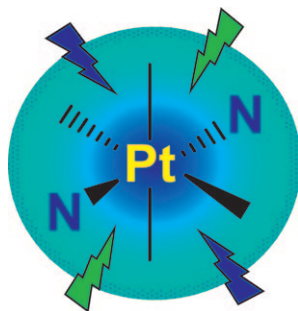
reviewed by A. Kapurniotu _____ 802

Highlights

Metallo drugs

S. J. Berners-Price* — 804–805

Activating Platinum Anticancer Complexes with Visible Light



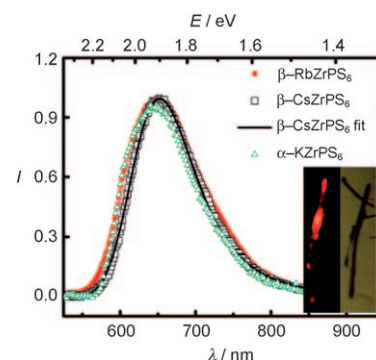
The next generation: Classical Pt^{II} anti-cancer compounds contain *cis* diam(m)ine ligands and are activated by ligand-substitution reactions. Pt^{IV} diam(m)ine diazido dihydroxo complexes are nontoxic to cells until activated by light. Replacement of the diam(m)ine ligands in a *trans* configuration by pyridine gives a complex that is potentially cytotoxic when irradiated with visible light and which has potential as a photochemotherapeutic agent.

Solid-State Chemistry

C. Wickleder* — 806–808

Luminescent Semiconductors

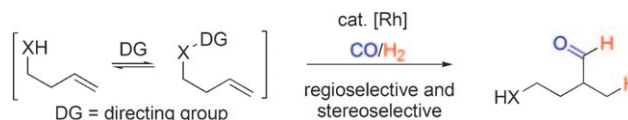
Bright light! Semiconductor materials are playing an ever-increasing role in optical applications, but the number of systems used is limited. The AZrPS₆ class of compounds (A = K, Rb, Cs) shows extremely interesting optical properties (see picture) and could thus smooth the way to the use of more complex materials.



Catalytic Directing Groups

C. S. Yeung, V. M. Dong* — 809–812

A New Direction in Enantioselective Catalysis: Scaffolding Ligands in Olefin Hydroformylation



A designer phosphine ligand capable of bonding covalently to an olefin substrate directed rhodium-catalyzed hydroformylation to generate branched aldehydes

with high regio- and enantioselectivity. The use of such scaffolding ligands opens up new directions in asymmetric synthesis.

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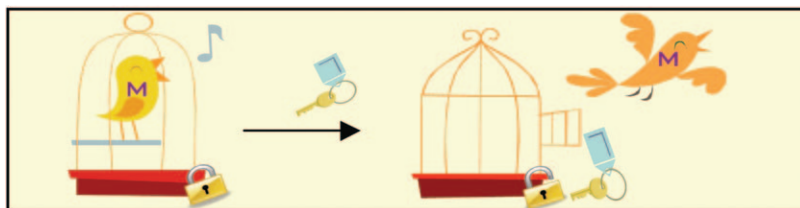
individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.

Minireviews

Photochemistry

K. L. Ciesienski, K. J. Franz* — 814–824

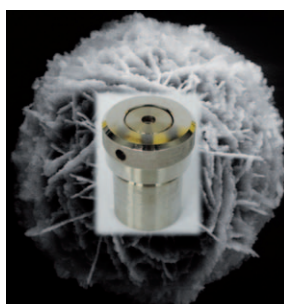
Keys for Unlocking Photolabile Metal-Containing Cages



The key to the door: Photolabile metal cages utilize light as the “key” to unlock a change in the coordination environment around the metal center. These triggerable agents can be useful tools for manipulating

the bioavailability of metals or their coordinating ligands in order to study biological pathways or for potential therapeutic purposes.

Plans for profit: Oxide nanomaterials (see picture) offer a limitless spectrum of structures, properties, and applications. In recent years, new synthetic approaches have been developed to access them and the most sophisticated in situ monitoring techniques are applied to understand their growth processes. This Review shows how these developments open up new design perspectives for the technical application of oxide nanomaterials in all current fields.



Reviews

Nanotechnology

G. R. Patzke,* Y. Zhou, R. Kontic, F. Conrad — 826–859

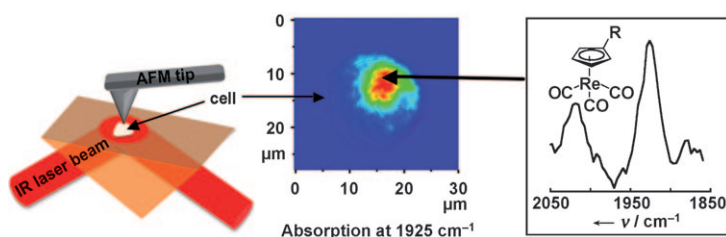
Oxide Nanomaterials: Synthetic Developments, Mechanistic Studies, and Technological Innovations

Communications

Subcellular IR Spectromicroscopy

C. Policar,* J. B. Waern, M.-A. Plamont, S. Clède, C. Mayet, R. Prazeres, J.-M. Ortega, A. Vessièrès, A. Dazzi — 860–864

Subcellular IR Imaging of a Metal–Carbonyl Moiety Using Photothermally Induced Resonance



Some like it hot! The photothermally induced resonance technique, in which an AFM microscope is coupled to a tunable pulsed IR laser, allows IR mapping and gives access to local IR spectra at the subcellular level. A metal–carbonyl com-

pound was internalized in cells and detected in the cell nucleus thanks to its IR signature. The local IR spectrum at the nucleus showed the characteristic IR bands of the $\{\text{Re}(\text{CO})_3\}$ unit.



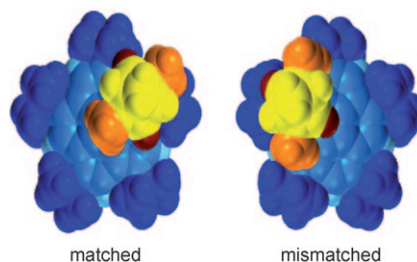
Dynamic Resolution

D. Bandera, K. K. Baldrige,* A. Linden,
R. Dorta, J. S. Siegel* — 865–867



Stereoselective Coordination of
 C_5 -Symmetric Corannulene Derivatives
with an Enantiomerically Pure
[Rh^I(nbd*)] Metal Complex

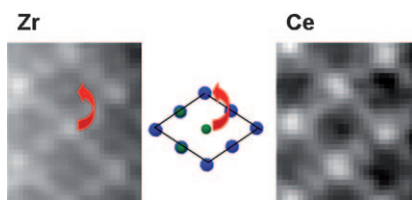
Catching the bowl! Enantiopure Rh^I dimethylnorbornadiene fragments selectively catch interconverting enantiomers of C_5 -sym-pentasubstituted corannulene derivatives in one bowl form and allow the observation and isolation of enantiopure metal-buckybowl complexes. A quantum mechanical model (see picture) predicts the mechanism of molecular dynamics and degree of stereoselective recognition.



Nanocrystal Structures

S. Trasobares,* M. López-Haro,
M. Kociak, K. March, F. de La Peña,
J. A. Perez-Omil, J. J. Calvino, N. R. Lugg,
A. J. D'Alfonso, L. J. Allen,
C. Colliex — 868–872

Chemical Imaging at Atomic Resolution
as a Technique To Refine the Local
Structure of Nanocrystals



New order: Ce₂Zr₂O₈ nanocrystals are characterized by aberration-corrected electron microscopy, core-loss electron energy-loss spectroscopy, and simulations. Direct chemical evidence of an ordered cation sublattice in nanosized (20–30 nm) crystallites is found for the first time. Local deviations in the chemical composition are also detected, with Zr occupying Ce sites (see scheme).



Gaseous Proteins



K. Breuker,* S. Brüscheiler,
M. Tollinger — 873–877



Electrostatic Stabilization of a Native
Protein Structure in the Gas Phase



One, two, three, whee! After transfer into the gas phase, the three-helix bundle protein KIX is sufficiently stabilized by electrostatic interactions to compensate for the loss of hydrophobic bonding. It thus retains its global fold on a timescale of more than 4 s.

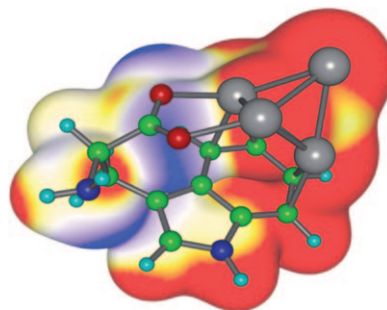
Silver Clusters

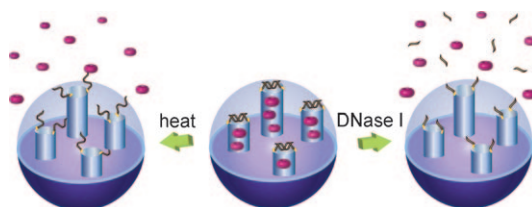
A. Kulesza, R. Mitrić,
V. Bonačić-Koutecký,* B. Bellina,
I. Compagnon, M. Broyer,
R. Antoine, P. Dugourd — 878–881



Doubly Charged Silver Clusters Stabilized
by Tryptophan: Ag₄²⁺ as an Optical Marker
for Monitoring Particle Growth

The effect of the environment on doubly charged metallic subunits has been investigated in the gas phase through a combined experimental and theoretical study. The hybrid system consisting of an Ag₄²⁺ cluster and a tryptophan molecule exhibits an unambiguous optical fingerprint, which can be useful to gain mechanistic insights into the aggregation and growth of nanoparticles (see figure; blue N, gray Ag, green C, red O, turquoise H).





Blocked tubes: Attachment of self-complementary duplex DNA to the openings of mesoporous silica nanoparticles results in a cap for trapping guest mole-

cules. The cargo can be released either by thermal stimuli or by the introduction of DNase I, both of which open the capping DNA structure (see picture).

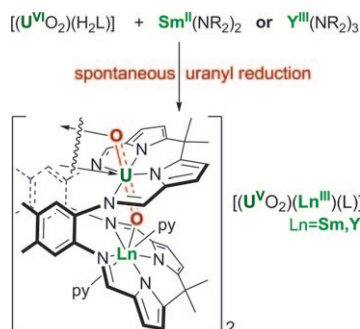
Drug Delivery

C. Chen, J. Geng, F. Pu, X. Yang, J. Ren,*
X. Qu* ————— **882–886**

Polyvalent Nucleic Acid/Mesoporous Silica Nanoparticle Conjugates: Dual Stimuli-Responsive Vehicles for Intracellular Drug Delivery



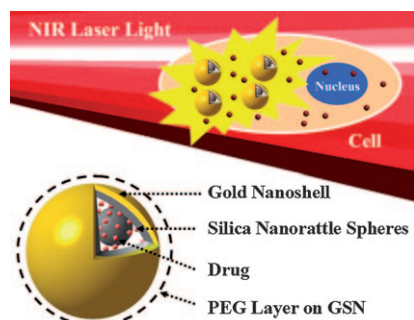
Reducing the irreducible: Incorporation of a lanthanide cation into the vacant coordination pocket of a uranyl Pacman complex results in single electron reduction to form stable pentavalent uranyl–rare-earth complexes with uranyl–oxo–rare-earth bonds (see scheme; py = pyridine, R = SiMe₃).



Uranyl Reduction

P. L. Arnold,* E. Hollis, F. J. White,
N. Magnani, R. Caciuffo,
J. B. Love* ————— **887–890**

Single-Electron Uranyl Reduction by a Rare-Earth Cation



Magic bullets: A drug-loaded structure comprising a PEGylated (PEG = polyethylene glycol) gold nanoshell on silica nanorattle spheres (GSNs; see picture) combines remote-controlled photothermal therapy with chemotherapy. Tumor cells are killed with higher efficacy and less toxicity than the free drug.

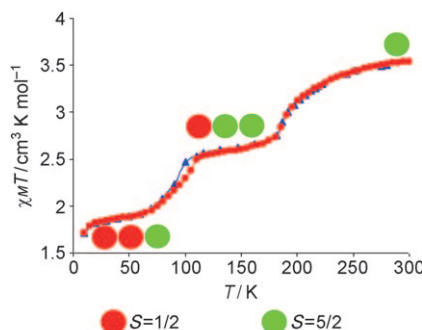
Nanomedicine

H. Liu, D. Chen, L. Li, T. Liu, L. Tan, X. Wu,
F. Tang* ————— **891–895**

Multifunctional Gold Nanoshells on Silica Nanorattles: A Platform for the Combination of Photothermal Therapy and Chemotherapy with Low Systemic Toxicity



Stepping up: A two-step magnetic spin transition with accompanying structural phase transitions is reported for the first time for Fe^{III}. The transitions are observed at 187 K and 90 K on cooling with a hysteretic transition recorded upon heating during the first crossover at 106 K. The intermediate phase persists over 97 K and contains an unprecedented [HS-HS-LS] motif with tripling of the unit cell.



Two-Step Transitions

M. Griffin, S. Shakespeare, H. J. Shepherd,
C. J. Harding, J.-F. L  tard, C. Desplanches,
A. E. Goeta, J. A. K. Howard, A. K. Powell,
V. Mereacre, Y. Garcia, A. D. Naik,
H. M  ller-Bunz,*
G. G. Morgan* ————— **896–900**

A Symmetry-Breaking Spin-State Transition in Iron(III)

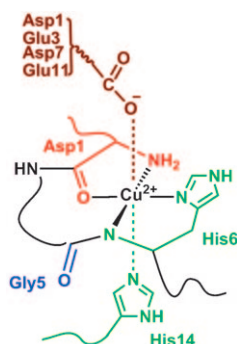


Disease Mechanisms

H. Eury, C. Bijani, P. Faller,
C. Hureau* 901–905



Copper(II) Coordination to Amyloid β :
Murine versus Human Peptide



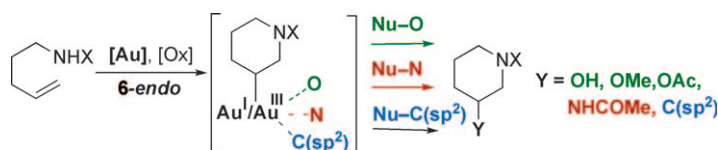
Be wary of mice: At physiological pH values, Cu^{II} binding to the human and murine amyloid β peptides differs significantly. The key mutation R5G in the murine Cu^{II} species results in coordination of the amidyl nitrogen atom of the Gly5–His6 bond (see scheme). The higher binding affinity observed for the murine peptide limits the relevance of transgenic mice (in which both peptides coexist) as models for Alzheimer's disease.

Gold Catalysis

T. de Haro, C. Nevado* 906–910



Flexible Gold-Catalyzed Regioselective
Oxidative Difunctionalization of
Unactivated Alkenes



$\text{Au}^{\text{I}}/\text{Au}^{\text{III}}$ catalytic cycles can trigger three highly regioselective alkene difunctionalization processes that involve the formation of $\text{C}(\text{sp}^3)\text{--O}$, $\text{C}(\text{sp}^3)\text{--N}$, and $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ bonds. The reaction can proceed by

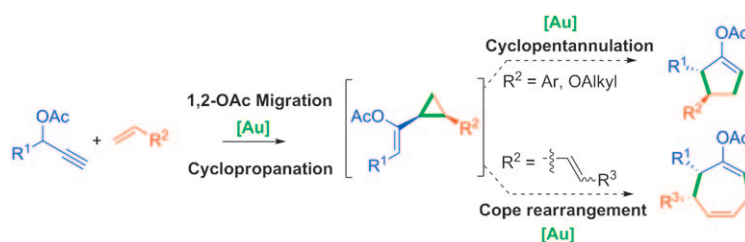
reductive elimination on the oxidized gold center with complete retention of the configuration or through two subsequent nucleophilic substitution reactions via an aziridine intermediate.

Gold Catalysis

D. Garayalde, K. Krüger,
C. Nevado* 911–915



Gold-Catalyzed Cyclopenta- and
Cycloheptannulation Cascades:
A Stereocontrolled Approach to the
Scaffold of Frondosins A and B



Golden cascades: Two diastereoselective gold-catalyzed cascade processes in which propargyl acetates react with alkenes or 1,4-dienes afford highly substituted five- and seven-membered rings,

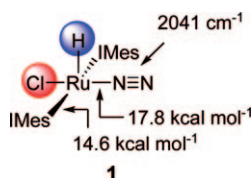
respectively (see scheme). The concerted nature of the gold-catalyzed Cope rearrangement has been used in the formal enantioselective synthesis of marine norsesquiterpenoids Frondosins A and B.

N_2 Activation

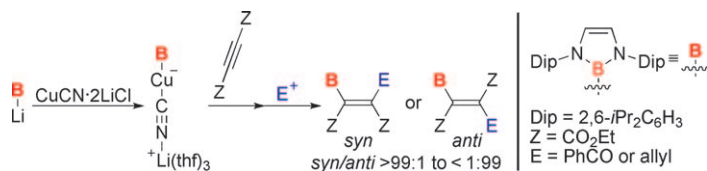
J. M. Blacquiere, C. S. Higman,
S. I. Gorelsky, N. J. Beach, S. J. Dalgarno,
D. E. Fogg* 916–919



Unusually Strong Binding of Dinitrogen to
a Ruthenium Center



Stuck on Ru: The lability of the N_2 ligand is thought to limit the efficacy of late-transition-metal complexes for the catalytic activation of N_2 . However, complex **1** is found to bind N_2 with unprecedented strength. This species resists displacement of N_2 by CO at room temperature, while computational and experimental data suggest that the $\text{Ru}\text{--}\text{N}_2$ binding is stronger than the $\text{Ru}\text{--}\text{IMes}$ binding. IMes = *N,N'*-bis(mesityl)imidazol-2-ylidene.



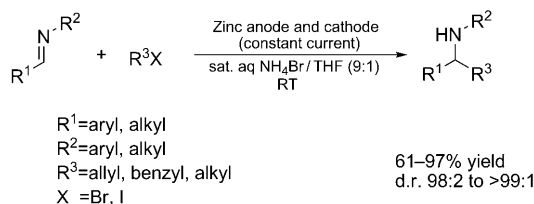
A key reactive species, lithium borylcyanoacrylate, was isolated and fully characterized in a one-pot carboboration of alkynes. The carboboration involves a boryllithium, $\text{CuCN} \cdot 2\text{LiCl}$, an ester-sub-

stituted alkyne, and an organic electrophile (see scheme). By changing the reaction temperature, the *syn/anti* ratio of the carboborated products can also be changed.

Borylcyanoacrylates

Y. Okuno, M. Yamashita,*
K. Nozaki* 920–923

Borylcyanoacrylate in a One-Pot Carboboration by a Sequential Reaction with an Electron-Deficient Alkyne and an Organic Carbon Electrophile



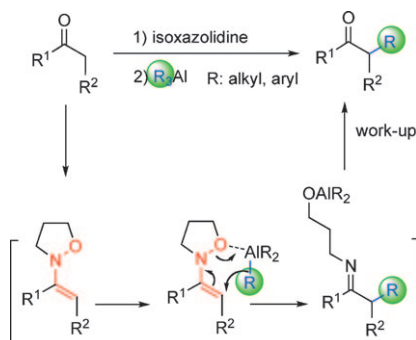
I zinc we're alone now: The title reactions were achieved in an undivided cell fitted with a pair of zinc electrodes in aqueous solution. A preliminary study on the

relationship of reaction activity and surface morphology showed that the deposited zinc powders with nanoscale architectures had very high activity.

Electrochemistry

J.-M. Huang,* X.-X. Wang,
Y. Dong 924–927

Electrochemical Allylation Reactions of Simple Imines in Aqueous Solution Mediated by Nanoscale Zinc Architectures

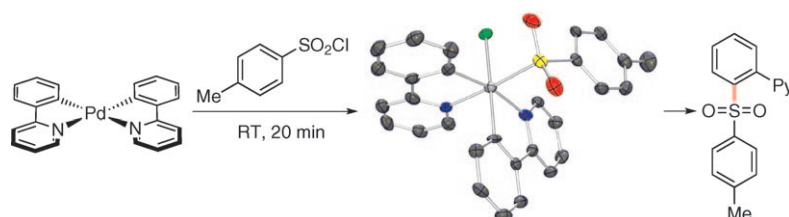


A new aspect of enamine chemistry: The formation of *N*-alkoxyenamines from ketones has led to an efficient umpolung reaction. The alkylation of *N*-alkoxyenamines with trialkylaluminum compounds proceeded smoothly and gave α -alkylated ketones (see scheme). This reaction offers a simple transformation of ketones into α -substituted ketones without the need to isolate enamines and intermediary imines.

Umpolung Reaction

T. Miyoshi, T. Miyakawa, M. Ueda,
O. Miyata* 928–931

Nucleophilic α -Arylation and α -Alkylation of Ketones by Polarity Inversion of *N*-Alkoxyenamines: Entry to the Umpolung Reaction at the α -Carbon Position of Carbonyl Compounds



Sulfurin succotash: The oxidation of Pd^{II} complexes with sulfonyl chlorides leads to a series of stable palladium(IV) sulfinate complexes. These complexes undergo reductive elimination to afford products

with C–S, C–C, and C–Cl bonds, as well as a desulfated product (see scheme; Py = pyridyl, Pd gray, N blue, S yellow, O red).

C–S Bond Formation

X. Zhao, V. M. Dong* 932–934

Carbon–Sulfur Reductive Elimination from Palladium(IV) Sulfinate Complexes

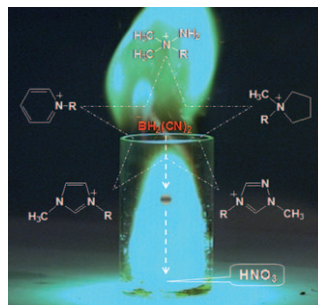


Hypergolics

Y. Zhang, J. M. Shreeve* — 935–937



Dicyanoborate-Based Ionic Liquids as Hypergolic Fluids



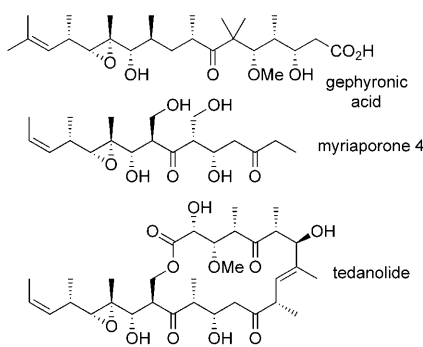
Explosive though stable: Dicyanoborate-based ionic liquids are hypergolic fuels in the presence of white fuming nitric acid as oxidizer (see high-speed picture of the ignition process). With long liquid ranges, low viscosities, and short ignition delay times, these thermally and hydrolytically stable ionic liquids appear to be very promising substitutes for hydrazine and its derivatives as bipropellants.

Structure Elucidation

L. Nicolas, T. Anderl, F. Sasse,*
H. Steinmetz, R. Jansen, G. Höfle,
S. Laschat,* R. E. Taylor* — 938–941



Gephyronic Acid, a Missing Link between Polyketide Inhibitors of Eukaryotic Protein Synthesis (Part I): Structural Revision and Stereochemical Assignment of Gephyronic Acid



Solving the puzzle: The correct structure and configuration of the natural product gephyronic acid has been determined by NMR analysis and correlation with synthetic reference compounds, as well as with myriaporone 4 and tedanolide. Gephyronic acid, isolated from culture supernatants of *Archangium gephyra*, displays intriguing antibiotic activity.

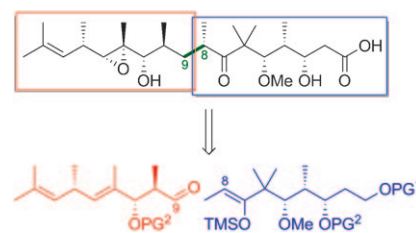
Natural Product Synthesis

T. Anderl, L. Nicolas, J. Münkemer,
A. Baro, F. Sasse, H. Steinmetz,
R. Jansen, G. Höfle, R. E. Taylor,*
S. Laschat* — 942–945



Gephyronic Acid, a Missing Link between Polyketide Inhibitors of Eukaryotic Protein Synthesis (Part II): Total Synthesis of Gephyronic Acid

19 steps in the longest linear sequence are required in the 27 step total synthesis of gephyronic acid. A key step is a diastereodifferentiating Mukaiyama aldol reaction of an aldehyde and an enolsilane (see picture, PG: protecting group). The strongly cytotoxic target compound is a structural relative of the polyketide tedanolide and was isolated from the myxobacterium *Archangium gephyra*.

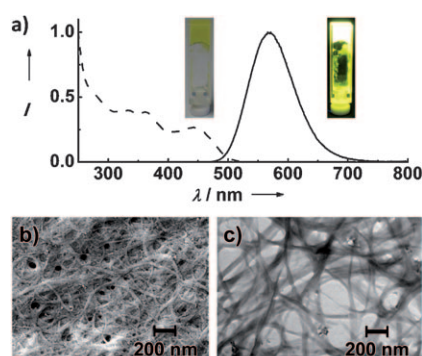


Light from Thin Assemblies

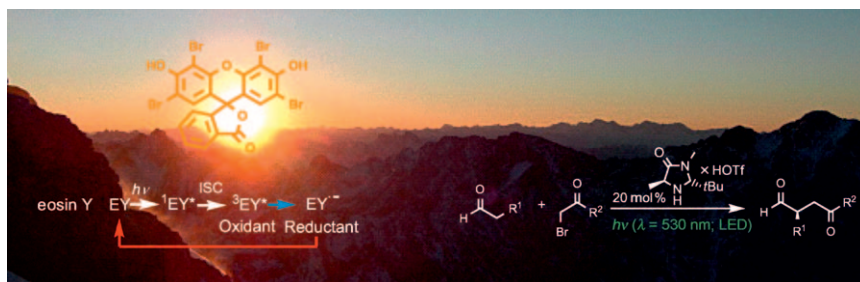
C. A. Strassert,* C.-H. Chien,
M. D. Galvez Lopez, D. Kourkoulos,
D. Hertel, K. Meerholz,
L. De Cola* — 946–950



Switching On Luminescence by the Self-Assembly of a Platinum(II) Complex into Gelating Nanofibers and Electroluminescent Films



A platinum(II) emitter is able to self-assemble into gelating nanofibers, leading to an unprecedented 90% photoluminescence quantum yield. Electroluminescent devices processed in solution can be doped with the aforementioned complex. Picture: a) Emission (—) and excitation spectra (----) and photos of the gel, b) REM, and c) TEM images of the nanofibers.



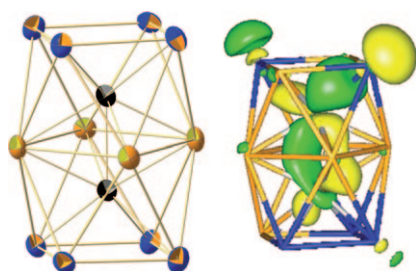
The dawn of old stars: Classic xanthene dyes like eosin Y (gr. εως = goddess of dawn) and green-light irradiation can replace precious metal complexes for the

organocatalytic asymmetric α -alkylation of aldehydes, thus rendering the process purely organic.

Photocatalysis

M. Neumann, S. Földner, B. König, K. Zeitler* 951–954

Metal-Free, Cooperative Asymmetric Organophotoredox Catalysis with Visible Light



The birdcage: The title anion, which contains two endohedral d^{10} metal atoms, is the second known ternary cluster anion comprising only metal atoms (see picture: Sn orange, Sn/Bi blue, Ni black). The $K([2.2.2]crypt)$ salt was obtained upon reaction of the binary precursor $[Sn_2Bi_2]^{2-}$ with $[Ni(cod)_2]$ in ethylenediamine/toluene by a complicated fragmentation/re-arrangement process. X-ray diffraction and DFT calculations confirm the composition of the anion.

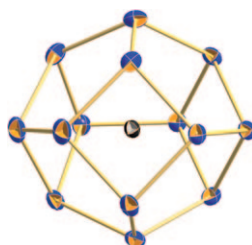
Ternary Cluster Anions

F. Lips, S. Dehnen* 955–959

Neither Electron-Precise nor in Accordance with Wade–Mingos Rules: The Ternary Cluster Anion $[Ni_2Sn_7Bi_5]^{3-}$



La cage aux folles: The $[Eu@Sn_6Bi_8]^{4-}$ anion (see picture: Sn/Bi blue/orange, Eu black) is the first example of an intermetalloid cluster anion that embeds a lanthanide ion in the solid state. Magnetic measurements and calculations both point to an $S = 7/2$ ground state and indicate ionic interactions of the Eu^{II} ion with the main-group-metal cage. ESI mass spectrometry suggest that the cage forms from two seven-atom hemispheres.



Intermetalloid Clusters

F. Lips, R. Clérac, S. Dehnen* 960–964

$[Eu@Sn_6Bi_8]^{4-}$: A Mini-Fullerane-Type Zintl Anion Containing a Lanthanide Ion



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



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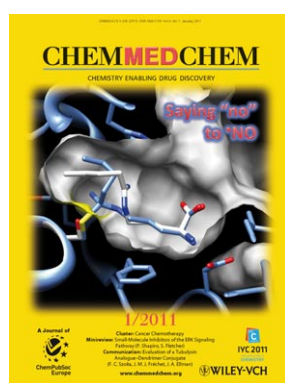
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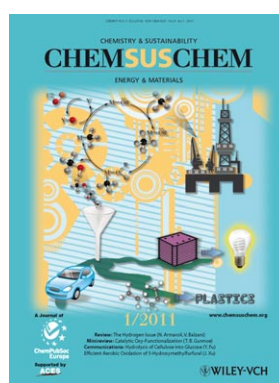
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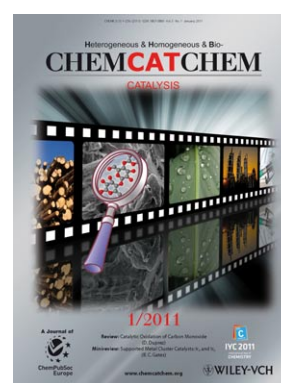
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