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:

*S. T. Scroggins, Y. Chi, J. M. J. Fréchet**
Polarity-Directed One-Pot Asymmetric Cascade Reactions Mediated by Two Catalysts in an Aqueous Buffer

D. Loffreda, F. Delbecq, F. Vigné, P. Sautet*
Fast Prediction of Selectivity in Heterogeneous Catalysis from Extended Brønsted–Evans–Polanyi Relations: A Theoretical Insight

*S. Joseph, M. Hamberger, F. Mutzbauer, O. Härtl, M. Meier, N. Korber**
Chemistry with Bare Silicon Clusters in Solution: A Transition Metal Complex of a Polysilicide Anion

*M. H. Kox, K. F. Domke, J. P. Day, G. Rago, E. Stavitski, M. Bonn, B. M. Weckhuysen**
Label-Free Chemical Imaging of Catalytic Solids by Coherent Anti-Stokes Raman Scattering and Synchrotron-Based Infrared Microscopy

*M. Griesser, D. Neshchadin, K. Dietliker, N. Moszner, R. Liska, G. Gescheidt**
Decisive Reaction Steps at Initial Stages of Photoinitiated Radical Polymerizations

*J.-G. Liu, T. Ohta, S. Yamaguchi, T. Ogura, S. Sakamoto, Y. Maeda, Y. Naruta**
Spectroscopic Characterization of a Hydroperoxo–Heme Intermediate of a Synthetic Model: Conversion of a Side-on Peroxy to an End-on Hydroperoxy Complex

*A. B. Chaplin, A. S. Weller**
B–H Activation at a Rhodium(I) Center: A Missing Link in the Transition-Metal-Catalyzed Dehydrocoupling of Amine–Boranes

Author Profile

*“The biggest challenge facing scientists is the capture and utilization of solar energy.
The secret of being a successful scientist is loving to solve problems and to share new findings with others …”*
This and more about Lawrence T. Scott can be found on page 8402.

News

J. M. J. Fréchet

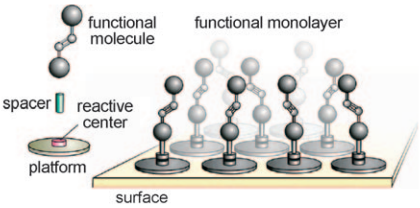
K. Nozaki

P. Braunstein

Books

Highlights

Chemistry at Interfaces



Flexible linkers: Surface chemists have long strived to prepare surfaces with properties that can be adjusted by a external stimulus. In a new platform method a substrate-bound triacatriangulinium spacer provides the attached azobenzene molecule enough room so that it can change configurations upon irradiation (see picture).

Selenium Catalysts

Selenium goes green! Recent advances in organoselenium chemistry clearly demonstrate that selenium-based catalysts can be used conveniently in a series of functional group transformations. Organoselenium compounds are promising "green catalysts" as they can transfer oxygen from environmentally friendly oxidants such as H_2O_2.

Minireviews

Asymmetric Materials

One particle, two faces: The synthesis of Janus particles is an emerging area of research. Such particles resemble the two-faced Roman god Janus who, according to mythology, had a face on either side of his head (see picture). Polymeric asymmetric particles in particular have recently received significant attention. Synthetic strategies and potential applications of such Janus particles are described.

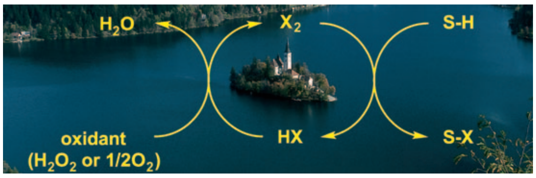
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 9442/8583 (valid for print and electronic / print or electronic delivery); for 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.

Reviews

Sustainable Chemistry

A. Podgoršek, M. Zupan,
J. Iskra* ——— **8424 – 8450**

Oxidative Halogenation with “Green” Oxidants: Oxygen and Hydrogen Peroxide



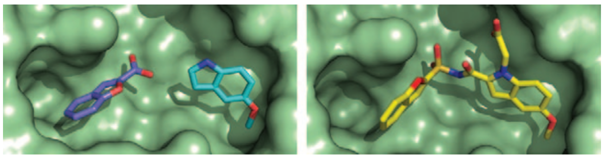
The friendly approach: The use of hazardous molecular halogens can be avoided by applying an oxidative halogenation strategy. Hydrogen peroxide and oxygen are suitable oxidants to promote the oxidation of a halide, either in the presence of a catalyst or uncatalyzed, into an active halogenating species (see scheme). The uncatalyzed transformation occurs with 100% halogen atom economy and can be improved further by using alternative reaction media.

Communications

Drug Discovery

A. W. Hung, H. L. Silvestre, S. Wen,
A. Ciulli, T. L. Blundell,
C. Abell* ——— **8452 – 8456**

Application of Fragment Growing and Fragment Linking to the Discovery of Inhibitors of *Mycobacterium tuberculosis* Pantothenate Synthetase

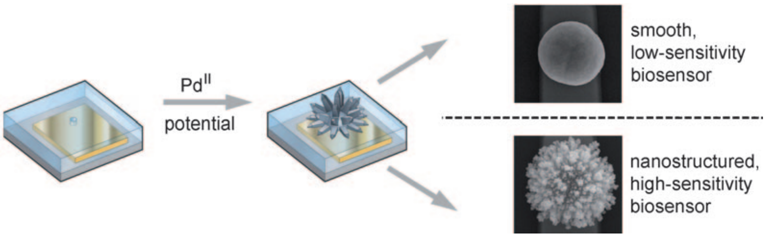


Two distinct strategies uncovered potent inhibitors of the title enzyme. X-ray crystallography and isothermal titration calorimetry guided the systematic elaboration of fragments identified from biophysical screens. The excellent inhibitor shown in the enzyme active site on the right was formed by connection of the lead fragments (left) with an acyl sulfonamide linker and resembles the best inhibitor discovered by the fragment-growing strategy.

Nanobiosensing (1)

L. Soleymani, Z. Fang, X. Sun, H. Yang,
B. J. Taft, E. H. Sargent,*
S. O. Kelley* ——— **8457 – 8460**

Nanostructuring of Patterned Microelectrodes To Enhance the Sensitivity of Electrochemical Nucleic Acids Detection



Take the rough without the smooth: The electrodeposition of patterned metal microelectrodes on a chip-based platform led to biosensors with varying sensitivity according to the degree of surface nanostructuring, which could be controlled systematically (see picture). The sensitivity of microelectrodes with highly nanostructured surfaces was superior to that of smooth microelectrodes.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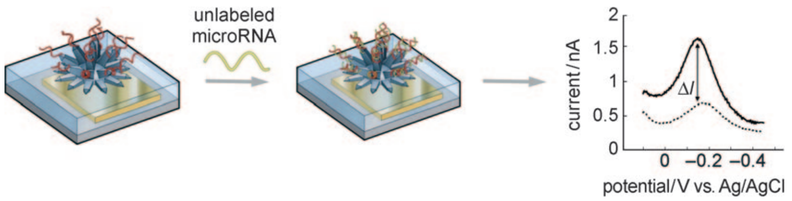
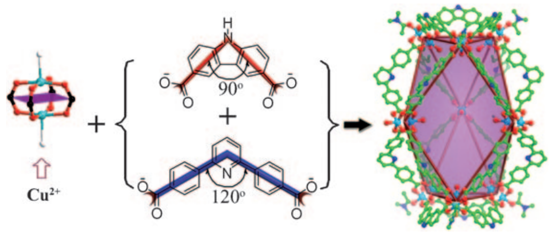
Nanobiosensing (2)



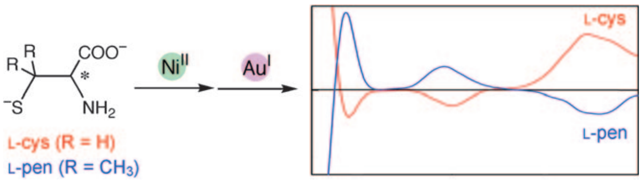
In the time it takes for lunch: An electronic chip featuring nanostructured microelectrodes (NMEs) enables the analysis of microRNA expression profiles in just 30 min in small RNA samples without enzymatic amplification or sequence labeling. The multiplexed chip detects the hybridization of microRNA targets to NME surfaces and provides large electrocatalytic gain through the use of an ultrasensitive redox reporter system (see picture).

Metal–Organic Polyhedra



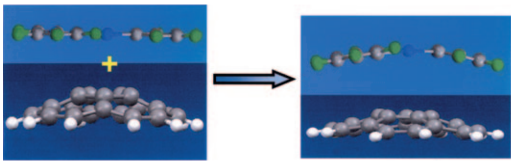
Don't be square: The title cages were synthesized by cooperative assembly of four-connected units and mixtures of two bridging dicarboxylate ligands (see picture). This work may open a new synthetic path towards complex coordination polyhedra that are inaccessible through reported synthetic procedures.

Chirality



Same but different: L-Cysteine (L-cys) and L-penicillamine (L-pen) ligands are incorporated in similar pentanuclear $Au^I_3M_2$ ($M = Ni^{II}$, Co^{III}) structures with, however, opposite stereochemical configurations. This phenomenon is explained in terms of intramolecular hydrogen bonding and steric interactions, which may provide insight into why D-penicillamine behaves like L-cysteine in nature.

Strained Molecules



Close encounters: Bending a flat molecule to make better contact with the surface of a curved molecule introduces strain. If the curved molecule can flatten somewhat (see picture), the overall energy cost of maximizing the surface contact is shared by both partners. X-ray crystal structures illustrate this geometrical mutual adaptation phenomenon.

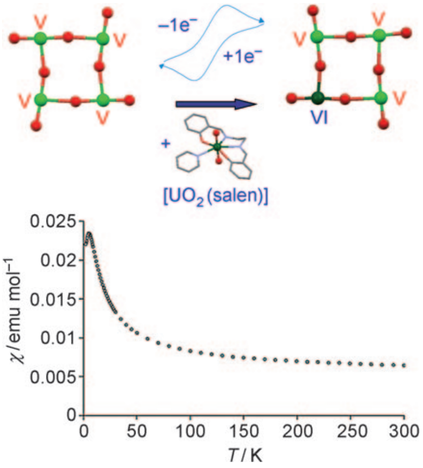
Contents

Uranium Clusters

V. Mougel, P. Horeglad, G. Nocton, J. Pécaut, M. Mazzanti* ____ **8477 – 8480**

Stable Pentavalent Uranyl Species and Selective Assembly of a Polymetallic Mixed-Valent Uranyl Complex by Cation–Cation Interactions

Useful connection: The self-assembly of four salen complexes of pentavalent uranyl ions by mutual coordination affords a tetrametallic complex that is highly stable toward disproportionation and hydrolysis, and shows an unambiguous antiferromagnetic coupling between the four oxo-bridged uranium centers (see picture; O red, U green). The first mixed-valent U^{V}_{3}/U^{VI} compound has been selectively synthesized from this complex.

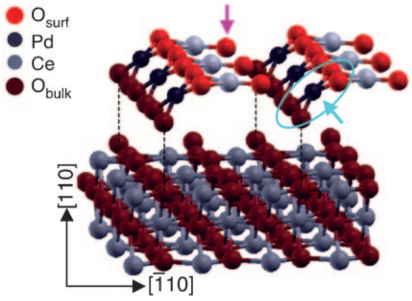


Heterogeneous Catalysis

S. Colussi, A. Gayen, M. Farnesi Camellone, M. Boaro, J. Llorca, S. Fabris, A. Trovarelli* ____ **8481 – 8484**

Nanofaceted Pd–O Sites in Pd–Ce Surface Superstructures: Enhanced Activity in Catalytic Combustion of Methane

An open superstructure: A Pd/CeO_2 catalyst prepared by solution combustion synthesis is three to five times more active for CH_4 combustion than the best conventional palladium-based systems. The catalyst contains an ordered, stable Pd-O-Ce surface superstructure (see picture; cyan arrow is a square-planar Pd site, red arrow is an undercoordinated O atom) and is an example of ultra-highly dispersed, stable Pd–O within an oxide carrier.

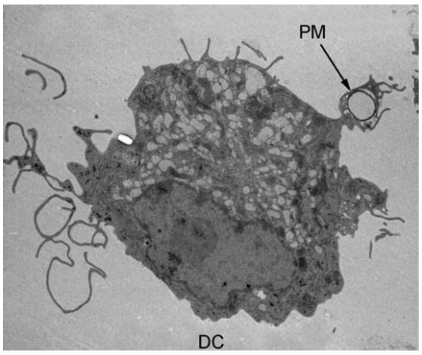


Medicinal Chemistry

S. De Koker, B. G. De Geest,* S. K. Singh, R. De Rycke, T. Naessens, Y. Van Kooyk, J. Demeester, S. C. De Smedt, J. Grooten ____ **8485 – 8489**

Polyelectrolyte Microcapsules as Antigen Delivery Vehicles To Dendritic Cells: Uptake, Processing, and Cross-Presentation of Encapsulated Antigens

Stand and deliver: Degradable polyelectrolyte microcapsules (PMs; see picture) as antigen delivery vehicles are taken up by dendritic cells (DCs) by macropinocytosis. Following uptake, the shell of the microcapsules ruptures, resulting in the invasion of the capsules by the cellular cytoplasm, thus allowing DCs to efficiently process encapsulated antigen.

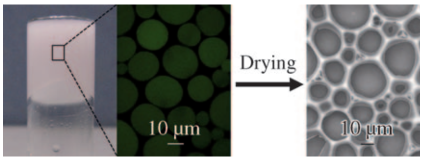


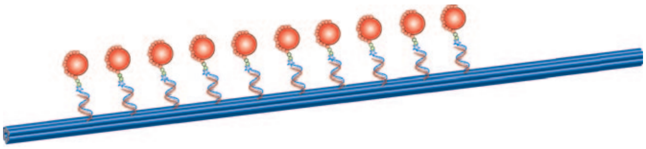
Emulsions

Z. F. Li, T. Ming, J. F. Wang, T. Ngai* ____ **8490 – 8493**

High Internal Phase Emulsions Stabilized Solely by Microgel Particles

Smart microgels: High internal phase emulsions (HIPEs) with a volume fraction up to 0.9 are prepared using soft microgel particles as stabilizer. Adsorption of microgels at the interface can effectively hinder droplet coalescence, and the excess particles form a gel in the continuous phase to inhibit creaming and phase inversion. Drying such HIPEs in air leads to porous materials.





DNA origami: A DNA nanotube containing gold-binding peptides can nucleate nanoparticles of a discrete size from soluble chemical precursors. The peptide–DNA nanostructure was used to direct the assembly of an inorganic nanostructure, with gold nanoparticles distributed along the surface of the DNA nanotube (see picture). The resulting nanostructure is an important step forward in the synthesis of programmable inorganic materials by self-assembly.

DNA Nanotechnology

L. A. Stearns, R. Chhabra, J. Sharma, Y. Liu, W. T. Petuskey, H. Yan,* J. C. Chaput* ———— **8494 – 8496**

Template-Directed Nucleation and Growth of Inorganic Nanoparticles on DNA Scaffolds

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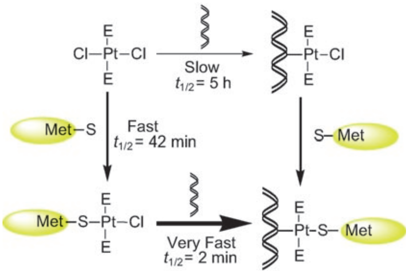

It happens at the Met: The DNA platination rate is substantially enhanced by methionine binding to *trans*-coordinated platinum antitumor drugs (see scheme). Platinum–methionine intermediates were also formed in a cell system and could play a major role in the mechanism of action of *trans* compounds.

Platinum Antitumor Agents

C. Li, Z. Li, E. Sletten, F. Arnesano, M. Losacco, G. Natile, Y. Liu* ———— **8497 – 8500**

Methionine Can Favor DNA Platination by *trans*-Coordinated Platinum Antitumor Drugs

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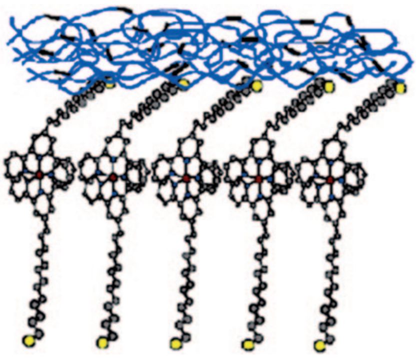

An unforgettable monolayer: Dialkylthiolate-tethered metal complex self-assembled monolayers (see picture; thickness 3 nm) provide stable and reproducible molecular monolayer nonvolatile memory (MMNVM) characterized by its hysteretic current–voltage (*I*–*V*) properties and retention time for write–multiple read–erase–multiple read pulse cycles. This is the first known voltage-driven MMNVM using only a molecular monolayer.

Molecular Devices

J. Lee, H. Chang, S. Kim, G. S. Bang, H. Lee* ———— **8501 – 8504**

Molecular Monolayer Nonvolatile Memory with Tunable Molecules

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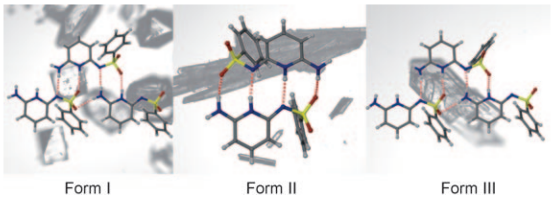


Polymorph hunting: The crystal structure of a third polymorph (form III; see picture: N blue, S yellow, O red) of 6-amino-2-phenylsulfonylimino-1,2-dihydropyridine, a crystal-structure-prediction blind-test molecule, was obtained using polymer-induced heteronucleation. Experimental stability determination finds that the in silico predicted thermodynamically stable form (form II) is actually least stable among the three polymorphs.

Crystal Polymorphism

S. Roy, A. J. Matzger* ———— **8505 – 8508**

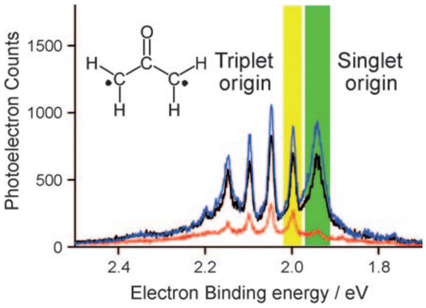
Unmasking a Third Polymorph of a Benchmark Crystal-Structure-Prediction Compound

Diradicals

T. Ichino, S. M. Villano, A. J. Gianola, D. J. Goebbert, L. Velarde, A. Sanov, S. J. Blanksby, X. Zhou, D. A. Hrovat, W. T. Borden, W. C. Lineberger* ________ **8509 – 8511**

The Lowest Singlet and Triplet States of the Oxyallyl Diradical

Small S–T splitting: The photoelectron spectrum of the oxyallyl radical anion (see picture) reveals that the electronic ground state of oxyallyl is singlet, and the lowest triplet state is separated from the singlet state by only (55 ± 2) meV in adiabatic energy.

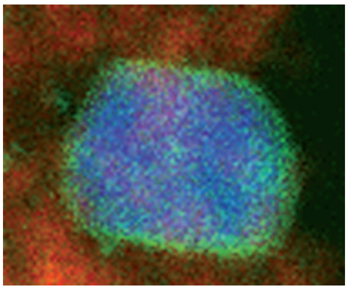


Nanoparticles

J. K. Edwards, E. Ntainjua N, A. F. Carley, A. A. Herzing, C. J. Kiely, G. J. Hutchings* ________ **8512 – 8515**

Direct Synthesis of H_2O_2 from H_2 and O_2 over Gold, Palladium, and Gold–Palladium Catalysts Supported on Acid-Pretreated TiO_2

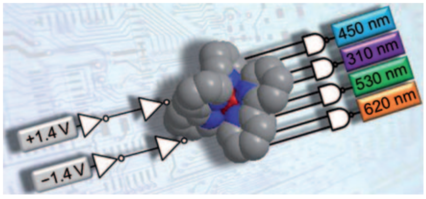
Palladium-ringed gold: The acid-pretreated Au–Pd catalysts supported on TiO_2 have a well-defined gold-rich core (blue) and palladium-rich shell (green). This type of core and shell enhances the catalytic activity of the catalyst for the direct synthesis of H_2O_2 from H_2 and O_2.



Molecular Logic

P. Ceroni, G. Bergamini, V. Balzani* ________ **8516 – 8518**

Old Molecules, New Concepts: $[Ru(bpy)_3]^{2+}$ as a Molecular Encoder–Decoder

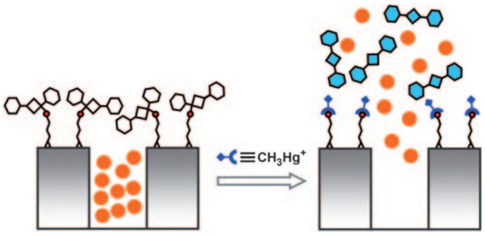


Totally logical: The well-known complex $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) can perform as both a 4-to-2 encoder and a 2-to-4 decoder (see picture; gray C, blue N, red Ru) by a combination of electronic and photonic inputs and outputs. The system can be reset in situ without the addition of chemical reagents. This approach is considered as an alternative route to solid-state molecular electronics and the design and construction of chemical computers.

Methylmercury Determination

E. Climent, M. D. Marcos, R. Martínez-Máñez,* F. Sancenón, J. Soto, K. Rurack,* P. Amorós ____ **8519 – 8522**

The Determination of Methylmercury in Real Samples Using Organically Capped Mesoporous Inorganic Materials Capable of Signal Amplification



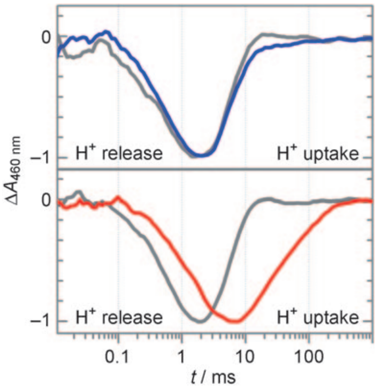
The affinity of methylmercury towards capping leuko-squaraine groups (see picture, white) induces the opening of the pores of a capped mesoporous hybrid material and the release of entrapped safranine dyes (orange), thus allowing the selective optical detection of methylmercury in complex biological samples.

Membrane Proteins

R. Simón-Vázquez, T. Lazarova,
A. Perálvarez-Marín, J.-L. Bourdelande,
E. Padrós* ______ **8523 – 8525**

Cross-Linking of Transmembrane Helices Reveals a Rigid-Body Mechanism in Bacteriorhodopsin Transport

A flashy protein: The flash-induced transient protonation of pyranine has been studied in the presence of the cross-linked double mutant E166C/A228C (red trace), a reduced mutant (blue trace), and wild-type bacteriorhodopsin (gray traces). If helices F and G are cross-linked, there is a delay in both proton release (extracellular side) and proton uptake (cytoplasmic side). Together with flash photolysis and FTIR studies, these data support a rigid-body mechanism of bacteriorhodopsin proton transport.

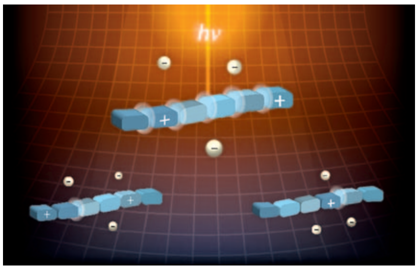


Peptide Activation

A. R. Ledvina, G. C. McAlister,
M. W. Gardner, S. I. Smith, J. A. Madsen,
J. C. Schwartz, G. C. Stafford, Jr.,
J. E. P. Syka, J. S. Brodbelt,
J. J. Coon* ______ **8526 – 8528**

Infrared Photoactivation Reduces Peptide Folding and Hydrogen-Atom Migration following ETD Tandem Mass Spectrometry

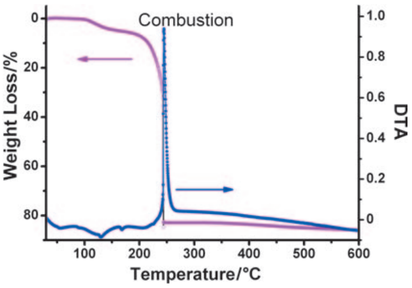
Peptides see the light: The photoactivation of peptide precursor cations during electron transfer dissociation (ETD) led to the generation of isotopic cluster peaks that more closely resembled theoretically predicted product-ion distributions. This method should enable the application of ETD to low-charge-density peptide precursors, the gas-phase secondary structure of which prevents the direct formation of *c*- and *z*$^•$-type fragment ions.



Metal Synthesis

Y. W. Jiang, S. G. Yang,* Z. H. Hua,
H. B. Huang ______ **8529 – 8531**

Sol–Gel Autocombustion Synthesis of Metals and Metal Alloys

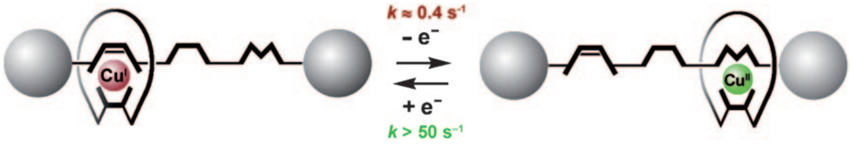


Go for the burn! Sol–gel autocombustion is an energy-efficient approach to synthesizing metals, such as Co, Ni, Cu, Ag, Bi, and Co–Ni alloy. Based on differential thermal analysis (DTA) and mass spectrometry measurements (see picture for Ni gel), a reaction mechanism is proposed that leads to the formation of metals and metal alloys instead of metal oxides.

Molecular Devices

J.-P. Collin, F. Durola, J. Lux,
J.-P. Sauvage* ______ **8532 – 8535**

A Rapidly Shuttling Copper-Complexed [2]Rotaxane with Three Different Chelating Groups in Its Axis



Fast and furious: The mobile ring of a copper-complexed [2]rotaxane incorporates an endocyclic but nonsterically hindering bidentate chelate. The rotaxane axis contains three different chelates (see picture), and both terminal coordination sites are separated by about 23 Å. The shuttling motion is triggered by oxidation or reduction of the copper center and is as fast as that in a related two-station rotaxane whose terminal stations are 10 Å apart.

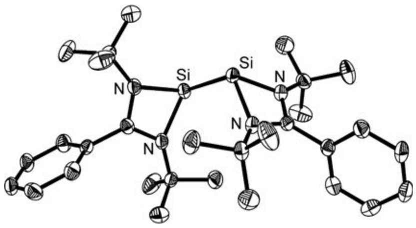
Contents

Silicon Chemistry

S. S. Sen, A. Jana, H. W. Roesky,*
C. Schulzke ________ **8536 – 8538**

A Remarkable Base-Stabilized Bis(silylene) with a Silicon(I)–Silicon(I) Bond

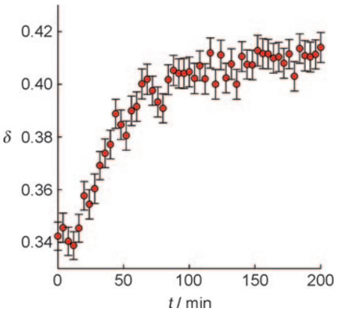
Singles party: A compound with a Si$^{\text{I}}$–Si$^{\text{I}}$ bond was prepared by the reduction of amidinatotrichlorosilane with potassium graphite. There is no multiple-bond character in the Si–Si bond, and the X-ray structural analysis (see picture) shows that this bis(silylene) possesses a *gauche*-bent geometry.



Time-Resolved Diffraction

L. Malavasi,* C. Tealdi,
C. Ritter ________ **8539 – 8542**

In Situ Time-Resolved Neutron Diffraction Investigation during Oxygen Exchange in Layered Cobaltite Cathode Materials

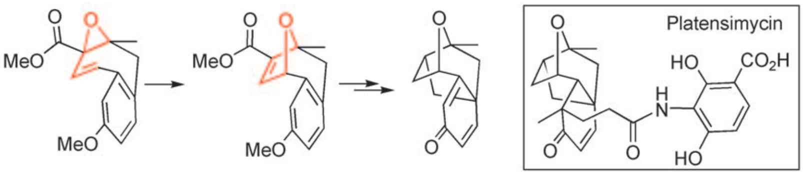


Keep your eye on the oxygen: In situ time-resolved neutron diffraction measurements can be used to study the structural changes occurring during oxygen exchange in a material (see graph of the increase in oxygen content when the gas flux is switched from Ar to O$_2$). The method is demonstrated for a layered cobaltite, which is a promising cathode material for intermediate-temperature fuel cells.

Natural Products

N. A. McGrath, E. S. Bartlett, S. Sittihan,
J. T. Njardarson* ________ **8543 – 8546**

A Concise Ring-Expansion Route to the Compact Core of Platensimycin

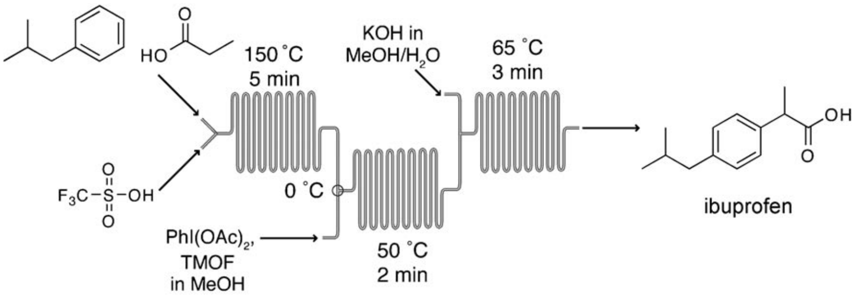


Oxatropanes from oxiranes: An expedient assembly of the compact platensimycin core is described. The synthetic approach relies on a Suzuki cross-coupling, a late-stage dearomatization reaction, and a copper-catalyzed vinyl oxirane ring expansion for accessing the oxatropane moiety of the natural product.

Synthesis Design

A. R. Bogdan, S. L. Poe, D. C. Kubis,
S. J. Broadwater,
D. T. McQuade* ________ **8547 – 8550**

The Continuous-Flow Synthesis of Ibuprofen

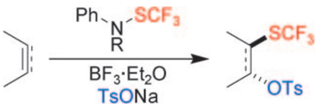


Let relief flow forth! A three-step, continuous-flow synthesis of ibuprofen was accomplished using a simplified microreactor. By designing a synthesis in which excess reagents and byproducts are compatible with downstream reactions, no intermediate purification or isolation steps are required.

Organofluorine Chemistry

A. Ferry, T. Billard,* B. R. Langlois, E. Bacqué ________ **8551 – 8555**

Trifluoromethanesulfanylamides as Easy-to-Handle Equivalents of the Trifluoromethanesulfanyl Cation (CF_3S^+): Reaction with Alkenes and Alkynes

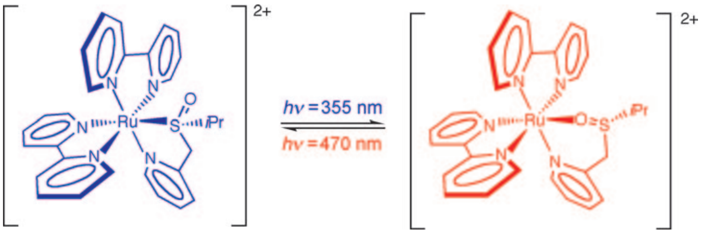


Making introductions: The CF_3S unit can be added in an electrophilic fashion to alkenes and alkynes in reactions with trifluoromethanesulfanylamide reagents (see scheme; Ts = toluene-4-sulfonyl). The products obtained may be of interest, for example, in pharmaceutical chemistry and materials science.

Photochromic Complexes

B. A. McClure, J. J. Rack* ____ **8556 – 8558**

Two-Color Reversible Switching in a Photochromic Ruthenium Sulfoxide Complex

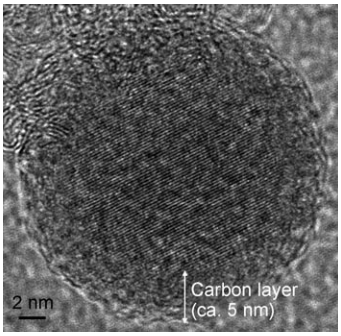


On the flipside: A reversible photochromic mechanism for the complex $[Ru(bpy)_2(pySO)]^{2+}$ (bpy = 2,2′-bipyridine, pySO = 2-(isopropylsulfinylmethyl)pyridine) is presented. Isomerization from the S-bonded (see picture; blue) to the O-bonded form (red) occurs upon excitation with UV light with a time constant τ of 1.5 ns ($\Phi = 0.11$), for the reverse process $\tau = 6.3$ ns ($\Phi = 0.027$).

Electrochemistry

S. K. Martha, J. Grinblat, O. Haik, E. Zinigrad, T. Drezen, J. H. Miners, I. Exnar, A. Kay, B. Markovsky, D. Aurbach* ________ **8559 – 8563**

$LiMn_{0.8}Fe_{0.2}PO_4$: An Advanced Cathode Material for Rechargeable Lithium Batteries

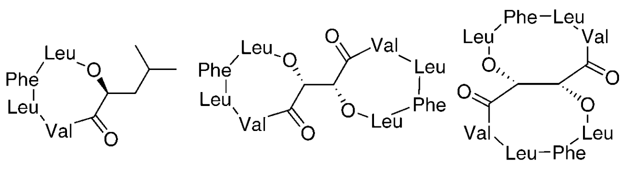


Capable and efficient: Carbon-coated nanoparticles of $LiMn_{0.8}Fe_{0.2}PO_4$ (see TEM image) synthesized by a solid-state reaction were found to be an excellent cathode material for lithium-ion batteries: A stable reversible capacity of up to 165 $mA\,h\,g^{-1}$ was observed, along with excellent cycling, very fast rate capabilities, excellent thermal stability, and very low surface reactivity in lithium-battery electrolyte solutions.

Depsipeptides

J. Ruiz-Rodríguez, J. Spengler,* F. Albericio* ________ **8564 – 8567**

Siamese Depsipeptides: Constrained Bicyclic Architectures



sansalvamide A (SA) siamese depsipeptide analogues of SA

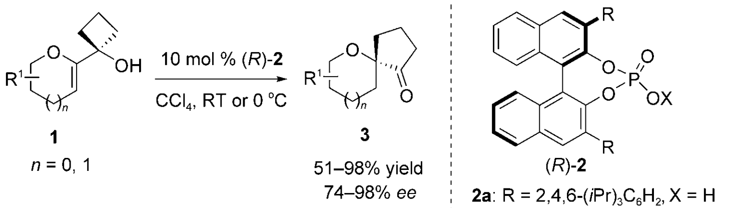
The first members of a new class of depsipeptides with tartaric acid as the core unit, called Siamese depsipeptides, are described. These compounds were synthesized from a branched precursor in only one cyclization step. The structural manipulation of a natural bioactive depsipeptide (sansalvamide A) gives analogues with greater activity, and thereby provides additional information on structure–activity relationships (see structures).

Contents

Bond Cleavage

Feeling the pinch: Remarkably facile Si–C(sp^3) and Si–C(sp^2) bond cleavage processes occur in [(Cy–PSiP)M(alkyl)] species (M = Ni, Pd; see picture); in the case of Ni, these Si–C bond activation processes are reversible on the NMR timescale in solution. Such examples of metal-mediated cleavage of an unstrained Si–C(sp^3) bond are extremely rare and are unprecedented for Ni.

Asymmetric Catalysis



2a: R = 2,4,6-(*i*Pr)$_3$C$_6$H$_2$, X = H
2b: R = 2,4,6-(*i*Pr)$_3$C$_6$H$_2$, X = Ag

A new twist: The catalytic asymmetric semipinacol rearrangement reaction of 2-oxo allylic alcohols **1** in the presence of a catalytic amount of chiral phosphoric acid (*R*)-**2a** or its silver salt (*R*)-**2b** affords enantiomerically pure spiroethers **3**.

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).

Service

Corrigendum

Asymmetric Total Synthesis of Soraphen A: A Flexible Alkyne Strategy

B. M. Trost,* J. D. Sieber, W. Qian,
R. Dhawan, Z. T. Ball ______ 5478–5481

The stereochemical descriptor for the enantiomer of glycidol used is incorrect. Scheme 2 and the first sentence of the fourth paragraph (page 5479, left column) should read (*R*)-glycidol not (*S*)-glycidol. This error also appears in the Supporting Information (pages 7–10). The authors apologize for this oversight and note that this correction does not affect the results presented in the original Communication.

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