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:

*H. Chinen, K. Mawatari, Y. Pihosh, K. Morikawa, Y. Kazoe, T. Tsukahara, T. Kitamori**
Enhancement of Proton Mobility in Extended Nanospace Channels

*A. Marrero, S. Duquerroy, S. Trapani, T. Goulas, T. Guevara, G. R. Andersen, J. Navaza, L. Sottrup-Jensen, F. X. Gomis-Rüth**
The Crystal Structure of Human α_2-Macroglobulin Shows a Unique Molecular Cage

*A. Patzer, M. Schütz, T. Möller, O. Dopfer**
IR Spectrum and Structure of the Adamantane Cation: Direct Evidence for Jahn–Teller Distortion

*C. Parthier, S. Görlich, F. Jaenecke, C. Breithaupt, U. Bräuer, U. Fandrich, D. Clausnitzer, U. F. Wehmeier, C. Böttcher, D. Scheel, M. T. Stubbs**
The *O*-Carbamoyl Transferase TobZ Catalyzes an Ancient Enzymatic Reaction

*D. Globisch, C. A. Lowery, K. C. McCague, K. D. Janda**
Uncharacterized DPD Molecules Shown by NMR Analysis: Implications for a Greater Signaling Diversity in Bacterial Species

*M. Murakami, R. Okamoto, M. Izumi, Y. Kajihara**
Chemical Synthesis of a Homogeneous Erythropoietin Analogue Having a Complex Type Disialyloligosaccharide by Use of the Improved *tert*-Boc Conditions

*C. Lux, M. Wollenhaupt, T. Bolze, Q. Liang, J. Köhler, C. Sarpe, T. Baumert**
Circular Dichroism in the Photoelectron Angular Distributions of Camphor and Fenchone from Multiphoton Ionization with Femtosecond Laser Pulses

*C. Giese, F. Zosel, C. Puorger, R. Glockshuber**
The Most Stable Protein/Ligand Complex: Applications for One-Step Affinity Purification and Identification of Protein Assemblies

Author Profile

*"My favorite piece of research is the next result.
The most important thing I learned from my parents is to find other people's merits. …"*
This and more about Ning Jiao can be found on page 3056.

News

G. Mugesh

S. You

H. W. Lam

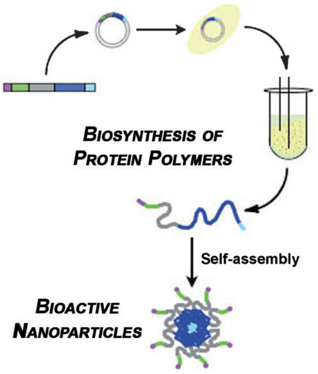
A. M. Beauchemin

N. K. Garg

Books

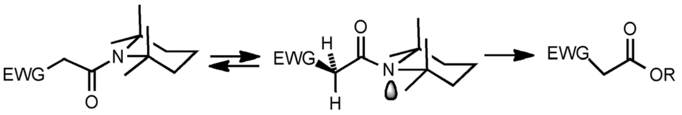
Highlights

Protein Polymers



Interdisciplinary: The application of protein-engineering techniques to polymer materials can lead to the design and preparation of biocompatible, biodegradable, stimuli-sensitive copolymers bearing biologically responsive peptide motifs (see picture).

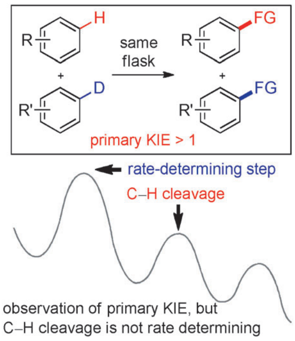
Enhanced Solvolysis



Planar but destabilized: Amides prepared from hindered amines and carbonyl compounds containing an electron-withdrawing substituent (EWG) have recently been shown to undergo solvolysis at greatly enhanced rates under neutral conditions. The key is increased access to a twisted amide conformation that undergoes a proton switch, ultimately leading to the observed products.

Essays

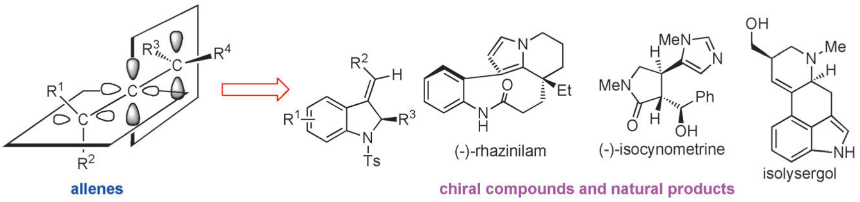
C–H Functionalization



Rate versus selectivity determining: The measurement of a kinetic isotope effect (KIE) can provide valuable information about the mechanism of a reaction, but care must be taken in the design and interpretation of KIE experiments. Depending on the experiment that is conducted, the observation of a primary KIE resulting from H/D substitution does not necessarily imply that C–H bond cleavage occurs during the rate-determining step of a reaction. FG = functional group.

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*, Journal Customer Services, John Wiley & Sons Inc., 350 Main St., Malden, MA 02148-5020. Annual subscription price for institutions: US$ 11.738/10.206 (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.

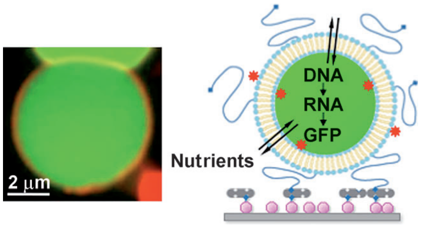
Reviews



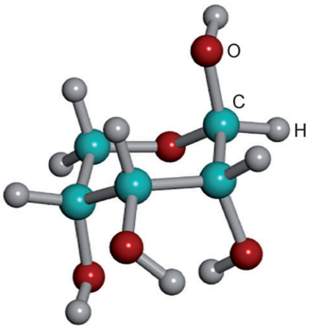
Creative and easy syntheses of chiral compounds and natural products are possible by using allenes. These compounds display exceptional physical and chemical properties, and thus offer new possibilities in catalytic asymmetric synthesis and the total synthesis of natural products. The remarkable progress made in these two topics is summarized selectively in this Review.

Communications

A minimal gene expression machinery has been encapsulated within large lipid vesicles that are immobilized on a microscope coverslip for fluorescence imaging (see picture). The engineered vesicle membrane acts as an exchange platform that enables the uptake of all necessary nutrients and tRNAs supplied in the outside environment, which initiates the internal synthesis of green fluorescent proteins (GFP) from a DNA template. Red: membrane dye, green: synthesized GFP.



Sweet truth: The search for sugars in interstellar space is hampered by a lack of spectroscopic information. D-Ribose is now the first C_5 sugar observed in the gas phase using microwave spectroscopy. The rotational spectrum revealed six conformations of free ribose, adopting preferentially β-pyranose rings and higher-energy α-pyranose forms. No evidence of α-/β-furanoses or linear forms was found, unlike biological systems, where β-furanoses are found in RNA.

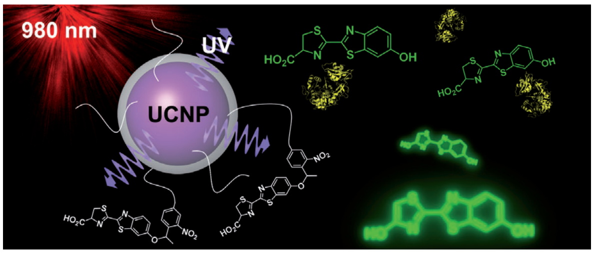


Bioimaging

Y. Yang, Q. Shao, R. Deng, C. Wang,
X. Teng, K. Cheng, Z. Cheng, L. Huang,
Z. Liu, X. Liu,* B. Xing* ____ **3125 – 3129**

In Vitro and In Vivo Uncaging and Bioluminescence Imaging by Using Photocaged Upconversion Nanoparticles

Inside Back Cover

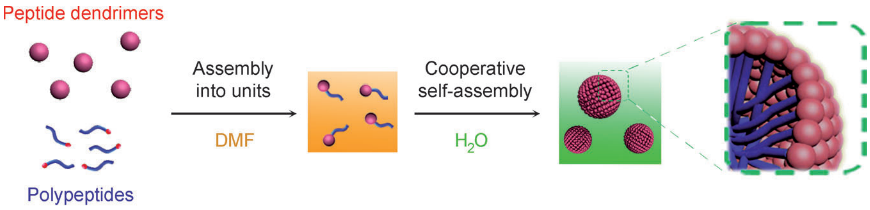


Trading up: A bioimaging system that is based on caged D-luciferin/upconversion nanoparticle conjugate has been developed. The nanoparticles upconvert near-infrared light into UV light, which triggers the photorelease of D-luciferin (see scheme) and leads to enhanced fluorescence and bioluminescence signals in vitro and in vivo. The use of near-infrared light enables deep penetration into tissue in vivo with minimum cellular damage.

Peptide Self-Assembly

X. Xu, H. Yuan, J. Chang, B. He,*
Z. Gu* ____ **3130 – 3133**

Cooperative Hierarchical Self-Assembly of Peptide Dendrimers and Linear Polypeptides into Nanoarchitectures Mimicking Viral Capsids



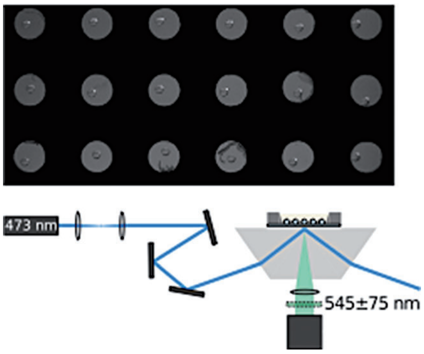
Peptidesomes are nanoparticles that are built by a two-step self-assembly of globular peptide dendrimers with lysine endgroups (red spheres in picture) and poly(L-leucine) carrying one glutamic acid residue (blue lines with red dot). These viral-capsid-mimicking nanoarchitectures exhibit high gene transfection efficacy and thus are promising nonviral vectors for biomedical applications.

Membrane Proteins

O. K. Castell, J. Berridge,
M. I. Wallace* ____ **3134 – 3138**

Quantification of Membrane Protein Inhibition by Optical Ion Flux in a Droplet Interface Bilayer Array

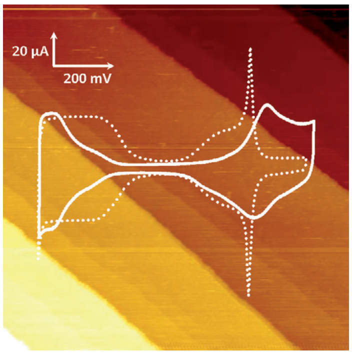
Optical platforms for assaying membrane protein function offer a promising route to scalable high-throughput screening (see picture). For the first time quantitative measurements of membrane protein inhibition are reported in an optically addressable lipid bilayer array. Wide-field total internal reflection fluorescence (TIRF) imaging of Ca^{2+} flux enables the quantification of α-hemolysin inhibition by γ-cyclodextrin.



Surface Chemistry

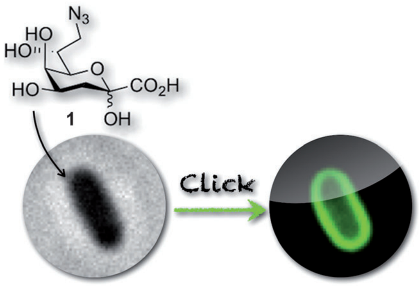
D. F. van der Vliet, C. Wang, D. Li,
A. P. Paulikas, J. Greeley, R. B. Rankin,
D. Strmcnik, D. Tripkovic, N. M. Markovic,
V. R. Stamenkovic* ____ **3139 – 3142**

Unique Electrochemical Adsorption Properties of Pt-Skin Surfaces



Thin skin: Pt-alloy catalysts, such as annealed $Pt_3Ni(111)$ (see STM image; color changes mark a single atomic step), with a surface layer of pure platinum, termed a Pt-skin surface, have very different electrochemical adsorption properties to monometallic Pt. The adsorption of hydrogen is largely suppressed (see CV, (——) $Pt_3Ni(111)$-skin versus (•••••) Pt(111)), making it hard to determine the electrochemically active surface area of catalysts with Pt-skin surfaces.

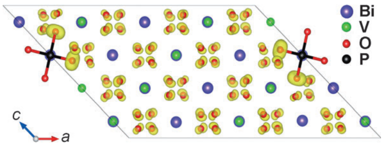
Clicking bugs: Metabolically active Gram-negative bacteria can specifically incorporate an azide-modified analogue of 3-deoxy-D-manno-octulosonic acid (**1**; see scheme) into the lipopolysaccharides on their membranes. This process adds a bioorthogonal chemical reporter onto the cell surface and allows the rapid fluorescent labeling of viable cells by click chemistry.



Bioimaging

A. Dumont, A. Malleron, M. Awwad, S. Dukan,* B. Vauzeilles* **3143 – 3146**

Click-Mediated Labeling of Bacterial Membranes through Metabolic Modification of the Lipopolysaccharide Inner Core



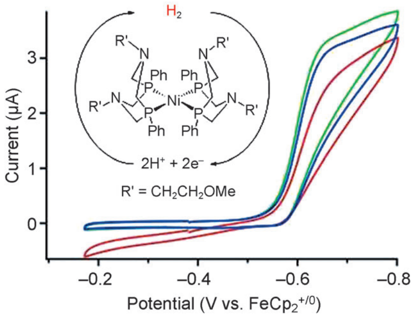
A monoclinic BiVO$_4$ lattice was doped with phosphate to enhance photoelectrochemical and photocatalytic water oxidation activity under visible light by a factor of about 30 compared with pristine BiVO$_4$. Electrochemical impedance spectroscopy measurements and density functional calculations revealed that much improved charge transfer characteristics of BiVO$_4$ are mainly responsible for the greatly enhanced photoelectrochemical activity.

P-Doped Photocatalysts

W. J. Jo, J.-W. Jang, K.-j. Kong, H. J. Kang, J. Y. Kim, H. Jun, K. P. S. Parmar, J. S. Lee* **3147 – 3151**

Phosphate Doping into Monoclinic BiVO$_4$ for Enhanced Photoelectrochemical Water Oxidation Activity

An efficient ligand combination: A new bis(diphosphine) nickel(II) complex (see picture) is described. A $\Delta G°$ value of 0.84 kcal mol^{-1} for hydrogen addition for this complex was calculated from the experimentally determined equilibrium constant. This complex displayed reversible electrocatalytic activity for hydrogen production and oxidation at low overpotentials, which are characteristic for hydrogenase enzymes.

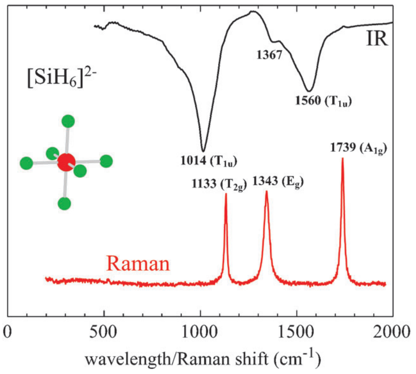


Hydrogen

S. E. Smith, J. Y. Yang,* D. L. DuBois, R. M. Bullock* **3152 – 3155**

Reversible Electrocatalytic Production and Oxidation of Hydrogen at Low Overpotentials by a Functional Hydrogenase Mimic

High-pressure conditions afford unique all-hydrido hypervalent complexes [SiH$_6$]$^{2-}$ in the crystalline hydridosilicates A$_2$SiH$_6$ (A = K, Rb). Compared to normal-valent silanes the Si–H bond appears considerably enlarged, by about 0.15 Å. Accordingly, Si–H stretching frequencies are drastically reduced, by about 400–500 cm^{-1}, thus reflecting the weakness of a hypervalent Si–H bond.



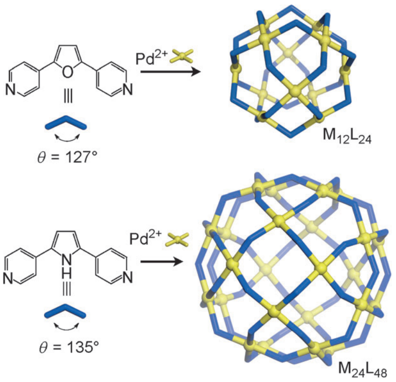
High-Pressure Chemistry

K. Puhakainen, D. Benson, J. Nylén, S. Konar, E. Stoyanov, K. Leinenweber, U. Häussermann* **3156 – 3160**

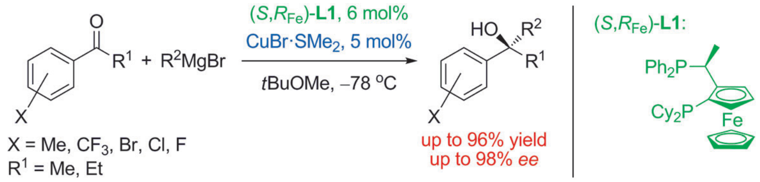
Hypervalent Octahedral SiH$_6^{2-}$ Species from High-Pressure Synthesis

Self-Assembly

Critical structural switch: A small initial difference in the angle within bidentate ligands (see scheme) is amplified into an incommensurable difference in the resultant structures ($M_{12}L_{24}$ or $M_{24}L_{48}$). This molecular-level emergent behavior was predicted from the empirical threshold of the ligand bend angle, determined by a ligand mixing experiment, for the critical $M_{12}L_{24}$/$M_{24}L_{48}$ switchover.

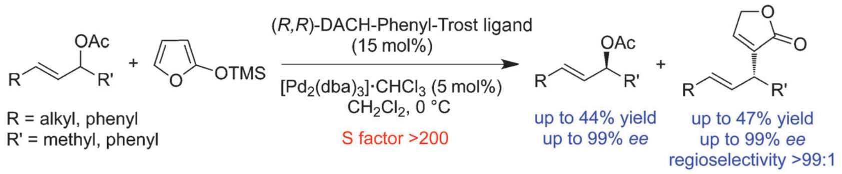


Asymmetric Catalysis



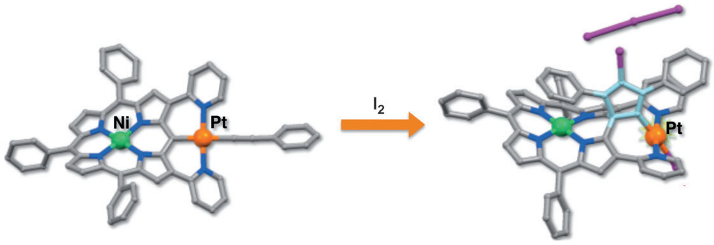
Chiral tertiary alcohols: A copper(I) catalyst with a chiral ferrocenyl diphosphine ligand facilitates the additive-free 1,2-addition of readily available Grignard reagents to aromatic ketones, thus providing access to chiral tertiary alcohols with excellent yields and enantioselectivities.

Asymmetric Catalysis

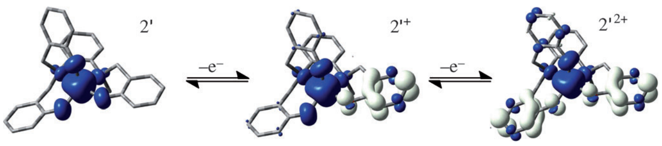


Resolving the issue: A near-perfect Pd-catalyzed kinetic resolution of 1,3-disubstituted unsymmetrical allylic acetates uses silyl enol ethers as nucleophiles to access the important 3-substituted-furanone scaffold (see scheme; DACH = diaminocyclohexyl, dba = dibenzylideneacetone). The reaction proceeds under mild conditions and provides the desired products with excellent chemo-, regio-, and enantioselectivity.

Porphyrinoids



A good catch: The oxidation of a phenylethynyl Pt^{II} pincer complex with iodine led to formal reductive elimination but without the liberation of Pt^{II}, which was caught by the 2-pyridyl substituents on the Ni^{II} porphyrin. The unique reactivity of the Pt^{II} pincer complex led to the formation of a *meso*-spiro[cyclopentadiene-isoporphyrin].



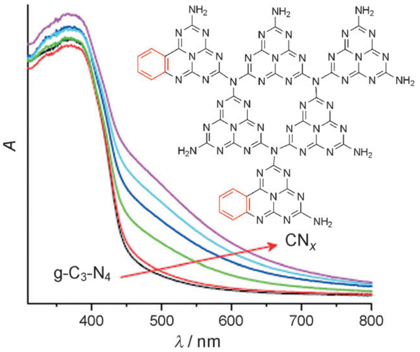
Give me five! Two five-coordinate complexes of iron with geometries that are based on those found in redox-versatile enzymes have been synthesized. The phenolate-rich, pentadentate N_2O_3 phenylene–diamine/triphenolate ligands confer a low local symmetry on the complex so that only subtle modifications in the structure of the ligands are sufficient to completely change the sequence in which the metal and the ligands are oxidized (see scheme).

Coordination Chemistry

M. M. Allard, J. A. Sonk, M. J. Heeg,
B. R. McGarvey, H. B. Schlegel,
C. N. Verani* ____________ **3178 – 3182**

Bioinspired Five-Coordinate Iron(III) Complexes for Stabilization of Phenoxyl Radicals

Back Cover



Bottom–up synthesis of graphitic carbon nitride semiconductor catalysts for the photocatalytic evolution of hydrogen by visible light is achieved through the polymerization of dicyandiamide with organic monomers bearing cyano groups, amino groups, or both. This strategy allows ample opportunity to adjust the physical and chemical properties of the resulting heterogeneous carbon-nitride-based organocatalysts.

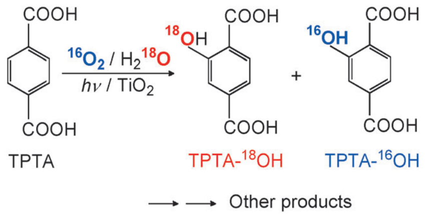
Photocatalysis

J. Zhang, G. Zhang, X. Chen, S. Lin,
L. Möhlmann, G. Dołęga, G. Lipner,
M. Antonietti, S. Blechert,
X. Wang* ____________ **3183 – 3187**

Co-Monomer Control of Carbon Nitride Semiconductors to Optimize Hydrogen Evolution with Visible Light

---

The reaction pathways by which oxygen is incorporated into the substrate in the photocatalytic oxidation of terephthalic acid (TPTA) are vastly different on {001} and {101} facets of an anatase single crystal. This was established by controlling the percentage of {101} and {001} facets, isotopically tracing the origins of the hydroxy group, and studying dioxygen consumption and variance in the concentration of hydroxylation intermediate.



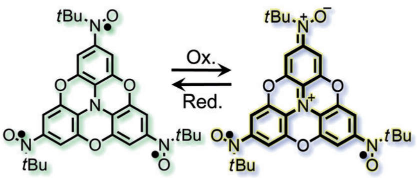
Photocatalysis

Y. Zhao, W. Ma, Y. Li, H. Ji, C. Chen,
H. Zhu, J. Zhao* ____________ **3188 – 3192**

The Surface-Structure Sensitivity of Dioxygen Activation in the Anatase-Photocatalyzed Oxidation Reaction

---

Spin-state conversion: Oxidation of trinitroxide-trioxytriphenylamine introduces extended π conjugation, resulting in a ground-state spin conversion from the antiferromagnetic coupling in the neutral spin-doublet state to the ferromagnetic coupling in the cation spin-triplet state. The reversible conversion between the two states was confirmed by a change in the UV/Vis absorption under electrochemical oxidative/reductive conditions.



π-Conjugation Control

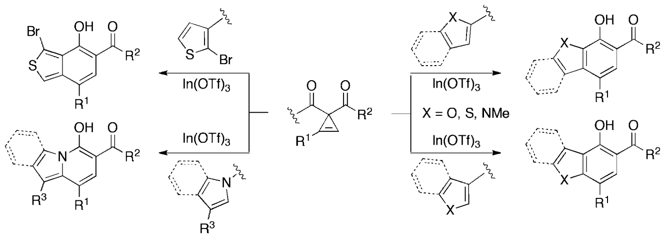
S. Suzuki, A. Nagata, M. Kuratsu,
M. Kozaki, R. Tanaka, D. Shiomi,
K. Sugisaki, K. Toyota, K. Sato, T. Takui,
K. Okada* ____________ **3193 – 3197**

Trinitroxide-Trioxytriphenylamine: Spin-State Conversion from Triradical Doublet to Diradical Cation Triplet by Oxidative Modulation of a π-Conjugated System

Diazo Compounds

L. H. Phun, J. Aponte-Guzman,
S. France* ______ 3198–3202

Indium-Catalyzed Cycloisomerizations of Cyclopropene-3,3-Dicarbonyl Compounds: Efficient Access to Benzo-Fused Heteroaromatics and Heterobiaryls



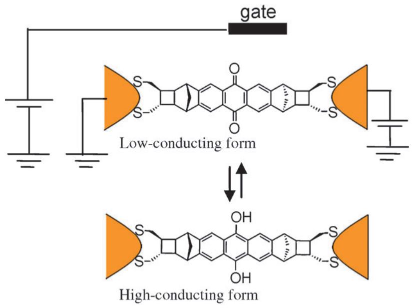
Rapid access: The title reaction generates highly functionalized benzo-annulated heterocycles and heterobiaryls. This method is amenable to a diverse array of heteroaromatics, thus allowing rapid access to benzothiophenes, benzofurans, indoles, indolizines, and pyrido[1,2-*a*]-indoles (see scheme; Tf = trifluoromethanesulfonyl).

Single-Molecule Switches

N. Darwish, I. Díez-Pérez, P. Da Silva,
N. Tao,* J. J. Gooding,*
M. N. Paddon-Row* ______ 3203–3206

Observation of Electrochemically Controlled Quantum Interference in a Single Anthraquinone-Based Norbornylogous Bridge Molecule

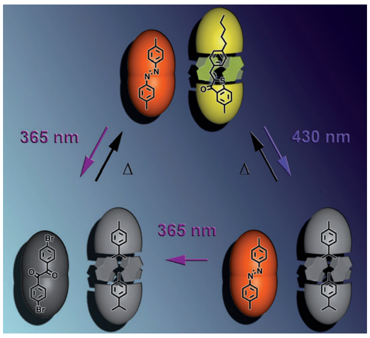
A single-molecular switch based on the anthraquinone/hydroanthraquinone redox reaction is reported (see picture). A single norbornyl anthraquinone unit can be switched between a low-conducting and a high-conducting form using electrochemical gating. The potential range, upon which the conductance enhancement is observed, can be varied using different pH values of the electrolyte.



Inclusion Complexes

H. Dube, J. Rebek, Jr.* ______ 3207–3210

Selective Guest Exchange in Encapsulation Complexes Using Light of Different Wavelenghts

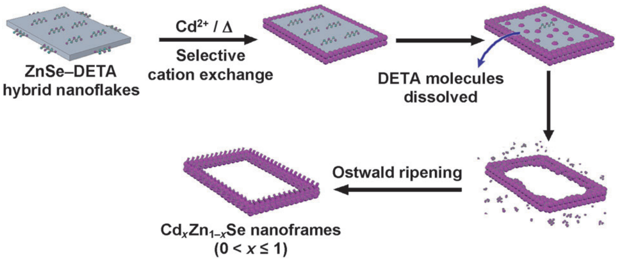


A matter of light: Selective control over the assembly of two distinct encapsulation complexes in solution is achieved by using light of two wavelengths and heat. Guest exchange can be triggered in a sequential or parallel fashion, depending on the wavelength applied, and three combinations of encapsulation complexes (see scheme) are accessible. Photoisomerization of azobenzene (red capsule) and hemithioindigo guests (yellow capsule) are used as triggers.

Nanostructures

X. Wu, Y. Yu, Y. Liu, Y. Xu, C. Liu,
B. Zhang* ______ 3211–3215

Synthesis of Hollow $Cd_xZn_{1-x}Se$ Nanoframes through the Selective Cation Exchange of Inorganic–Organic Hybrid ZnSe–Amine Nanoflakes with Cadmium Ions

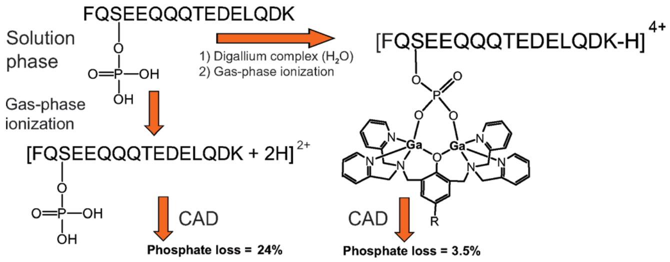


Tiny frames: The selective cation-exchange of unpurified ZnSe–diethylenetriamine (DETA) hybrid nanosheets with cadmium ions, followed by the dissolution of DETA and subsequent Ostwald ripening, leads to hollow $Cd_xZn_{1-x}Se$ nanoframes with tunable compositions (see scheme). These nanoframes are highly active in the photocatalytic hydrogen evolution from water-splitting.

Phosphoproteomics

S. Svane, F. Kryuchkov, A. Lennartson, C. J. McKenzie, F. Kjeldsen* **3216 – 3219**

Overcoming the Instability of Gaseous Peptide Phosphate Ester Groups by Dimetal Protection

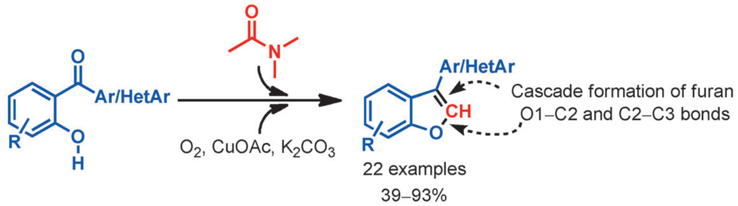


Complex protection: Fragmentation of phosphorylated peptide ions by collision-activated dissociation (CAD) is possible without facile detachment of the phosphate ester group when it is protected by a digallium complex (see scheme). The application of this dimetal phosphate ester stabilization (DIMPES) approach is believed to hold enormous potential for application in phosphoproteomics.

Cascade Cyclization

M. J. Moure, R. SanMartin,* E. Dominguez* **3220 – 3224**

Benzofurans from Benzophenones and Dimethylacetamide: Copper-Promoted Cascade Formation of Furan O1–C2 and C2–C3 Bonds Under Oxidative Conditions

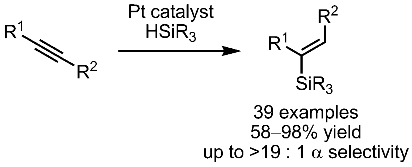


DMA donates: Copper(II) acetate and 8-hydroxyquinoline promote the formation of a benzofuran core through a cascade of copper-catalyzed processes wherein the key carbon atom comes from the dimethylacetamide (DMA) solvent. Strong evidence for the participation of a Wacker cyclization catalyzed solely by copper is provided, not only in the title reaction from benzophenones but also from 2-hydroxy-α-arylstyrene derivatives.

Homogeneous Catalysis

D. A. Rooke, E. M. Ferreira* **3225 – 3230**

Platinum-Catalyzed Hydrosilylations of Internal Alkynes: Harnessing Substituent Effects to Achieve High Regioselectivity



Rule of thumb: The high yielding title reaction is described with a focus on understanding the factors that govern the regioselectivity of the process (see scheme). Electronic, steric, and functional group properties all influence the selectivity, an understanding of which allows the selective formation of trisubstituted vinylsilanes, which are synthetically useful compounds for accessing stereodefined alkenes.

Synthetic Methods

Z. Liu, J. Zhang, S. Chen, E. Shi, Y. Xu, X. Wan* **3231 – 3235**

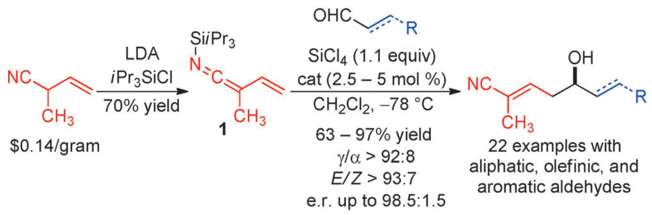
Cross Coupling of Acyl and Aminyl Radicals: Direct Synthesis of Amides Catalyzed by Bu$_4$NI with TBHP as an Oxidant

A radical solution: A Bu$_4$NI/*tert*-butyl hydroperoxide (TBHP) catalyzed synthesis of amides through a cross-coupling reaction between acyl and aminyl radicals is described. This method involves the combination of aldehyde C–H bond functionalization and decarbonylation of *N*,*N*-disubstituted formamides (see scheme). The cross-coupling is metal-free, has a wide substrate scope, operational simplicity, and gives high yields on scale-up.

Asymmetric Catalysis

S. E. Denmark,*
T. W. Wilson ______ **3236–3239**

Lewis Base Catalyzed Enantioselective Additions of an *N*-Silyl Vinylketene Imine



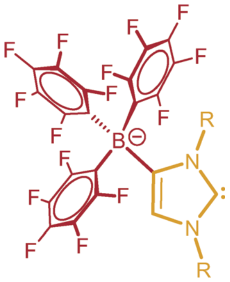
Outside the limits: In the title reaction the nucleophile **1** represents a synthetic equivalent of nucleophilic allylic nitriles and addresses some of the current limitations associated with reactions of allylic nitrile anions. Unsaturated nitriles containing a trisubstituted double bond are obtained in high yield, with excellent site selectivity and good to excellent stereoselectivity (see scheme; LDA = lithium diisopropylamide).

Carbene Chemistry

S. Kronig, E. Theuergarten, C. G. Daniliuc,
P. G. Jones, M. Tamm* ______ **3240–3244**

Anionic N-Heterocyclic Carbenes That Contain a Weakly Coordinating Borate Moiety

Piggyback ride: Anionic N-heterocyclic carbenes are presented that bear their negative charge in the form of a weakly coordinating anionic borate moiety in the backbone. This class of carbene can be used in silver-free routes for the preparation of neutral, single-source gold(I) catalysts, the performance of which is comparable with that of other cationic gold(I) catalysts in enyne rearrangements.



DOI: 10.1002/anie.201201199

50 Years Ago . . .

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

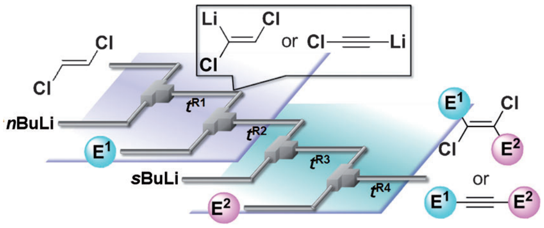
Already by Issue 4 in 1962, the new International Edition of *Angewandte Chemie* had started to attract contributions from all over the world. In a Communication from the former Czechoslovakia, J. Tomiška and E. Spousta reported the cleavage of the trioxane ring in acetic anhydride solution in the presence of strong mineral acids. The observed reaction was presumed to occur by a cationic cleavage of the ring followed by acylation of the resulting products. Acylated carbodiimides were the subject of two Communications from researchers in Chile, who discussed ring closures and elimination of hydrogen sulfide with these compounds.

Fifty years ago, the measurement of chemical shifts was still relatively new, but the link between the effects measured by IR and NMR spectroscopy was already being explored. In a Communication, W. Seiffert reported the relationship between the C–H vibrational energy and the chemical shift of the protons in a series of substituted quinolines. A linear relation was found between the chemical shift of an isolated hydrogen atom in a ring and the deformation energy of its out-of-plane vibration.

Side reactions can always be problematic, not least for H. Elsner and S. Saure, who reported an explosion during the uncatalyzed addition of trichlorobromomethane to ethylene in a high-pressure autoclave. Following three incident-free experiments, the autoclave exploded with great force, resulting in the autoclave and manometer being shattered and the laboratory walls to be covered in soot. It was assumed that a previously unknown side reaction had occurred.

Enzymes were a common theme in the Reviews section, which contained articles on isozymes and heteroenzymes by Theodor Wieland and Gerhard Pfleiderer, and on microbial enzymes by Christoph Tamm. The latter Review discusses microbial transformations in natural products, including steroids, estrogens, and terpenes. These reactions were valuable in elucidating the biosynthesis and metabolism of the natural products.

Read more in Issue 4/1962



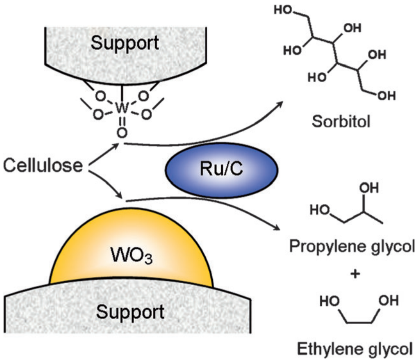
It's all about the timing: Precise control of the residence time (t^{Rx}; see picture) of reactive intermediates in flow microreactors enables the reaction pathway of lithiated 1,2-dichloroethene to be switched to produce either alkenes or alkynes. This method also allows versatile syntheses of asymmetric disubstituted dichloroalkenes and alkynes.

Microreactors

A. Nagaki, C. Matsuo, S. Kim, K. Saito, A. Miyazaki, J.-i. Yoshida* ______ **3245 – 3248**

Lithiation of 1,2-Dichloroethene in Flow Microreactors: Versatile Synthesis of Alkenes and Alkynes by Precise Residence-Time Control

---



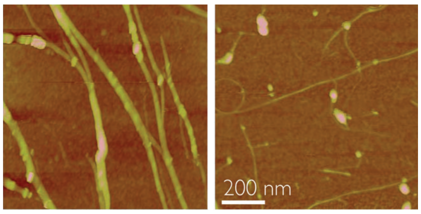
Chopped up: The success of the title reaction strongly depends on the domain size of the WO_3 crystallites, and the type of support. Structurally stable WO_3 plays a bifunctional role in the promotion of the hydrolysis of cellulose into sugar intermediates, and more significantly in the selective cleavage of the C–C bonds in these sugars.

Renewable Resources

Y. Liu, C. Luo, H. Liu* ______ **3249 – 3253**

Tungsten Trioxide Promoted Selective Conversion of Cellulose into Propylene Glycol and Ethylene Glycol on a Ruthenium Catalyst

---



$T > T_K$ $T < T_K$

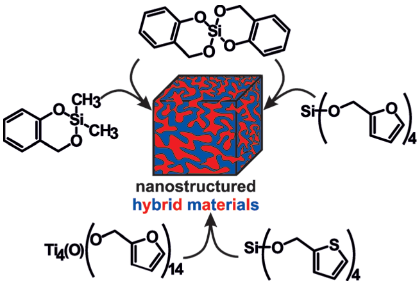
Cool tubes: Micelle formation is inhibited at temperatures below the Krafft temperature T_K, therefore the dispersion of carbon nanotubes (CNTs) below T_K results in better exfoliation, higher particle loading, and a dramatically reduced final amount of surfactant (see AFM images). The concept is not restricted to CNTs but is also readily applicable to other nanoparticle types.

Nanoparticle Colloids

S. Dölle, B.-D. Lechner, J. H. Park, S. Schymura, J. P. F. Lagerwall,* G. Scalia* ______ **3254 – 3257**

Utilizing the Krafft Phenomenon to Generate Ideal Micelle-Free Surfactant-Stabilized Nanoparticle Suspensions

---



A third twin: Homopolymers are formed by the copolymerization of two twin monomers. Using the new method of simultaneous twin polymerization, complex hybrid materials can be synthesized in a targeted manner (see scheme), in which, depending upon the combination of twin monomers used, nanostructured hybrid materials with different compositions and properties can be obtained.

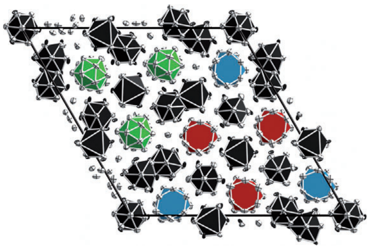
Hybrid Materials

T. Löschner, A. Mehner, S. Grund, A. Seifert, A. Pohlers, A. Lange, G. Cox, H.-J. Hähnle, S. Spange* ___ **3258 – 3261**

A Modular Approach for the Synthesis of Nanostructured Hybrid Materials with Tailored Properties: The Simultaneous Twin Polymerization

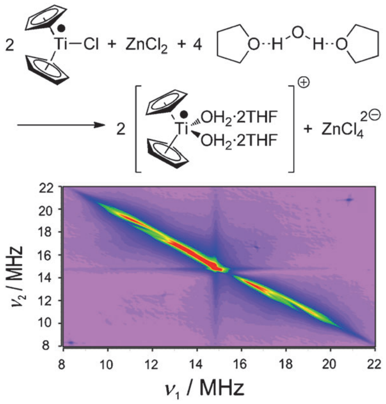
Sodium Mercury Amalgams

Front Cover



The mercury puzzle: Using the new technique of electrocrystallization the sodium mercury alloy $Na_{11}Hg_{52}$ could be obtained in a phase pure form. This amalgam is a key component in the industrially important chloralkali process. The combination of different bonding situations in this phase results in it having the typical properties of a “bad” metal.

Hydrogen-Atom Transfer



In contradiction to what has been postulated before, the formation of cationic hydrated Ti^{III} complexes is crucial for the activation of H_2O towards hydrogen-atom transfer (HAT). The relevant intermediates have been characterized by modern EPR methods (see spectrum) and cyclic voltammetry. The structural assignments were verified by a comprehensive computational study. The calculated bond dissociation energies are in agreement with a previous kinetic investigation.

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).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

Service