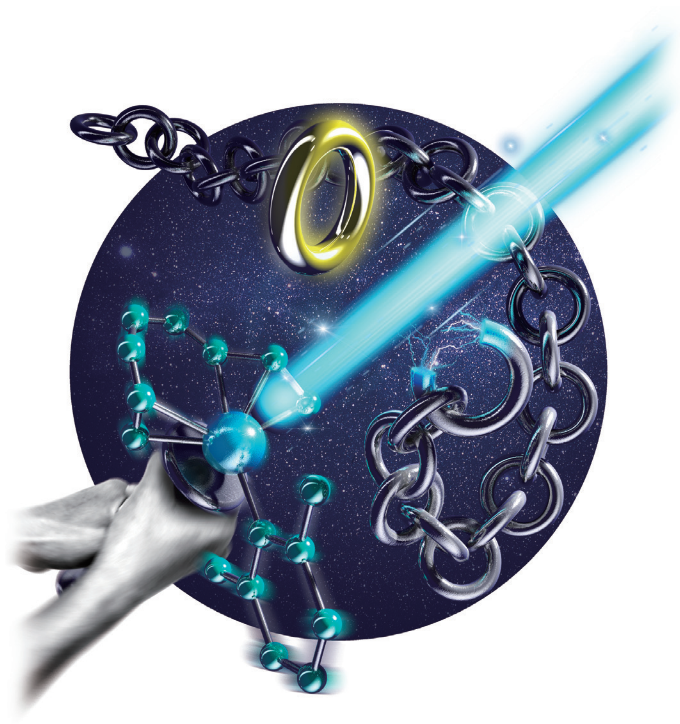
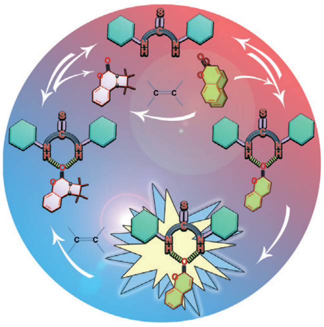
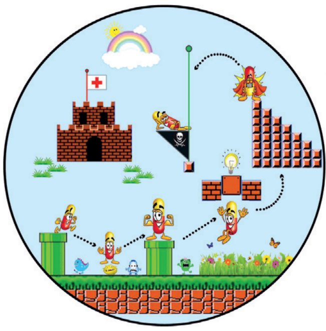
Strong C–F bonds ...



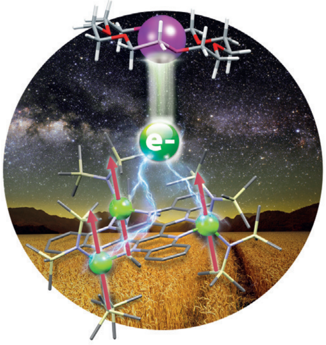
… were cut by an anionic nickel complex to incorporate the alkyl chains of the alkyl fluorides into the desired coupling products. In their Communication on page 5550 ff., N. Kambe, T. Iwasaki, and co-workers describe the nickel-catalyzed regio- and stereoselective multicomponent coupling of alkyl fluorides, aryl Grignard reagents, and two molecules of 1,3-butadiene, showcasing the unique reactivity of anionic bis(allyl)nickel complexes towards C–F bonds.

Photochemistry
How thiourea catalysts enhance the efficiency of the intermolecular [2+2] photocycloaddition of coumarin with tetramethylethylene is elucidated by J. Sivaguru, M. P. Sibi, and co-workers in their Communication on page 5446 ff.





Photodynamic Therapy
In their Communication on page 5477 ff., W. Tan and co-workers show that a photosensitizer–MnO_2 nanosystem depletes intracellular glutathione and generates singlet oxygen with light irradiation, thus increasing its efficiency in killing cancer cells.



Molecular Magnets
The $[\mathrm{HAN}]^{\bullet-}$ radical anion is synthesized and transferred intact to $\mathrm{Co}^{\mathrm{II}}$ as described by R. A. Layfield et al. in their Communication on page 5521 ff. The resulting complex anion $[\{(\mathrm{HAN})\{\mathrm{Co}(\mathrm{N}')_2\}_3]^-$ is a rare radical-bridged trimetallic complex.

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Editorial

"... Most transition-metal catalysts and organocatalysts do not meet the requirements for modern industrial manufacturing processes. Their main limitation is low efficiency. The need to develop highly efficient catalysts and related catalytic reactions is a never-ending challenge in synthetic chemistry ..."
Read more in the Editorial by Qi-Lin Zhou.

Service

Author Profile

"When I was eight, I wanted to be a surgeon. Chemistry is fun because there is always something new and it is full of surprises ..."
This and more about Wolfgang Kroutil can be found on page 5372.

News

N. Metzler-Nolte

E. A. Lemke

R. Schlögl

J. M. Thomas

Highlights

DNAzymes

J. Wirmer-Bartoschek,
H. Schwalbe* **5376 – 5377**

Understanding How DNA Enzymes Work

Tied up in knots: The crystal structure of a DNA enzyme in its post-catalytic state was solved. The results provide insight into the structural possibilities for DNA and the mechanism of DNA catalysis.

Essays

History of Science

B. Friedrich* **5378 – 5392**

How Did the Tree of Knowledge Get Its Blossom? The Rise of Physical and Theoretical Chemistry, with an Eye on Berlin and Leipzig

W. Ostwald

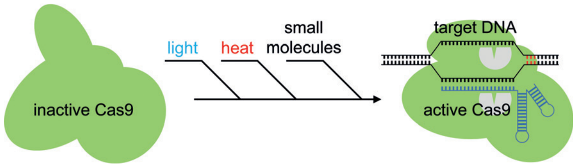
“Physical chemistry is not just a branch on but the blossom of the tree of knowledge,” declared Ostwald, a most vocal advocate of his field, conceived as the basis for all of chemistry. This Essay describes the historical development of physical and theoretical chemistry with a focus on Berlin and Leipzig, its foremost centers in Germany.

Minireviews

Gene Regulation

W. Zhou, A. Deiters* **5394 – 5399**

Conditional Control of CRISPR/Cas9 Function



Tools for genome editing: CRISPR/Cas9, an efficient and customizable genome engineering tool, has a major impact on modern biology. Conditional control of its function not only expands the applicability of gene editing and gene activation, but also provides researchers with a versatile toolbox for temporal and spatial control of gene function.

For the USA and Canada:
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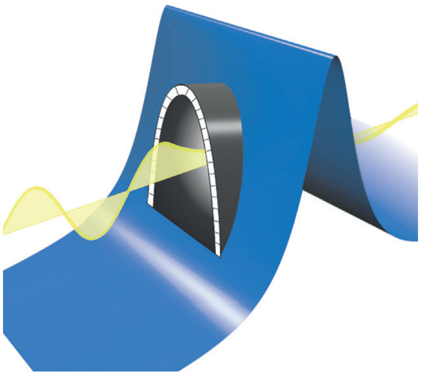
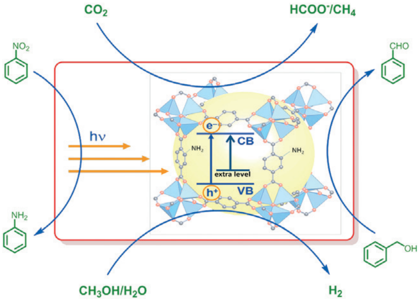
Reviews



Tunnel vision: The quantum mechanical tunnel effect is increasingly found to influence many chemical reactions. Although it can only be detected indirectly in experiments, computational investigations allow direct observation. Here, we highlight cases in which the tunnel effect changes reaction paths and branching ratios, enables chemical reactions in an astrochemical environment, and influences biochemical processes.

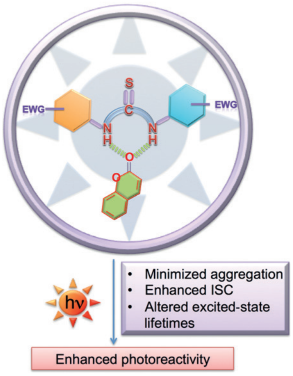
Atom Tunneling

MOFs, filling up with sun: Metal–organic frameworks (MOFs) can be constructed from light-absorbing units—organic linkers and metal complexes—thus offering the possibility of photoexcitation and charge separation. The advantages of using MOFs in photocatalysis, in particular in H_2 evolution and CO_2 reduction, are discussed.



Photocatalysis with MOFs

Communications

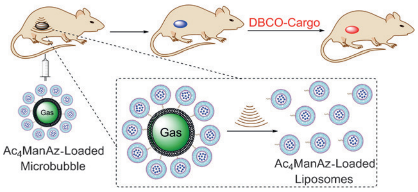


Thiourea catalysts enhance the efficiency of the intermolecular [2+2] photocycloaddition of coumarin with tetramethylethylene by a combination of minimized aggregation, enhanced intersystem crossing (ISC), and altered excited-state lifetime(s). A third mechanistic pathway for thiourea-mediated photocatalysis has thus been revealed.

Photochemistry

Frontispiece

What's that sound? High ultrasound pressure induces microbubble permeation and release of an azido sugar (Ac_4ManAz), which can be taken up by the surrounding cancer cells. The azido-modified cells can subsequently be labeled and treated with dibenzocyclooctyne (DBCO)-bearing therapeutics using click chemistry. This method could easily be adapted to a variety of cancers and cancer therapies.



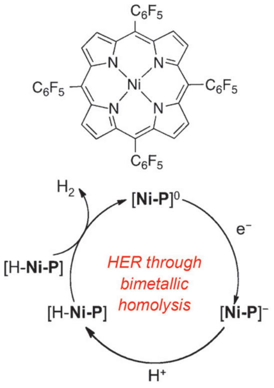
Cell Labeling

Electrocatalysis

Y. Z. Han, H. Y. Fang, H. Z. Jing, H. L. Sun, H. T. Lei, W. Z. Lai,* R. Cao* **5457 – 5462**

Singly versus Doubly Reduced Nickel Porphyrins for Proton Reduction: Experimental and Theoretical Evidence for a Homolytic Hydrogen-Evolution Reaction

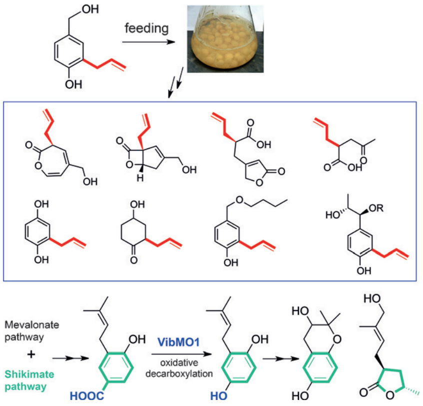
Learning to understand HER: A nickel porphyrin bearing four *meso*-C_6F_5 groups catalyzed H_2 evolution from acetic acid and trifluoroacetic acid by different mechanisms initiated by doubly and singly reduced species, respectively. Experimental and theoretical evidence suggest that bimetallic homolysis of a hydride intermediate formed by oxidative protonation of singly reduced species may be involved in the catalytic cycle.



Biosynthesis

Y.-L. Yang, H. Zhou, G. Du, K.-N. Feng, T. Feng, X.-L. Fu, J.-K. Liu,* Y. Zeng* ———— **5463 – 5466**

A Monooxygenase from *Boreostereum vibrans* Catalyzes Oxidative Decarboxylation in a Divergent Vibralactone Biosynthesis Pathway



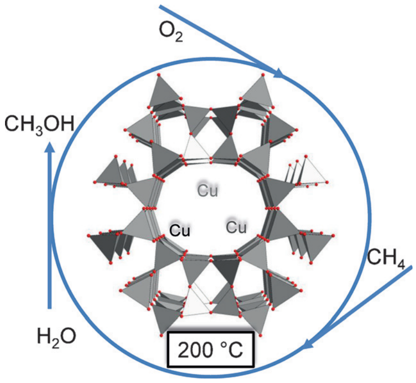
One to all and all from one: A monooxygenase (VibMO1) was identified that converts prenyl 4-hydroxybenzoate into prenylhydroquinone for the biosynthesis of vibralactones and other meroterpenoids in the basidiomycete *B. vibrans*. Based on the traditional platform of precursor-directed biosynthesis, divergent pathways were demonstrated to produce skeletally different compounds from a single precursor.

Methane to Methanol Conversion

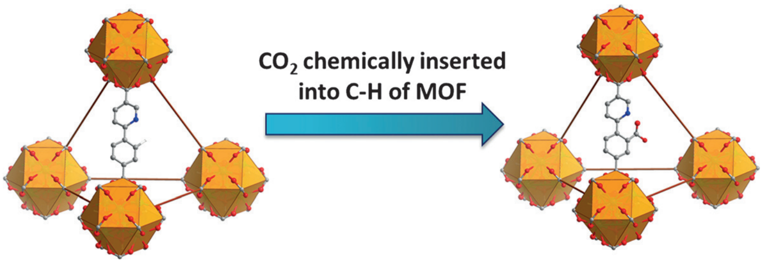
P. Tomkins, A. Mansouri, S. E. Bozbag, F. Krumeich, M. B. Park, E. M. C. Alayon, M. Ranocchiari, J. A. van Bokhoven* ———— **5467 – 5471**

Isothermal Cyclic Conversion of Methane into Methanol over Copper-Exchanged Zeolite at Low Temperature

Under pressure: Direct, stepped oxidation of methane into methanol was realized in an isothermal reaction. Otherwise inactive copper clusters were activated by employing higher methane pressures. This method provides new material design and process development opportunities that enable direct conversion of methane into methanol.

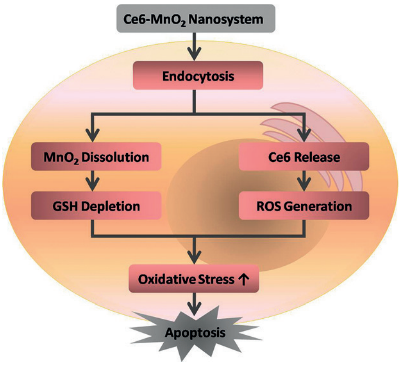


Heterogeneous Catalysis



Framed: CO_2 is utilized for heterogeneous C—H activation and carboxylation reactions on metal–organic frameworks (MOFs). The formed carboxylate groups serve as Brønsted acid sites and were shown to efficiently catalyze the methanolysis of epoxides. This work introduces a new avenue for CO_2 chemical transformations under mild reaction conditions.

Photodynamic Therapy

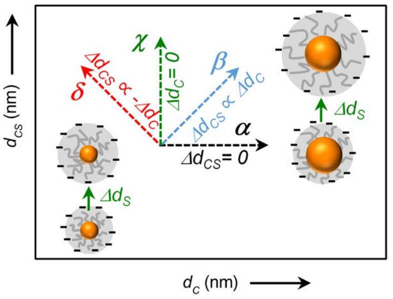


A photosensitizer–MnO_2 nanosystem has been designed for highly efficient photodynamic therapy. The nanosystem can react with intracellular glutathione (GSH), decreasing the level of GSH, releasing the photosensitizer completely, and thus improving the therapeutic efficiency.

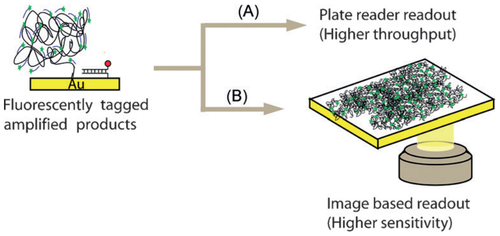
Inside Back Cover

Nanoparticle Uptake

A homologous library of gold nanoparticles coated with polyethylene glycol was synthesized, whereby the diameter of the gold cores, as well as the thickness of the shell of polyethylene glycol, was varied. Basic physicochemical parameters of this two-dimensional nanoparticle library were determined. Cell uptake of selected nanoparticles and their effect on basic structural and functional cell parameters were determined.



Mechanobiology

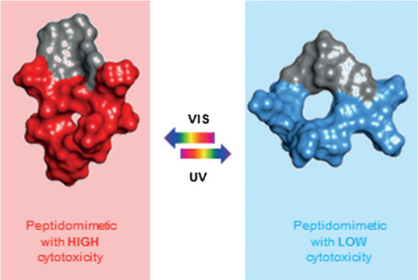


A mechanically induced catalytic amplification reaction (MCR) for readout of receptor-mediated forces in cells is described. This catalytic reaction is triggered by molecular piconewton forces. A) Dehybridization of FISH probe; B) direct imaging.

Photoswitchable Drugs

O. Babii, S. Afonin, L. V. Garmanchuk,
V. V. Nikulina, T. V. Nikolaienko,
O. V. Storozhuk, D. V. Shelest,
O. I. Dasyukevich, L. I. Ostapchenko,
V. Iurchenko, S. Zozulya, A. S. Ulrich,*
I. V. Komarov* **5493 – 5496**

Direct Photocontrol of Peptidomimetics: An Alternative to Oxygen-Dependent Photodynamic Cancer Therapy

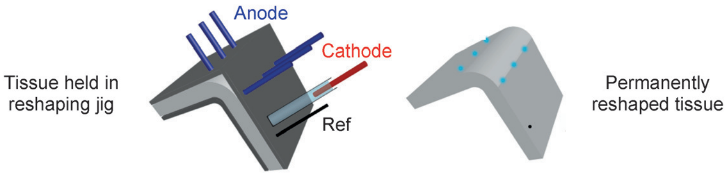


Leading light: A diarylethene-derived peptidomimetic is presented that is suitable for oxygen-independent photocontrolled cancer therapy since the light-sensitive molecule is not a mediator but the cytotoxic agent. The gramicidin S derivative exists in two thermally stable photoforms, and the isomer generated by visible light shows much stronger toxicity against tumor cells than the UV-generated isomer.

Cartilage Remodeling

B. M. Hunter, J. Kallick, J. Kissel,
M. Herzig, C. Manuel, D. Protsenko,
B. J. F. Wong,* M. G. Hill* **5497 – 5500**

Controlled-Potential Electromechanical Reshaping of Cartilage

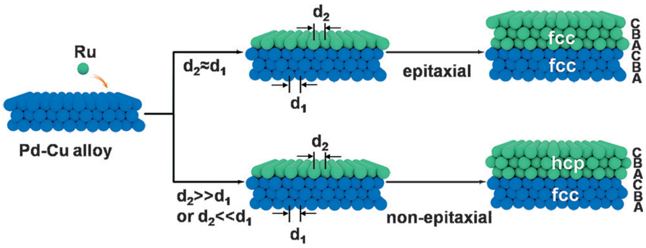


Changing shape: In a molecular-based alternative to "cut-and-suture" cartilage surgery, electrodes are inserted into tissues held under mechanical deformation. Electrolysis at the water-oxidation limit generates highly localized regions of low pH that chemically relax the stressed tissue. Re-equilibration to physiological pH yields cartilage permanently remodeled to the new shape of the jig.

Nanoparticles

Y. Yao, D. S. He, Y. Lin, X. Feng, X. Wang,
P. Yin, X. Hong, G. Zhou, Y. Wu,*
Y. Li* **5501 – 5505**

Modulating fcc and hcp Ruthenium on the Surface of Palladium–Copper Alloy through Tunable Lattice Mismatch

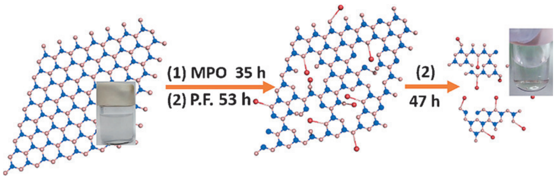


On the face of it: Epitaxial growth of the rare face-centered cubic (fcc) Ru phase is possible on the surface of a Pd–Cu alloy to build a unique Pd–Cu@Ru yolk–shell structure. Through varying the lattice spacing of the Pd–Cu substrate both fcc and hexagonal close packed (hcp) Ru can be selectively grown.

Hexagonal Boron Nitride

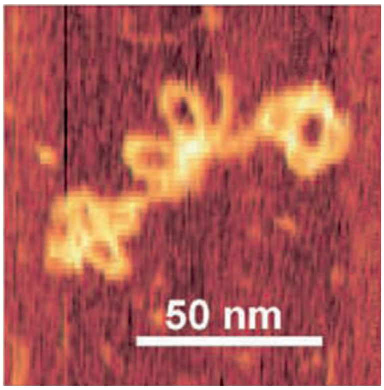
R. Kurapati, C. Backes, C. Ménard-Moyon,
J. N. Coleman, A. Bianco* **5506 – 5511**

White Graphene undergoes Peroxidase Degradation



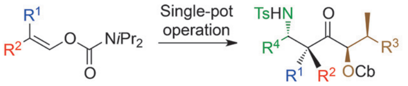
Between the sheets: Biodegradability of hexagonal boron nitride (hBN) nanosheets was investigated using different conditions including treatment with human myeloperoxidase (MPO) and the UV-assisted photo-Fenton (P.F.) reaction. The photo-Fenton reaction almost completely degrades hBN nanosheets. These studies are important for designing safer hBN-based materials for biomedical uses and polymer-composites.

DNA Nanotechnology



Chained up: Mechanically bonded daisy chain rotaxanes (DCRs) made from double-stranded DNA (dsDNA) comprise a macrocycle connected to an axle bearing a stopper at its end that circumscribes the axle of a second such unit and vice versa (see image). Mechanically interlocked DCRs have higher degrees of freedom in their movement along the thread axle than the DCR-precursors in which the macrocycles are still hybridized to the axle.

Quaternary Carbons



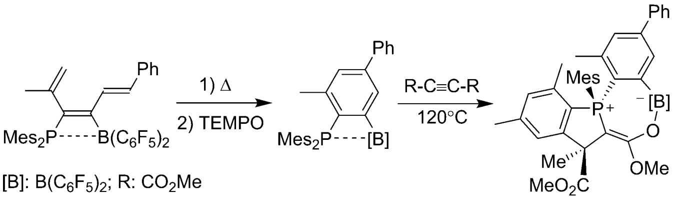
The formation of several new stereogenic centers via α,α-disubstituted ketone enolates as single stereoisomers is enabled by an approach that combines metalation, carbonyl addition, and carbamoyl transfer. A series of aldol and Mannich products are obtained from enol carbamates with excellent diastereomeric ratios in a single-pot operation.

Molecular Magnetism

Back Cover

The $[HAN]^{\bullet-}$ radical anion (see scheme, left) is synthesized as a stable potassium salt and transferred intact to Co^{II}. The resulting complex anion $[\{(HAN)\{Co(N'')_2\}_3]^-$ is a rare radical-bridged trimetallic complex, with very strong antiferromagnetic exchange between the Co^{II} ions and the non-innocent ligand.

Frustrated Lewis Pairs

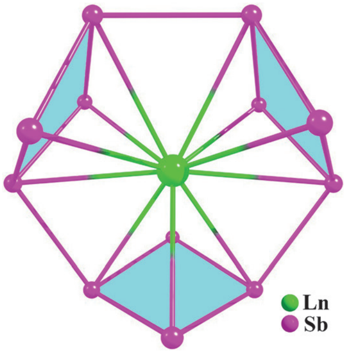


The phosphorus/boron-substituted hexatriene gave the phenylene-bridged P/B frustrated Lewis pairs (FLP) by thermally induced electrocyclic ring closure followed by oxidation with the 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical. The thermally robust FLP reacted with dimethyl acetylenedicarboxylate by C–C coupling with the mesityl group (see picture).

Antiaromaticity

X. Min, I. A. Popov, F. X. Pan, L. J. Li, E. Matito, Z. M. Sun,* L. S. Wang, A. I. Boldyrev* **5531 – 5535**

All-Metal Antiaromaticity in Sb_4-Type Lanthanocene Anions

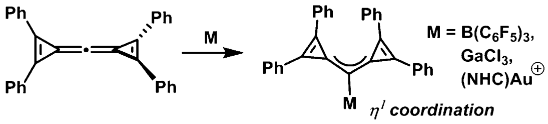


Several unique lanthanocene compounds, $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ (Ln = La, Y, Ho, Er, or Lu), were isolated as the K([2.2.2]crypt) salts and characterized by single-crystal X-ray diffraction. They feature a central lanthanide atom coordinated by three rhombic Sb_4 units. Chemical bonding analysis revealed all three *cyclo*-Sb_4 units in $[Ln(\eta^4\text{-}Sb_4)_3]^{3-}$ to be locally π-antiaromatic.

Bent Allenes

C. Pranckevicius, L. Liu, G. Bertrand, D. W. Stephan* **5536 – 5540**

Synthesis of a Carbodicyclopropenylidene: A Carbodicarbene based Solely on Carbon

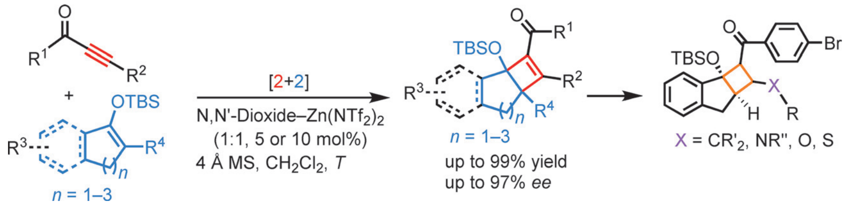


Carbo loading: The first carbodicarbene stabilized by flanking cyclopropenylidenes is accessed by deprotonation of the corresponding triafulvene cyclopropenium salt. Main-group and transition-metal complexes of it have been accessed, and have revealed the high σ-donating ability, and exclusive η^1 binding of this neutral all carbon ligand.

Asymmetric Catalysis

T. F. Kang, S. L. Ge, L. L. Lin, Y. Lu, X. H. Liu,* X. M. Feng* **5541 – 5544**

A Chiral *N*,*N*′-Dioxide–Zn^{II} Complex Catalyzes the Enantioselective [2+2] Cycloaddition of Alkynones with Cyclic Enol Silyl Ethers

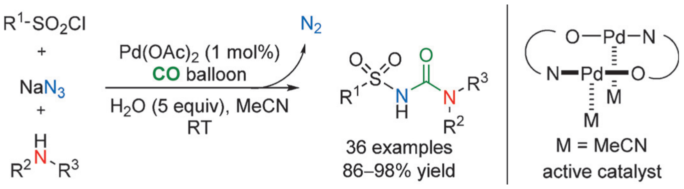


Fused cyclobutenes: The title reaction was realized by using a chiral *N*,*N*′-dioxide–$Zn(NTf_2)_2$ catalyst. The reaction functions well for a variety of terminal alkynes and cyclic enol silyl ethers, providing good to excellent enantioselectivity. Internal alkynes were utilized in this reaction to give fully substituted cyclobutenes. TBS = *tert*-butyldimethylsilyl.

Reaction Mechanisms

J. Zhao, Z. Li, S. Song, M. Wang, B. Fu, Z. Zhang* **5545 – 5549**

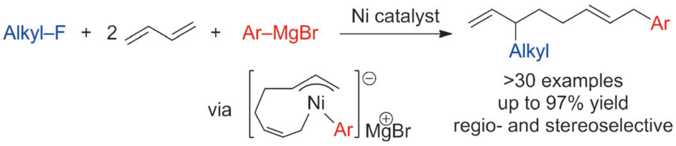
Product-Derived Bimetallic Palladium Complex Catalyzes Direct Carbonylation of Sulfonylazides



Doubling up on Pd: A product-derived bimetallic palladium complex catalyzes a sulfonylazide-transfer reaction with the σ-donor/π-acceptor ligand CO, which is advantageous given its broad substrate scope, high efficiency, and mild reaction conditions under 1 bar of CO at room temperature. Mechanistically, the generation of the sulfonylurea-derived bridged bimetallic palladium species is the crucial step for this catalytic cycle.

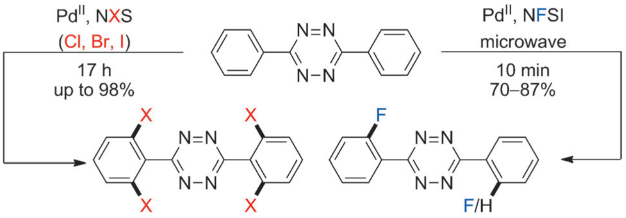
Multicomponent Reactions

Front Cover



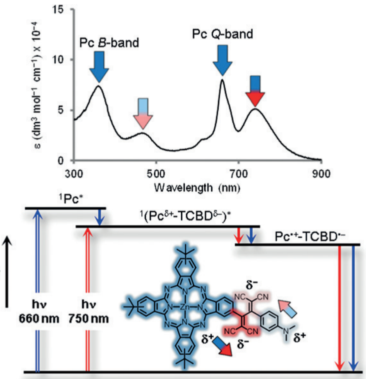
Change the charge: An anionic nickel complex catalyzes the trapping of dimerized 1,3-butadiene by alkyl fluorides and thus enables the regioselective dimerization and alkylarylation of this compound. The overall process entails the consecutive formation of three carbon–carbon bonds and provides access to 1,6-octadienes with alkyl and aryl groups in the 3- and 8-position, respectively.

C–H Activation



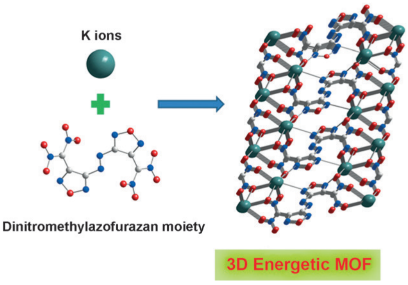
Ring me up: The selective palladium-catalyzed *ortho*-C–H halogenation of *s*-tetrazine has been achieved. Fast fluorination is performed within 10 minutes by using *N*-fluorobenzenesulfonimide (NFSI). By this method, di-, tri-, and tetrahalogenated aryltetrazines are accessible in a straightforward manner.

Photophysics



Two Pc-TCBD-aniline conjugates (phthalocyanine–tetracyanobutadiene–aniline conjugates) have been prepared. The intense ground-state charge transfer between Pc and TCBD, the panchromatic absorption of these derivatives in the visible and near-infrared regions, the low HOMO–LUMO gaps, and the photoinduced electron-transfer behavior upon photoexcitation render these systems promising materials for applications in molecular photovoltaics.

Energetic Materials

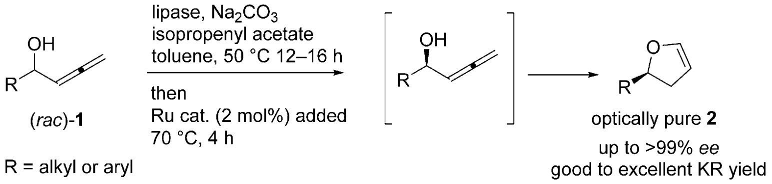


A bundle of energy: Potassium 4,4′-bis(dinitromethyl)-3,3′-azofurazanate, composed of K⁺ ions and dinitromethylazofurazan moieties, was synthesized and isolated as a nitrogen-rich 3D metal–organic framework (MOF). The material shows attractive energetic properties which make it a promising candidate as a next-generation green primary explosive. Atom colors: C = gray; O = red; N = blue.

Asymmetric Catalysis

B. Yang, C. Zhu, Y. Qiu,
J.-E. Bäckvall* ______ **5568 – 5572**

Enzyme- and Ruthenium-Catalyzed Enantioselective Transformation of α-Allenic Alcohols into 2,3-Dihydrofurans



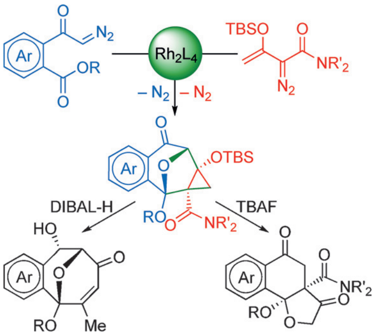
Enzyme- and ruthenium catalysis: In an efficient one-pot enzyme- and ruthenium-catalyzed enantioselective transformation of α-allenic alcohols, an enzymatic kinetic resolution (KR) was followed by a cycloisomerization step thought to involve a ruthenium carbene intermediate. The reaction provided a variety of 2-substituted 2,3-dihydrofurans with excellent enantioselectivity (see scheme).

Annulation

Q.-Q. Cheng, J. Yedoyan, H. Arman,
M. P. Doyle* ______ **5573 – 5576**

Dirhodium(II)-Catalyzed Annulation of Enoldiazoacetamides with α-Diazoketones: An Efficient and Highly Selective Approach to Fused and Bridged Ring Systems

Inside Cover

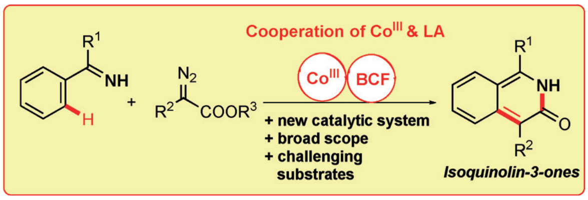


One, two, three: A dirhodium(II)-catalyzed annulation reaction between two structurally different diazocarbonyl compounds was achieved with excellent chemo-, regio-, and diastereoselectivity under mild conditions. This reaction, along with further one-step transformations, allows the efficient construction of three natural-product-related ring systems from two easily accessible diazo compounds with one commercially available catalyst.

C–H Activation

J. H. Kim, S. Greßies,
F. Glorius* ______ **5577 – 5581**

Cooperative Lewis Acid/Cp*$\mathrm{Co^{III}}$ Catalyzed C–H Bond Activation for the Synthesis of Isoquinolin-3-ones

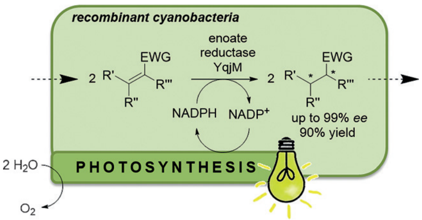


$\mathrm{Co^{III}}$-operative catalysis: The first facile route toward the synthesis of isoquinolin-3-ones through cooperative C–H bond activation with $B(C_6F_5)_3$ (BCF in picture) and Cp*$\mathrm{Co^{III}}$ (Cp* = C_5Me_5) is presented. The newly developed catalytic system is highly reactive, thus unstable NH imines can serve as substrates.

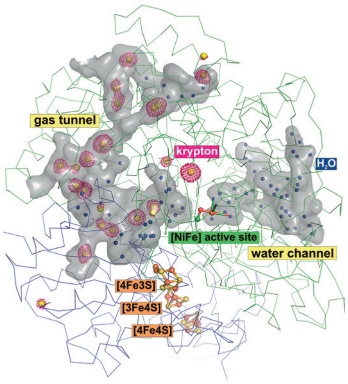
Biotechnology

K. Köninger, Á. Gómez Baraibar,
C. Mügge, C. E. Paul, F. Hollmann,
M. M. Nowaczyk,
R. Kourist* ______ **5582 – 5585**

Recombinant Cyanobacteria for the Asymmetric Reduction of C=C Bonds Fueled by the Biocatalytic Oxidation of Water

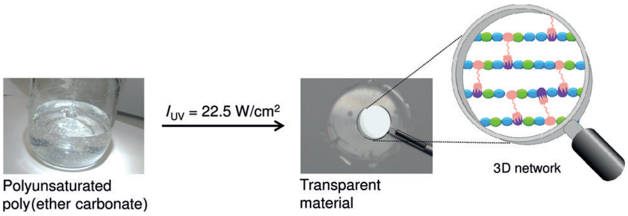


Useful bacteria: Recombinant cyanobacteria are able to perform enantioselective redox reactions without the addition of cofactors or sacrificial substrates. This increases the atom efficiency of the process and removes an intrinsic limitation for the use of enzymes in mainstream industrial processes. EWG = electron-withdrawing group.



At the end of the tunnel: The active site in [NiFe] hydrogenases is buried deep within the protein and accessible to gas-phase substrates through tunnels. The structure of the O_2-tolerant, membrane-bound [NiFe] hydrogenase of *Ralstonia eutropha* has now been determined from krypton-derivatized protein crystals. The positions of the krypton atoms and corresponding calculations provided information on the gas tunnel network within the enzyme.

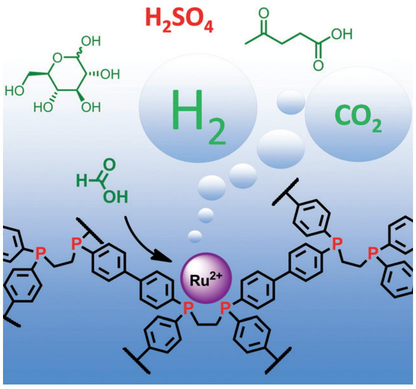
[NiFe] Hydrogenase



Well connected: Transparent films were obtained by cross-linking polyunsaturated poly(ether carbonate)s, which were obtained by the one-pot multicomponent polymerization of CO_2, epoxide, maleic anhydride, and allyl glycidyl ether. The presence of double bonds substituted with electron-acceptor and electron-donor groups accelerates the curing step and enables the facile preparation of coatings by UV-initiated free-radical curing.

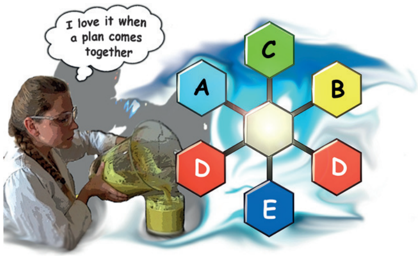
Transparent Materials

High activity, selectivity, and recyclability are exhibited by Ru-loaded phosphine polymers, which are promising heterogeneous catalysts for on-site hydrogen production from biomass-derived formic acid. These catalysts can be used to selectively remove formic acid from crude reaction mixtures.



Biomass Utilization

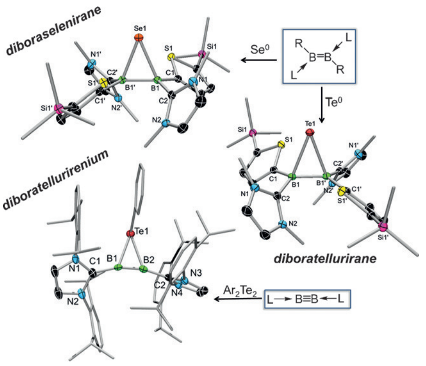
Bulk discount on hexaarylbenzenes (HABs): A rational and scalable synthesis of uncommon and highly functionalized HABs utilizes 4-nitroaniline as the starting material. This approach can potentially provide 18 novel HABs and 26 substitution geometries in total, which are not available or only difficult to obtain by standard techniques.



Substituted Hexaarylbenzenes

Main-Group Chemistry

Heavy heterocycles: The reaction of diborenes with Se and Te resulted in the formation of diboraseleniranes and diboratelluriranes, while the reaction of diborynes with diarylditellurides yielded diboratellurirenium cations with aryltelluride anions. Such reactions are unique to boron–boron multiple bonds because of their reducing nature and the relatively low electronegativity of boron.



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A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

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