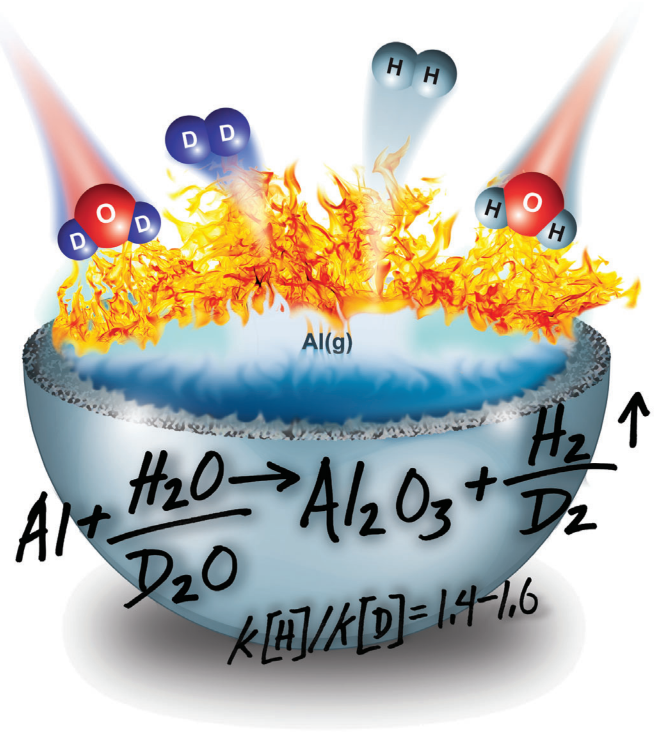
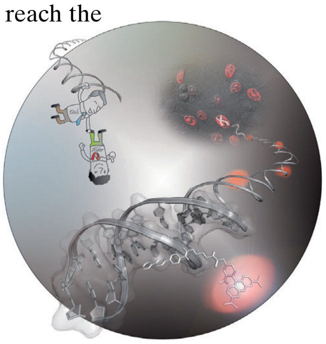
Kinetic limitation ...

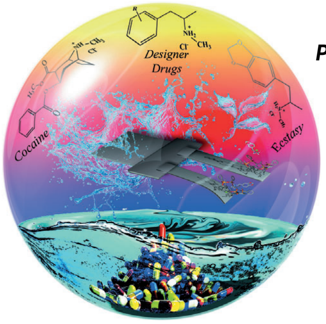


… of nanoparticulate aluminum (nAl) combustion has never been observed. Therefore the reaction is often described as solely diffusion-controlled. In their Communication on page 9218 ff., B. C. Tappan and co-workers present the combustion analysis of nAl with H_2O or D_2O and measure a distinct kinetic isotope effect. This observation verifies that reaction kinetics play a major role in determining the global burning rate as particle sizes reach the nanoscale.

DNA Labeling

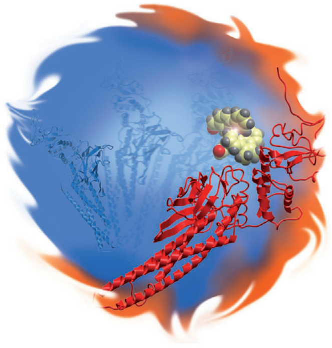
U. Rieder and N. W. Luedtke report the incorporation of 5-vinyl-2′-deoxyuridine (VdU) into cellular DNA in their Communication on page 9168 ff. The VdU can then be visualized through Diels–Alder reactions with fluorescent tetrazines.





Protein Mass Spectrometry

In their Communication on page 9183 ff. Bergese, E. Dalcanale, et al. describe a supramolecular nanomechanical device for the label-free detection of the whole class of methamphetamines in water.



STAT3 Dimerization

A substitutionally inert, organometallic rhodium(III) complex inhibits the dimerization of STAT3 in vitro and in vivo, as reported by D.-L. Ma, C.-H. Leung, H.-M. D. Wang et al. in their Communication on page 9178 ff.

How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 6201–606-331
Telephone: (+49) 6201–606-315

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Fax: (+49) 6201–606-331
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Courier Services:
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Regular Mail:
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Service

Author Profile

"If I were a car I would be a Formula One car. My favorite saying is "Chance favors only the prepared mind" (Louis Pasteur). …"
This and more about Yoichiro Kuninobu can be found on page 9122.

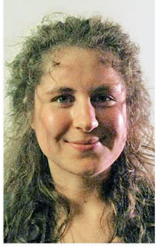
News

R. D. Süssmuth

A. B. Smith III

S. Linic

G. H. Clever



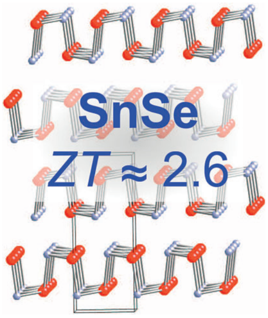
F. Schoenebeck

Books

Highlights

Thermoelectric Materials

A thermoelectric figure of merit that is unprecedentedly high has been observed in SnSe crystals. This finding suggests that bulk materials with a layered structure and highly anharmonic lattice vibrations can feature an intrinsically low thermal conductivity and high thermoelectric efficiency. Together with other recent findings in this field, it urges us to revisit basic design principles for thermoelectric materials.



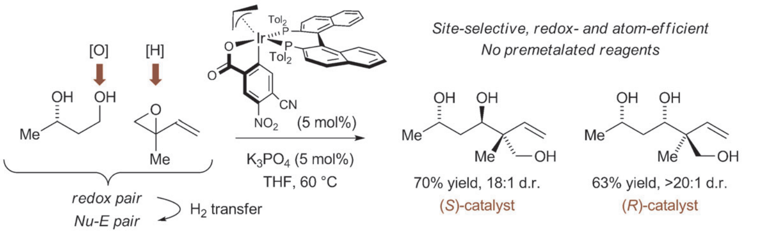
Essays

Drug Development

Concerted effort: What is the current state of the art and science of drug design and discovery? How can the cooperation between academic investigators and industry be improved? This Essay is meant to inspire and motivate, especially those in academia, to think about how to use their expertise to contribute to the drug discovery and development process. Photograph: Fotolia.

Minireviews

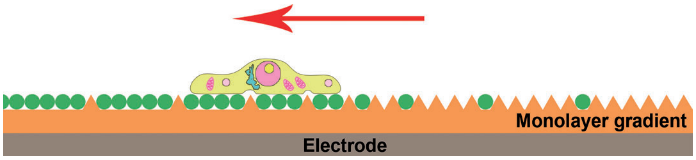
Enantioselective Catalysis



Borrowing with interest: The concept of exploiting alcohols and unsaturated reactants for the redox-triggered generation of nucleophile–electrophile pairs reinvents the chemistry of carbonyl addition, enabling a broad, new family of catalytic enantioselective C–C couplings.

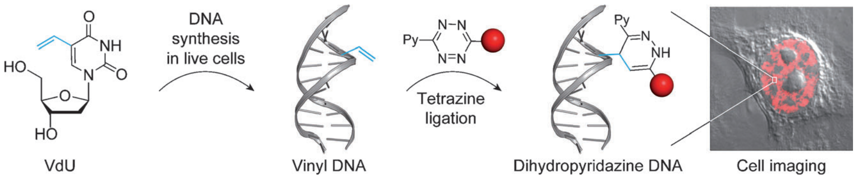
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. 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

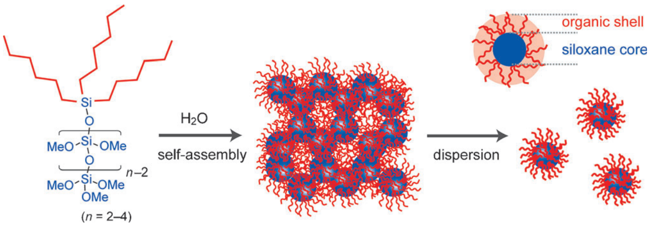


Biased toward gradient formation: The use of electrochemistry to generate gradients (see picture) has many benefits, such as the ability to generate dynamic solution and surface gradients, the integration of electronics, and compatibility with automation. The resulting gradients have been employed extensively for biological and technological applications, such as high-throughput screening, high-throughput deposition, and device development.

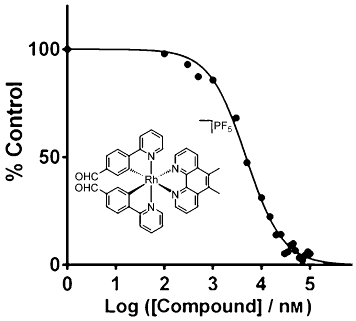
Communications



Diels–Alder on DNA: 5-Vinyl-2′-deoxyuridine (VdU) is metabolically incorporated into cellular DNA where it can be visualized by using inverse electron demand Diels–Alder reactions with fluorescent tetrazines. VdU–tetrazine ligation reactions are rapid ($k \approx 0.02\ \text{M}^{-1}\text{s}^{-1}$) and chemically orthogonal to alkyne–azide “click” reactions, thereby enabling time-resolved, multicolor labeling of DNA synthesis in individual cells.



Self-assembled hybrid nanoparticles: A new type of oligosiloxane precursor self-assembles into reverse-micellar mesostructures, which can be transformed to nanoparticles with a siloxane core and an organic shell by dispersion in nonpolar organic solvents.



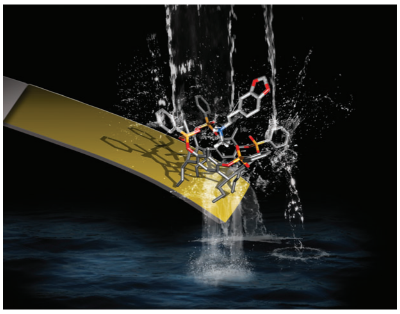
Saving your skin: A rhodium(III) complex is the first example of a substitutionally inert, Group 9 organometallic compound which serves as a direct inhibitor of the signal transducer and activator of transcription 3 (STAT3) dimerization. The rhodium(III) complex inhibited STAT3 activity in vitro and in vivo and showed potent and selective anticancer activity against melanoma cell lines and melanoma xenografts in an in vivo mouse model.

Drug Detection

E. Biavardi, S. Federici, C. Tudisco, D. Menozzi, C. Massera, A. Sottini, G. G. Condorelli, P. Bergese,* E. Dalcanale* **9183 – 9188**

Cavitand-Grafted Silicon Microcantilevers as a Universal Probe for Illicit and Designer Drugs in Water

Inside Back Cover

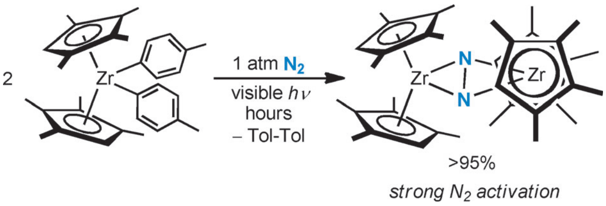


Get them all! The widespread diffusion of methamphetamines and related designer drugs is a great challenge for our society, with significant impact on human health and social security. A cavitand-grafted microcantilever device has been developed that is able to detect the whole class of methamphetamine drugs in water. This method acts independently of the type of residue attached to the target methylammonium unit.

Photochemical Nitrogen Reduction

G. W. Margulieux, S. P. Semproni, P. J. Chirik* **9189 – 9192**

Photochemically Induced Reductive Elimination as a Route to a Zirconocene Complex with a Strongly Activated N_2 Ligand



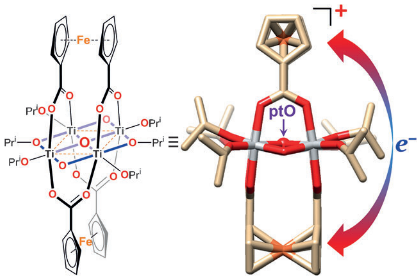
The zirconocene dinitrogen complex $[\{(\eta^5\text{-}C_5Me_4H)_2Zr\}_2(\mu_2,\eta^2,\eta^2\text{-}N_2)]$ was synthesized by photochemical reductive elimination from the corresponding Zr bis(aryl) or aryl hydride complexes. Mechanistic studies support the intermediacy of zirconocene arene complexes that in the absence of sufficient N_2 promote C–H activation. When N_2 is in excess arene displacement gives rise to strong dinitrogen activation.

Titanium-Oxo Clusters

Z. Liu, J. Lei, M. Frasconi, X. Li, D. Cao, Z. Zhu, S. T. Schneebeli, G. C. Schatz, J. F. Stoddart* **9193 – 9197**

A Square-Planar Tetracoordinate Oxygen-Containing Ti_4O_{17} Cluster Stabilized by Two 1,1′-Ferrocenedicarboxylato Ligands

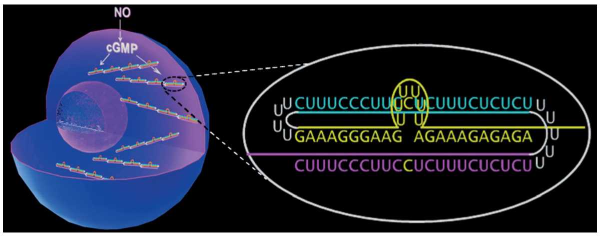
A square-planar tetracoordinate oxygen (ptO) is realized in an edge-sharing Ti_4O_{17} octahedron tetramer stabilized by two orthogonal 1,1′-ferrocenedicarboxylato ligands. Whereas the two ferrocene units are separated spatially by the ptO with an Fe⋯Fe separation of 10.4 Å, the electronic communication between them still takes place as indicated by the cluster's two distinct one-electron electrochemical oxidation processes.



cGMP Capture

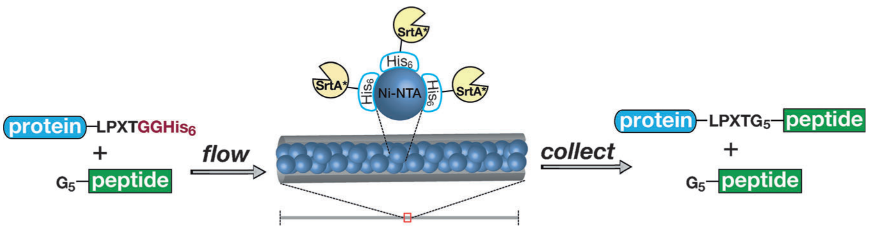
C. Kröner, M. Thunemann, S. Vollmer, M. Kinzer, R. Feil, C. Richert* **9198 – 9202**

Endless: A Purine-Binding RNA Motif that Can Be Expressed in Cells



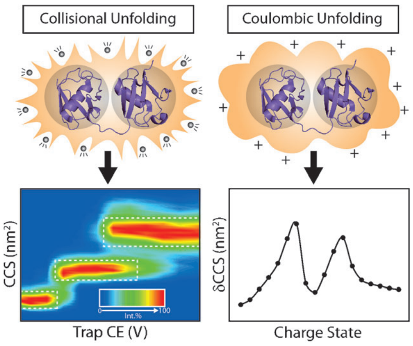
A sink for a second messenger: A de novo designed RNA motif, termed *endless*, binds the second messenger 3′,5′-cyclic guanosine monophosphate (cGMP) with low micromolar affinity. The binding pocket of *endless* does not involve the strand termini, which makes it suitable for expression in cells. There, it suppresses NO-induced cGMP signals, which suggests that it can act as a genetically encoded cGMP sink.

Protein Modification



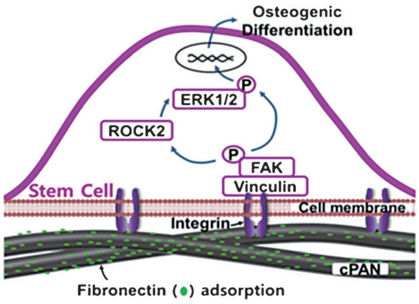
Flow-based sortagging: A simple Ni-NTA flow reactor containing the immobilized enzyme sortase A was constructed and used to perform the sortase-mediated ligation reaction at low substrate concentrations. By limiting substrate contact time with sortase, side reactions were suppressed and pure protein bioconjugates were obtained directly from the reactor effluent.

Protein Structures



Gas-phase unfolding is used as a means to determine the number of autonomously folded domains within monomeric proteins. Ion-mobility mass spectrometry data show a strong, positive correlation between the number of protein unfolding transitions observed in the gas phase and the number of known domains within a group of sixteen proteins ranging from 8–78 kDa. CCS = collision cross-section.

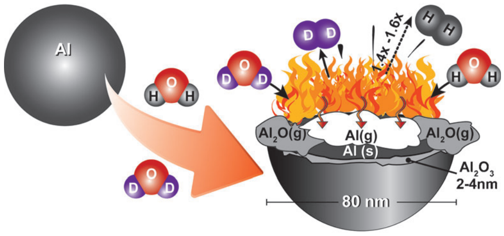
Scaffolds for Tissue Engineering



Carbonized polyacrylonitrile (cPAN) scaffolds prepared from electrospinning–lyophilization–carbonization have a 3D macrostructure with graphite-like molecular structure that could not be achieved from pure carbon materials. Fabrication of microporous 3D scaffolds of cPAN, which impose excellent biocompatibility and osteoinductivity, was demonstrated.

Nanoparticles

Front Cover

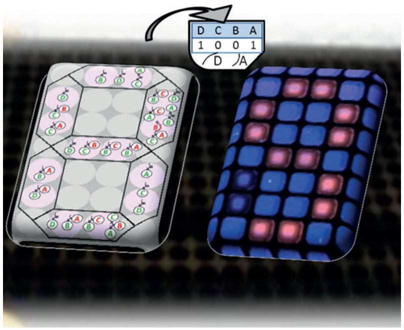


Burning insights: Kinetic limitation of nanoparticulate aluminum (nAl) combustion has never been observed and therefore is often described as solely diffusion controlled. The combustion analysis of nAl with H_2O or D_2O is presented and a distinct kinetic isotope effect measured. This first-ever observed kinetic isotope effect in metal combustion verifies that reaction kinetics play a major role in determining the global burning rate as particle sizes reach the nanoscale.

Molecular Automata

J. E. Poje, T. Kastratovic, A. R. Macdonald, A. C. Guillermo, S. E. Troetti, O. J. Jabado, M. L. Fanning, D. Stefanovic, J. Macdonald* ______ **9222 – 9225**

Visual Displays that Directly Interface and Provide Read-Outs of Molecular States via Molecular Graphics Processing Units

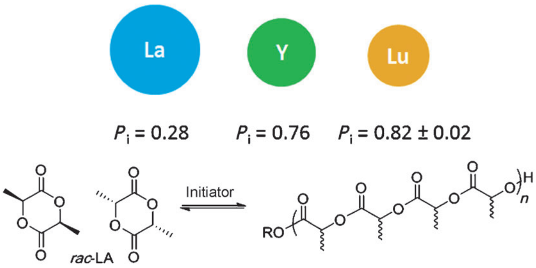


Molecular computing: Graphics processing units made from molecular circuits can monitor nucleic acids and output alphanumerical read-outs via a fluorescent display. A molecular 7-segment display, a molecular calculator able to add and multiply small numbers, and a molecular automaton able to diagnose viral nucleic acid sequences are reported. These units provide insight for the construction of autonomous biosensing devices and computing platforms devoid of electronics.

Polymerization Catalysis

C. Bakewell, A. J. P. White, N. J. Long,* C. K. Williams* ______ **9226 – 9230**

Metal-Size Influence in Iso-Selective Lactide Polymerization

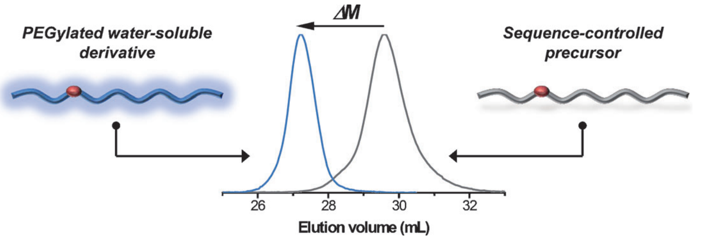


Small is beautiful: Lutetium phosphasalen complexes are developed as highly iso-selective initiators for the ring-opening polymerization of *rac*-lactide (LA), and show excellent rates and high degrees of polymerization control. The corresponding La derivative exhibits moderate heteroselectivity. The order of rates for the series of complexes is inversely related to metallic covalent radius.

Sequence-Controlled Polymers

S. Srichan, H. Mutlu, N. Badi, J.-F. Lutz* ______ **9231 – 9235**

Precision PEGylated Polymers Obtained by Sequence-Controlled Copolymerization and Postpolymerization Modification



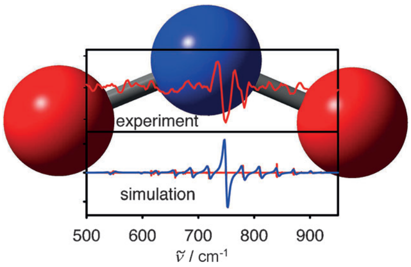
Precise and purposeful: PEGylated water-soluble polymers containing precisely positioned fluorescent, switchable, and reactive functionalities, such as pyrene, azobenzene, and activated ester groups, were prepared by sequence-controlled radical polymerization of donor styrene and acceptor *N*-substituted-maleimide comonomers, followed by postpolymerization modification (see picture).

Paramagnetic Raman Optical Activity

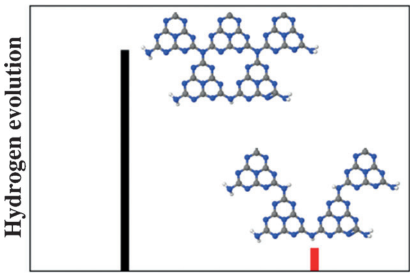
J. Šebestík,* P. Bouř* ______ **9236 – 9239**

Observation of Paramagnetic Raman Optical Activity of Nitrogen Dioxide

Paramagnetic gases: Paramagnetic Raman optical activity of nitrogen dioxide was observed for the first time and explained on the basis of angular momentum theory (see picture). The technique provides enhanced information about molecular properties, and the results suggest that the technique can be immediately used for discrimination and analysis of similar paramagnetic gases.



A recipe for success: Graphitic carbon nitride exhibited an internal quantum yield of 26.5 % at 400 nm when prepared by a specific tailored recipe. The activity was shown to be inversely proportional to the protonation status at specific nitrogen sites in heptazine units (see picture; N blue, C gray, H white). Theoretical results indicated that protonation significantly influences reductive power and charge migration to active sites.



Water Splitting

D. J. Martin, K. Qiu, S. A. Shevlin, A. D. Handoko, X. Chen, Z. Guo, J. Tang* ______ **9240 – 9245**

Highly Efficient Photocatalytic H_2 Evolution from Water using Visible Light and Structure-Controlled Graphitic Carbon Nitride

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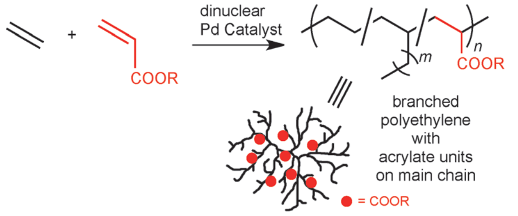

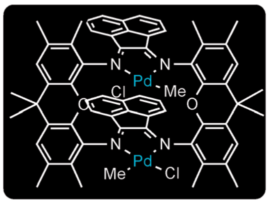

Double-decker: A dinuclear palladium complex with a double-decker structure promotes ethylene–acrylate copolymerization to produce a branched polymer with an acrylate unit in the polymer chain. The copolymer and its hydrolysis product, having COOH groups on the polymer chain, are soft and its cast film can be stretched. The cooperation of the two palladium centers is proposed to have a dinuclear effect on the copolymerization.

Homogeneous Catalysis

S. Takano, D. Takeuchi,* K. Osakada, N. Akamatsu, A. Shishido __ **9246 – 9250**

Dipalladium Catalyst for Olefin Polymerization: Introduction of Acrylate Units into the Main Chain of Branched Polyethylene

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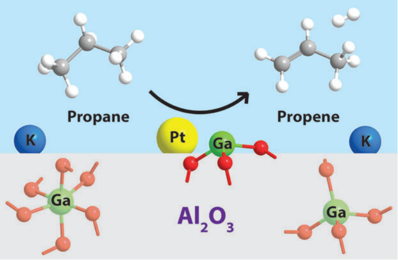

Alkane activation: The selective dehydrogenation of propane is achieved with a catalyst material consisting of 1000 ppm Pt, 3 wt % Ga, and 0.25 wt % K supported on alumina. The synergy between Ga and Pt results in a highly active and stable catalyst. A bifunctional active phase is proposed, in which coordinately unsaturated Ga^{3+} species are the active species and Pt functions as promoter.

Heterogeneous Catalysis

J. J. H. B. Sattler, I. D. Gonzalez-Jimenez, L. Luo,* B. A. Stears, A. Malek, D. G. Barton, B. A. Kilos, M. P. Kaminsky, T. W. G. M. Verhoeven, E. J. Koers, M. Baldus, B. M. Weckhuysen* ______ **9251 – 9256**

Platinum-Promoted Ga/Al_2O_3 as Highly Active, Selective, and Stable Catalyst for the Dehydrogenation of Propane

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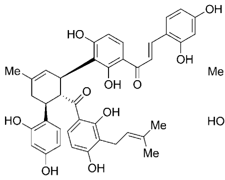
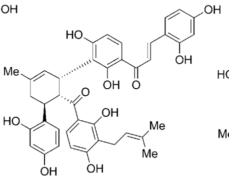
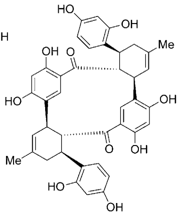
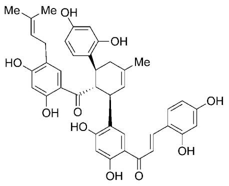

(−)-kuwanon I


(+)-kuwanon J


(−)-brosimone A


(−)-brosimone B

Four in a row: The first enantioselective total syntheses of the prenylflavonoid natural products (−)-kuwanon I, (+)-kuwanon J, (−)-brosimone A, and (−)-brosimone B have been accomplished based on a concise synthetic strategy. Key elements of the synthesis include a biosynthesis-inspired asymmetric Diels–Alder cycloaddition mediated by a chiral ligand/boron Lewis acid, as well as a process involving regioselective Schenck ene reaction, reduction, and dehydration.

Natural Products

J. Han, X. Li, Y. Guan, W. Zhao, W. D. Wulff,* X. Lei* ______ **9257 – 9261**

Enantioselective Biomimetic Total Syntheses of Kuwanons I and J and Brosimones A and B

Analytical Chemistry

A. Doménech-Carbó,*
M. T. Doménech-Carbó, S. Capelo,
T. Pasíes, I. Martínez-Lázaro **9262 – 9266**

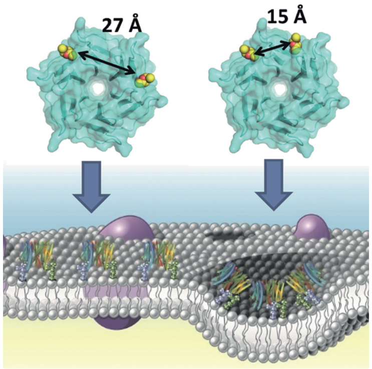
Dating Archaeological Copper/Bronze Artifacts by Using the Voltammetry of Microparticles

The dating game: A method for dating copper/bronze archaeological objects (see example) aged in atmospheric environments is proposed based on the measurement of specific voltammetric signals for cuprite and tenorite corrosion products. The tenorite/cuprite ratio increased with the corrosion time, fitting to a potential law that yielded a calibration curve usable for dating purposes.

Glycosciences

J. Arnaud, K. Tröndle, J. Claudinon,
A. Audfray, A. Varrot, W. Römer,*
A. Imberty* **9267 – 9270**

Membrane Deformation by Neolectins with Engineered Glycolipid Binding Sites

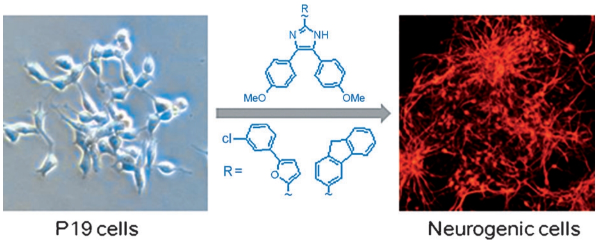


Neolectins, which are based on a β-propeller architecture, have been designed with controlled number and position of binding sites to decipher the role of multivalency on avidity to a glycosylated surface and on membrane dynamics of glycolipids. Whereas the avidity only depends on the presence of at least two binding sites, the ability to bend and invaginate membranes critically depends on the distance between two adjacent binding sites.

Neurochemistry

G.-H. Kim, D. Halder, J. Park,
W. Namkung, I. Shin* **9271 – 9274**

Imidazole-Based Small Molecules that Promote Neurogenesis in Pluripotent Cells

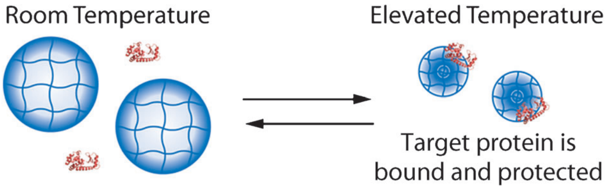


A small world: Imidazole-based small molecules can induce neuronal differentiation of pluripotent cells. These substances promote production of physiologically active neurons because P19-cell-derived neurons induced by these substances have functional glutamate responsiveness.

Hydrogel Nanoparticles

J. M. Beierle, K. Yoshimatsu, B. Chou,
M. A. A. Mathews, B. K. Lesel,
K. J. Shea* **9275 – 9279**

Polymer Nanoparticle Hydrogels with Autonomous Affinity Switching for the Protection of Proteins from Thermal Stress

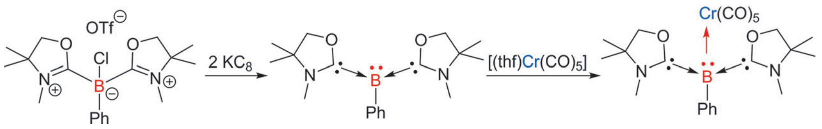


Enzyme protector: Thermally responsive *N*-isopropylacrylamide-based polymer nanoparticle (NP) hydrogels are engineered to protect a protein from thermal stress. The NP hydrogels bind and protect a target enzyme from activity loss at elevated temperature but readily release the enzyme when the solution is cooled.

Nucleophilic Boron

L. Kong, Y. Li, R. Ganguly, D. Vidovic, R. Kinjo* ______ 9280–9283

Isolation of a Bis(oxazol-2-ylidene)–Phenylborylene Adduct and its Reactivity as a Boron-Centered Nucleophile

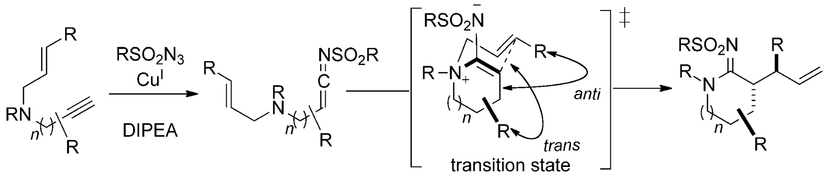


Two oxazol-2-ylidene ligands effectively stabilize a phenylborylene fragment that features a lone pair of electrons on the boron atom. There are eight electrons around the tricoordinate boron center (8-B-3), and the nucleophilic boron center readily reacts with an electrophile, such as a proton or a transition-metal species, to form a boronium species and a metal–borylene complex, respectively.

Heterocycle Synthesis

H. Xu,* Z. Jia, K. Xu, M. Han, S. Jiang, J. Cao, J. Wang, M. Shen* __ 9284–9288

Copper-Catalyzed Cyclization/aza-Claisen Rearrangement Cascade Initiated by Ketenimine Formation: An Efficient Stereocontrolled Synthesis of α-Allyl Cyclic Amidines



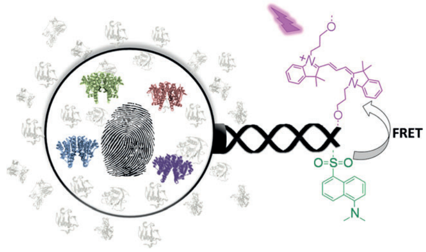
After a pattern: A convenient copper-catalyzed method for cyclic amidine synthesis with high yield under mild reaction conditions has been established. By using this method, tertiary allyl enynes, with broad substitution patterns, can be converted stereoselectively into α-allyl cyclic amidines bearing multiple functionalities for potential elaboration. DIPEA = diisopropylethylamine.

Protein Surface Recognition

L. Motiei, Z. Pode, A. Koganitsky, D. Margulies* ______ 9289–9293

Targeted Protein Surface Sensors as a Tool for Analyzing Small Populations of Proteins in Biological Mixtures

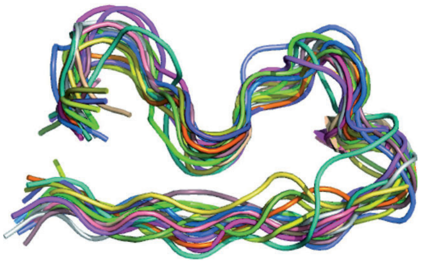
Taking protein "fingerprints": A general methodology for endowing an optical cross-reactive sensor array (the so-called "chemical noses/tongues") with selectivity toward specific protein groups has been developed. With this approach an array can be "programmed" to generate patterns that reflect the composition of closely related biomarkers, even in the presence of abundant serum proteins or within human urine.



β-amyloid Aggregation

Z. Niu, W. Zhao, Z. Zhang, F. Xiao, X. Tang, J. Yang* ______ 9294–9297

The Molecular Structure of Alzheimer β-Amyloid Fibrils Formed in the Presence of Phospholipid Vesicles

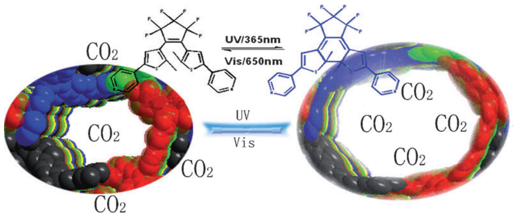


Fickle fibers: An atomic-resolution molecular structure of β-amyloid fibrils formed in the presence of lipid vesicles was obtained by using highly ordered fibril samples and multidimensional solid-state NMR (monomeric unit shown). The structure of the fibrils formed in the presence of lipid vesicles is different from those formed in solution. This study provides new structural insights into the molecular mechanism of Aβ aggregation.

Functional Materials

F. Luo, C. B. Fan, M. B. Luo, X. L. Wu,
Y. Zhu, S. Z. Pu,* W.-Y. Xu,
G.-C. Guo* ———— **9298 – 9301**

Photoswitching CO_2 Capture and Release in a Photochromic Diarylethene Metal–Organic Framework

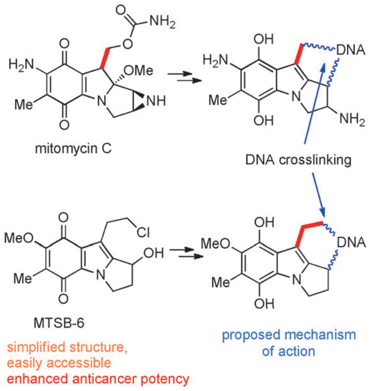


Low-energy CO_2 capture and release was possible with a metal–organic framework containing a photosensitive diarylethene ligand. The local framework flexibility caused by the photoswitchable diarylethene ligand (see picture) led to a record high CO_2-desorption capacity of 75% under static irradiation and 76% under dynamic irradiation.

Anticancer Drugs

Z. Zheng, M. Touve, J. Barnes, N. Reich,*
L. Zhang* ———— **9302 – 9305**

Synthesis-Enabled Probing of Mitosene Structural Space Leads to Improved IC_{50} over Mitomycin C

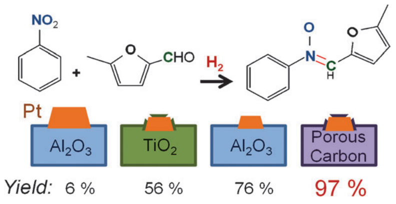


CH_2 makes a difference: By incorporating an additional CH_2 unit into mitomycin C and making other structural simplifications, a new mode for double alkylation of DNA is hypothesized. Rational design and synthesis led to MTSB-6, which is twice as potent as mitomycin C and of similar toxicity. This discovery opens up novel mitosene structural space for further improvement.

Selective Reductions

L. Cisneros, P. Serna,*
A. Corma* ———— **9306 – 9310**

Selective Reductive Coupling of Nitro Compounds with Aldehydes to Nitrones in H_2 Using Carbon-Supported and -Decorated Platinum Nanoparticles

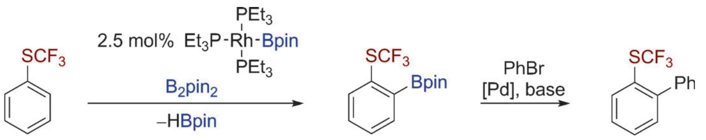


Support and decoration: Nitrones were synthesized in high yields directly from nitro compounds, aldehydes, and H_2 using platinum nanoparticles supported on and decorated with carbon. The high selectivity is in contrast to that obtained with typical supported metal catalysts.

Synthetic Methods

S. I. Kalläne, T. Braun* ———— **9311 – 9315**

Catalytic Borylation of SCF_3-Functionalized Arenes by Rhodium(I) Boryl Complexes: Regioselective C—H Activation at the *ortho*-Position

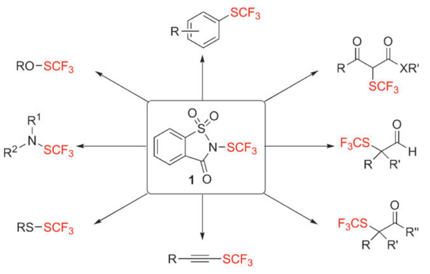


SCF_3 building blocks: A unique reaction route allows access to SCF_3-functionalized arenes, which are borylated at the *ortho*-position. The functionalization proceeds by C—H borylation with $[Rh(Bpin)(PEt_3)_3]$ (pin = pinacolato), and the SCF_3 group likely serves as directing group. The generated borylated SCF_3 compounds are versatile building blocks for further transformations.

Synthetic Methods

C.-F. Xu, B.-Q. Ma,
Q. Shen* **9316 – 9320**

N-Trifluoromethylthiosaccharin: An Easily Accessible, Shelf-Stable, Broadly Applicable Trifluoromethylthiolating Reagent

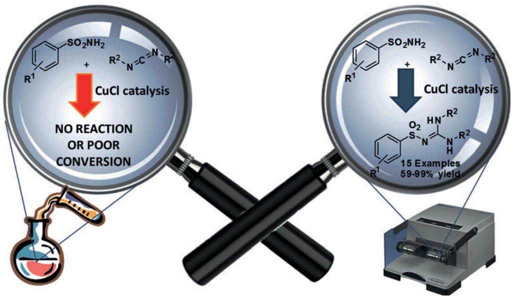


‘Sacch’ed out: A new, electrophilic trifluoromethylthiolating reagent, *N*-trifluoromethylthiosaccharin (**1**) can be synthesized in two steps from saccharin within 30 minutes. The reagent **1** allows the trifluoromethylthiolation of a variety of nucleophiles such as alcohols, amines, thiols, electron-rich arenes, aldehydes, ketones, acyclic β-ketoesters, and alkynes under mild reaction conditions.

Synthetic Methods

D. Tan, C. Mottillo, A. D. Katsenis,
V. Štrukil, T. Friščić* **9321 – 9324**

Development of C–N Coupling Using Mechanochemistry: Catalytic Coupling of Arylsulfonamides and Carbodiimides

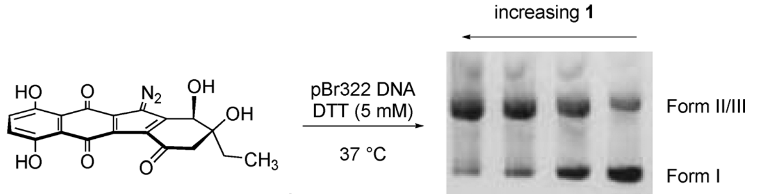


Milling around: Mechanochemistry is used to develop a method for the direct coupling of carbodiimides and arylsulfonamides using a copper catalyst. Attempts to reproduce this C–N coupling reaction under conventional solution-based conditions either failed or gave very poor conversions.

Anticancer Agents

C. M. Woo, N. Ranjan, D. P. Arya,
S. B. Herzon* **9325 – 9328**

Analysis of Diazofluorene DNA Binding and Damaging Activity: DNA Cleavage by a Synthetic Monomeric Diazofluorene



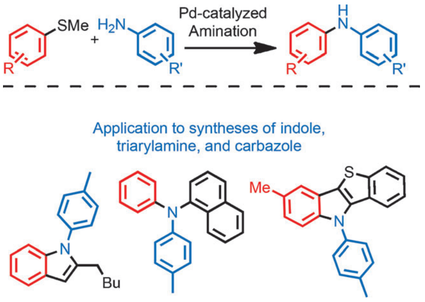
(–)-monomeric lomaivicin aglycon (**1**)

A potent cleaving agent: Diazofluorene-containing natural products are potent cytotoxic agents that damage DNA. The factors governing DNA binding and cleavage by synthetic and natural diazofluorenes are elucidated, and it is shown that the simple monomeric diazofluorene **1** cleaves DNA in tissue culture, suggesting its application in translational development.

Synthetic Methods

T. Sugahara, K. Murakami,*
H. Yorimitsu,* A. Osuka **9329 – 9333**

Palladium-Catalyzed Amination of Aryl Sulfides with Anilines

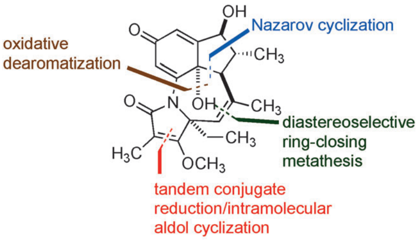


Switching S to N: Transformation of inert C–S bonds of aryl sulfides into C–N bonds is achieved using a palladium complex with an N-heterocyclic carbene ligand. Thanks to the efficient conditions for amination of bulky sulfides, the synthesis of carbazole products from 2-biphenylylamine is achieved through oxidative C–N bond formation. When combined with extended Pummerer reactions, intriguing nitrogen-containing molecules are prepared.

Natural Product Synthesis

P. N. Carlsen, T. J. Mann, A. H. Hoveyda, A. J. Frontier* ______ **9334 – 9338**

Synthesis of (±)-Tetrapetalone A-Me Aglycon



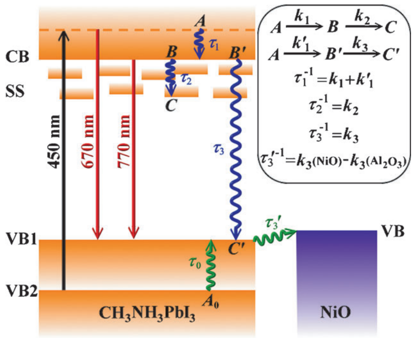
Keyed up: In the synthesis of (±)-tetrapetalone A-Me aglycon the key bond-forming reactions include Nazarov cyclization, a ring-closing metathesis promoted with complete diastereoselectivity by a chiral molybdenum-based complex, tandem conjugate reduction/intramolecular aldol cyclization, and oxidative dearomatization.

Perovskite Solar Cells

H.-Y. Hsu, C.-Y. Wang, A. Fathi, J.-W. Shiu, C.-C. Chung, P.-S. Shen, T.-F. Guo, P. Chen, Y.-P. Lee, E. W.-G. Diau* ______ **9339 – 9342**

Femtosecond Excitonic Relaxation Dynamics of Perovskite on Mesoporous Films of Al_2O_3 and NiO Nanoparticles

Femtosecond optical gating (FOG) technique was employed to investigate the excitonic relaxation mechanism in a NiO-supported p-type perovskite. The effect of photoluminescence quenching and the excellent photovoltaic performance were rationalized based on this measurement.

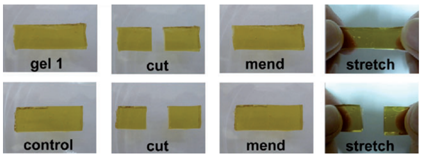


Self-Healing Materials

Y. Z. Gao, Q. Luo, S. P. Qiao, L. Wang, Z. Y. Dong, J. Y. Xu, J. Q. Liu* ______ **9343 – 9346**

Enzymetically Regulating the Self-Healing of Protein Hydrogels with High Healing Efficiency

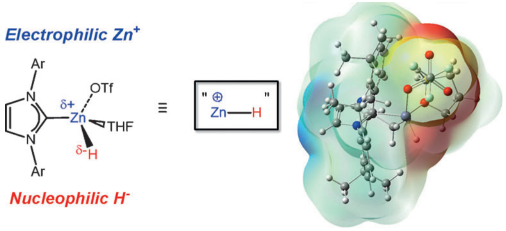
Enzyme-mediated self-healing of dynamic covalent bond-driven protein hydrogels was realized by the synergy of two enzymes, glucose oxidase (GOX) and catalase (CAT). The dual-enzyme-mediated protein hydrogels exhibit excellent self-healing properties with 100% recovery. The self-healing process was reversible and effective with an external glucose stimulus at room temperature.



Zinc Hydride Cations

P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, M. Miskolzie, A. Brown,* E. Rivard* ______ **9347 – 9351**

Accessing Zinc Monohydride Cations through Coordinative Interactions



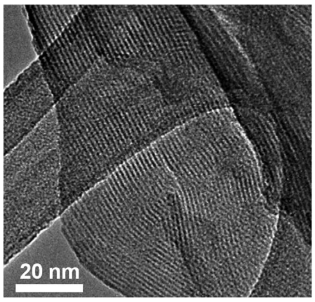
A positive approach: Isolable examples of formal zinc hydride cations supported by N-heterocyclic carbene donors are prepared. The dual electrophilic and nucleophilic (hydridic) character of the encapsulated $[ZnH]^+$ units was investigated by computational methods and hydrosilylation catalysis.

Lithium-Ion Batteries

D. Yang, Z. Y. Lu, X. H. Rui, X. Huang, H. Li, J. X. Zhu, W. Y. Zhang, Y. M. Lam, H. H. Hng, H. Zhang,* Q. Y. Yan* ______ **9352 – 9355**

Synthesis of Two-Dimensional Transition-Metal Phosphates with Highly Ordered Mesoporous Structures for Lithium-Ion Battery Applications

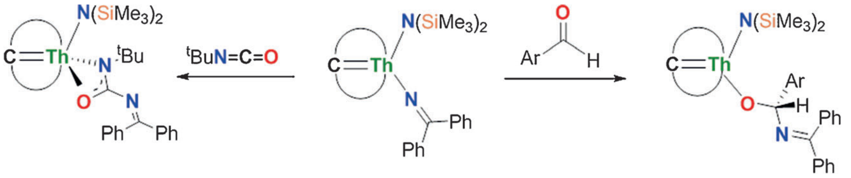
Ultrathin two-dimensional (2D) nanoflakes of transition-metal phosphates, including $FePO_4$ (see TEM image), $Mn_3(PO_4)_2$, and $Co_3(PO_4)_2$, with highly ordered mesoporous structures have been successfully synthesized in a nonpolar solvent. The use of the 2D mesoporous $FePO_4$ nanoflake as a cathode in a lithium-ion battery resulted in excellent stability and high rate capabilities.



Ketimide Reactivity

E. Lu, W. Lewis, A. J. Blake, S. T. Liddle* ______ **9356 – 9359**

The Ketimide Ligand is Not Just an Inert Spectator: Heteroallene Insertion Reactivity of an Actinide–Ketimide Linkage in a Thorium Carbene Amide Ketimide Complex

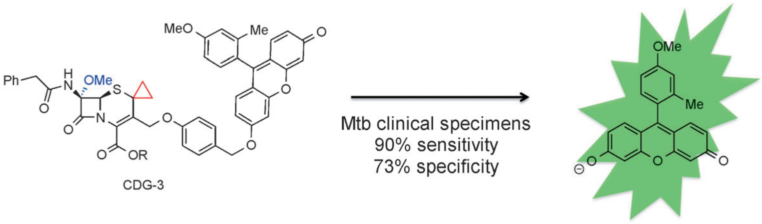


Inert no more: The thorium carbene amide ketimide complex $[Th(BIPM^{TMS})\{N(SiMe_3)_2\}(N{=}CPh_2)]$ $[BIPM^{TMS}{=}C(PPh_2NSiMe_3)_2]$ features Th=C, Th–N_{amide}, and Th–$N_{ketimide}$ bonds in one molecule. Reactivity studies show that reactions preferentially involve the traditionally inert Th–$N_{ketimide}$ linkage rather than the usually reactive Th=C or Th–N_{amide} bonds, and overturn the established view of ketimides as purely inert spectator ligands.

Fluorescent Probes

Y. Cheng, H. Xie, P. Sule, H. Hassounah, E. A. Graviss, Y. Kong, J. D. Cirillo, J. Rao* ______ **9360 – 9364**

Fluorogenic Probes with Substitutions at the 2 and 7 Positions of Cephalosporin are Highly BlaC-Specific for Rapid *Mycobacterium tuberculosis* Detection

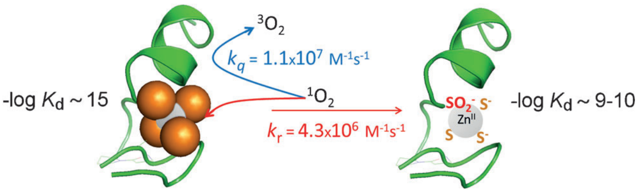


TB or not TB? A fluorogenic probe (CDG-3) was developed for BlaC, a biomarker expressed by *Mycobacterium tuberculosis* (Mtb). CDG-3 is based on cephalosporin with substitutions at both the 2 and 7 positions and it demonstrates over 120000-fold selectivity for BlaC over the common β-lactamase TEM-1 Bla. This rapid, low cost, sensitive, and selective method shows great potential for point-of-care tuberculosis (TB) testing in resource-limited settings.

Oxidative Stress

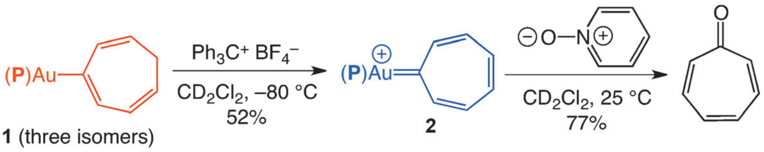
V. Lebrun, A. Tron, L. Scarpantonio, C. Lebrun, J.-L. Ravanat J.-M. Latour, N. D. McClenaghan,* O. Sénèque* ______ **9365 – 9368**

Efficient Oxidation and Destabilization of $Zn(Cys)_4$ Zinc Fingers by Singlet Oxygen



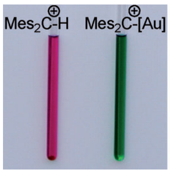
No zinc, no finger: The efficient oxidation of cysteines of a $Zn(Cys)_4$ zinc finger into sulfinates was achieved with singlet oxygen. This oxidation drastically decreases the Zn^{2+} affinity thereby allowing the destruction of the zinc finger under cellular conditions.

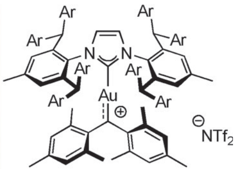
Carbenoids



Hydride abstraction from the neutral gold cycloheptatrienyl complex **1** (**P** = P(*t*Bu)$_2$(*o*-biphenyl)) with $Ph_3C^+ BF_4^-$ formed the cationic gold cycloheptatrienylidene complex **2**, which was characterized by single-crystal X-ray diffraction. The cycloheptatrienylidene ligand of **2** is reactive; it can be reduced by mild hydride donors, and converted into tropone in the presence of pyridine *N*-oxide.

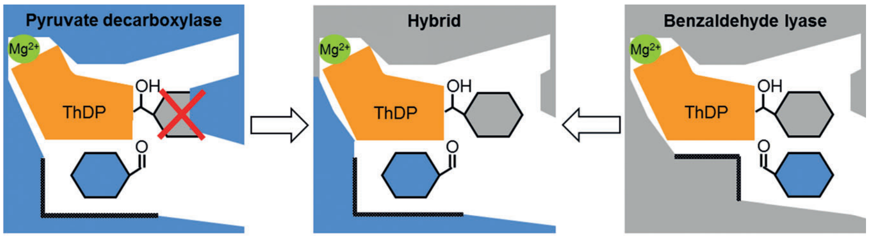
Stable Gold Carbene





Gold: more than just a "soft proton": The preparation of the gold complex [IPr**Au═CMes$_2$]NTf$_2$ was made possible by the extreme steric shielding of the IPr** ancillary ligand (Ar = *para*-C_6H_4*t*Bu) and the dimesitylcarbene. The strong bathochromic shift from the red-purple carbenium ion [Mes$_2$CH]$^+$ to the emerald-green gold–carbene cation literally shows that the carbene interaction with gold is more complex than its bonding to a proton.

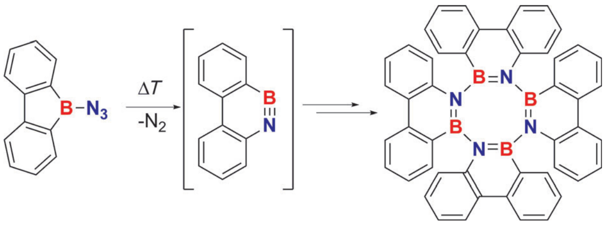
Biocatalysis



no benzoin (**S**)-benzoin 98 % *ee* (**R**)-benzoin > 99 % *ee*

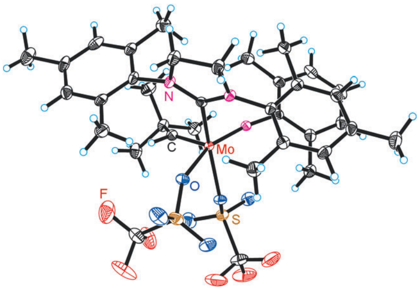
Hybrid vigor: Combining the active-site characteristics of two thiamine diphosphate (ThDP) dependent enzymes solved the long-standing problem of enzymatic asymmetric (*S*)-benzoin synthesis starting from commercially available benzaldehydes. The resulting rationally designed hybrid enzyme provides access to various (*S*)-benzoins with excellent enantiomeric excess and good conversion.

BN-Arynes



Making a first appearance: A BN-aryne analogous to 9,10-phenanthryne can be formed by thermolysis of the 9-azido-9-borafluorene and can undergo cyclotetramerization.

To be or not to be (cationic)? In the presence of monomer, neutral 16-electron N-heterocyclic carbene adducts of high oxidation state Mo^{VI} N-arylimidoalkylidene bis(triflate) complexes convert into cationic 16-electron complexes that are active and functional-group tolerant polymerization catalysts.



Molybdenum–NHC Complexes

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

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

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