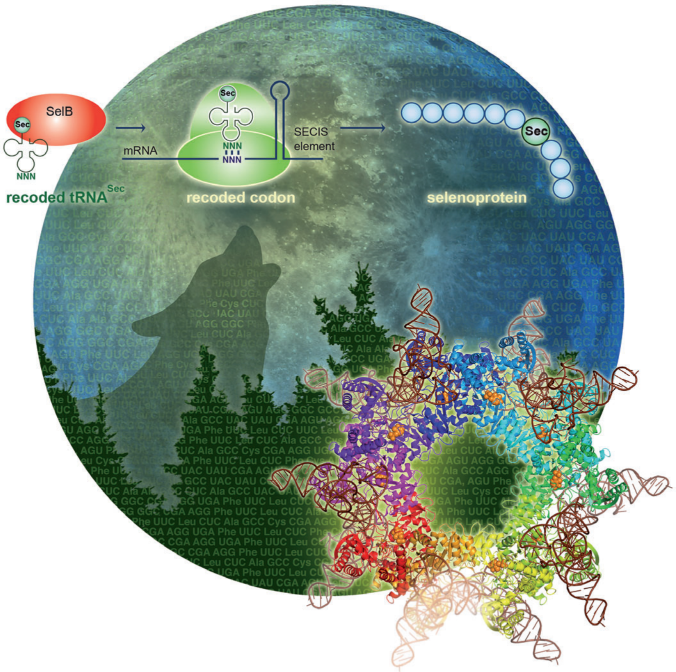
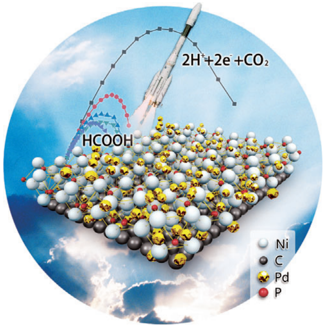
Named after Selene, goddess of the moon …

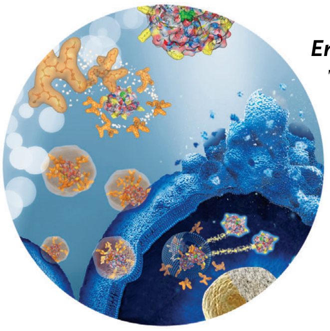


… selenocysteine (Sec) is unique in its unrivaled catalytic power and its insertion into proteins by redefinition of specific UGA stop codons to Sec. In their Communication on page 319 ff., D. Söll, P. O'Donoghue et al. describe the engineering of the Sec-insertion machinery to redefine nearly all 64 codons. Here, the ring-shaped decameric selenocysteine synthase SelA is essential in providing tRNA-bound Sec as the central building block for selenoprotein translation.

Electrocatalysis

In their Communication on page 122 ff., W. Xing, X. L. Hu et al. describe a novel Pd–Ni_2P/C electrocatalyst that gives superior performance to a state-of-the-art commercial Pd/C catalyst for the oxidation of formic acid in fuel cells.





Enzyme Hybrids

T. Weil and co-workers describe dendrimer-coated enzymes in their Communication on page 324 ff. These structurally defined biohybrids show pH-responsive activity and the capability for membrane translocation and localization.

Self-Replication

B. A. Grzybowski, M. O. de la Cruz et al. present the self-replication of light-sensitive nanoparticle dimers in their Communication on page 173 ff. What matters is not constant energetic expenditure but the timing with which energy is delivered to the system.

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Editorial

With some reflections on the anniversary year 2013, a look ahead to some important changes in 2014, and an introduction to the new members of the Editorial Board and the International Advisory board, Peter Gölitz's Editorial opens the new volume.

P. Gölitz* ——— **4–7**

Angewandte Chemie Always New

"… Mankind will need synthetic chemistry as well as synthetic biology (which can indeed be considered a branch of chemistry) to solve the many challenges it is facing. Rather than spending time on 'religious warfare' within the community, we should lobby together for adequate support for the best science …"
Read more in the Editorial by Alois Fürstner.

*A. Fürstner** ——— ***8–9***

What Matters?

"… 'My Angewandte *belongs to me—anywhere' was once an advertising slogan for the journal. It has never been more true than today …"*
Read all about alerts, feeds, apps, and more in the Editorial by Mario Müller.

*M. Müller** ——— ***10–12***

Angewandte Chemie Online, Anywhere

Miscellaneous

Spotlight on Angewandte's Sister Journals **32–35**

Editorial Board and International Advisory Board of ***Angewandte Chemie*** **43–45**

Author Profile

"I would have liked to have discovered a new element. The most exciting thing about my research is working closely with young co-workers and watching their transition from science students into scientists. …"
This and more about Steven H. Strauss can be found on page 34.

Steven H. Strauss ______ **36–37**

News


F. Diederich


A. Fürstner


A. G. Beck-Sickinger


T. Carell


S. Grimme


H. Grützmacher


W. J. Parak


F. Schüth


P. S. Baran


H. Bayley


F. Caruso


A. Corma


J. M. DeSimone


K. Ding


M. Fontecave

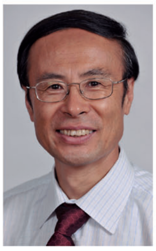

J. F. Hartwig


E. N. Jacobsen


D. A. Leigh


I. Marek


K. Nozaki


L.-J. Wan


R. Weissleder


Q.- L. Zhou

New Members of the Editorial Board and International Advisory Board of *Angewandte Chemie* ______ **38–41**

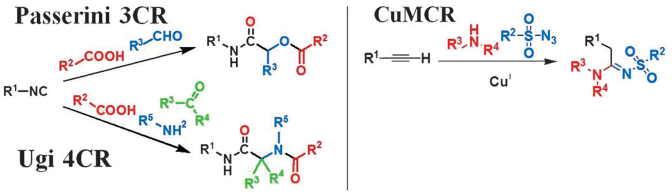
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. 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.

Highlights

Multicomponent Reactions

R. Kakuchi* ______ 46 – 48

Multicomponent Reactions in Polymer Synthesis

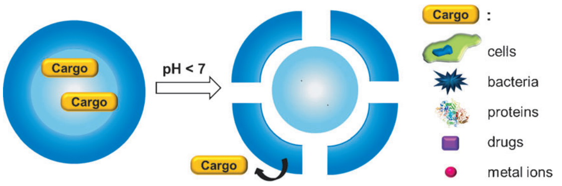


More participants, yet efficient reactions: Multicomponent reactions (MCRs) have found application in polymer chemistry both in the synthesis of multifunctional monomers and in post-polymerization modification. Examples include the Passerini three-component reaction, the Ugi four-component reaction, and the copper-catalyzed MCR (see scheme).

Drug Delivery

S. Nowag, R. Haag* ______ 49 – 51

pH-Responsive Micro- and Nanocarrier Systems



Release on demand: The pH gradients between extra- and intracellular regions can be utilized for the controlled release of drugs and biological cargos from delivery systems. Biocompatible carrier systems with pH-cleavable units must fulfill many other criteria as well, for example, a long blood circulation time. This can be achieved by tailored micro- and nanocarriers based on macromolecular architectures or stable self-assembled systems.

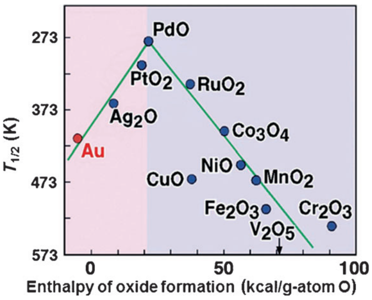
Essays

Gold Nanoparticle Catalysts

M. Haruta* ______ 52 – 56

Chance and Necessity: My Encounter with Gold Catalysts

“Have you tried gold?” This question after a presentation on hydrogen oxidation steered Masatake Haruta’s research on heterogeneous catalysis. He found that gold combined with 3d transition metal oxides could exhibit surprisingly high catalytic activity for carbon monoxide oxidation at temperatures as low as 203 K.

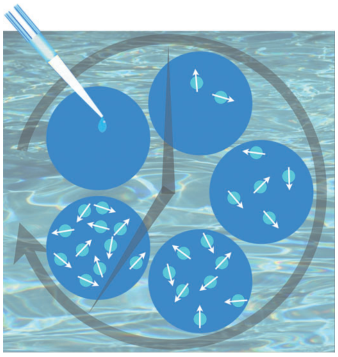


Minireviews

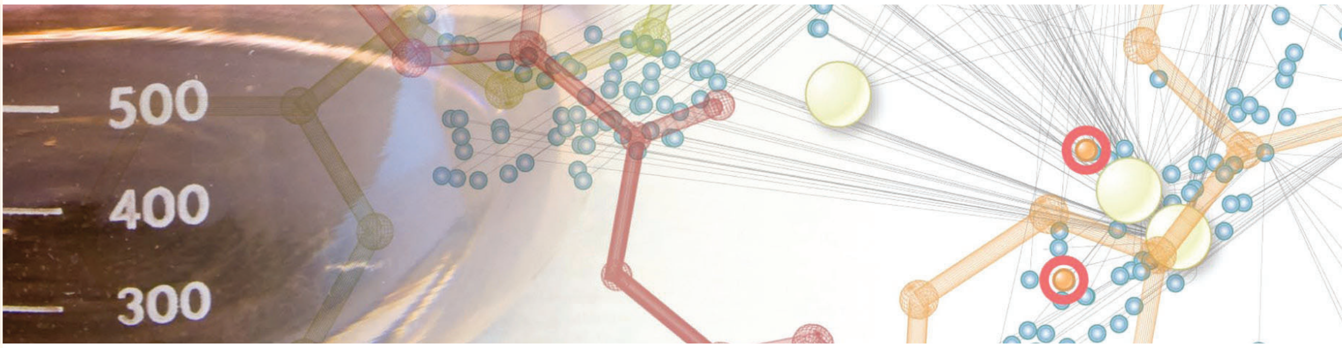
Magnetogenic Probes

J. Hasserodt,* J. L. Kolanowski, F. Touti ______ 60 – 73

Magnetogenesis in Water Induced by a Chemical Analyte



No way back: Molecules that change the magnetic properties of a solution-phase sample in response to a chemical stimulus all operate through a reversible mechanism. The lessons learned can be used in the design of high-performance probes that, similar to optically responsive agents, react irreversibly. A discussion of the capabilities of two recently reported irreversible probes allow the readers to form their own views on this field.



Novartis is pleased to announce the 2013 recipients of the

Novartis Early Career Award in Organic Chemistry

Professor Nicolai Cramer, *EPF Lausanne, Switzerland*

Nicolai Cramer earned his Ph.D. in 2005 in the group of Professor Sabine Laschat at the University of Stuttgart. After a stay with Professors Michio Murata and Sumihiro Hase at Osaka University he joined the group of Professor Barry M. Trost at Stanford University as a postdoctoral fellow. In 2007, he started his habilitation at the ETH Zürich associated to Professor Erick M. Carreira and in 2010 took his current position at EPF Lausanne. Professor Cramer has made major contributions to the field of enantioselective metal-catalyzed transformations and has been a pioneer in the development of catalytic methods for selective functionalization of relatively inert C-H and C-C bonds.

Professor Daniel Rauh, *Technische Universität, Dortmund, Germany*

Daniel Rauh earned his Ph.D. in 2002 from Phillips-Universität Marburg working with Professor Gerhard Klebe. Later that year he spent time as a Research Fellow at the Genomics Institute of the Novartis Research Foundation (GNF) in San Diego. His postdoctoral studies began with Professor Milton Stubbs at Martin-Luther-Universität Halle-Wittenberg and then with Professor Kevan Shokat at the University of California, San Francisco. Professor Rauh started his independent career at Dortmund in 2006 and has made truly innovative contributions to the field of chemical biology in the development of high-throughput assay methodologies for the identification of allosteric kinase inhibitors, and in the creative design of functional probes for targeting proteins and dissecting oncogene dependencies.

The Novartis Early Career Award in Organic Chemistry is presented annually to outstanding scientists within 10 years of having established an independent academic research career, in the areas of organic or bioorganic chemistry in the broadest sense. Two winners are identified, from the Global Research community, each of whom receives an unrestricted research grant.

Past Awardees:

2012	Sarah E. Reisman and Corey R.J. Stephenson
2011	David Chen and David Spiegel
2010	Karl Gademann and Jin-Quan Yu
2009	Christopher J. Chang and Magnus Rueping
2008	Matthew J. Gaunt and Jeffrey S. Johnson
2007	Lukas J. Goossen and Anna K. Mapp
2006	Armido Studer and F. Dean Toste
2005	Benjamin List and Dirk Trauner
2004	J. Stephen Clark and Jonathan P. Clayden
2003	Thorsten Bach
2002	Bernhard Breit and Thomas Carell
2001	Tim Donohoe
2000	Andrew Miller
1999	Alan Armstrong
1998	Mark Bradley

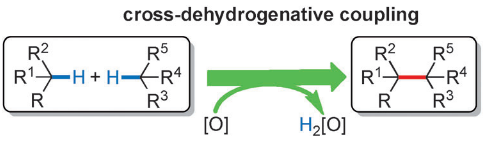
NOVARTIS

Reviews

Cross-Coupling

S. A. Girard, T. Knauber,
C.-J. Li* **74–100**

The Cross-Dehydrogenative Coupling of C_{sp^3}—H Bonds: A Versatile Strategy for C—C Bond Formations



Waste not, want not: The title CDC reactions have emerged as versatile tools for selective and waste-minimized C—C bond formations. They rely on the direct coupling of two different C—H bonds under oxidative conditions. This Review focuses on the recent progress in cross-dehydrogenative C_{sp^3}—C formation and provides a comprehensive overview on existing procedures and employed methodologies.

Nanostructured Electrocatalysts

I. Katsounaros,* S. Cherevko,
A. R. Zeradjanin,
K. J. J. Mayrhofer* **102–121**

Oxygen Electrochemistry as a Cornerstone for Sustainable Energy Conversion

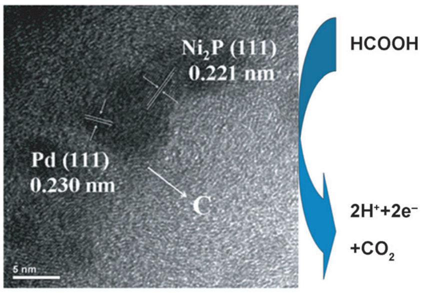
The deployment of sustainable energy technologies is limited by severe challenges in the design of nanostructured electrocatalysts. Efficient catalysts must meet the criteria of high activity, long-term stability, and abundance of the materials used. Integrated solutions will be provided only by multidisciplinary approaches that include fundamental electrochemistry, materials science, and chemical engineering. ORR/OER = O_2 reduction/evolution reaction.

Communications

Electrocatalysis

J. F. Chang, L. G. Feng, C. Liu, W. Xing,*
X. L. Hu* **122–126**

An Effective Pd–Ni_2P/C Anode Catalyst for Direct Formic Acid Fuel Cells

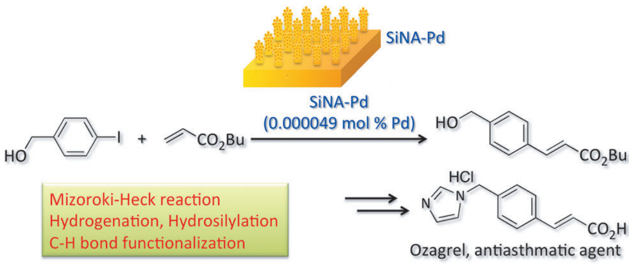


Giving Pd a boost: A novel Pd–Ni_2P/C electrocatalyst has been developed for formic acid oxidation. A direct formic acid fuel cell integrating this catalyst showed superior power density and discharge stability than a state-of-the-art commercial Pd/C catalyst.

Nanocatalyst

Y. M. A. Yamada,* Y. Yuyama, T. Sato,
S. Fujikawa, Y. Uozumi **127–131**

A Palladium-Nanoparticle and Silicon-Nanowire-Array Hybrid: A Platform for Catalytic Heterogeneous Reactions

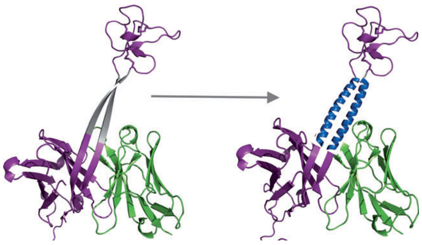


An array of reactions: A silicon-nanowire-array-stabilized palladium-nanoparticle catalyst, SiNA-Pd, was designed and used in the palladium-catalyzed Mizoroki–Heck reaction. It can catalyze a variety of other reactions and has a high reusability.

Protein Engineering

Y. Zhang, D. Goswami, D. Wang,
T. S. A. Wang, S. Sen, T. J. Magliery,
P. R. Griffin, F. Wang,*
P. G. Schultz* **132 – 135**

An Antibody with a Variable-Region Coiled-Coil "Knob" Domain

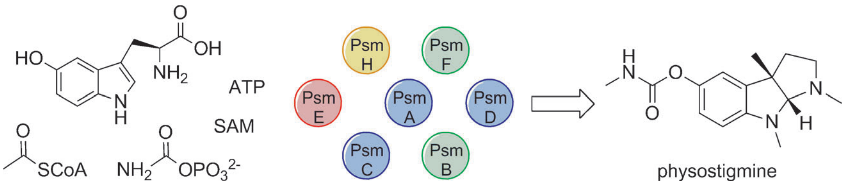


With knob and stalk: A bovine antibody is featured with a unique solvent exposed, antiparallel β-strand "stalk" fused to a disulfide cross-linked "knob" domain in its complementarity determining region 3 (CDR3). Substitution of the stalk with an antiparallel heterodimeric coiled-coil generates a novel coiled-coil CDR3 motif that provides a new strategy for generating stable, potent antibody chimeras.

Drug Biosynthesis

J. Liu, T. Ng, Z. Rui, O. Ad,
W. Zhang* **136 – 139**

Unusual Acetylation-Dependent Reaction Cascade in the Biosynthesis of the Pyrroloindole Drug Physostigmine

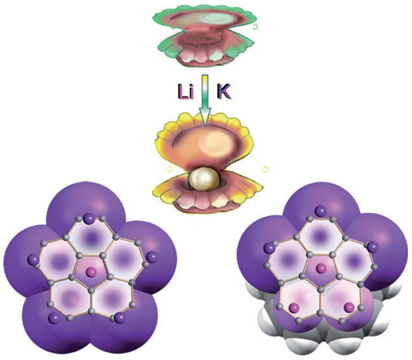


A tightly choreographed act: A biosynthetic gene cluster for physostigmine was identified by genome mining. In vitro reconstitution showed that seven enzymes, PsmA–F and PsmH, are required for the synthesis of physostigmine from 5-hydroxytryptophan (see scheme; ATP = adenosine 5′-triphosphate, CoA = coenzyme A, SAM = *S*-adenosylmethionine) through a series of highly coordinated methylation and acetylation/deacetylation reactions.

Mixed-Metal Aggregates

A. S. Filatov, A. V. Zabula, S. N. Spisak,
A. Yu. Rogachev,
M. A. Petrukhina* **140 – 145**

Clamshell Opening in the Mixed-Metal Supramolecular Aggregates Formed by Fourfold Reduced Corannulene for Maximizing Intercalated Metal Content

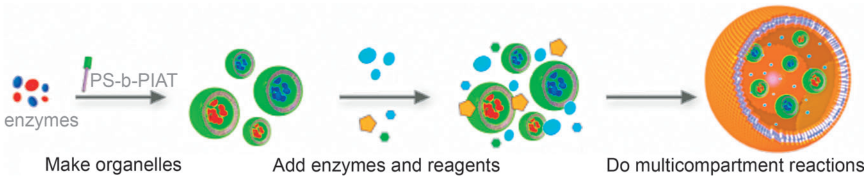


Pearls in a clamshell: A new class of supramolecular organometallic compounds with mixed-alkali-metal clusters, LiK$_5$ and Li$_3$K$_3$, sandwiched between two highly reduced corannulene decks have been prepared and characterized. They show a coordination record for corannulene tetraanions able to bind six alkali-metal ions. Previously unseen engagement of the hub-site of C$_{20}$H$_{10}^{4-}$ in lithium binding is accompanied by unprecedented shifts up to −24 ppm in ^{7}Li NMR spectra.

Multicompartment Cascade Reactions

R. J. R. W. Peters, M. Marguet, S. Marais,
M. W. Fraaije, J. C. M. van Hest,*
S. Lecommandoux* **146 – 150**

Cascade Reactions in Multicompartmentalized Polymersomes

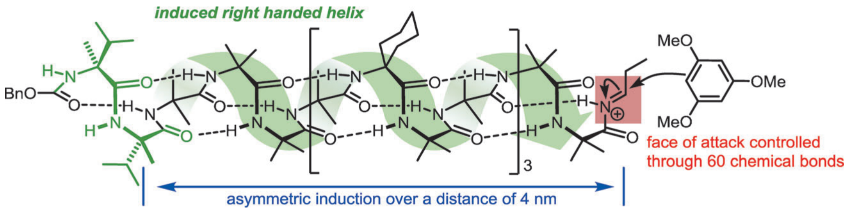


Mimicking cells: Enzyme-filled polystyrene-*b*-poly(3-(isocyano-L-alanylamino-ethyl)thiophene) (PS-*b*-PIAT) nanoreactors have been encapsulated together with free enzymes and substrates in a larger polymersome to form a multicompartmentalized structure, which shows structural resemblance to a cell and its organelles (see picture). An original cofactor-dependent three-enzyme cascade reaction, with either compatible or incompatible enzymes, takes place across multiple compartments.

Remote Stereocontrol

L. Byrne, J. Solà, T. Boddaert, T. Marcelli,
R. W. Adams, G. A. Morris,
J. Clayden* 151 – 155

Foldamer-Mediated Remote Stereocontrol: >1,60 Asymmetric Induction

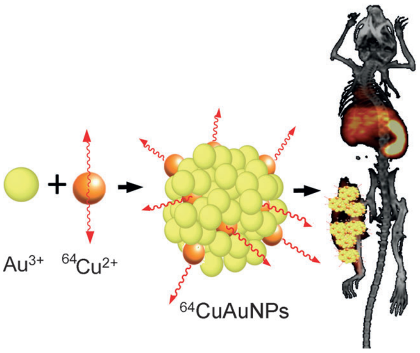


Reaction at a distance: By inducing a quantitative, persistent preference for right-handed helicity, chirality at one end of an otherwise achiral helical molecule is able to control the stereoselectivity of reactions at sites located up to 60 bonds away, shattering previous records for remote stereochemical control.

Imaging

Y. Zhao, D. Sultan, L. Detering, S. Cho,
G. Sun, R. Pierce, K. L. Wooley,
Y. Liu* 156 – 159

Copper-64-Alloyed Gold Nanoparticles for Cancer Imaging: Improved Radiolabel Stability and Diagnostic Accuracy



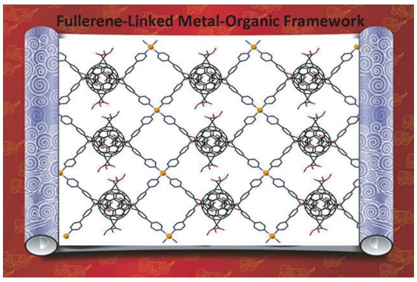
Copper goes for gold: Alloyed copper–gold nanoparticles with controlled integration of ^{64}Cu (^{64}CuAuNPs) are ideal for positron emission tomography imaging. The direct incorporation of ^{64}Cu into the lattice of gold nanoparticles ensured greatly improved radiolabel stability and detection sensitivity. The superior biodistribution profile and imaging capability demonstrated the potential of these alloyed nanoparticles for further investigation.

Supramolecular Chemistry

P. Peng, F.-F. Li, V. S. P. K. Neti,
A. J. Metta-Magana,
L. Echegoyen* 160 – 163

Design, Synthesis, and X-Ray Crystal Structure of a Fullerene-Linked Metal–Organic Framework

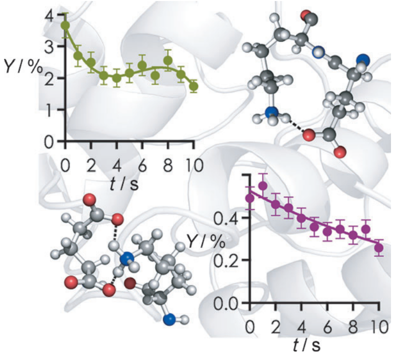
Linked in: A new hexakisfullerene derivative, possessing two pairs of phenyl pyridine groups attached to two methanocarbon atoms located at *trans*-1 positions, was designed, synthesized, and used to assemble the first fullerene-linked metal–organic framework.



Mass Spectrometry

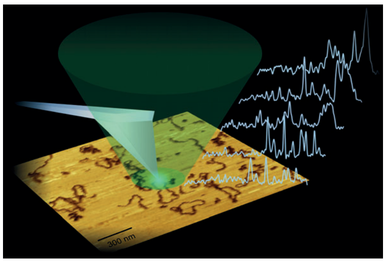
M. Schennach, K. Breuker* 164 – 168

Proteins with Highly Similar Native Folds Can Show Vastly Dissimilar Folding Behavior When Desolvated



Electron capture dissociation has been used to study horse (example at the top) and tuna (example at the bottom) heart cytochromes *c* in the complete absence of solvent. It was shown that in the absence of hydrophobic bonding, folding is slow, complex, and driven by electrostatic interactions. Y = Yield.

Individual DNA double strand breaks (DSBs) were first detected and located by atomic force microscopy, and the molecular structure of this damage was characterized with tip-enhanced Raman scattering (see picture) using a top-down configuration and a reflective substrate. The first experimental evidence is reported confirming that individual DSBs result from cleavage at the 3′- and 5′-bonds of deoxyribose upon exposure to ultraviolet C radiation.



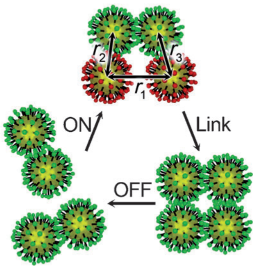
DNA Damage

E. Lipiec, R. Sekine, J. Bielecki, W. M. Kwiatek, B. R. Wood* ___ **169 – 172**

Molecular Characterization of DNA Double Strand Breaks with Tip-Enhanced Raman Scattering

---

A finger on the pulse: The rate of self-replication can be significantly enhanced by delivering energy to the system in pulses rather than continuously. In other words, optimal self-replication does not necessarily require constant energetic expenditure; instead what matters is the timing with which energy is delivered to the system.



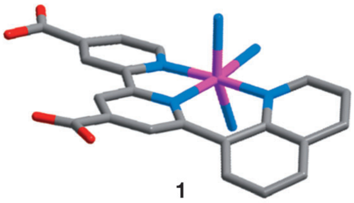
Self-Replication

R. Zhang, D. A. Walker, B. A. Grzybowski,* M. Olvera de la Cruz* ___ **173 – 177**

Accelerated Self-Replication under Non-Equilibrium, Periodic Energy Delivery

Back Cover

Go with the flow: The increased π conjugation of panchromatic Ru^{II} sensitizers of type **1** containing a 6-quinolin-8-yl-2,2′-bipyridine rather than a traditional 2,2′:6′,2′′-terpyridine anchor (structure **2**) led to a remarkable improvement in absorptivity across the whole UV/Vis/NIR spectral regime. A bulky *tert*-butyl substituent on the quinolinyl fragment caused an increase in the short-circuit current by suppressing dye aggregation.



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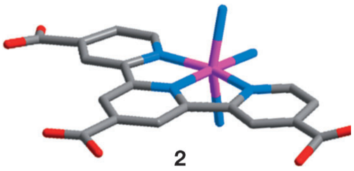

2

Panchromatic Sensitizers

C.-C. Chou, F.-C. Hu, H.-H. Yeh, H.-P. Wu, Y. Chi,* J. N. Clifford,* E. Palomares, S.-H. Liu, P.-T. Chou,* G.-H. Lee ___ **178 – 183**

Highly Efficient Dye-Sensitized Solar Cells Based on Panchromatic Ruthenium Sensitizers with Quinolinylbipyridine Anchors

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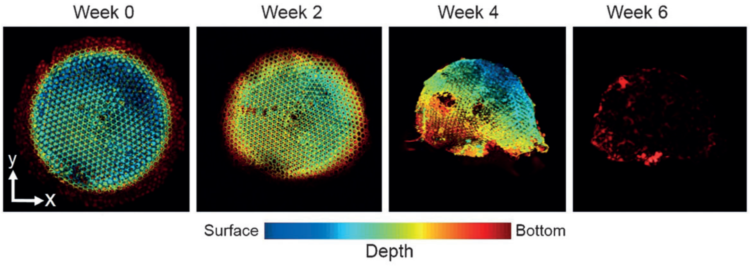


Seeing is believing: By doping a polymer scaffold with an absorption contrast agent, the degradation of this scaffold could be non-invasively monitored and quantified using volumetric photoacoustic microscopy (see pictures). Dual-wavelength imaging further provided the capability to record the vascular remodeling and scaffold degradation simultaneously and in vivo.

Photoacoustic Imaging

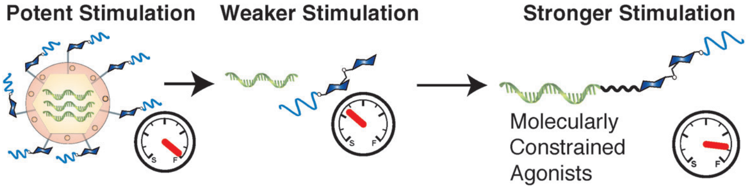
Y. S. Zhang, X. Cai, J. Yao, W. Xing, L. V. Wang,* Y. Xia* ___ **184 – 188**

Non-Invasive and In Situ Characterization of the Degradation of Biomaterial Scaffolds by Volumetric Photoacoustic Microscopy

Immunology

R. J. Mancini, J. K. Tom,
A. P. Esser-Kahn* ———— 189 – 192

Covalently Coupled Immunostimulant Heterodimers

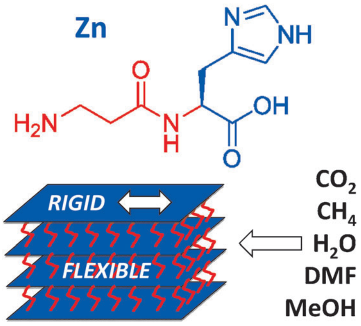


Big PAMPin': Many vaccines present spatially organized agonists known as pathogen-associated molecular patterns (PAMPs) to immune-cell receptors (see picture, left). In a study to probe the spatial aspects of immune-cell activation involving multiple, unique receptors, greater stimulation of dendritic cells was observed with heterodimers of covalently linked immunostimulants than with a mixture of the two unconjugated immunostimulants.

Metal–Organic Frameworks

A. P. Katsoulidis, K. S. Park, D. Antypov,
C. Martí-Gastaldo, G. J. Miller,
J. E. Warren, C. M. Robertson, F. Blanc,
G. R. Darling, N. G. Berry, J. A. Purton,
D. J. Adams,
M. J. Rosseinsky* ———— 193 – 198

Guest-Adaptable and Water-Stable Peptide-Based Porous Materials by Imidazolate Side Chain Control

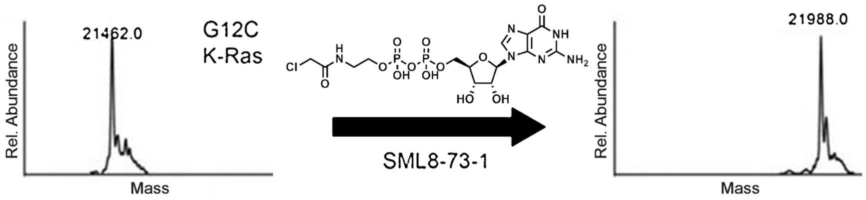


A peptide-based porous framework (ZnCar·DMF), which is formed by the assembly of Zn with carnosine, exhibits permanent microporosity and has pores of chiral shape. Zn–imidazolate bonding to the histidine side chain affords the chemical stability of the framework in water, and the His-β-Ala main chain provides flexibility while conferring structural adaptability on the framework in the presence of different guest molecules.

Drug Design

S. M. Lim, K. D. Westover, S. B. Ficarro,
R. A. Harrison, H. G. Choi, M. E. Pacold,
M. Carrasco, J. Hunter, N. D. Kim, T. Xie,
T. Sim, P. A. Jänne, M. Meyerson,
J. A. Marto, J. R. Engen,
N. S. Gray* ———— 199 – 204

Therapeutic Targeting of Oncogenic K-Ras by a Covalent Catalytic Site Inhibitor



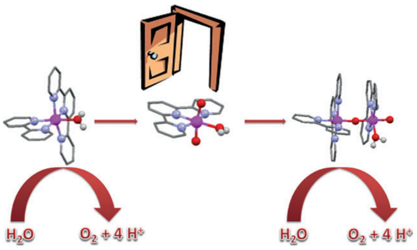
Putting a stop to Ras: Two new selective, direct-acting covalent inhibitors of the K-Ras G12C mutant are reported. Studies suggest that the modification of K-Ras with SML-8-73-1 renders the protein inactive. These novel covalent inhibitors demonstrate that irreversible targeting of the K-Ras guanine-nucleotide binding site is potentially a viable therapeutic strategy for inhibition of Ras signaling.

Water Oxidation

I. López, M. Z. Ertem, S. Maji,
J. Benet-Buchholz, A. Keidel,
U. Kuhlmann, P. Hildebrandt,
C. J. Cramer,* V. S. Batista,*
A. Llobet* ———— 205 – 209

A Self-Improved Water-Oxidation Catalyst: Is One Site Really Enough?

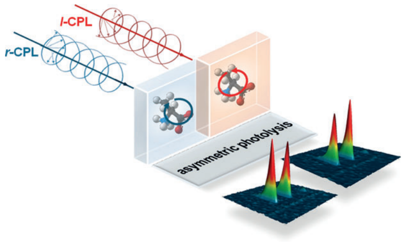
In for the long haul: The transformation of a highly active mononuclear ruthenium–aqua water-oxidation catalyst into a dinuclear complex during oxygen-evolution catalysis led to the coexistence of two different catalytic cycles in solution (see picture; Ru pink, N blue, O red). The dinuclear species was much more robust than its mononuclear counterpart and remained an active catalyst for water oxidation for extended periods of time.



Photochemistry

C. Meinert,* S. V. Hoffmann,
P. Cassam-Chenaï, A. C. Evans, C. Giri,
L. Nahon,* U. J. Meierhenrich **210–214**

Photonenergy-Controlled Symmetry Breaking with Circularly Polarized Light

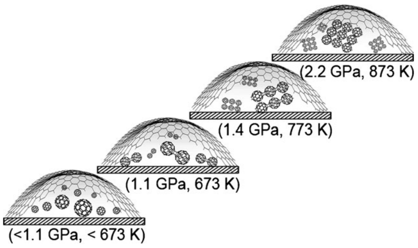


Light-induced chirality: Exposure of *rac*-alanine to tunable circularly polarized light (CPL) has led to the highest optical purities ever generated for this family of compounds by asymmetric photolysis. These enantiomeric enrichments are dependent upon the helicity and energy of the CPL used.

High-Pressure Chemistry

C. H. Y. X. Lim, M. Nesladek,
K. P. Loh* **215–219**

Observing High-Pressure Chemistry in Graphene Bubbles

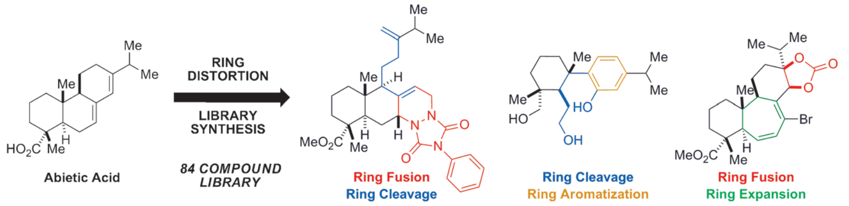


Graphene anvil: Graphene bubbles can be used as a bench-top anvil cell for studying high-pressure chemistry. Pressure-sensitive molecules that undergo conformational changes were used to probe the internal pressures inside the bubbles, which are 0.5–1 GPa over a temperature window of up to 673 K. The pressure-induced oligomerization of C_{60} molecules occurring at distinct *P*–*T* windows could be followed using FTIR spectroscopy.

Molecular Diversity

R. J. Rafferty, R. W. Hicklin, K. A. Maloof,
P. J. Hergenrother* **220–224**

Synthesis of Complex and Diverse Compounds through Ring Distortion of Abietic Acid

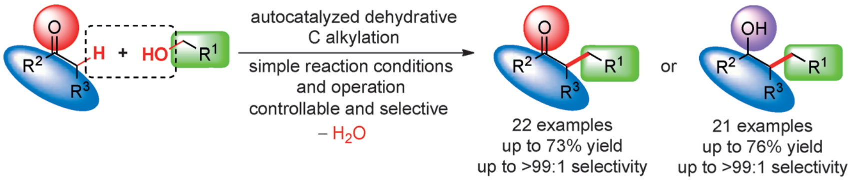


Abietic acid was used as the starting point for the synthesis of 84 complex and diverse small molecules. Their complexity was assessed by the fraction of sp^3-hybridized carbon atoms and the number of stereogenic centers, and their diversity was evaluated by Tanimoto analysis. The 84 compounds constructed herein, and those created through similar efforts, should find utility in a variety of biological screens.

Synthetic Methods

Q. Xu,* J. Chen, H. Tian, X. Yuan, S. Li,
C. Zhou, J. Liu **225–229**

Catalyst-Free Dehydrative α-Alkylation of Ketones with Alcohols: Green and Selective Autocatalyzed Synthesis of Alcohols and Ketones

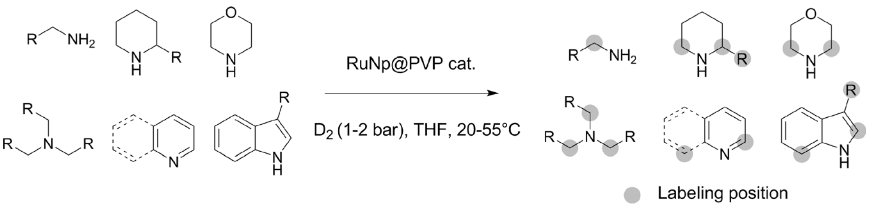


Plain and simple: The title reaction has been realized under simple and practical conditions without using external catalysts, and can afford alkylated ketone or alcohol products in a one-pot manner and on a large scale. The reaction proceeds by C=C bond formation of the in situ generated intermediates with subsequent controllable and selective Meerwein–Pondorf–Verley–Oppenauer-type redox processes.

Isotopic Exchange

G. Pieters, C. Taglang, E. Bonnefille,
T. Gutmann, C. Puente, J.-C. Berthet,
C. Dugave, B. Chaudret,*
B. Rousseau* ______ 230–234

Regioselective and Stereospecific Deuteration of Bioactive Aza Compounds by the Use of Ruthenium Nanoparticles

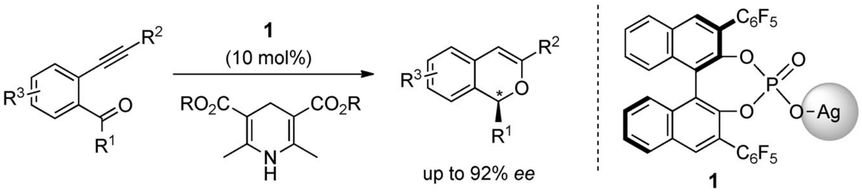


Don't just slap a label on it! A regioselective and stereospecific method for the deuteration of nitrogen-containing compounds has been developed on the basis of a C—H activation process triggered by Ru nanoparticles (RuNps). This general and efficient approach to deuterium labeling was applied to 22 compounds, including 8 biologically active substances (see scheme; PVP = polyvinylpyrrolidone).

Asymmetric Catalysis

M. Terada,* F. Li, Y. Toda ______ 235–239

Chiral Silver Phosphate Catalyzed Transformation of *ortho*-Alkynylaryl Ketones into 1*H*-Isochromene Derivatives through an Intramolecular-Cyclization/Enantioselective-Reduction Sequence

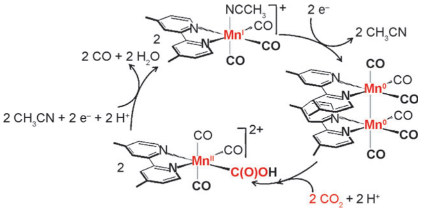


Dependent on its other half: The title reaction of *ortho*-alkynylaryl ketones in the presence of a silver catalyst with a chiral counteranion afforded 1*H*-isochromene derivatives in high yield with good to high enantioselectivity (see scheme; R^1 = alkyl, aryl; R^2 = aryl; R^3 = H, F). An asymmetric synthesis of the 9-oxabicyclo[3.3.1]nona-2,6-diene framework found in biologically active molecules highlights the synthetic utility of this method.

Electrocatalysis

M. Bourrez, M. Orio,* F. Molton,
H. Vezin, C. Duboc, A. Deronzier,
S. Chardon-Noblat* ______ 240–243

Pulsed-EPR Evidence of a Manganese(II) Hydroxycarbonyl Intermediate in the Electrocatalytic Reduction of Carbon Dioxide by a Manganese Bipyridyl Derivative

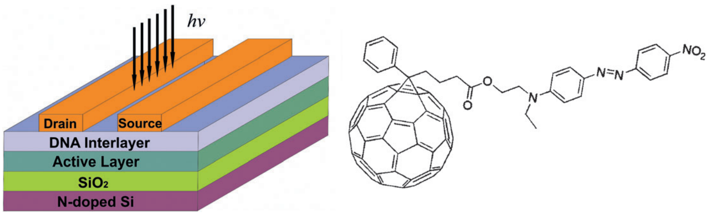


New insights into the catalytic mechanism pathway for selective electrocatalytic reduction of carbon dioxide to carbon monoxide by a manganese(I) carbonyl catalyst are given by using pulsed-EPR spectroscopy combined with DFT calculations. The results directly show the formation of a metal(II)–carboxylic acid–CO_2 adduct (see picture) after oxidative addition of CO_2 and H^+ to a Mn^0 carbonyl dimer.

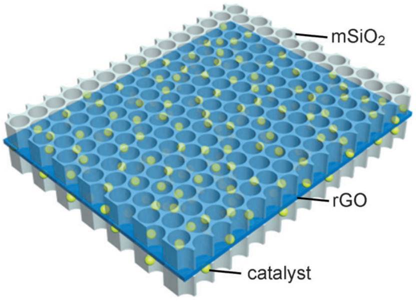
Photoresponsive Materials

Y. Zhang, M. Wang, S. D. Collins, H. Zhou,
H. Phan, C. Proctor, A. Mikhailovsky,
F. Wudl, T.-Q. Nguyen* ______ 244–249

Enhancement of the Photoresponse in Organic Field-Effect Transistors by Incorporating Thin DNA Layers



With a thin DNA layer inserted beneath the top source and drain electrodes, the photoresponse of n-type field-effect transistors based on PCBDR (chemical structure shown in the picture) increases remarkably at low gate bias. This result is primarily attributable to the improved exciton dissociation assisted by the interfacial dipole created at the DNA/PCBDR interface.



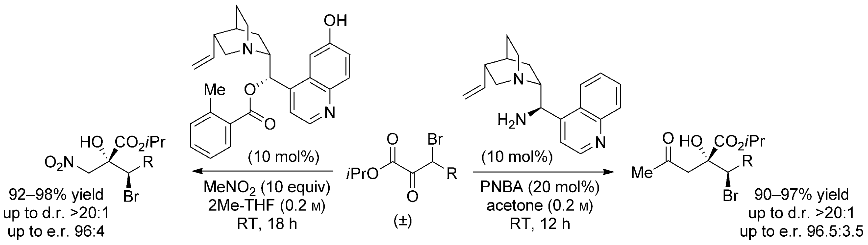
Layer cake: The synthesis of graphene-nanosheet-supported ultrafine metal nanoparticles encapsulated by thin mesoporous silica layers is reported. The resulting class of robust catalysts was shown to possess high activity, good stability under high temperature conditions, and excellent recyclability and reusability in both gas- and solution-phase reactions.

Hetergeneous Catalysts

L. Shang, T. Bian, B. H. Zhang, D. H. Zhang, L.-Z. Wu, C.-H. Tung, Y. Yin,* T. R. Zhang* **250 – 254**

Graphene-Supported Ultrafine Metal Nanoparticles Encapsulated by Mesoporous Silica: Robust Catalysts for Oxidation and Reduction Reactions

Inside Cover



Dynamic and efficient: Dynamic kinetic asymmetric transformations of racemic β-bromo-α-ketoesters through the direct aldolization of nitromethane and acetone provided access to fully substituted α-glycolic acid derivatives bearing a β-stereocenter (see scheme; PNBA = *p*-nitrobenzoic acid). The aldol adducts were obtained in excellent yield with high relative and absolute stereocontrol under mild reaction conditions.

Asymmetric Catalysis

M. T. Corbett, J. S. Johnson* **255 – 259**

Dynamic Kinetic Asymmetric Transformations of β-Stereogenic α-Ketoesters by Direct Aldolization

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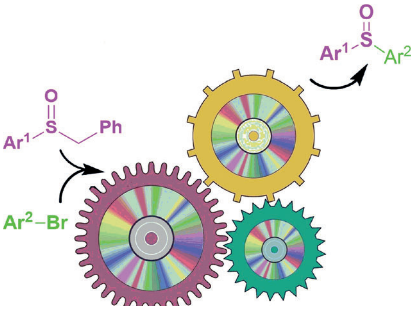

Three for one: The [Pd(dba)$_2$]/NiXantPhos (dba = dibenzylideneacetone) catalyst system successfully promotes a triple relay process involving sulfoxide α-arylation, C–S bond cleavage, and C–S bond formation to give diaryl sulfoxides (see picture). Aryl benzyl sulfoxides, as well as alkyl benzyl sulfoxides reacted with various (hetero)aryl bromides.

Homogeneous Catalysis

T. Jia, A. Bellomo, S. Montel, M. Zhang, K. EL Baina, B. Zheng, P. J. Walsh* **260 – 264**

Diaryl Sulfoxides from Aryl Benzyl Sulfoxides: A Single Palladium-Catalyzed Triple Relay Process

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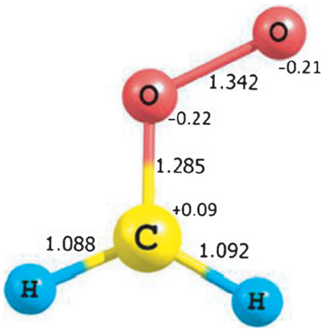


Reading the wave function: The isomerization and decomposition dynamics of the simplest Criegee intermediate CH_2OO were studied by classical trajectory simulations using the multireference ab initio MR-T2 potential on the fly (see picture, numbers are bond lengths (Å) and partial charges). The contributions of different configurations to the multiconfigurational total electronic wave function vary dramatically along the trajectories.

Molecular Dynamics Simulations

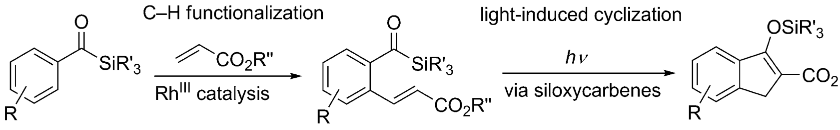
J. Kalinowski,* M. Räsänen, P. Heinonen, I. Kilpeläinen, R. B. Gerber **265 – 268**

Isomerization and Decomposition of a Criegee Intermediate in the Ozonolysis of Alkenes: Dynamics Using a Multireference Potential

Photochemistry

P. Becker, D. L. Priebbenow, R. Pirwerdjan,
C. Bolm* ——— 269 – 271

Acylsilanes in Rhodium(III)-Catalyzed Directed Aromatic C–H Alkenylations and Siloxycarbene Reactions with C=C Double Bonds

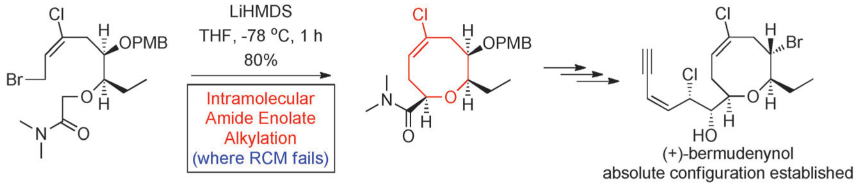


Circle of light: A rhodium(III)-catalyzed olefination process allows access to *ortho*-olefinated aroylsilanes through C–H functionalization in high yields. A light-induced cyclization leads to silyl ethers of indanones in excellent yields as determined by NMR spectroscopy. Mechanistically, the latter transformation proceeds via siloxycarbene intermediates.

Natural Product Synthesis

G. Kim, T. Sohn, D. Kim,*
R. S. Paton ——— 272 – 276

Asymmetric Total Synthesis of (+)-Bermudenynol, a C_{15} *Laurencia* Metabolite with a Vinyl Chloride Containing Oxocene Skeleton, through Intramolecular Amide Enolate Alkylation

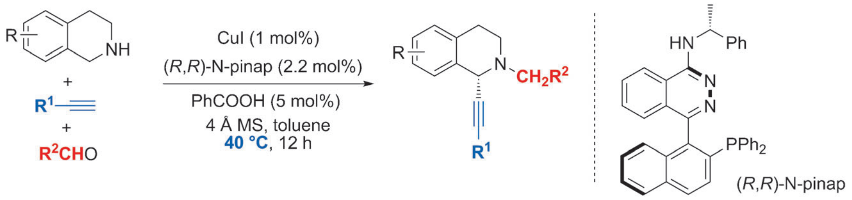


Bermuda octagon: A substrate-controlled asymmetric total synthesis of the title compound was developed. The oxocene core (shown in red), which contains a vinyl chloride unit, was constructed by an efficient and highly stereoselective intramolecular amide enolate alkylation (IAEA). This work demonstrates the utility of the IAEA method, which provides a useful alternative for cases in which ring-closing metathesis (RCM) is inefficient.

Asymmetric Catalysis

W. Lin, T. Cao, W. Fan, Y. Han, J. Kuang, H. Luo, B. Miao, X. Tang, Q. Yu, W. Yuan, J. Zhang, C. Zhu, S. Ma* ——— 277 – 281

Enantioselective Double Manipulation of Tetrahydroisoquinolines with Terminal Alkynes and Aldehydes under Copper(I) Catalysis

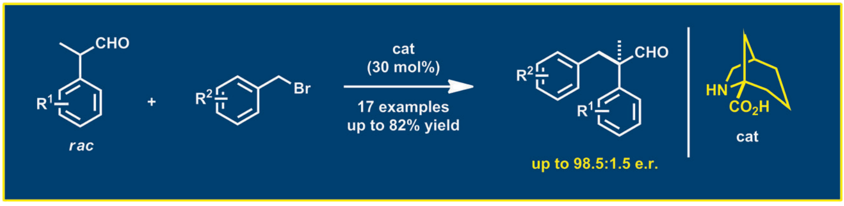


Two groups for the price of one: A mild copper-catalyzed α-alkynylation of unsubstituted tetrahydroisoquinolines with aldehydes and terminal alkynes proceeded with high chemo- and enantioselectivity at a low catalyst loading to provide the core structure of a large class of alkaloids (see scheme). This reaction offers access to a broad range of alkaloid precursors with an *N*-benzyl group and a C–C triple bond for further manipulation.

Aminocatalysis

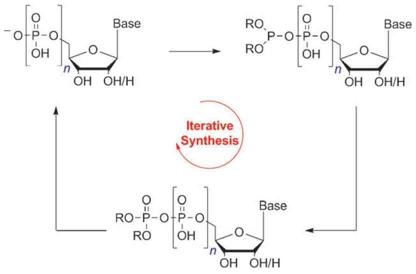
B. List,* I. Čorić, O. O. Grygorenko,
P. S. J. Kaib, I. Komarov, A. Lee,
M. Leutzsch, S. Chandra Pan,
A. V. Tymtsunik,
M. van Gemmeren ——— 282 – 285

The Catalytic Asymmetric α-Benzylation of Aldehydes



A sterically demanding proline derivative promotes the first aminocatalyzed α-alkylation of α-branched aldehydes with benzyl bromides as alkylating agents. Racemic α-branched aldehydes react with alkylating agents in a DYKAT process to give the corresponding α-alkylated aldehydes with quaternary stereogenic centers in good yields and high enantioselectivities.

Omne trium perfectum: Nucleoside triphosphates can be synthesized by an iterative approach based on P-amidite chemistry (coupling, oxidation, deprotection). The reactions occur under ambient conditions without drying of any solvent or reagent. The process is very convenient, fast, and works with all canonical nucleosides. An extension of this approach is the iterative coupling applied to a controlled pore glass bound nucleoside.



Iterative Synthesis

G. S. Cremosnik, A. Hofer, H. J. Jessen* ——— 286–289

Iterative Synthesis of Nucleoside Oligophosphates with Phosphoramidites

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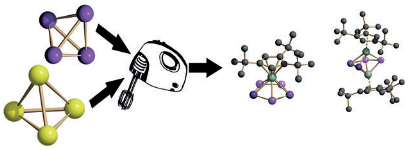
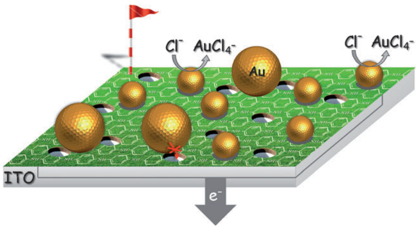
A P_4 butterfly complex reacts with yellow arsenic to yield the largest mixed P_nAs_m ligand complexes synthesized to date. Mass spectrometry together with NMR spectroscopy and X-ray crystallography give clear evidence about the arrangement of the E positions within the *cyclo*-E_5 and E_4 moieties of the products. Moreover, the results of DFT calculations agree well with the experimental determined outcomes.



Mixed-Element Ligands

C. Schwarzmaier, M. Bodensteiner, A. Y. Timoshkin, M. Scheer* ——— 290–293

An Approach to Mixed P_nAs_m Ligand Complexes



Suitable refills: Gold nanoparticles transferred together with monolayers of polyaniline onto a conducting substrate can be electro-oxidized leaving behind cavities of uniform size in the polymer films. The cavities show size-exclusion properties and the films can be used as an analytical tool for the recognition of nanoparticles.

Nanoparticle Detection

S. Kraus-Ophir, J. Witt, G. Wittstock, D. Mandler* ——— 294–298

Nanoparticle-Imprinted Polymers for Size-Selective Recognition of Nanoparticles

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DOI: 10.1002/anie.201309444

Flashback: 50 Years Ago . . .

Manfred Eigen, who was awarded the 1967 Nobel Prize in Chemistry together with Ronald G. W. Norrish and George Porter, published a classic Review on proton transfer mechanisms and the modes of acid–base and enzymatic catalysis. The systems discussed include proton mobility in ice crystals, and pseudo acids. A review of his latest book entitled *From Strange Simplicity to Complex Familiarity: A Treatise on Matter, Information, Life and Thought* appeared in Issue 52/2013.

Albert Eschenmoser et al. reported on the use of *N,N*-dimethylformamide dineopentylacetal for the esterification of carboxylic acids with benzyl alcohols. Use of this reagent is advantageous as only one equivalent of the alcohol is required and only volatile by-products are produced in some cases. Eschenmoser's most recent contribution is a grand Review on prebiotic chemistry (*Angew. Chem. Int. Ed.* **2011**, *50*, 12412).

The preparation of pure disulfur monoxide was reported by P. W. Schenk and R. Steudel, who reacted thionyl chloride with metal sulfides that act as dehalogenating reagents. The reaction of thionyl chloride and silver sulfide provided disulfur monoxide in 96% purity.

H. Rheinheckel published two Communications on triethylaluminum, and reported how an ice-cold mixture of triethylaluminum and carbon tetrachloride exploded when the ice bath was taken away. The explosion was so violent that the hood was destroyed and not a single fragment of glass could be found.

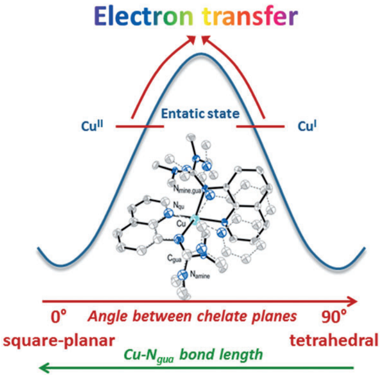
Read more in Issue 1/1964.

Electron Transfer

A. Hoffmann, S. Binder, A. Jesser,
R. Haase, U. Flörke, M. Gnida,
M. Salomone Stagni, W. Meyer-Klaucke,
B. Lebsanft, L. E. Grünig, S. Schneider,
M. Hashemi, A. Goos, A. Wetzel,
M. Rübhausen,
S. Herres-Pawlis* ______ **299 – 304**

Catching an Entatic State—A Pair of Copper Complexes

Independent of the oxidation state, two guanidine–quinoline copper complexes have structures that are virtually identical in both the solid state and in solution. They can be interconverted by a reversible electron transfer at 0.33 V. By resonant excitation of the two copper complexes, the transition state of the electron transfer is accessible through vibrational modes.

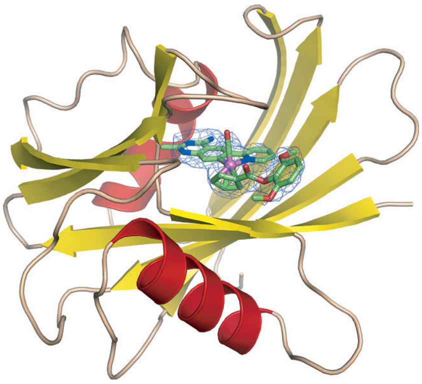


Metal-Containing Inhibitors

M. Streib, K. Kräling, K. Richter, X. Xie,
H. Steuber,* E. Meggers* ______ **305 – 309**

An Organometallic Inhibitor for the Human Repair Enzyme 7,8-Dihydro-8-oxoguanosine Triphosphatase

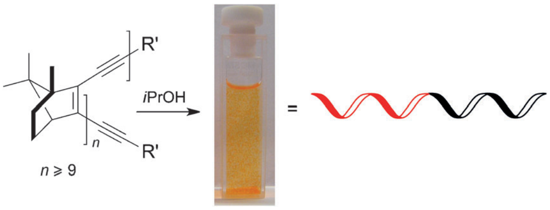
Not a canonical inhibitor: A ruthenium complex has been shown to be a low-nanomolar and selective inhibitor of an enzyme that hydrolyzes oxidized purine nucleoside triphosphates. This work provides a blueprint for the discovery and development of organometallic inhibitors of other purine nucleotide binding proteins which rely on ruthenium-coordinated adenine and quinazoline derivatives with tailored coordination spheres.



Oligodiacetylenes

E. T. Chernick, G. Börzsönyi, C. Steiner,
M. Ammon, D. Gessner, S. Frühbeißer,
F. Gröhn, S. Maier,
R. R. Tykwinski* ______ **310 – 314**

Optically Pure, Monodisperse *cis*-Oligodiacetylenes: Aggregation-Induced Chirality Enhancement

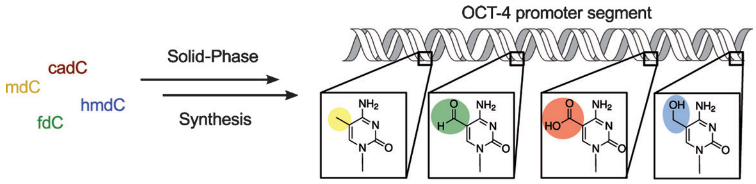


Conformation, conjugation: A series of optically pure, monodisperse *cis*-oligodiacetylenes (*cis*-ODAs) based on D-camphor building blocks has been synthesized up to the tridecamer length, which represents the longest *cis*-ODA reported to date. Optical spectroscopy and STM/AFM measurements indicate that the oligomers assume a linear, planar conformation in THF. Conversely, in *i*PrOH solution ODAs with $n \geq 9$ form chiral aggregates.

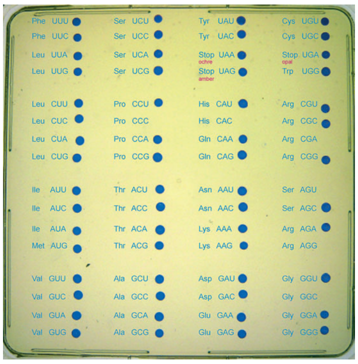
Epigenetics

A. S. Schröder, J. Steinbacher,
B. Steigenberger, F. A. Gnerlich,
S. Schiesser, T. Pfaffeneder,
T. Carell* ______ **315 – 318**

Synthesis of a DNA Promoter Segment Containing All Four Epigenetic Nucleosides: 5-Methyl-, 5-Hydroxymethyl-, 5-Formyl-, and 5-Carboxy-2′-Deoxycytidine



Biologically relevant promoter segments with all four epigenetic nucleosides are finally accessible by solid-phase synthesis. With the fdC-phosphoramidite building block introduced herein, no side reactions of 5-formylcytosine were observed. Furthermore, mild deprotection conditions prevented oxidative or reductive lesions, which was proven by detailed mass spectrometric analysis.



The selenocysteine insertion machinery was engineered to recode multiple sense codons. This was demonstrated for *Escherichia coli* formate dehydrogenase and recombinant human thioredoxin reductase. In the picture the canonical genetic code table is overlaid with a single assay in which purple-colored cells express active Sec-containing enzymes.

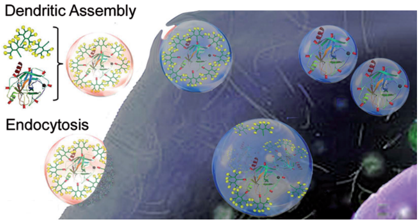
RNA Engineering

M. J. Bröcker, J. M. L. Ho, G. M. Church, D. Söll,* P. O'Donoghue* ____ **319–323**

Recoding the Genetic Code with Selenocysteine

Front Cover

The programmed self-assembly of a dendritic shell onto enzymes was used to modulate enzyme activity as well as induce cellular entry and release of the active proteins. The defined dendritic construct represents a contemporary avenue for smart protein therapeutics.



Supramolecular Enzyme Hybrids

D. Y. W. Ng, M. Arzt, Y. Wu, S. L. Kuan, M. Lamla, T. Weil* ________ **324–328**

Hybrid Protein Zymogens with a Self-Assembled Protective Dendrimer Shell

Inside Back Cover

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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