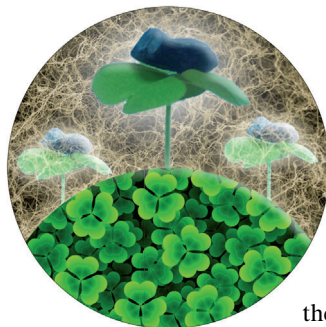
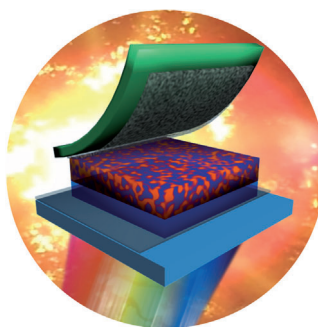


In their Communication on page 2874 ff., A. J. Heeger et al. show how to insert electron-transport layers of transferable graphene oxide into bulk-heterojunction solar cells for enhanced power-conversion efficiency.



Ultralight, flexible, and fire-resistant carbon nanofiber aerogels, which can be fabricated in large scale by using bacterial cellulose as a precursor, are described by S. H. Yu and co-workers in their Communication on page 2925 ff.

Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

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In this issue, many articles are accompanied by a special symbol:



The articles marked with this symbol are by speakers at the Anniversary Symposium celebrating 125 years of *Angewandte Chemie*.



"...Angewandte Chemie is probably the only scientific journal of such standing that not only comes from Germany, but even has a German title, and has established itself on the international stage ..."
Read more in the Editorial by Wolfram Koch.

Editorial

W. Koch* _____ 2614

Made in Germany: 125 Years of
Angewandte Chemie



"... What has so far been largely missing in bottom-up synthetic biology, however, is the power of true chemical synthesis ..."
Read more in the Editorial by Petra Schwill.

P. Schwill* _____ 2616 – 2617

Chemistry Needed: Synthetic Biology as
a New Incentive for Interdisciplinarity

Spotlight on Angewandte's Sister Journals

Editorial Board and International Advisory Board of *Angewandte Chemie*

2640 – 2642

2644 – 2645

Miscellaneous



*"If I won the lottery, I would buy a Steinway for me and a house for my Steinway.
My favorite place on earth is Paris ..."*
This and more about Paul Knochel can be found on page 2646.

Author Profile

Paul Knochel _____ 2646 – 2647

News



B. List



M. Christmann



E. E. Wille



R. Schlögl



F. Glorius



M. Beller



N. Maulide

Horst Pracejus Prize: B. List _____ **2648**

Carl Duisberg Memorial Prize:
M. Christmann _____ **2648**

Carl Duisberg Plaque: E. E. Wille — **2648**

Honorary Professorship:
R. Schlögl _____ **2648**

Gottfried Wilhelm Leibniz Prize:
F. Glorius _____ **2648**

Karl Ziegler Guest Professorship:
M. Beller _____ **2648**

Bayer Early Excellence in Science Award:
N. Maulide _____ **2648**

Books

Catalysis

Matthias Beller, Albert Renken, Rutger A. van Santen

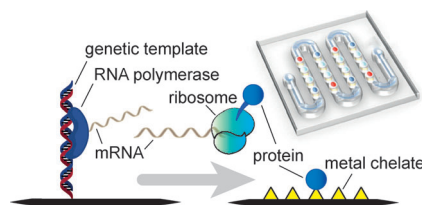
reviewed by F. E. Kühn _____ **2650**

Highlights

On-Chip Biosynthesis

C. Timm, C. M. Niemeyer* — **2652–2654**

On-Chip Protein Biosynthesis

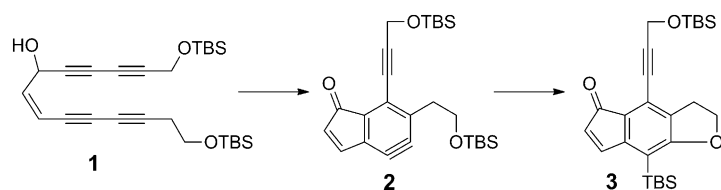


Spot on! Cell-free protein expression on surfaces can be implemented in biosensors and in microfluidic devices like that shown in the picture. Proteins are generated and immobilized successively on separated spots in a microfluidic reactor. This approach opens up novel opportunities for basic and applied biomedical research.

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.



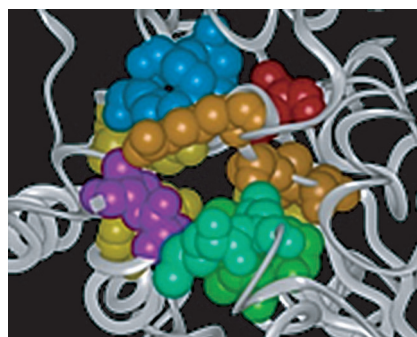
Fundamental aspects of chemically activated reactive intermediates can possibly be learned from the novel generation of arynes. The intramolecular [4+2] cycloaddition

between a diyne and an (electronically activated) alkyne also provides a new route to generate arynes (see scheme).

Reactive Intermediates

R. W. Hoffmann,* K. Suzuki 2655–2656

A “Hot, Energized” Benzyne



Additive or non-additive, that is the question: The increasing awareness of non-additive cooperative mutational effects in protein engineering is currently providing new theoretical and practical insights. In particular, the directed evolution of stereoselective enzymes as catalysts in organic chemistry and biotechnology profits from this intriguing development.

Essays

Protein science

M. T. Reetz* 2658–2666

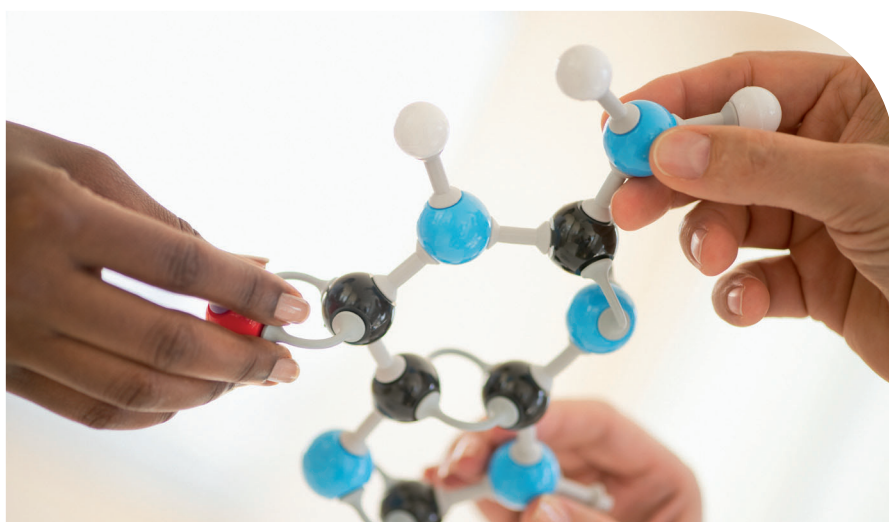
The Importance of Additive and Non-Additive Mutational Effects in Protein Engineering

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Unpredictability of Science

E. Keinan* _____ 2667–2672

Gloomy Forecast for the Prophets of Apocalypse and Bright Forecast for Chemists

The human population, doubling every 50 years, creates global problems, including limitations on energy, raw materials, food, water, health, and air. However, the future of humankind seems bright thanks to the even faster growth of human knowledge,

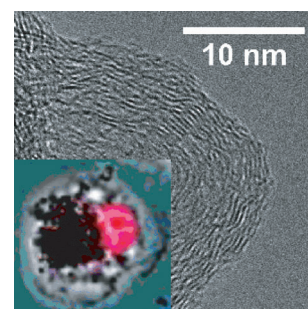
doubling every 18 months, and the unpredictability of science. Our global challenges are likely to be met by yet unknown technologies, mostly invented by chemists.

Exhaust Emission

B. Frank, M. E. Schuster, R. Schlögl,
D. S. Su* _____ 2673–2677

Emission of Highly Activated Soot Particulate—The Other Side of the Coin with Modern Diesel Engines

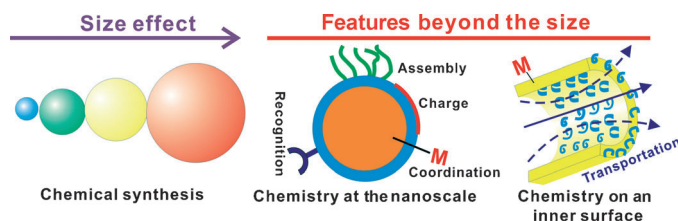
Soot toxification: The increasing chemical activity of the emitted soot particulate produced by modern diesel engines is an unwanted side effect of modification of the motors. This makes Euro IV and VI soots chemically and biologically highly active and hazardous. Taking these factors into consideration, the question arises whether the reduced net mass of diesel soot particulate emitted overcompensates for the induced micro- and nano-structure.



Nanoscience

C. Bai,* M. Liu _____ 2678–2683

From Chemistry to Nanoscience: Not Just a Matter of Size



Size matters: Chemistry has contributed strongly to the rapid development of nanoscience resulting in an ever-growing amount of nanosized systems and materials. The properties of these systems do not only arise from their size, but also

surface modifications and structures. Nanomaterials thus have unique properties and can contribute to the development of chemistry, including nanocatalysts and nanomedicine.

Drug Development

H. Wild,* C. Huwe, M. Lessl _____ 2684–2687

“Collaborative Innovation”—Regaining the Edge in Drug Discovery

Sharers are winners: The concept of “Collaborative Innovation” has the potential to overcome the significant challenges the pharmaceutical industry faces in its effort to improve the lives of patients by fighting increasingly complex diseases. In order to succeed, it is crucial

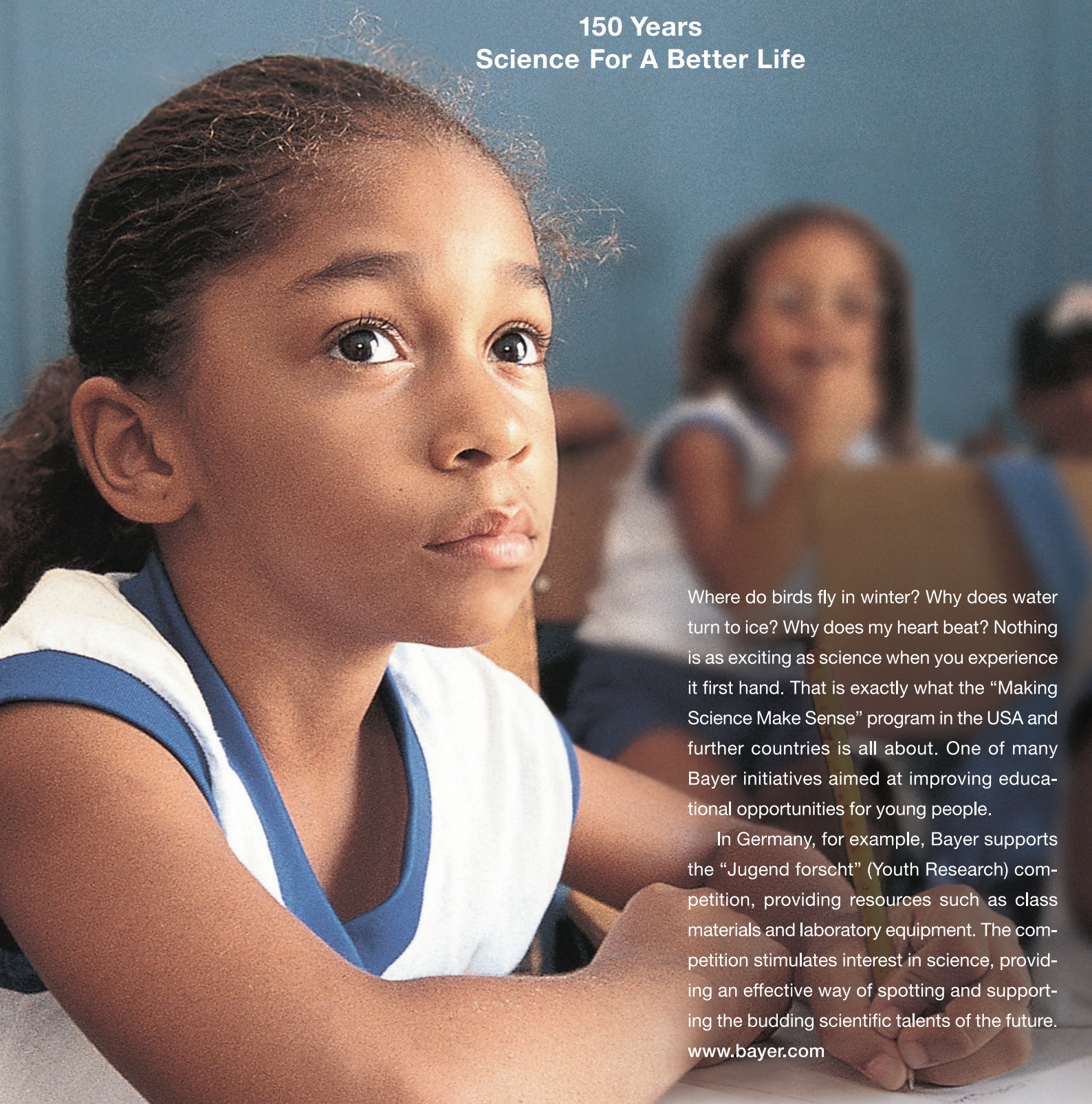
to join forces on a global level and to combine different approaches in a flexible way, requiring the right mindset of all involved parties, a combination of internal excellence and external openness, and the right organizational setup.

Supporting Education



Promoting Talent

**150 Years
Science For A Better Life**



Where do birds fly in winter? Why does water turn to ice? Why does my heart beat? Nothing is as exciting as science when you experience it first hand. That is exactly what the "Making Science Make Sense" program in the USA and further countries is all about. One of many Bayer initiatives aimed at improving educational opportunities for young people.

In Germany, for example, Bayer supports the "Jugend forscht" (Youth Research) competition, providing resources such as class materials and laboratory equipment. The competition stimulates interest in science, providing an effective way of spotting and supporting the budding scientific talents of the future.
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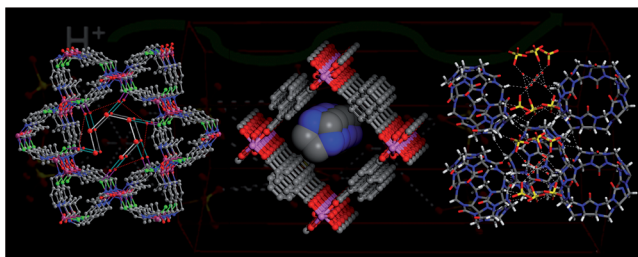
MaterialScience

Minireviews

Proton-Conducting Materials

M. Yoon, K. Suh, S. Natarajan,*
K. Kim* ————— 2688 – 2700

Proton Conduction in Metal–Organic Frameworks and Related Modularly Built Porous Solids



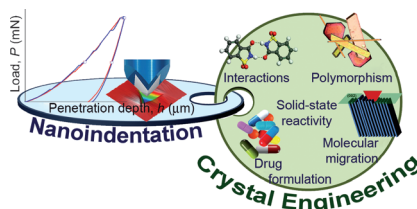
Pores and protons: Development of new types of proton-conducting materials is important in fuel-cell technology. Newly developed proton-conducting materials

formed from modularly built porous solids, including coordination polymers (CPs) or metal–organic frameworks (MOFs) are discussed (see scheme).

Crystal Engineering

S. Varughese, M. S. R. N. Kiran,
U. Ramamurty,*
G. R. Desiraju* ————— 2701 – 2712

Nanoindentation in Crystal Engineering: Quantifying Mechanical Properties of Molecular Crystals



Poking crystals: The application of nano-indentation in crystal engineering provides an important breakthrough in establishing links between microscopic structures and macroscopic properties. This Minireview highlights some of the advantages of this technique for studying the mechanical behavior of organic crystals.

Reviews

History of Chemistry

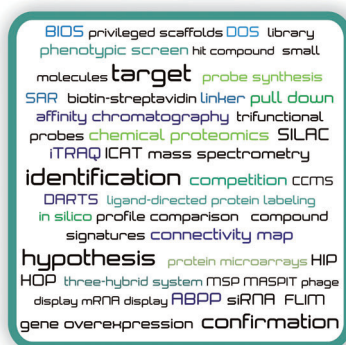
F. Diederich* ————— 2714 – 2742

125 Years of Chemistry in the Mirror of “Angewandte”



The development of Angewandte Chemie and the changes in chemical research over the first 125 years of its existence are the topic of this Review. Even from the content of its first 50 years, the journal offers numerous milestones in chemical research, and today, with its attractive layout and successful mix of articles, it covers chemical research worldwide in its full breadth.

How to solve the riddle? When phenotypic screens are performed, mostly there are missing pieces (of information) that would explain the link between a biologically active compound and the appearance of a certain phenotype. The interplay of organic synthesis, cell biology, proteomics, genetics, molecular biology, biochemistry, informatics, and biophysics is required to find the missing pieces and to assemble the whole puzzle of a compound's cellular activity.



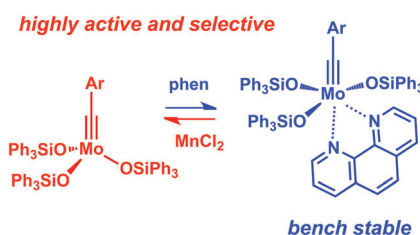
Drug Discovery

S. Ziegler,* V. Pries, C. Hedberg,*
H. Waldmann* 2744–2792

Target Identification for Small Bioactive Molecules: Finding the Needle in the Haystack



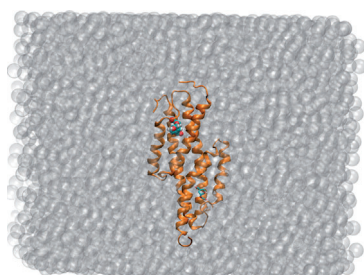
Making connections: The latest generation of alkyne metathesis catalysts holds considerable promise for synthesis, as they are exceptionally active, remarkably tolerant, and, in the form of their phenanthroline adducts, bench stable (see scheme). Numerous applications to material science and natural product synthesis illustrate the excellent performance and structural scope of this method.



Catalysis for Synthesis

A. Fürstner* 2794–2819

Alkyne Metathesis on the Rise

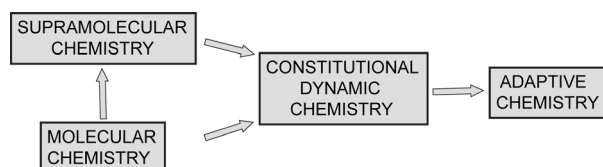


Various levels of resolution, for example, electronic, atomic, supramolecular, are combined in one model in multi-resolution simulations. The basic choices when setting up a multi-resolution model are reviewed. As an illustration the differential catalytic properties of two enzymes with similar folds are explored using multi-resolution simulation at three different levels of resolution.

Computational Chemistry

K. Meier, A. Choutko, J. Dolenc,
A. P. Eichenberger, S. Riniker,
W. F. van Gunsteren* 2820–2834

Multi-Resolution Simulation of Biomolecular Systems: A Review of Methodological Issues



Chemistry is key for understanding the fundamental processes that underlie the evolution of matter towards states of increasing complexity through self-organization. It has developed from the molec-

ular to the supramolecular level and has, through constitution dynamic systems, acquired the features of adaptive chemistry. Hence, chemistry opens the door towards complex matter.

Towards Complex Matter

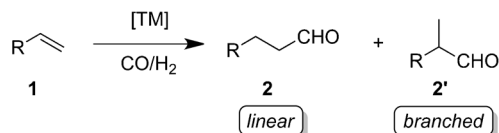
J.-M. Lehn* 2836–2850

Perspectives in Chemistry—Steps towards Complex Matter

Homogeneous Hydroformylation

J. Pospech, I. Fleischer, R. Franke,*
S. Buchholz, M. Beller* — 2852–2872

Alternative Metals for Homogeneous
Catalyzed Hydroformylation Reactions



New possibilities: There is a growing awareness that organometallic complexes based on ruthenium, iridium, palladium, and even iron as the central metal offer new opportunities for catalytic hydrofor-

mylations (see scheme; TM = transition metal). Research from the past few decades is critically summarized in this Review.

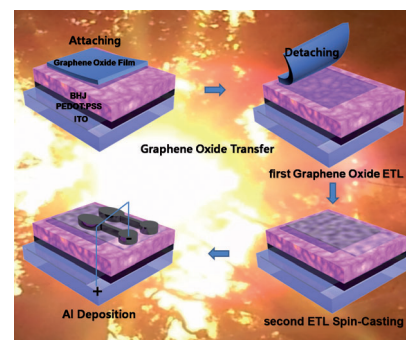
Communications

Organic Electronics

D. H. Wang, J. K. Kim, J. H. Seo, I. Park,
B. H. Hong, J. H. Park,
A. J. Heeger* — 2874–2880

Transferable Graphene Oxide by Stamping
Nanotechnology: Electron-Transport
Layer for Efficient Bulk-Heterojunction
Solar Cells

Layer by layer: Electron-transport layers (ETLs) of transferable graphene oxide (GO) inserted by using a stamping nanotechnology (see picture) result in bulk-heterojunction (BHJ) solar cells with enhanced power conversion efficiency because of enhanced electron-charge transport and reduced electronic charge barrier with low series resistance. The GO ETL also increases the stability of the device in air.

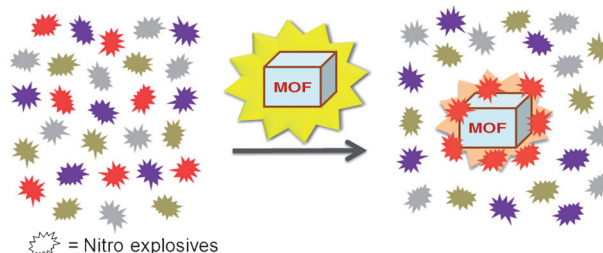


Frontispiece

Metal–Organic Frameworks

S. S. Nagarkar, B. Joarder, A. K. Chaudhari,
S. Mukherjee, S. K. Ghosh* — 2881–2885

Highly Selective Detection of Nitro
Explosives by a Luminescent Metal–
Organic Framework



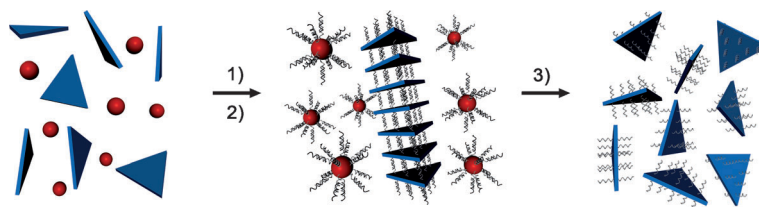
TNP can't hide from MOF: A three-dimensional fluorescent metal–organic framework (MOF), $[\text{Cd}(\text{NDC})_{0.5}(\text{PCA})]\cdot\text{G}_x$, can be used for the detection of 2,4,6-trinitrophenol (TNP). The MOF exhibits

high selectivity towards TNP, even in the presence of other nitro explosives in aqueous and organic solutions, owing to electron- and energy-transfer mechanisms and electrostatic interactions.

Nanoparticle Separation

M. R. Jones, C. A. Mirkin* — 2886–2891

Bypassing the Limitations of Classical
Chemical Purification with DNA-
Programmable Nanoparticle
Recrystallization



And then there was one: Anisotropic nanoparticle syntheses often contain impurity nanostructures. Functionalization of the products of such syntheses with DNA (see scheme (1)) allows the relative interaction strengths between

particles to be tailored. The desired nanoparticle component can then be crystallized selectively (2) and separated to arrive at samples of significantly improved purity (3).



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help millions of people by
alleviating their suffering and
improving their quality of life.
We give them hope.



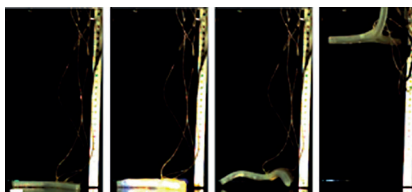
We Innovate Healthcare

Soft Robots

R. F. Shepherd, A. A. Stokes, J. Freake,
J. Barber, P. W. Snyder, A. D. Mazzeo,
L. Cademartiri, S. A. Morin,
G. M. Whitesides* — 2892–2896



Using Explosions to Power a Soft Robot



Combustion causes a soft robot to jump:

Rapid actuation of a soft robot (composed of silicone elastomers) was achieved using high-temperature chemical reactions. Computer-controlled electrical sparks triggered the combustion of premixed CH_4 and O_2 gases inside the robot, which pressurized the pneumatic channels of the robot and caused it to jump (see figure). The heat from the explosions dissipated quickly and did not damage the robot even over many jumps.

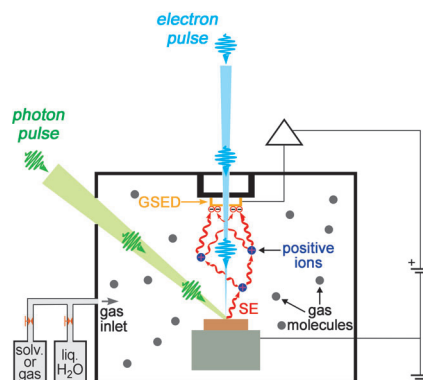
Ultrafast Electron Microscopy

D.-S. Yang, O. F. Mohammed,
A. H. Zewail* — 2897–2901



Environmental Scanning Ultrafast
Electron Microscopy: Structural
Dynamics of Solvation at Interfaces

On the surface: CdSe surfaces have been used as a prototype for the investigation of the spatiotemporal characteristics of solvation by environmental scanning ultrafast electron microscopy (see picture, GSED = gaseous secondary electron detector). This study has shown that the ultrafast relaxation dynamics of polar molecules, such as water, in the adsorbate layers exhibit a striking dependence on the CdSe surface structure.

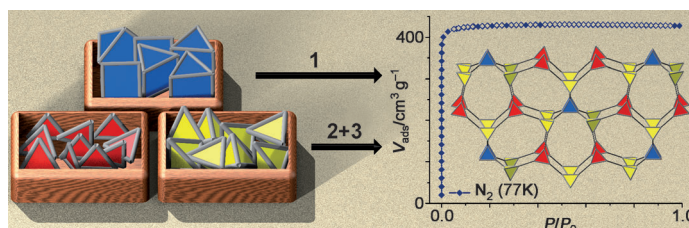


Metal–Organic Materials

A. Schoedel, A. J. Cairns, Y. Belmabkhout,
L. Wojtas, M. Mohamed, Z. Zhang,
D. M. Proserpio, M. Eddaoudi,
M. J. Zaworotko* — 2902–2905



The asc Trinodal Platform: Two-Step
Assembly of Triangular, Tetrahedral, and
Trigonal-Prismatic Molecular Building
Blocks



The self-assembly of triangular, tetrahedral, and trigonal-prismatic molecular building blocks affords the first example of a trinodal family of metal–organic materials. Four examples of isorecticular

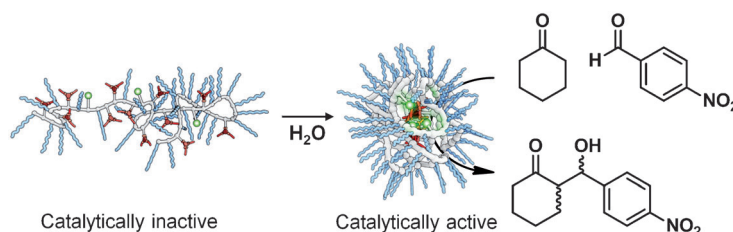
expanded and functionalized frameworks are detailed. Gas adsorption experiments validated the permanent porosity of the parent structure.

Supramolecular Chemistry

E. Huerta, P. J. M. Stals, E. W. Meijer,*
A. R. A. Palmans* — 2906–2910

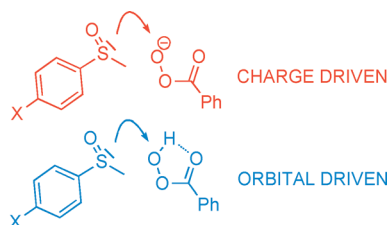
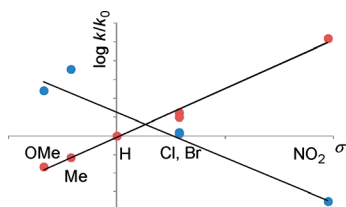


Consequences of Folding a Water-Soluble
Polymer Around an Organocatalyst



Give 'em structure: The presence of structuring elements in polymers that were functionalized with catalytic units resulted in a new class of enzyme mimics, which are only active in the folded state

(see picture). The conformationally adaptive hydrophobic environment that surrounds the catalytic site allows the very efficient catalysis of an aldol reaction in water with Michaelis–Menten kinetics.



Nucleophilic Substitution

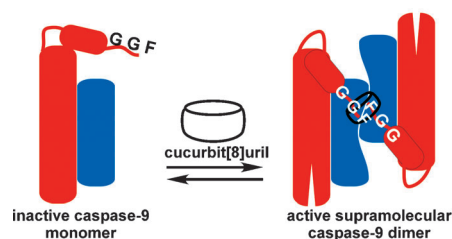
G. Licini, C. Zonta* — 2911–2914

Revisiting the Hammett ρ Parameter for the Determination of Philicity: Nucleophilic Substitution with Inverse Charge Interaction



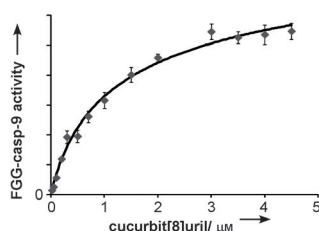
Too OT to handle? In oxygen transfer (OT) reactions the inversion of the ρ value is not representative of a change in mechanism. Substituents bonded to aromatic

sulfoxides have the opposite effect on the rates of oxidation depending on whether the reaction is dominated by electrostatic or orbital-overlap effects (see picture).



At the double: Cucurbit[8]uril-mediated protein dimerization enables reversible control over strong enzyme activation of caspases. Simple addition of a short N-

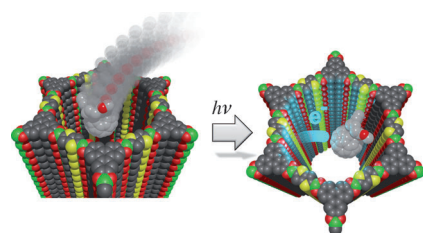
terminal FGG motif allows for a supramolecular-mediated 50-fold enhancement of caspase-9 catalytic activity.



Host–Guest Chemistry

D. T. Dang, H. D. Nguyen, M. Merckx, L. Brunsvelde* — 2915–2919

Supramolecular Control of Enzyme Activity through Cucurbit[8]uril-Mediated Dimerization

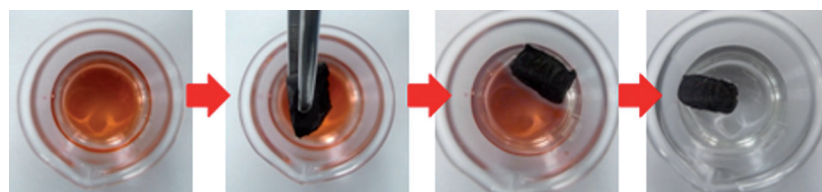


Filling a honeycomb: The thienothiophene-based covalent organic framework (COF) can be loaded with a complementary semiconductor, such as a fullerene derivative, and electronic interactions are observed (see figure). The novel periodic interpenetrated donor–acceptor system shows the spectroscopic signatures of efficient charge transfer on the nanoscale. Photovoltaic activity was demonstrated upon integrating the COF:fullerene film into a device.

Energy Transfer

M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel,* T. Bein* — 2920–2924

A Photoconductive Thienothiophene-Based Covalent Organic Framework Showing Charge Transfer Towards Included Fullerene



Thirsty fibers: The aerogels described in the title can be fabricated in large scale by using a low-cost biomass, bacterial cellulose, as a precursor, which can be produced at industrial level in a microbial

fermentation process. The carbon nanofiber aerogels (black pieces in picture) exhibit superior absorption capacity for organic solvents (red solution) and high potential for pressure sensing.

Carbon Nanomaterials

Z. Y. Wu, C. Li, H. W. Liang, J. F. Chen, S. H. Yu* — 2925–2929

Ultralight, Flexible, and Fire-Resistant Carbon Nanofiber Aerogels from Bacterial Cellulose



Inside Back Cover



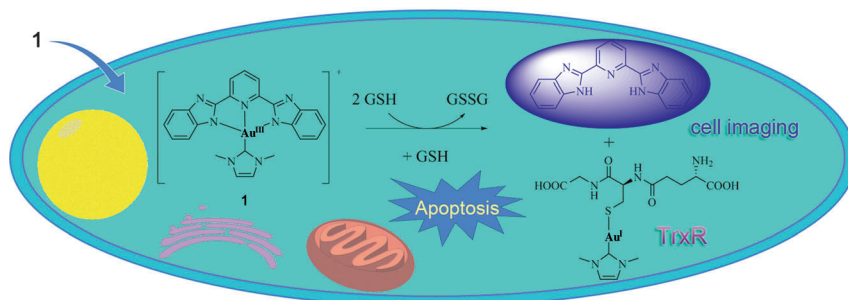


In Vivo Gold Chemistry

T. Zou, C. T. Lum, S. S.-Y. Chui,
C.-M. Che* 2930–2933



Gold(III) Complexes Containing N-
Heterocyclic Carbene Ligands: Thiol
“Switch-on” Fluorescent Probes and Anti-
Cancer Agents



Illuminating results: Activation of non-emissive $[\text{Au}^{\text{III}}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{NHC})]^+$ complexes (such as **1**) through reduction by intracellular glutathione gives active Au^{I} -NHC complexes, which show promising

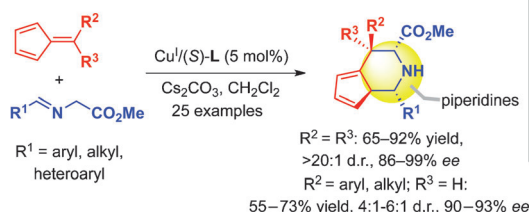
anti-cancer properties, accompanied by release of the highly fluorescent ligand. The high fluorescence “switch-on” efficiency makes these Au^{III} complexes excellent probes for cellular thiol detection.

Asymmetric Catalysis

Z.-L. He, H.-L. Teng,
C.-J. Wang* 2934–2938



Fulvenes as Effective Dipolarophiles in
Copper(I)-Catalyzed [6+3] Cycloaddition
of Azomethine Ylides: Asymmetric
Construction of Piperidine Derivatives



As easy as π : Fulvenes serve as 6π dipolarophiles in the title reaction in the presence of the chiral $\text{Cu}^{\text{I}}/(\text{S})\text{-L}$ complex. The present system provides a unique and straightforward access to enantioen-

riched, highly functionalized piperidine derivatives in good yields and excellent diastereoselectivities and enantioselectivities.

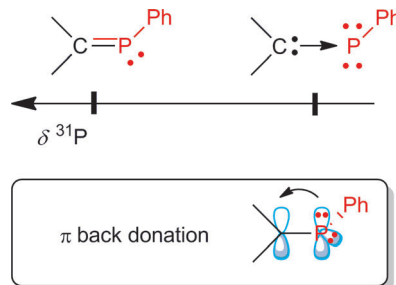
Stable Carbenes

O. Back, M. Henry-Ellinger, C. D. Martin,
D. Martin, G. Bertrand* 2939–2943



^{31}P NMR Chemical Shifts of Carbene-
Phosphinidene Adducts as an Indicator of
the π -Accepting Properties of Carbenes

Beyond the Tolman electronic parameter: The ^{31}P NMR chemical shifts of easily synthesized carbene–phenylphosphinidene adducts allow the determination of the relative π -acceptor properties of carbenes. In combination with the Tolman electronic parameter value, the relative pure σ -donation of carbenes can also be evaluated.

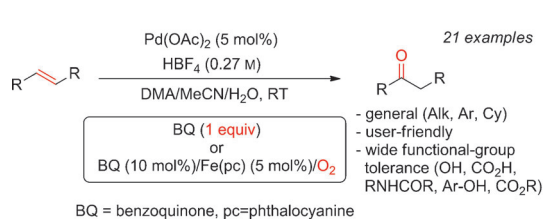


Synthetic Methods

B. Morandi, Z. K. Wickens,
R. H. Grubbs* 2944–2948



Practical and General Palladium-
Catalyzed Synthesis of Ketones from
Internal Olefins



Make it simple! A convenient and general palladium-catalyzed oxidation of internal olefins to ketones is reported. The transformation occurs at room temperature and shows wide substrate scope. Appli-

cations to the oxidation of seed-oil derivatives and a bioactive natural product (see scheme) are described, as well as intriguing mechanistic features.



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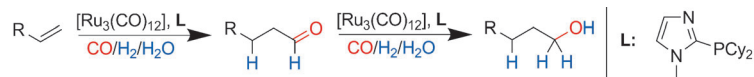
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Carbonylation

I. Fleischer, K. M. Dyballa, R. Jennerjahn,
R. Jackstell, R. Franke, A. Spannenberg,
M. Beller* 2949–2953



From Olefins to Alcohols: Efficient and
Regioselective Ruthenium-Catalyzed
Domino Hydroformylation/Reduction
Sequence



Exploring the alternatives: Ruthenium
imidazolyl phosphine complexes catalyze
the domino hydroformylation/reduction
of alkenes to alcohols in good yields and

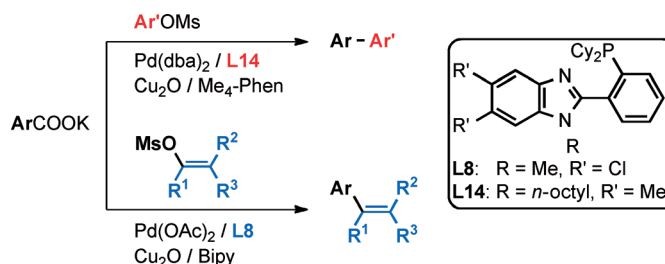
with good selectivities (see scheme).
Linear aliphatic alcohols are synthesized
under reaction conditions typically used in
industrial hydroformylations.

C–C Coupling

B. Song, T. Knauber,
L. J. Gooßen* 2954–2958



Decarboxylative Cross-Coupling of
Mesylates Catalyzed by Copper/Palladium
Systems with Customized Imidazolyl
Phosphine Ligands



The activation of the inert C–O bonds in
mesylates through the use of a new class
of imidazolyl phosphines allows the
decarboxylative coupling of aryl mesylates
as well as polysubstituted alkenyl mesy-

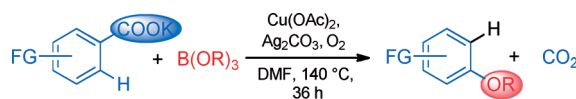
lates. Variation of the ligands leads to two
complementary methods providing the
corresponding biaryls and polysubstituted
olefins in good yields.

C–H Activation

S. Bhadra, W. I. Dzik,
L. J. Gooßen* 2959–2962



Synthesis of Aryl Ethers from Benzoates
through Carboxylate-Directed C–H-
Activating Alkoxylation with Concomitant
Protodecarboxylation



One in, one out: In the presence of
a copper/silver bimetallic catalyst system,
aromatic carboxylate salts undergo *ortho*
C–H alkoxylation with concomitant loss of
the carboxylate directing group in a proto-

decarboxylation step (see scheme, FG =
functional group). This process provides
a convenient synthetic access to the
important class of aromatic ethers from
widely available carboxylic acids.

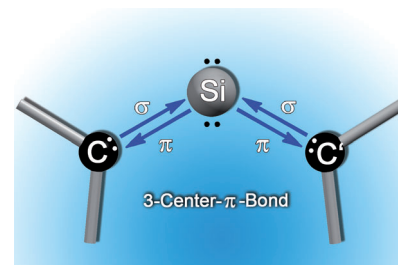
Low-Valent Silicon

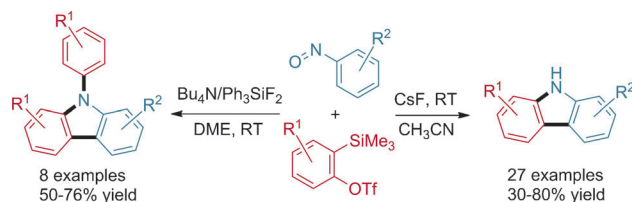
K. C. Mondal, H. W. Roesky,*
M. C. Schwarzer, G. Frenking,*
B. Niepötter, H. Wolf, R. Herbst-Irmer,
D. Stalke* 2963–2967



A Stable Singlet Biradicaloid
Siladibene: (L)₂Si

A trapped silicon atom: The compound
(L)₂Si with low-valent silicon was
synthesized from its dichloride biradical
precursor (L)₂SiCl₂ by reduction with K₂C₈.
Theoretical analysis suggest that there are
two donor–acceptor σ bonds L→Si←L.
There is one σ lone-pair orbital at Si and
one π orbital which features significant
π-back-donation L←Si→L giving short
Si–C bonds.





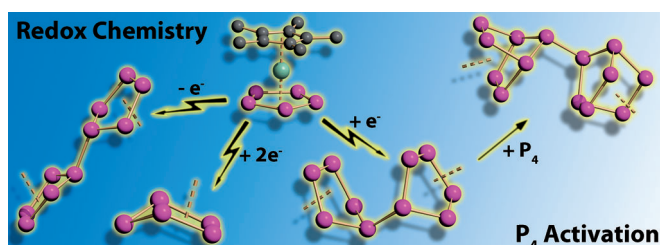
No transition metals are necessary in the reaction of in situ generated arynes with nitrosoarenes to give substituted carbazoles. Depending on the fluoride source and the solvent, either N-arylated carbazoles or NH-carbazoles are obtained (see

scheme; DME = dimethoxyethane, OTf = trifluoromethanesulfonate). In these cascades a C–C and one or two C–N bonds are formed. The reactions are easy to conduct and proceed under mild conditions.

Heterocycles

S. Chakrabarty, I. Chatterjee, L. Tebben, A. Studer* 2968–2971

Reactions of Arynes with Nitrosoarenes—An Approach to Substituted Carbazoles



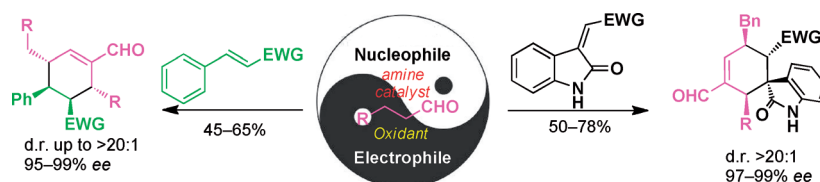
Pentaphosphaferrocene redox chemistry: Unprecedented dianionic and P–P coupled and monomeric products are obtained by the reduction of pentaphosphaferrocene with KH or K metal, whereas

by oxidation a P–P coupled P_{10}^{2+} ligand coordinated to two Cp^*Fe units is obtained. The redox behavior clearly distinguishes pentaphosphaferrocene from its organometallic relative, ferrocene.

Small-Molecule Activation

M. V. Butovskiy, G. Balázs, M. Bodensteiner, E. V. Peresypkina, A. V. Virovets, J. Sutter, M. Scheer* 2972–2976

Ferrocene and Pentaphosphaferrocene: A Comparative Study Regarding Redox Chemistry



Take two: By employing two equivalents of an aldehyde in an asymmetric organocatalytic domino reaction, the nucleophilic enamine intermediate is also converted into the corresponding iminium species through oxidation with *o*-iodoxy-

benzoic acid. Thus, polyfunctionalized cyclohexene derivatives are formed from two simple starting materials in good yields and stereoselectivities (see scheme; Bn = benzyl, EWG = electron-withdrawing group).

Asymmetric Synthesis

X. Zeng, Q. Ni, G. Raabe, D. Enders* 2977–2980

A Branched Domino Reaction: Asymmetric Organocatalytic Two-Component Four-Step Synthesis of Polyfunctionalized Cyclohexene Derivatives

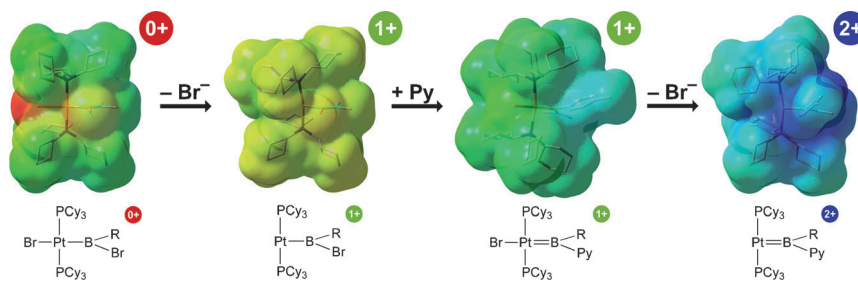


Low-Coordinate Complexes

H. Braunschweig,* P. Brenner,
R. D. Dewhurst, J. O. C. Jimenez-Halla,
T. Kupfer, D. Rais,
K. Uttinger ————— 2981–2984



Maximizing Coordinative and Electronic
Unsaturation: Three-Coordinate
Dicationic Platinum Complexes



Halide abstraction from cationic base-stabilized borylene complexes led to extremely electronically and coordinatively unsaturated platinum complexes. The formally 14-electron borylene complexes

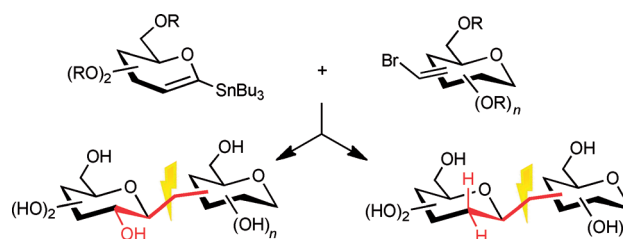
show no agostic interactions with the phosphine ligands, and only small Lewis donor ligands could be added to the Pt center.

Carbohydrate Mimics

D. C. Koester, E. Kriemen,
D. B. Werz* ————— 2985–2989



Flexible Synthesis of 2-Deoxy-C-
Glycosides and (1→2)-, (1→3)-, and
(1→4)-Linked C-Glycosides



Link! Two, three, four! A rapid and flexible synthesis of native (1→*n*)-linked C-di-saccharides (*n*=2, 3, 4; left) is possible. The configuration of the pseudoanomeric carbon was readily established by an

epoxidation/ring-opening sequence. The synthesis of (1→*n*)-linked 2-deoxy-C-di-saccharides (right) with high diastereoselectivity follows an even shorter route.

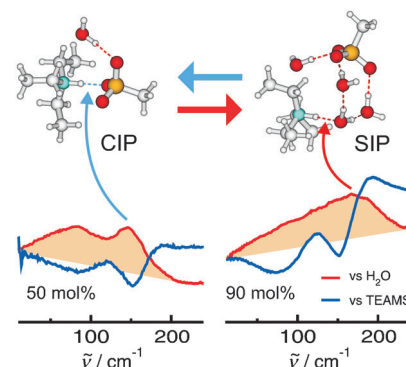
Ion Pairs

P. Stange, K. Fumino,
R. Ludwig* ————— 2990–2994



Ion Speciation of Protic Ionic Liquids in
Water: Transition from Contact to Solvent-
Separated Ion Pairs

The fab four: Far-infrared difference spectra and DFT-calculated properties for mixtures of protic ionic liquids (PILs) and water clearly indicate that a minimum of four water molecules are needed to transfer contact (CIPs) into solvent-separated (SIPs) ion pairs. SIPs are favored over CIPs owing to additional H-bonds and cooperative effects. This enthalpic advantage overcompensates for the entropic penalty of separation by water.

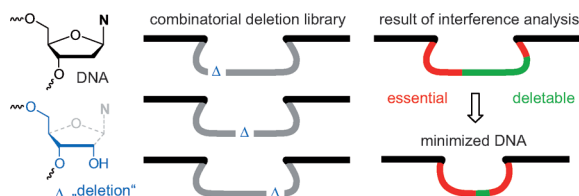


Nucleic Acid Chemistry

B. Samanta, C. Höbartner* — 2995–2999



Combinatorial Nucleoside-Deletion-
Scanning Mutagenesis of Functional DNA



Compact and informative: Individual nucleosides are statistically mutated by replacement with a non-nucleosidic spacer unit Δ that encodes the “deletion” in a single DNA library. This efficient

mutagenesis approach enables minimization of functional DNA, identifying essential nucleotides, as demonstrated for two nucleic-acid ligating deoxyribozymes.



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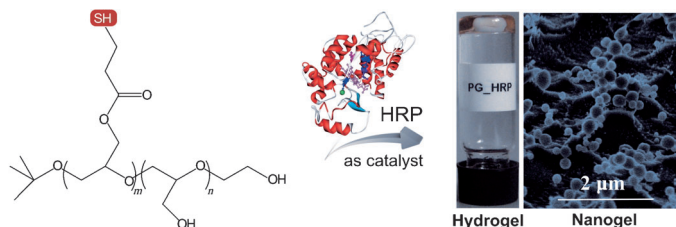
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Hydrogels

S. Singh, F. Topuz, K. Hahn, K. Albrecht, J. Groll* — 3000–3003

Embedding of Active Proteins and Living Cells in Redox-Sensitive Hydrogels and Nanogels through Enzymatic Cross-Linking



Horseradish peroxidase (HRP) can be used for the enzymatic cross-linking of thiol-functionalized polymers under mild conditions to form hydrogels and nanogels without the need for added H_2O_2 .

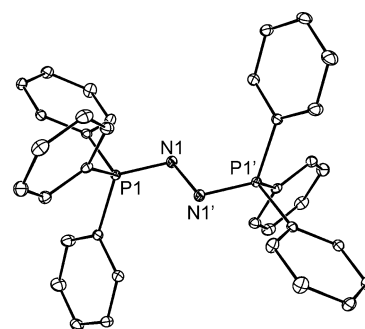
Cells can be embedded in the hydrogels and proteins can be entrapped and released from the nanogels. These gels are fully degradable under mild and cytocompatible reductive conditions.

Dinitrogen Species

N. Holzmann, D. Dange, C. Jones,* G. Frenking* — 3004–3008

Dinitrogen as Double Lewis Acid: Structure and Bonding of Triphenylphosphinazine $\text{N}_2(\text{PPh}_3)_2$

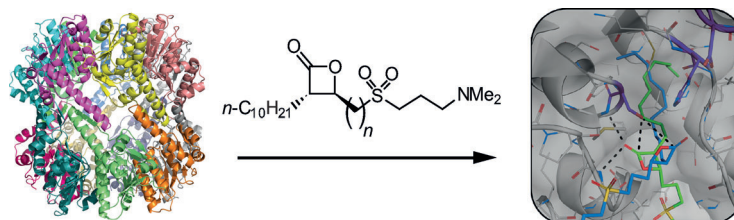
Making Ns meet: Triphenylphosphinazine $\text{N}_2(\text{PPh}_3)_2$ is a donor–acceptor complex between nitrogen in the highly excited $^1\Gamma_g$ state and two anti-periplanar coordinated phosphine ligands (see structure). Although the dissociation into $\text{N}_2 + 2 \text{PPh}_3$ is calculated to be exergonic by 75 kcal mol^{-1} , the compound is kinetically very stable as a result of the very large Lewis acidity of N_2 in the excited $^1\Gamma_g$ state.



Enzyme Inhibitors

M. Gersch, F. Gut, V. S. Korotkov, J. Lehmann, T. Böttcher, M. Rusch, C. Hedberg, H. Waldmann, G. Klebe, S. A. Sieber* — 3009–3014

The Mechanism of Caseinolytic Protease (ClpP) Inhibition



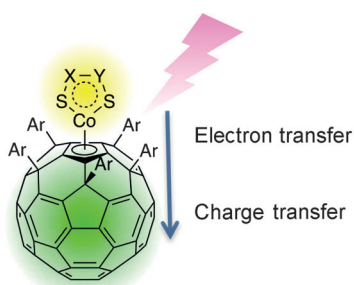
Catch me if you can: The ClpP protease mediates protein homeostasis and can be efficiently inhibited by β -lactones. A combination of molecular docking, mutagenesis, activity-based protein profiling, and kinetics studies now reveals the mechanism of ClpP inhibition.

A hydrophobic pocket next to the active site allows binding of long aliphatic and aromatic residues. The preferred stereoisomer binds into the oxyanion hole.

C–H Activation

M. Maruyama, M. König, D. M. Guldi,* E. Nakamura, Y. Matsuo* — 3015–3018

Reactivity of a Metastable Cobalt(III) Trisulfide Complex: Multiple C–H Functionalization of *p*-Xylene and Disulfides to Afford Photofunctional Cobalt Complexes



Unprecedented reactivity of a metastable cobalt trisulfide complex has been observed, and several direct C–S bond formation reactions by C–H functionalization were developed. These reactions produced a series of photofunctional motifs of sulfur-rich cobalt complexes (see picture). The measured photophysical properties of these complexes suggest promising molecular designs for photocurrent generating materials.

And Finally



What could be simpler than C_2 , a diatomic molecule that has the second strongest homonuclear bond? This molecule turns out to be a microcosm of the bonding issues that bother chemists, as is shown in this triologue. Join the three authors in their lively debate, light a candle, as Faraday did, and see the excited states of C_2 !

Chemical Bonding

S. Shaik,* H. S. Rzepa,*
R. Hoffmann* _____ 3020–3033

One Molecule, Two Atoms, Three Views,
Four Bonds?



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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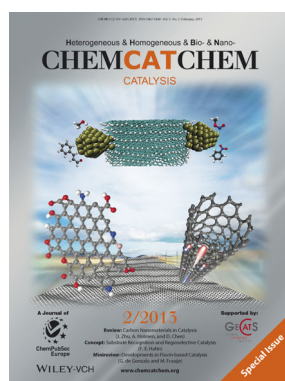


This article is accompanied by a cover picture (front or back cover, and inside or outside).

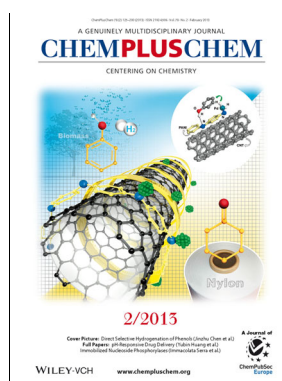
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