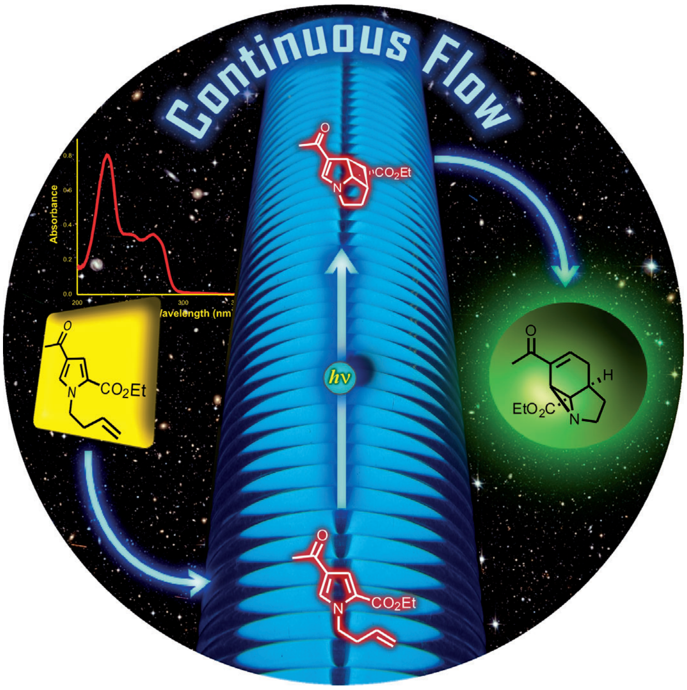
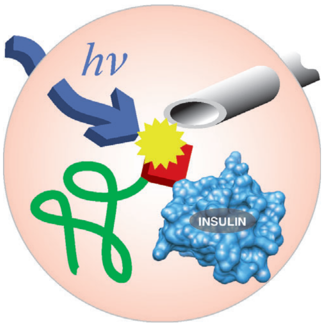
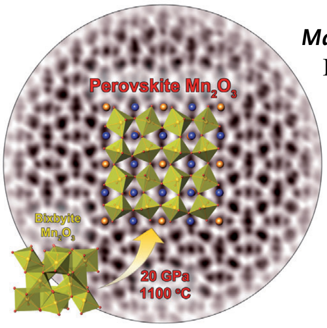
Complex tricylic aziridines ...



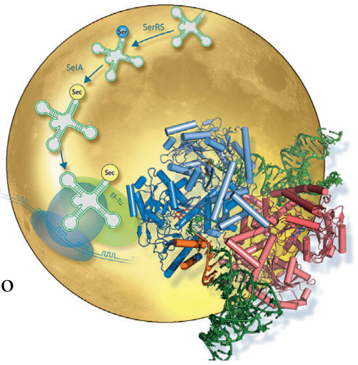
… can be prepared from simple pyrroles by UV irradiation. In their Communication on page 1499 ff., K. I. Booker-Milburn and co-workers show that the reaction proceeds by a two-stage photochemical sequence that involves [2+2] cycloaddition and rearrangement, and that the scale of the reaction can be increased using a customized FEP flow reactor.



Insulin
A photocleavable linker was used to connect insulin with an insoluble resin. In their Communication on page 1404 ff., S. H. Friedman et al. show that light pulses can be used to release insulin in a controlled fashion.



Manganese Oxides
In their Communication on page 1494 ff., S. V. Ovsyannikov et al. describe a new perovskite-like structure for Mn_2O_3, prepared under high-temperature high-pressure conditions. This structure contains Mn in three oxidation states within a distorted octahedral framework.



Protein Engineering
D. Söll et al. describe in their Communication on page 1441 ff. a synthetic tRNA that is accepted by the *E. coli* ribosome. This selenocysteine tRNA can be incorporated site-specifically into proteins to study their function.

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Service

Author Profile

"My favorite pieces of music are Beethoven's symphonies. If I were not a scientist, I would be a chef in a restaurant …"
This and more about Hiroshi Shinokubo can be found on page 1360.

News


R. Andersen


F. van Veggel


T. Lowary


L. Barriault


J. Pawliszyn


P. T. Gunning


S. Loeb


B. M. Pinto


M. Stradiotto


Y. Li

Obituaries

Nicholas J. Turro, who was a pioneer of supramolecular photochemistry and spin chemistry, died in November 2012. His research interests ranged from synthetic organic chemistry, colloidal and interface chemistry, chemical physics, magnetic resonance theory, and reaction mechanisms, to materials and biological chemistry.

Nicholas J. Turro (1938–2012)

V. Ramamurthy, J. Mattay** **1363 – 1364**

Books

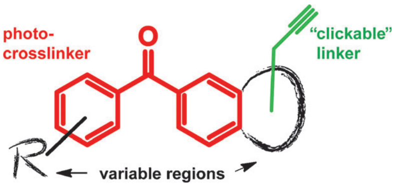
Organic Chemistry Principles in Context Mark M. Green *reviewed by H. Hopf* ____________ **1365**

Highlights

Chemical Biology

J. Oeljeklaus, F. Kaschani,
M. Kaiser* ____________ **1368 – 1370**

Streamlining Chemical Probe Discovery: Libraries of "Fully Functionalized" Small Molecules for Phenotypic Screening

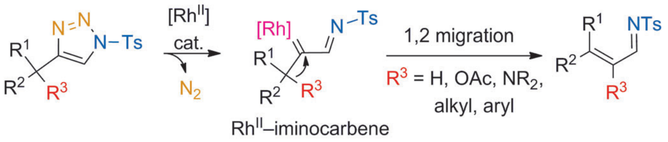


Cross-linked: The concept of phenotypic screening with probes of fully functionalized small molecules (see picture) has recently been introduced. This approach significantly increases the efficiency and success of target identification after the screening campaign.

Carbenes

A. V. Gulevich,
V. Gevorgyan* ____________ **1371 – 1373**

Versatile Reactivity of Rhodium–Iminocarbenes Derived from *N*-Sulfonyl Triazoles



The migrations of different groups to the metal–carbene center of Rh^{II}-stabilized iminocarbenes that were derived from *N*-sulfonyl triazoles are discussed (see scheme). The reactivity of these Rh-iminocabenes can be tuned easily by variation of substituents on the parent triazole.

For the USA and Canada:
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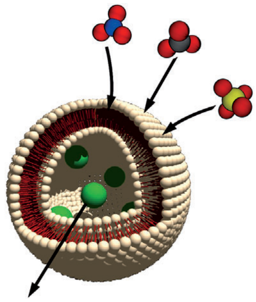
Minireviews

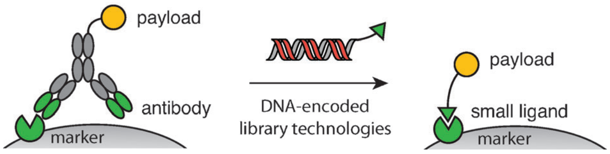
Anion Transport



Into the cell: The development of small-molecule lipid-bilayer anion transporters for potential future use in channel replacement therapy for the treatment of cystic fibrosis, and in treating cancer by perturbing chemical gradients within cells, is currently an area of intense interest. This Minireview looks at recent developments in the design of small-molecule transmembrane anion transporters and focuses on the progress so far in employing these compounds in biological systems.

Reviews

Drug Delivery

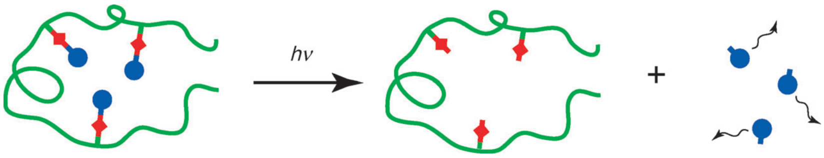


On target: Antibodies have emerged as promising vehicles for the targeted delivery of potent cytotoxic agents to sites of disease. This Review surveys how the use of smaller organic molecules can yield targeted constructs with improved properties and how DNA-encoded library technologies will facilitate the discovery of the necessary ligands (see scheme).

Communications

Protein Delivery

Frontispiece



Light controlled: A material that allows for insulin to be released in a controlled fashion by using light was prepared. A subcutaneous reservoir of such materials could allow for the non-invasive control of blood sugar. Insulin (blue in picture) was linked to an insoluble resin (green) through a photocleavable linker (red). Native insulin is released following a first-order process in response to pulses of light from an LED.

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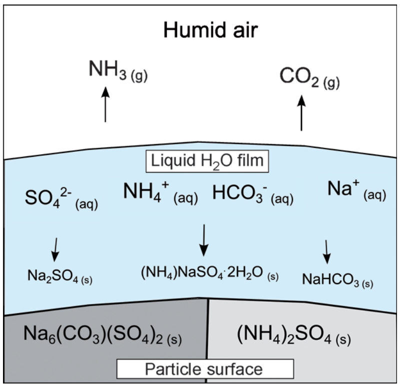
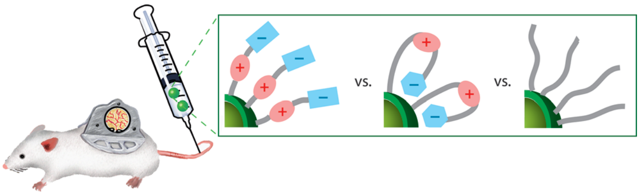
Climate science: When different salts occurring in atmospheric particles combine during a coagulation process and interact with humid air, some reactions can take place and modify the salt composition (see picture). The hygroscopicity of certain salts favors the formation of a liquid H_2O film on the solid material. The salts partially dissolve and the ions can react with each other.



Raman Spectroscopy

P. Vargas Jentzsch, V. Ciobotă, P. Rösch, J. Popp* ———— **1410–1413**

Reactions of Alkaline Minerals in the Atmosphere



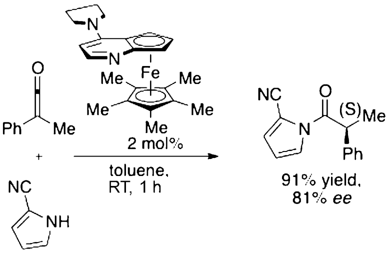
Detailed arrangements: A new set of zwitterionic quantum dots were synthesized and used to study the influence of microscopic charge arrangements on the in vivo behavior of nanoparticles. Experiments using cultured cells and live mice demonstrate that the microscopic arrangement of surface charges strongly influences nonspecific binding, clearance behavior, and in vivo transport of nanoparticles.

Nanoparticle Surface Chemistry

H.-S. Han, J. D. Martin, J. Lee, D. K. Harris, D. Fukumura, R. K. Jain, M. Bawendi* ———— **1414–1419**

Spatial Charge Configuration Regulates Nanoparticle Transport and Binding Behavior In Vivo

In control: The computational study of the title reaction catalyzed by the planar-chiral 4-(pyrrolidino)pyridine is reported (see scheme). The resting state is a chiral Brønsted acid complex and the rate-determining step involves a chiral base. The catalyst controls the enantioselectivity through a combination of stereoelectronic effects and CH⋯O interactions.

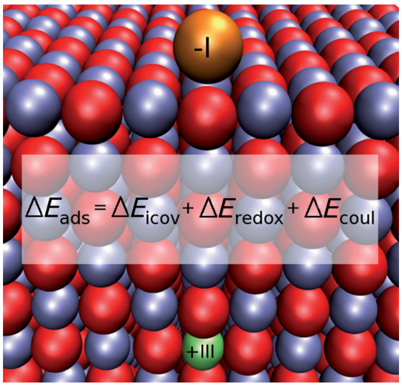


Computational Chemistry

O. Pattawong, T. J. L. Mustard, R. C. Johnston, P. H. Y. Cheong* ———— **1420–1423**

Mechanism and Stereocontrol: Enantioselective Addition of Pyrrole to Ketenes Using Planar-Chiral Organocatalysts

Red ox power! DFT calculations have been used to analyze the adsorption energy of gold on high-valent doped CaO in terms of iono-covalent, redox, and Coulomb contributions (see picture). Surprisingly, the dominant energy contribution originates from redox processes between the dopant and the adsorbate Au, not from the Coulomb interaction of charged species as currently presumed.



Gold Redox Chemistry

J. Andersin, J. Nevalaita, K. Honkala,* H. Häkkinen ———— **1424–1427**

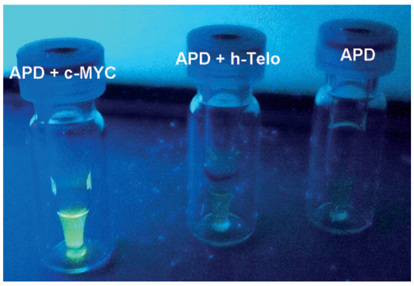
The Redox Chemistry of Gold with High-Valence Doped Calcium Oxide

G-Quadruplexes

M. Nikan, M. Di Antonio, K. Abecassis, K. McLuckie, S. Balasubramanian* ——— **1428 – 1431**

An Acetylene-Bridged 6,8-Purine Dimer as a Fluorescent Switch-On Probe for Parallel G-Quadruplexes

Lighting up: The systematic design and synthesis of a G-quartet-inspired fluorescence probe (APD), which is made of two acetylene-bridged purines, are reported. The APD lights up in the presence of parallel DNA (e.g. c-MYC) or RNA G-quadruplexes, while it shows no fluorescence enhancement with double-stranded DNA, antiparallel or mixed-type (e.g. h-Telo) G-quadruplexes (see picture). The utility of APD in the preferential staining of G-quadruplexes is also demonstrated.

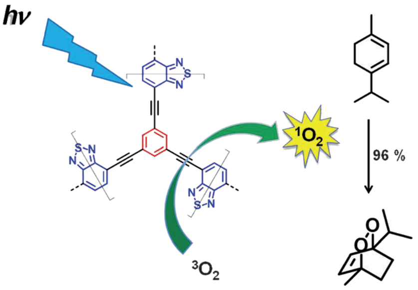


Microporous Polymers

K. Zhang, D. Kopetzki, P. H. Seeberger, M. Antonietti, F. Vilela* ——— **1432 – 1436**

Surface Area Control and Photocatalytic Activity of Conjugated Microporous Poly(benzothiadiazole) Networks

Conjugated microporous polymers (CMPs) with controlled specific surface area have been prepared through Sonogashira–Hagihara cross-coupling reactions in the presence of silica nanoparticles as templating agents. The CMPs act as heterogeneous photosensitizers for producing singlet oxygen in a continuous flow synthesis (see picture).

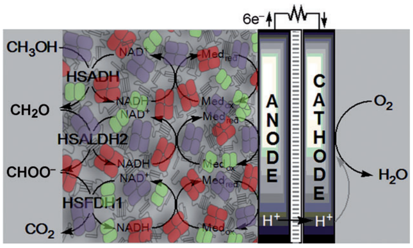


Protein Engineering

Y. H. Kim, E. Campbell, J. Yu, S. D. Minteer, S. Banta* ——— **1437 – 1440**

Complete Oxidation of Methanol in Biobattery Devices Using a Hydrogel Created from Three Modified Dehydrogenases

Enzyme catalysis: Three dehydrogenases have been engineered to self-assemble into a hydrogel that supports a synthetic metabolic network. The new catalytic biomaterial was used as an anode modification in two enzymatic biobatteries capable of the complete oxidation of methanol to CO_2 (see picture).



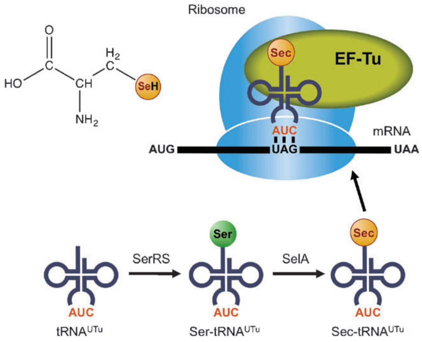
Protein Engineering

C. Aldag, M. J. Bröcker, M. J. Hohn, L. Prat, G. Hammond, A. Plummer, D. Söll* ——— **1441 – 1445**

Rewiring Translation for Elongation Factor Tu-Dependent Selenocysteine Incorporation

Back Cover

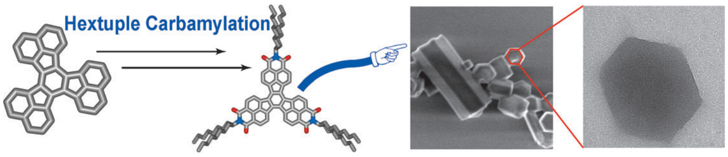
Enjoying UTu in concert: A synthetic tRNA ($tRNA^{UTu}$) was used as a substrate for three *E. coli* proteins: seryl-tRNA synthetase (SerRS) forming Ser-$tRNA^{UTu}$, selenocysteine (Sec) synthase (SelA) generating Sec-$tRNA^{UTu}$, and EF-Tu for Sec-$tRNA^{UTu}$ transport to the ribosome (see scheme). $tRNA^{UTu}$ can be used by the ribosome, thus allowing site-specific Sec insertion into proteins, including formate dehydrogenase H, selenoglutaredoxin, and glutathione peroxidase.



Polycyclic Hydrocarbons

T. V. Pho, F. M. Toma, M. L. Chabinyc,
F. Wudl* ———— 1446 – 1451

Self-Assembling Decacyclene Triimides Prepared through a Regioselective Hextuple Friedel–Crafts Carbamylation

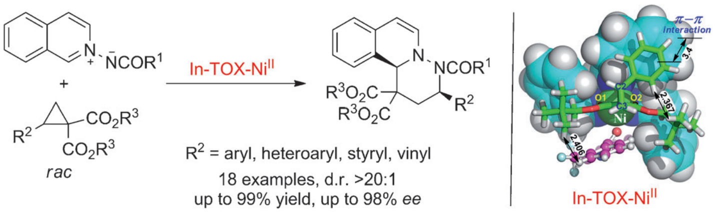


Molecular electronics: A hextuple Friedel–Crafts carbamylation is reported in the synthesis of the electroactive decacyclene triimides (see picture). These triimides self-assemble into different nanostructures through modification of the alkyl substituents and are promising n-type materials for organic semiconducting devices.

Asymmetric Catalysis

Y.-Y. Zhou, J. Li, L. Ling, S.-H. Liao,
X.-L. Sun,* Y.-X. Li,* L.-J. Wang,
Y. Tang* ———— 1452 – 1456

Highly Enantioselective [3+3] Cycloaddition of Aromatic Azomethine Imines with Cyclopropanes Directed by π–π Stacking Interactions

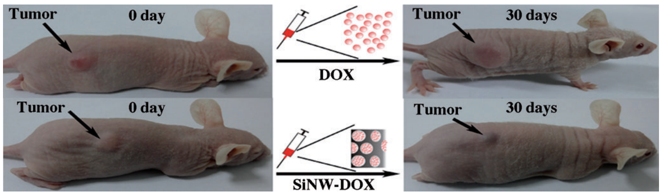


Designing armory: The side-arm-modified In-TOX/Ni^{II} complex was identified as a highly efficient and stereoselective catalyst for the [3+3] cycloaddition of aromatic azomethine imines with cyclopropanes (see picture). Density functional calculations and control experiments revealed that the directing effect of the side arm through π interactions is crucial to the stereochemical control.

Drug Delivery

F. Peng, Y. Y. Su, X. P. Wei, Y. M. Lu,
Y. F. Zhou, Y. L. Zhong, S. T. Lee,*
Y. He* ———— 1457 – 1461

Silicon-Nanowire-Based Nanocarriers with Ultrahigh Drug-Loading Capacity for In Vitro and In Vivo Cancer Therapy

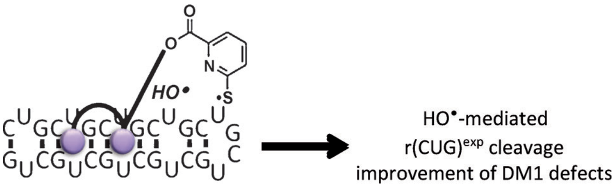


A pratical agent for cancer therapy: Silicon nanowires (SiNWs) were employed in the design of high-performance drug nanocarriers. The SiNWs were used as nanovectors for the delivery of an anticancer drug (DOX). SiNWs feature an ultrahigh drug-loading capacity. In vitro and in vivo experiments show that SiNW-based nanocarriers are highly efficacious for cancer therapy (see picture).

RNA Binding

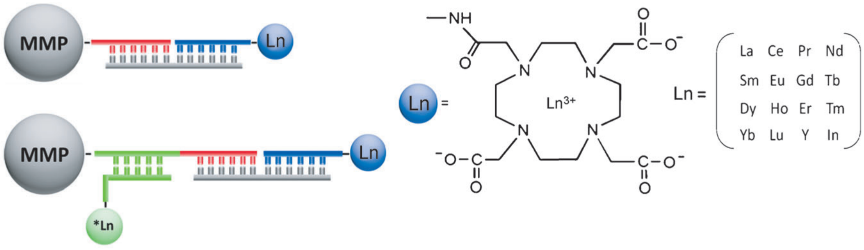
L. Guan, M. D. Disney* ———— 1462 – 1465

Small-Molecule-Mediated Cleavage of RNA in Living Cells



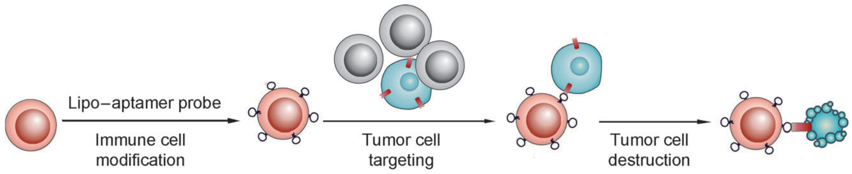
Killing the message: An approach to direct the cleavage of RNA targets with small molecules in living cells is described (see scheme). A bifunctional small molecule (purple) that recognizes a specific three nucleotide repeat sequence and cleaves that sequence in response to light was shown to be effective at degrading the myotonic dystrophy type 1 (DM1) extended repeat RNAs, thereby affecting biological functions.

Multiplex DNA Assays



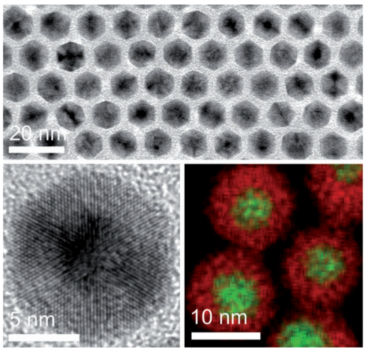
Elements and quantification: A nucleic acid assay has been developed, based on an elemental labeling strategy using magnetic microparticles (MMPs), which provides quantification of multiple DNA targets. Rare-earth elements, indium, and stable isotopes could be labeled with oligonucleotides serving as DNA probes. Quantitative analysis was then carried out using the designed systems (see picture) and elemental mass spectrometry.

Cell Targeting



An apt modification: A simple and effective way to modify the cell surface with target-specific ligands, such as DNA aptamers, while minimizing the effects on the modified cells has been developed. After incubating with lipo–aptamer probes, immune cells (red, see scheme) recognize and kill cancer cells (blue) in the cell mixture.

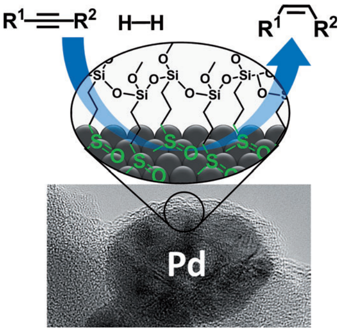
Bimetallic Nanoparticles

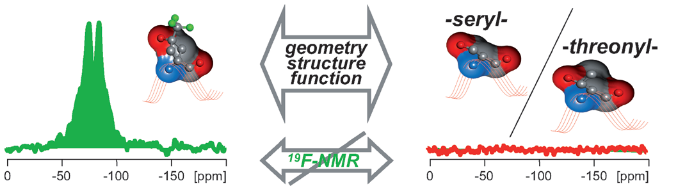


Right to the core: The design of nanocatalysts with maximized catalytic performance relies on control of the size, shape, and composition. The shell thickness of nanocrystals with core–shell structures can be controlled, thus enabling control over the nanocrystal electronic structure and catalytic properties. Monodisperse faceted icosahedral Au–Pd core–shell nanocrystals (see picture) were synthesized, and optimized for the oxidation of benzyl alcohol to benzaldehyde.

Heterogeneous Catalysis

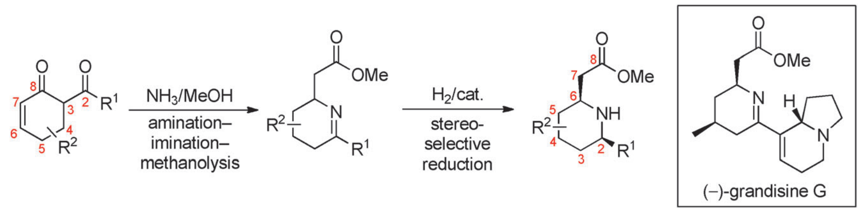
Catalysts with a sheltered upbringing: Novel core–shell nanocomposite catalysts consisting of active metal nanoparticles encapsulated by macroligands have been prepared. They have Pd nanoparticles (PdNPs) as an active core and shell ligands having sulfoxide moieties coordinated to the PdNPs. The shell protects the catalyst from coordination by alkenes and allows the lead-free selective semihydrogenation of a wide range of alkynes without any additives (see scheme).





Rigid & polar: The cyclobutane scaffold was used to design the first polar non-perturbing rigid CF_3-substituted amino acid (left in picture) suitable for replacing the serine/threonine residues in peptides. This amino acid imitates the geometry, structure, and function of serine and threonine, but in contrast to those, it can be used in structural studies of membrane-active Ser/Thr-containing peptides by solid-state ^{19}F NMR spectroscopy.

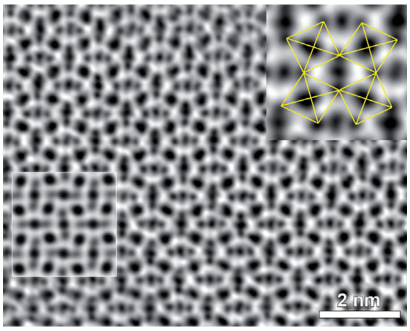
Amino Acids



A grand route to grandisines: A method for the conversion of 6-acyl cyclohexenones into 2,6-disubstituted 2,3,4,5-tetrahydropyridines and, after diastereoselective reduction, 2,6-*syn*-disubstituted piperidines has been developed. The scope of this process is outlined by the synthesis of *cis*-2-methoxycarbonylmethyl-6-pentylpiperidine and the first total synthesis of the *Elaeocarpus*-derived alkaloid (−)-grandisine G (see scheme).

Natural Product Synthesis

Phases of the Mn_2O_3: Two new phases of Mn_2O_3—corundum-type ε-Mn_2O_3 and perovskite-type ζ-Mn_2O_3—were obtained by high-pressure high-temperature synthesis. Manganese atoms were found to completely occupy the *A*- and *B*-positions of perovskite simultaneously. The perovskite-type ζ-Mn_2O_3 has an *A*-site-ordered perovskite structure (see picture) containing Mn in three different oxidation states (+II, +III, and +IV).



High-Pressure Perovskites

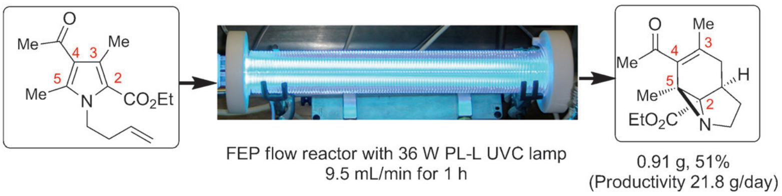
Inside Back Cover

Photochemical Synthesis

K. G. Maskill, J. P. Knowles, L. D. Elliott, R. W. Alder,
K. I. Booker-Milburn* ______ **1499 – 1502**

Complexity from Simplicity: Tricyclic Aziridines from the Rearrangement of Pyrroles by Batch and Flow Photochemistry

Front Cover



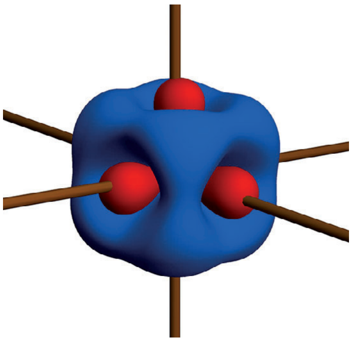
Molecular acrobatics: Irradiation of *N*-butenyl-substituted pyrroles that bear an electron-withdrawing group leads to complex tricyclic aziridines through an unprecedented photocycloaddition–rearrangement sequence. Gram quantities of these complex products could be produced by using a bespoke flow reactor (see picture, FEP = fluorinated ethylene propylene).

Electron Density

M. Stokkebro Schmøkel, L. Bjerg, J. Overgaard, F. Krebs Larsen, G. K. Hellerup Madsen, K. Sugimoto, M. Takata, B. Brummerstedt Iversen* _ **1503 – 1506**

Pushing X-ray Electron Densities to the Limit: Thermoelectric $CoSb_3$

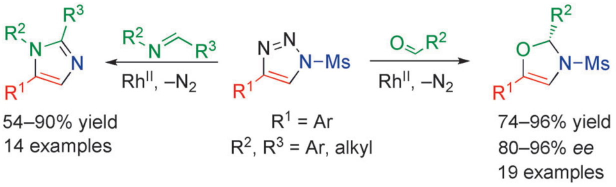
A big challenge: The experimental electron density of $CoSb_3$ was determined based on short-wavelength single-crystal synchrotron data (10 K), thereby giving a view of covalently bonded Co and Sb atoms that carry only small negative and positive charges, respectively. This result contradicts the conventional view of the electrostatic properties of the structure used in thermoelectric studies.



Heterocycles

M. Zibinsky, V. V. Fokin* ___ **1507 – 1510**

Sulfonyl-1,2,3-Triazoles: Convenient Synthones for Heterocyclic Compounds

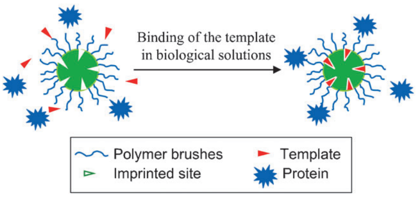


As easy as 1,2,3: Readily available and shelf-stable 1-sulfonyl-1,2,3-triazoles react with aldehydes and aldimines in the presence of Rh^{II} catalysts to produce 4-oxazolines and 1,2,5-trisubstituted imidazoles (see scheme).

Synthetic Receptors

Y. Ma, G. Pan, Y. Zhang, X. Guo, H. Zhang* ______________ **1511 – 1514**

Narrowly Dispersed Hydrophilic Molecularly Imprinted Polymer Nanoparticles for Efficient Molecular Recognition in Real Aqueous Samples Including River Water, Milk, and Bovine Serum

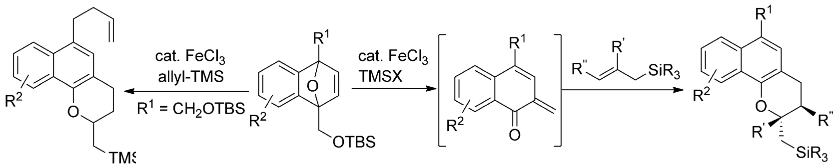


In river water, milk, and bovine serum, molecularly imprinted polymer nanoparticles with hydrophilic polymer brushes showed excellent molecular recognition (see picture). Readily prepared by precipitation polymerization with a macromolecular chain-transfer agent, such nanoparticles are promising alternatives to antibodies for many applications owing to their superior dispersion and binding properties in biological matrices.

Annulation Reactions

Y. Sawama,* Y. Shishido, T. Yanase,
K. Kawamoto, R. Goto, Y. Monguchi,
Y. Kita, H. Sajiki* **1515 – 1519**

Efficient Generation of *ortho*-Naphthoquinone Methides from 1,4-Epoxy-1,4-dihydronaphthalenes and Their Annulation with Allyl Silanes

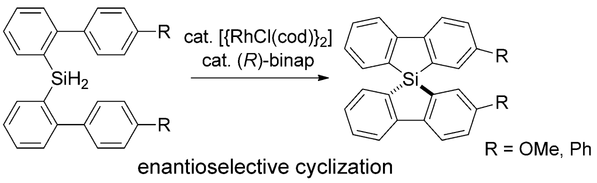


Pharmaceutically useful dihydronaphthopyran derivatives were obtained in good yield by the regio- and stereoselective annulation of *ortho*-naphthoquinone methides with allyl silanes. The *ortho*-naphthoquinone methides were generated in situ from 1-siloxymethyl-1,4-epoxy-1,4-dihydronaphthalenes under FeCl$_3$ catalysis (see scheme; allyl-TMS = allyltrimethylsilane, TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl).

Chirality

Y. Kuninobu,* K. Yamauchi, N. Tamura,
T. Seiki, K. Takai* **1520 – 1522**

Rhodium-Catalyzed Asymmetric Synthesis of Spirosilabifluorene Derivatives

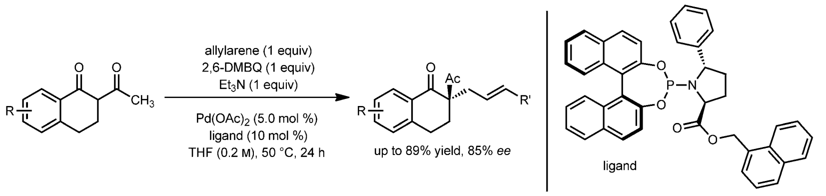


Si goes chiral: Treatment of a bis(biphenyl)silane with a catalytic amount of a rhodium complex gave a spirosilabifluorene bearing a quaternary silicon atom. By using a rhodium catalyst with a chiral phosphine ligand (see scheme), asymmetric dehydrogenative cyclization proceeded to give chiral derivatives in good yields and enantioselectivities.

Synthetic Methods

B. M. Trost,* D. A. Thaisrivongs,
E. J. Donckele **1523 – 1526**

Palladium-Catalyzed Enantioselective Allylic Alkylations through C–H Activation

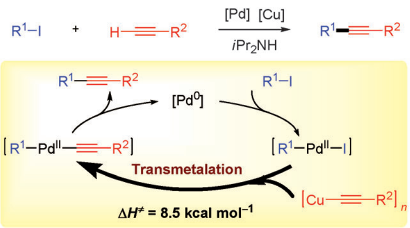


A new ligand class: The title reaction was made possible by the discovery of a new class of phosphoramidite ligands. A variety of sterically and electronically diverse allylarenes undergo reaction with 2-acetyl-1-tetralones to form quaternary carbon stereocenters. This is a conceptually and mechanistically distinct strategy from traditional methods for the synthesis of enantioenriched allylic substitution products. 2,6-DMBQ = 2,6-dimethylbenzoquinone.

Cross-Coupling

C. He, J. Ke, H. Xu, A. Lei* **1527 – 1530**

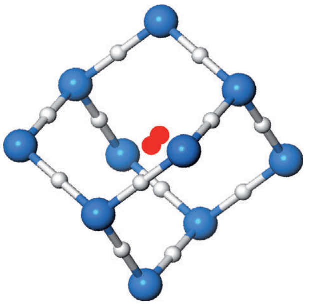
Synergistic Catalysis in the Sonogashira Coupling Reaction: Quantitative Kinetic Investigation of Transmetalation



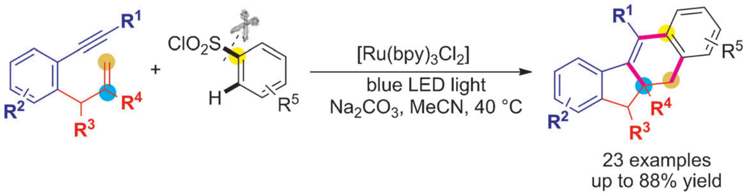
Rate-limiting: The transmetalation step of the Sonogashira coupling reaction has been established as the rate-limiting step. This cross-coupling has been demonstrated to be a Pd-catalyzed and Cu-catalyzed synergistic process, which exhibits a first-order kinetic dependence on both the [Pd] and [Cu] catalysts (see scheme).

Clathrate Hydrates

A hydrogen storage material: When vapor-deposited amorphous ice is exposed to a low pressure (about 12 MPa) of hydrogen at 140 K a hydrogen-filled cubic ice results (see picture). Calculations suggest that this material has the potential for hydrogen storage with a capacity of 10 wt% hydrogen at full loading.



Visible-Light Photocatalysis



23 examples
up to 88% yield

Ray of light: 10*a*,11-Dihydro-10*H*-benzo[*b*]fluorenes were synthesized by a visible-light-catalyzed tandem cyclization of 1,6-enynes with arylsulfonyl chlorides. This method extends the scope of enyne cyclizations and represents a new synthetic application of arylsulfonyl chlorides.

DOI: 10.1002/anie.201209344

50 Years Ago ...

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

NMR spectroscopy was already starting to revolutionize organic chemistry, and the applications of NMR to organic chemistry was the subject of a Review by J. D. Roberts, a true hero of physical organic chemistry from Caltech. As well as an introduction to the technique and to topics such as chemical shift and spin–spin coupling, several examples that have become standard textbook knowledge, such as the analysis of the interconversion of chair forms, were given. The author's prediction of a bright future for NMR was certainly not understated!

The rising popularity of organometallic chemistry was reflected in two articles by E. O. Fischer, who received the Nobel Prize in Chemistry in 1973. In a Review, he discussed the chemistry of metal π complexes with di- and oligo-olefinic ligands, and in a Communication, he reported the expansion of six-membered rings in metal π complexes.

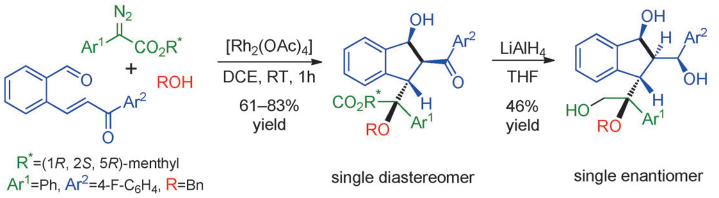
Hubert Schmidbaur, former Chairman of the Editorial Board of *Angewandte Chemie*, reported the formation of heterosiliconate anions containing organic groups. These anions correspond to the structural units of polymeric feldspars. The ionic structure of the compounds $[Me_4Sb][Al(OSiMe_3)_4]$ was confirmed by NMR spectroscopy and X-ray structural analysis.

Read more in Issue 2/1963

Domino Reactions

J. Jiang, X.-Y. Guan, S.-Y. Liu, B.-Y. Ren, X.-C. Ma, X. Guo, F.-P. Lv, X. Wu, W.-H. Hu* ______ 1539 – 1542

Highly Diastereoselective Multicomponent Cascade Reactions: Efficient Synthesis of Functionalized 1-Indanols

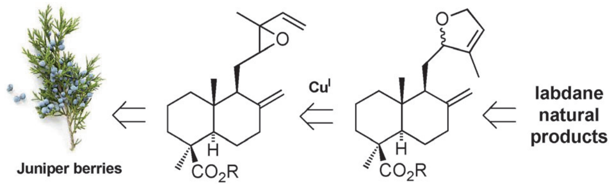


Trapped: A Michael-aldol-type cascade reaction including the trapping of an oxonium ylide through a delayed proton shift leads to the formation of multiple stereocenters in a mild one-pot synthesis. Enantiomerically pure indanol derivatives with four stereocenters and a stereogenic quaternary carbon center were easily obtained through this method in moderate to good yields.

Total Synthesis

D. J. Mack,
J. T. Njardarson* ______ 1543 – 1547

Syntheses and Structural Confirmations of Members of a Heterocycle-Containing Family of Labdane Diterpenoids

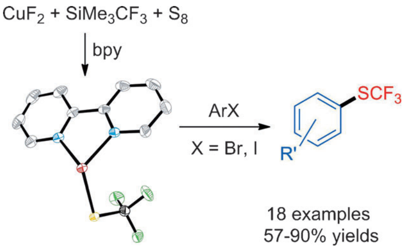


Building with berries! Several labdane natural products have been synthesized for the first time by the combination of a copper-catalyzed vinyl oxirane ring expansion reaction with an abundant, inexpensive, chiral natural source (juniper berries; see scheme). These expedient (1–5 step) syntheses have resulted in the structural confirmations of five natural products and one reassignment. Reagent-controlled oxidation and 1,3-diene isomerization results are also presented.

Trifluoromethylthiolation

Z. Weng,* W. He, C. Chen, R. Lee, D. Tan, Z. Lai, D. Kong, Y. Yuan, K.-W. Huang* ______ 1548 – 1552

An Air-Stable Copper Reagent for Nucleophilic Trifluoromethylthiolation of Aryl Halides

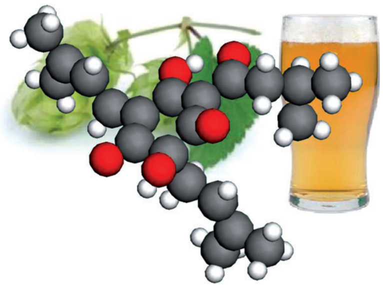


A series of copper(I) trifluoromethyl thiolate complexes have been synthesized from the reaction of CuF_2 with Me_3SiCF_3 and S_8 (see scheme; Cu red, F green, N blue, S yellow). These air-stable complexes serve as reagents for the efficient conversion of a wide range of aryl halides into the corresponding aryl trifluoromethyl thioethers in excellent yields.

Structure Elucidation

J. Urban, C. J. Dahlberg, B. J. Carroll, W. Kaminsky* ______ 1553 – 1555

Absolute Configuration of Beer's Bitter Compounds

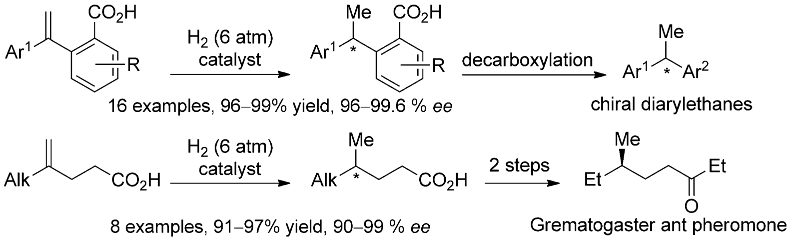


During the beer brewing process, bitter tasting *cis* and *trans* iso-α-acids are generated from the precursor α-acids found in hops. The absolute configurations of the α-acid (−)-humulone and several of its derivatives have now been elucidated by X-ray crystallography, thus resolving decades of confusion over the humulone isomerization mechanism.

Directed Asymmetric Hydrogenation

S. Song, S.-F. Zhu, Y.-B. Yu,
Q.-L. Zhou* ________ 1556 – 1559

Carboxy-Directed Asymmetric Hydrogenation of 1,1-Diarylethenes and 1,1-Dialkylethenes

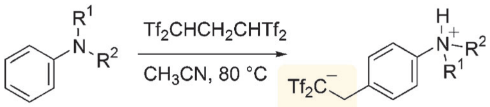


Carboxy marks the spot: A carboxy-directed asymmetric hydrogenation of 1,1-diarylethenes and 1,1-dialkylethenes with chiral iridium/spiro phosphine–oxazoline catalysts has been developed. A wide range of chiral diarylethanes and chiral γ-methyl fatty acids were synthesized with excellent enantioselectivity (see scheme).

Acids

H. Yanai,* T. Yoshino, M. Fujita,
H. Fukaya, A. Kotani, F. Kusu,
T. Taguchi* ________ 1560 – 1563

Synthesis, Characterization, and Applications of Zwitterions Containing a Carbanion Moiety

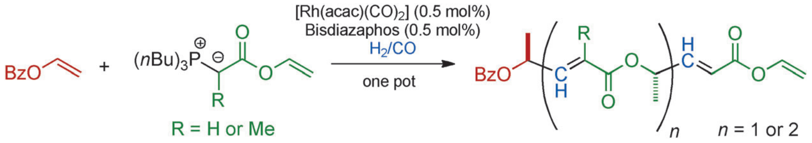


A trifle of triflyl: *N*-substituted anilines react with 1,1,3,3-tetrakis(triflyl)propane to give a 2,2-bis(triflyl)ethyl group at the *para* position of the ring. The product is a zwitterion with a carbanion and an ammonium moiety, and can be used as an acid catalyst for organic reactions (see scheme).

Asymmetric Synthesis

G. W. Wong, C. R. Landis* _ 1564 – 1567

Iterative Asymmetric Hydroformylation/ Wittig Olefination Sequence



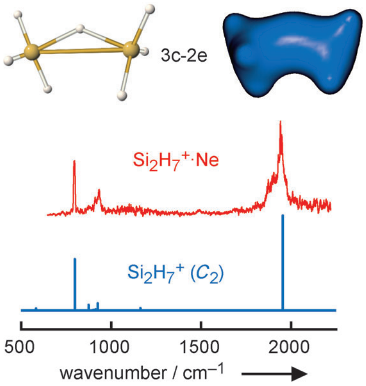
Over and over again: Various alkenes underwent the title reaction in the presence of rhodium/bis(diazaphospholane) complexes to give γ-chiral α,β-unsaturated carbonyl products (46–96 % yield) with high enantioselectivity (90–99 % *ee*). Iterative sequences of the reaction lead to stereoselective C–C bond formations between achiral reactants to produce products having multiple stereocenters (see scheme, acac = acetylacetonate).

Gas-Phase Chemistry

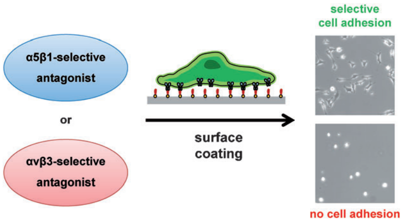
M. Savoca, J. Langer,
O. Dopfer* ________ 1568 – 1571

IR Spectrum and Structure of a Protonated Disilane: Probing the Si–H–Si Proton Bridge

Inside Cover



Structure elucidation: The IR spectrum of the protonated disilane $Si_2H_7^+$ has been derived by resonant IR photodissociation spectroscopy of weakly bound $Si_2H_7^+{\cdot}Ne$ clusters (see picture). Analysis of the spectra provides the first characterization of this fundamental polysilane cation and direct evidence for the nonlinear Si–H–Si proton bridge with a three-center two-electron bond.



Stuck with the right choice: αvβ3- or α5β1-selective integrin ligands were functionalized for surface coating without losing activity and selectivity. The coating of nanostructured gold surfaces with these compounds stimulated subtype-selective cell adhesion of genetically modified αvβ3- or α5β1-expressing fibroblasts in vitro.

Selective Cell Adhesion

F. Rechenmacher, S. Neubauer, J. Polleux,
C. Mas-Moruno, M. De Simone,
E. A. Cavalcanti-Adam, J. P. Spatz,
R. Fässler, H. Kessler* **1572–1575**

Functionalizing αvβ3- or α5β1-Selective Integrin Antagonists for Surface Coating: A Method To Discriminate Integrin Subtypes In Vitro

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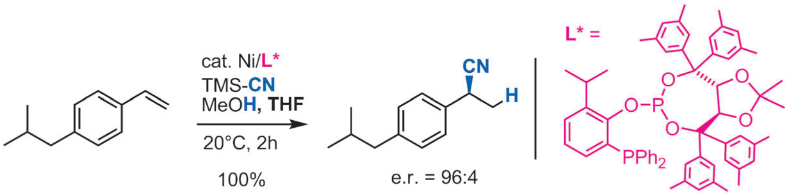
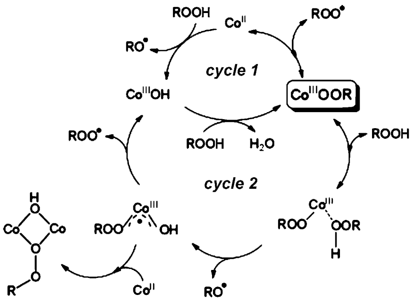


Anti-headache chemistry: In the presence of a tailored modular P,P ligand the nickel-catalyzed addition of HCN, generated in situ from TMS-CN, to styrene derivatives proceeds with an unprecedented level of stereocontrol (up to 97% *ee*) to give 2-aryl-acetonitriles, for example, the depicted precursor of Ibuprofen.

Hydrocyanation

A. Falk, A.-L. Göderz,
H.-G. Schmalz* **1576–1580**

Enantioselective Nickel-Catalyzed Hydrocyanation of Vinylarenes Using Chiral Phosphine–Phosphite Ligands and TMS-CN as a Source of HCN



Two cycles: Based on a computational study, Co^{III}OOR is put forward as the pivotal intermediate in the title reaction. Depending on the coordination environment of Co^{II}, two very different catalytic cycles are accessible (see scheme). Irreversible catalyst deactivation takes place via the formation of an inactive dimer. Immobilization of cobalt on alumina results in a stable heterogeneous catalyst that is not subject to deactivation, since dimerization is prohibited.

Cobalt Catalysis

E. Spier, U. Neuenschwander,
I. Hermans* **1581–1585**

Insights into the Cobalt(II)-Catalyzed Decomposition of Peroxide

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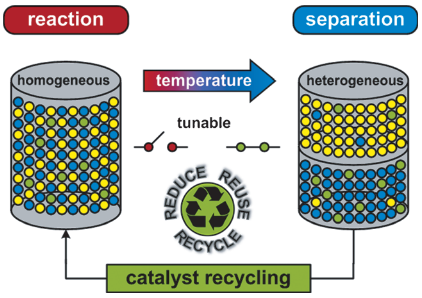
Reduce–reuse–recycle! One of the challenges in applied homogeneous catalysis is the efficient recycling of the valuable metal catalyst. The catalyst recycling concept of temperature-controlled multicomponent solvent systems was successfully applied to the hydroformylation of long-chain alkenes. The factors that signficantly influence catalyst leaching and how it can be minimized effectively were systematically investigated for the first time.

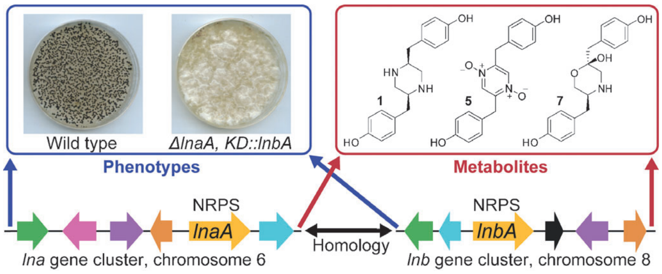


Catalyst Recycling

Y. Brunsch, A. Behr* **1586–1589**

Temperature-Controlled Catalyst Recycling in Homogeneous Transition-Metal Catalysis: Minimization of Catalyst Leaching

Natural Products



Biosynthetic crosstalk: Most gene clusters in fungi are orphans with no known associated metabolites. NMR-based comparative metabolomics was used to identify the products of two highly homologous orphan clusters in *Aspergillus flavus*. The two clusters encode partially redundant biosynthetic pathways that produce overlapping sets of novel fungal alkaloids, feature NRPS-like genes with unusual functions, and regulate fungal development.

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

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

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

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

Angewandte Corrigendum

Synthesis of Aromatic α-Aminoesters: Palladium-Catalyzed Long-Range Arylation of Primary C$_{sp^3}$–H Bonds

S. Aspin, A.-S. Goutierre, P. Larini,
R. Jazzar, O. Baudoin* ___ **10808–10811**

Angew. Chem. Int. Ed. **2012**, *51*

DOI: 10.1002/anie.201206237

Scheme 4 of this Communication contains two typesetting mistakes that need to be corrected: 1) The text above the chemical formula for **9a** must read “γ arylation” instead of “g arylation”, and 2) the isomeric ratio for **14a** is “$\beta/\gamma > 98{:}2$” and not “$\gamma/\beta > 98{:}2$”.