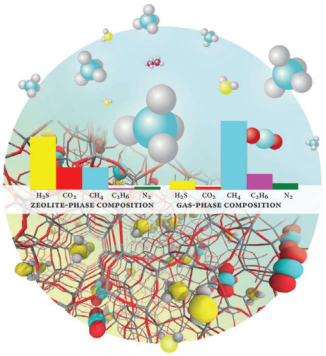
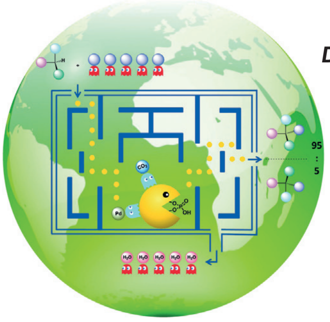
The male brown rat ...

… marks his territory with urine deposits, thereby deterring potential male intruders while retaining females within his deme and attracting wandering females to it. In their Communication on page 6062 ff., G. Gries et al. report the identification and field testing of the urine-derived sex pheromone, which, when added to food-baited traps, increases the capture of wild female rats by a factor of ten. The pheromone could improve the efficacy of rat control tactics (picture: S. McCann and S. DeMuth).

Natural Gas Desulfurization

Zeolites are potential adsorbants for the desulfurization of natural gas. To find potential candidates, J. I. Siepmann and co-workers computationally screened 386 zeolite structures, as reported in their Communication on page 5938 ff.



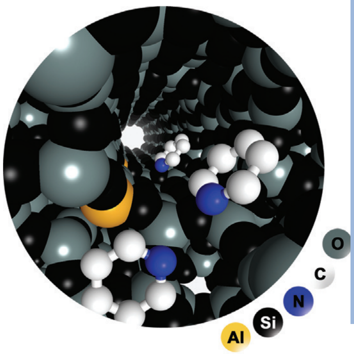


Direct Ketone Allylation

In their Communication on page 6099 ff., B. List et al. disclose a direct asymmetric Tsuji–Trost allylation of branched ketones with allylic alcohols. CO_2 serves as a co-catalyst together with a chiral phosphoric acid and a palladium catalyst.

Mesoporous Materials

In their Communication on page 5981 ff., S. C. E. Tsang et al. study the atomic positions and interactions between small pyridine molecules and zeolite H-ZSM-5 using in situ powder X-ray diffraction.



How to contact us:

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Fax: (+49) 6201–606-331
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Service

Author Profile

"My favorite place to spend a holiday is on the coast. When I was eighteen I wanted to be a scientist. I was impressed by a book about Max Planck …"
This and more about Marc Baldus can be found on page 5892.

News

R. Göttlich

N. Graulich

S. Schindler

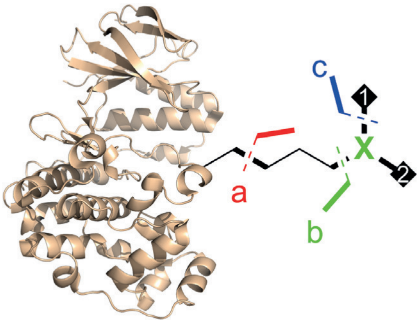
D. Rauh

Minireviews

Synthetic Biology

T. H. Wright, M. R. J. Vallée,
B. G. Davis* ______ **5896 – 5903**

From Chemical Mutagenesis to Post-Expression Mutagenesis: A 50 Year Odyssey



Taking control: Direct chemical control of the precise structure of residues in proteins has its origins in prescient ideas from 50 years ago, and now has the potential to allow the most free-ranging form of protein design and construction. Highlighted are prospects for new strategies in protein modification, alteration, and construction, which will enable protein science to achieve truly synthetic biology.

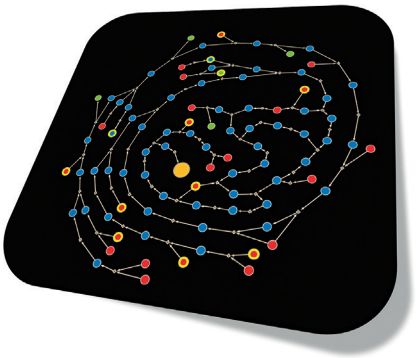
Reviews

Computer-Aided Synthetic Planning

S. Szymkuć, E. P. Gajewska, T. Klucznik,
K. Molga, P. Dittwald, M. Startek,
M. Bajczyk,
B. A. Grzybowski* ______ **5904 – 5937**

Computer-Assisted Synthetic Planning: The End of the Beginning

By combining chemical knowledge with network theory and chess-like algorithms, computers can, at last, design synthetic pathways to non-trivial targets. The picture shows a cost-optimized synthesis of Taxol (large yellow node) selected by the Chematica program from amongst 400+ million possibilities in just 7 s. Red nodes are commercially available chemicals, blue are intermediates, green are side products, and yellow halos indicate regulated substances.



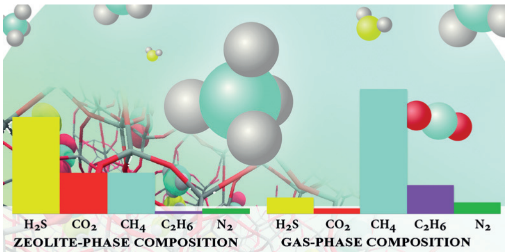
Communications

H_2S Capture

M. S. Shah, M. Tsapatsis,
J. I. Siepmann* ______ **5938 – 5942**

Identifying Optimal Zeolitic Sorbents for Sweetening of Highly Sour Natural Gas

Frontispiece



Sweet and sour: The sweetening of sour natural-gas mixtures (that is, the removal of H_2S) could be possible by zeolite-based adsorptive processes. The performance of all the 386 electrically neutral zeolite structures found in the IZA-SC database is assessed in a computational screening.

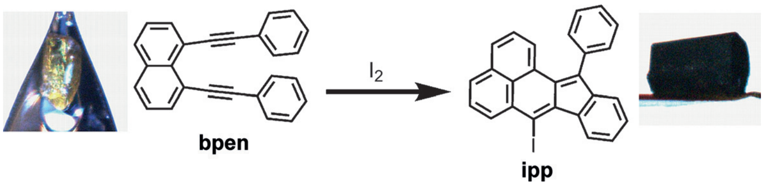
For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 101161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 16.862/14.051 (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.

Host–Guest Systems

J. V. Knichal, H. J. Shepherd, C. C. Wilson,
P. R. Raithby, W. J. Gee,*
A. D. Burrows* ______ 5943 – 5946

An Iodine-Vapor-Induced Cyclization in a Crystalline Molecular Flask

Inside Cover



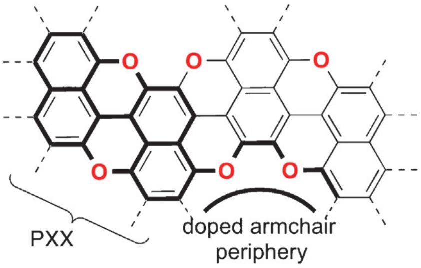
A crystalline flask: The iodine-vapor-induced cyclization of bpen into the corresponding indeno[2,1-α]phenalene species ipp in the host environment of a crystalline molecular flask, $[(\mathrm{ZnI}_2)_3(\mathrm{tpt})_2]\cdot x(\mathrm{G})$ (tpt = 2,4,6-tris(4-pyridyl)-1,3,5-triazine, G = guest), was monitored spectroscopically. The cyclization was found to proceed under mild conditions and without the need to suspend the crystals in solvent.

Supramolecular Chemistry

D. Stassen, N. Demitri,
D. Bonifazi* ______ 5947 – 5951

Extended O-Doped Polycyclic Aromatic Hydrocarbons

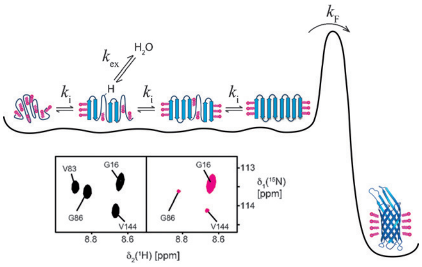
Dope up: O-doped benzorylenes, in which peripheral carbon atoms have been replaced by oxygen atoms, were synthesized. This includes key high-yielding ring-closure steps which, through intramolecular C–O bond formation, allow stepwise planarization of oligonaphthalenes. Single-crystal X-ray diffraction shows that the tetraoxa derivative forms remarkable face-to-face π–π stacks in the solid state, a favorable arrangement for organic electronics. PXX = peri-xanthenoxanthene.



Membrane Proteins

T. Raschle, P. Rios Flores, C. Opitz,
D. J. Müller, S. Hiller* ______ 5952 – 5955

Monitoring Backbone Hydrogen-Bond Formation in β-Barrel Membrane Protein Folding



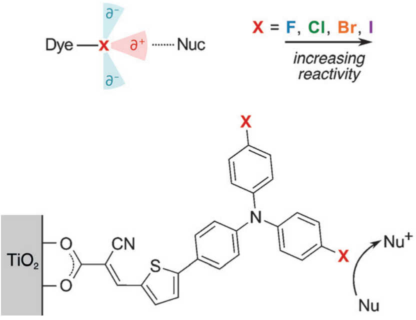
Folding mechanisms of β-barrel membrane proteins are not understood at the atomic level. H/D-exchange was applied to monitor hydrogen-bond formation during folding of the β-barrel membrane protein OmpX at atomic resolution. Hydrogen bond formation kinetics are uniform in the entire barrel, indicating cooperative formation of the hydrogen bond network.

Halogen Chemistry

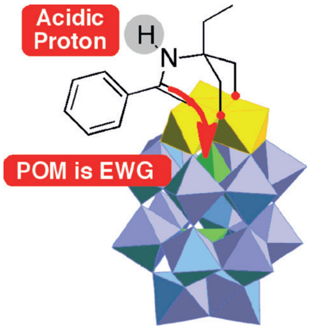
W. B. Swords, S. J. C. Simon,
F. G. L. Parlane, R. K. Dean, C. W. Kellett,
K. Hu, G. J. Meyer,*
C. P. Berlinguette* ______ 5956 – 5960

Evidence for Interfacial Halogen Bonding

Scratching the surface of halogen bonding: A homologous series of donor–π–acceptor dyes bearing different halogen substituents, adsorbed onto a semiconductor surface, showed differences in reactivity towards nucleophiles that track with the extent of halogen bonding. Transient spectroscopic methods were used to show that this intermolecular interaction is most significant for the most polarizable halogen substituent.

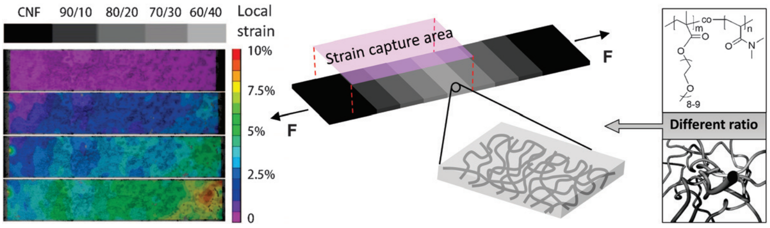


Polyoxometalates



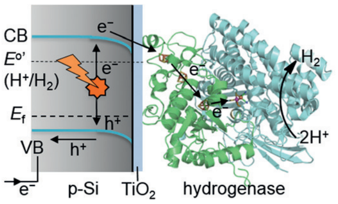
The interaction between an organic amide and the inorganic backbone of $[P_2W_{15}V_3O_{62}]^{9-}$ generates an organoheteropolyacid that can be used as a Brønsted organocatalyst (see picture; EWG = electron-withdrawing group). Modeling studies and high-field NMR spectroscopy indicate that the active site is on the nitrogen atom.

Bioinspired Gradients



Direct filament writing of nanocomposites formed by emerging cellulose nanofibrils and toughening polymers allows the engineering of strain field gradients. Such materials can find applications for tougher material joints, fundamental cell/material interaction studies, and as substrates for printed electronic circuitry.

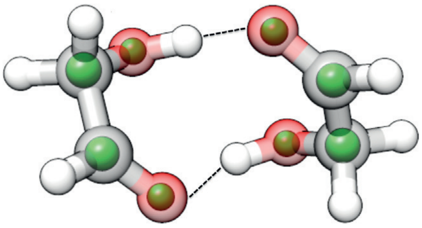
H_2 Evolution



Protect and make H_2: A layer of TiO_2 on a p-type silicon semiconductor enables the integration of a hydrogenase enzyme for photoelectrochemical H_2 generation onto a photocathode. The resulting semi-biological system generates H_2 with quantitative Faradaic yield and provides a widely applicable platform to adsorb redox enzymes on photocathodes.

Microwave Spectroscopy

The aggregation of glycolaldehyde was studied in a conformer-selective manner using high-resolution rotational spectroscopy. Two different dimer structures were observed that are influenced by both hydrogen bonding and disperion interactions.

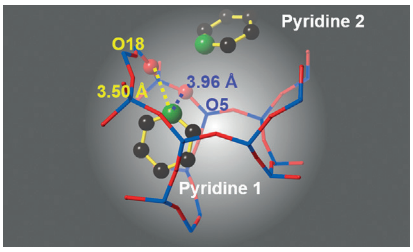


Microporous Materials

B. T. W. Lo, L. Ye, J. Qu, J. Sun, J. Zheng,
D. Kong, C. A. Murray, C. C. Tang,
S. C. E. Tsang* 5981 – 5984

Elucidation of Adsorbate Structures and Interactions on Brønsted Acid Sites in H-ZSM-5 by Synchrotron X-ray Powder Diffraction

Atomic positions and interactions between small adsorbate molecules and zeolite H-ZSM-5 are revealed in the confined zeolite channels by in situ synchrotron powder X-ray diffraction combined with Rietveld refinement. In this study the periodical lattice of H-ZSM-5 (one Brønsted acid site per asymmetric unit) was used as a template for trapping molecules (e.g. pyridine; see picture).

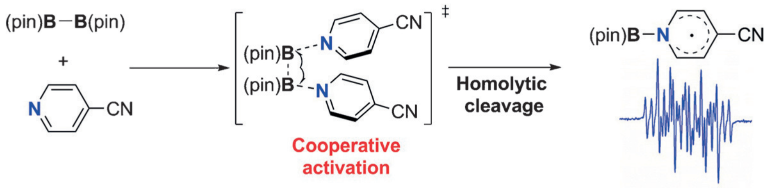


Back Cover

B–B Bond Activation

G. Wang, H. Zhang, J. Zhao, W. Li, J. Cao,
C. Zhu,* S. Li* 5985 – 5989

Homolytic Cleavage of a B–B Bond by the Cooperative Catalysis of Two Lewis Bases: Computational Design and Experimental Verification

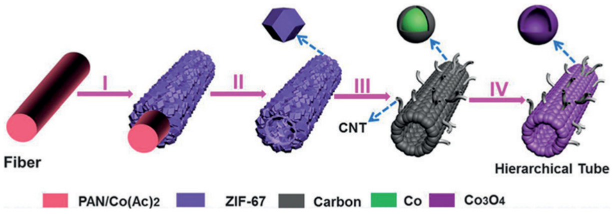


Breaking good: The diborane B–B bond can be homolytically cleaved via the cooperative catalysis of two 4-cyanopyridine molecules. Using this combination of a diborane ($B_2(pin)_2$) and 4-cyanopyridine also allows the catalytic reduction of the N=N double bond of azo-compounds to hydrazine derivatives, deoxygenation of sulfoxides to sulfides, and reduction of quinones under mild conditions.

Lithium Ion Batteries

Y. M. Chen, L. Yu,
X. W. Lou* 5990 – 5993

Hierarchical Tubular Structures Composed of Co_3O_4 Hollow Nanoparticles and Carbon Nanotubes for Lithium Storage



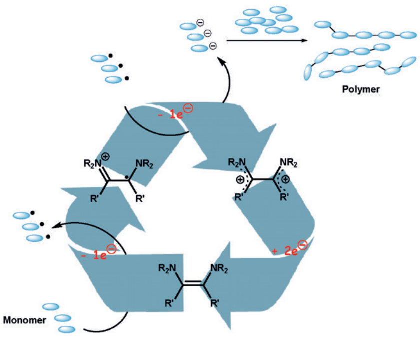
Forming hierarchies: Hierarchical tubular structures composed of Co_3O_4 hollow nanoparticles and carbon nanotubes are synthesized from the polymer/cobalt acetate composite nanofibers. Benefiting from unique structural and compositional features, the as-synthesized hierarchical tubular structures show excellent lithium storage properties.

Chain-Growth Polymerization

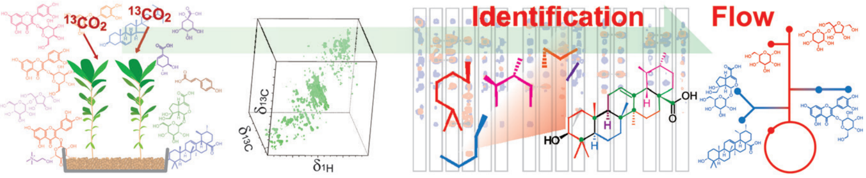
J. Broggi,* M. Rollet, J.-L. Clément,
G. Canard, T. Terme, D. Gigmes,
P. Vanelle* 5994 – 5999

Polymerization Initiated by Organic Electron Donors

Off to a good start: The metal-free polymerization of various activated alkenes and cyclic esters occurred rapidly under mild conditions in the presence of organic electron donors (OED) as initiators and without the need for co-initiators or external activation methods (see picture). The simple and efficient room-temperature process meets the technical standards of low energy consumption, cost-effectiveness, and safety.



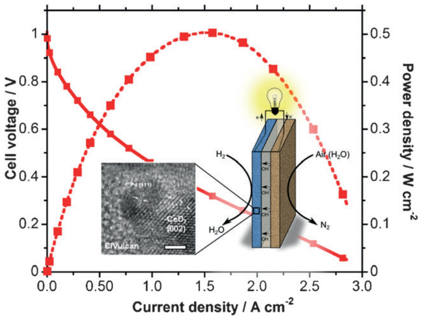
Natural Products



Tree of knowledge: Multidimensional NMR analysis with stable isotope labelling was applied to the comprehensive analysis of biological small molecules in the tree *Rhododendron japonicum*. This approach enabled the identification of unexpected molecules and provided information on their metabolic flow.

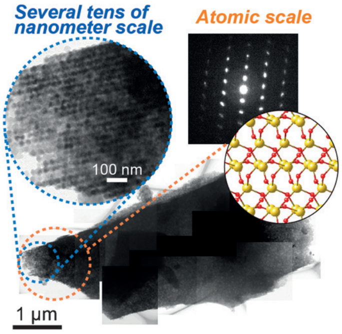
Fuel Cells

Low-cost cell: A platinum-free alkaline membrane fuel cell employing a Pd/C-CeO_2 anode electrocatalyst produces peak power densities of more than 500 mW cm^{-2}. Morphological analysis attests to a fine dispersion of the Pd nanoparticles accumulated mostly on the ceria part of the catalyst.



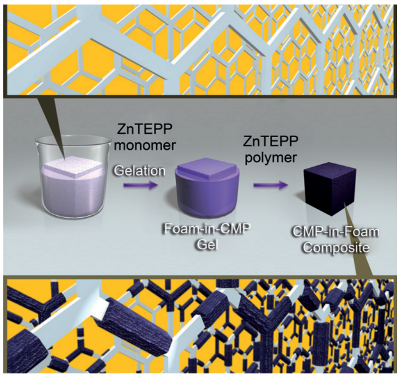
Ordered Materials

Order a double: A single-crystalline mesoporous quartz superlattice with periodic order on both the several tens of nanometer scale and the atomic scale is prepared by crystallization of amorphous silica nanospheres which constitute a colloidal crystal. The periodic arrangement of silica nanospheres is retained even though Li^+ ions are used as a strong flux.

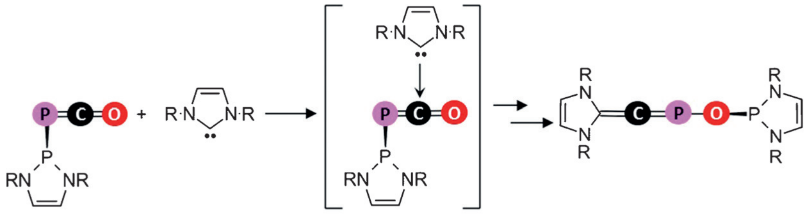


Foam Composites

Elastic and catalytic: A gel-mediated strategy was employed for the synthesis of a CMP-covered melamine foam composite (CMP = conjugated microporous polymer). The material retains elasticity and has interconnected micropores and macropores as a result of the coating of the melamine foam skeleton with ZnTEPP metalloporphyrin frameworks. ZnTEPP = Zn^{II} 5,10,15,20-tetra(4-ethynylphenyl)porphyrin.



Isomerism



Stable phosphaketenes react with N-heterocyclic carbenes to give phosphaheteroallenes. The PCO unit is converted to its constitutionally isomeric OPC group in this process (see scheme).

Z. Li, X. Chen, Z. Benkő, L. Liu, D. A. Ruiz,
J. L. Peltier, G. Bertrand,* C.-Y. Su,*
H. Grützmacher* ________ 6018 – 6022

N-Heterocyclic Carbenes as Promotors for the Rearrangement of Phosphaketenes to Phosphaheteroallenes: A Case Study for OCP to OPC Constitutional Isomerism

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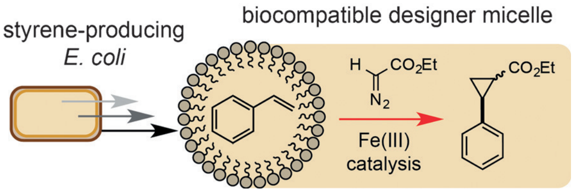
Micellar Catalysis



Micelles and microbes: Vitamin E derived micelles, originally developed for use as nanoreactors in water, are biocompatible and accelerate metabolic flux through an engineered styrene production pathway in *E. coli* NST74. These microbe-associated micelles can accommodate both heterogeneous and organic-soluble transition metal catalysts, and accelerate biocompatible cyclopropanation in vivo.

S. Wallace, E. P. Balskus* __ 6023 – 6027

Designer Micelles Accelerate Flux Through Engineered Metabolism in *E. coli* and Support Biocompatible Chemistry

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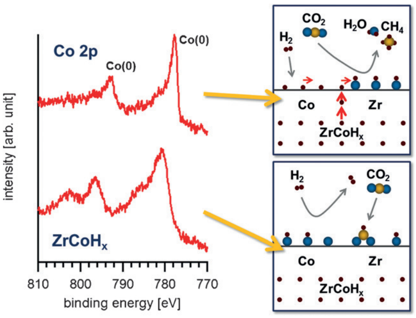
CO_2 Reduction



Tracking hydrogen: A mixture of hydrogen and carbon dioxide generates methane on the metal hydride $ZrCoH_x$ and not on the pristine intermetallic. The atomic hydrogen flux from the metal hydride is crucial for CO_2 reduction.

S. Kato,* S. K. Matam, P. Kerger,
L. Bernard, C. Battaglia, D. Vogel,
M. Rohwerder, A. Züttel* __ 6028 – 6032

The Origin of the Catalytic Activity of a Metal Hydride in CO_2 Reduction

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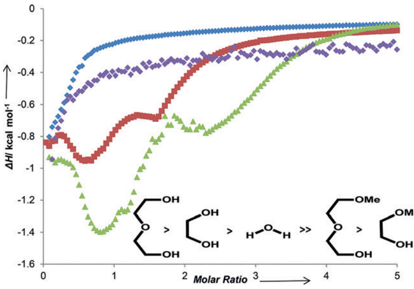
Proton Donors



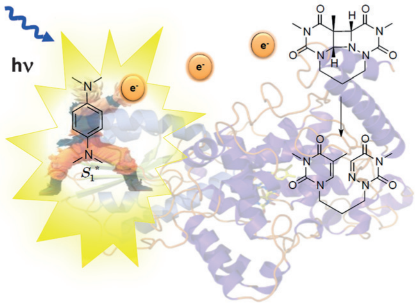
Very Sm-art! A combination of thermochemical, spectroscopic, and kinetic studies demonstrate that only proton donors with a high affinity for SmI_2 promote reduction of anthracene through a PCET process. In fact, any high-affinity ligand containing a strong X–H bond that is weakened upon coordination to a metal could be effective for reduction.

T. V. Chciuk, W. R. Anderson, Jr.,
R. A. Flowers, II* ________ 6033 – 6036

High-Affinity Proton Donors Promote Proton-Coupled Electron Transfer by Samarium Diiodide

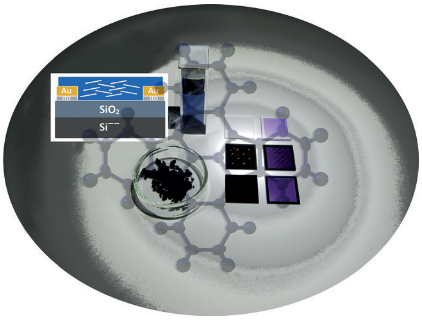
DNA Repair

Photoinduced injection of one electron into a dimeric azetidine derived from thymine leads to a clean cycloreversion and therefore to repair of the nucleobase. This result is relevant to understand the role of (6-4) photolyase and supports the feasibility of the mechanistic pathway involving reductive splitting of an azetidine intermediate.

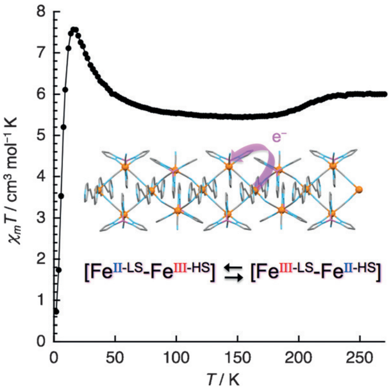


Conjugated Polycycles

When polymorphism rules: The orientation of individual molecules of a peri substituted acene with cross-conjugated π-systems differs significantly in its single-crystal and thin film structure. In the latter, a most efficient face-to-face overlap arranges its individual arene moieties in a slipped stacking mode resulting in a close π-π overlap. This gives rise to attractive hole carrier mobilities and decent thin film transistor properties.

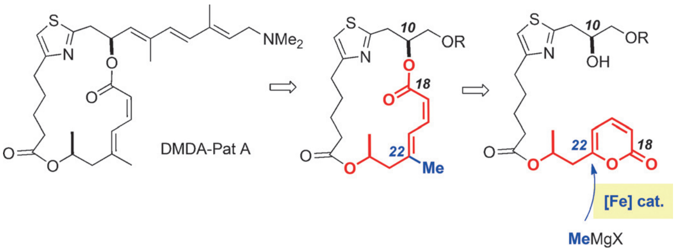


Switchable Cyanometalates

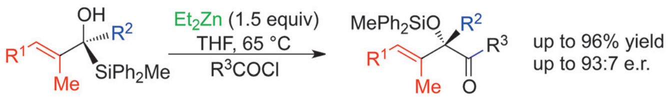


Feeling blue: A simple cyanide-bridged Fe^{II}/Fe^{III} complex, inspired by Prussian blue ($Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot x H_2O$), displays switchable optical and magnetic properties upon metal-to-metal charge-transfer phase transitions.

Macrolide Synthesis

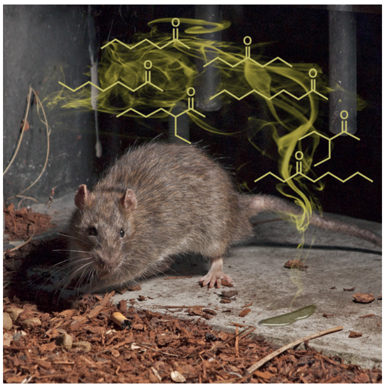


Closed and open: A pyrone ring, formed by a gold-catalyzed cycloisomerization, was used to encode the highly isomerization-prone *Z*,*E*-dienoate subunit of a pateamine-type macrolide. The closed, robust pyrone was unlocked to reveal the sensitive open dienoate by an unorthodox iron-catalyzed ring opening/cross coupling only immediately prior to macrocyclization.



All about control: A chiral allylzinc intermediate obtained from enantiomerically enriched α-hydroxy allylsilanes reacts with retention of configuration in the presence of an electrophile. Two remarkable features of this transformation are the stereochemical outcome during the formation of the allylzinc species and the complete stereocontrol in the six-membered transition state, which leads to an overall transfer of chirality within the reaction sequence.

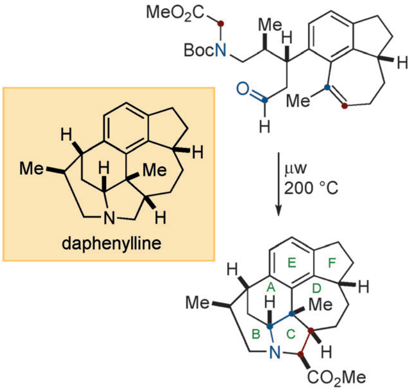
Allylic Compounds



The male brown rat marks his territory with urine deposits, thereby deterring potential male intruders while retaining females within his deme and attracting wandering females to it. The urine-derived sex pheromone comprises several ketones (2-heptanone, 4-heptanone, 3-ethyl-2-heptanone, 2-octanone, 2-nonanone, 4-nonanone), which when added to baited traps increase the captures of female rats by a factor of ten.

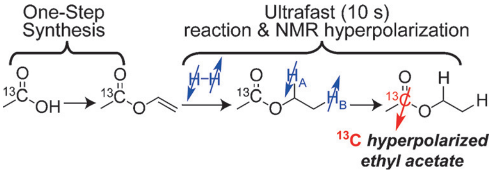
Pheromones

Front Cover



Ring ring ring: Total synthesis of daphenylline, a hexacyclic *Daphniphyllum* alkaloid, was achieved. The synthesis features a remote stereocontrolled Claisen rearrangement that takes advantage of the characteristic conformation of the tricyclic DEF core, and intramolecular cycloaddition of a cyclic azomethine ylide to simultaneously construct the ABC ring system.

Natural Product Synthesis



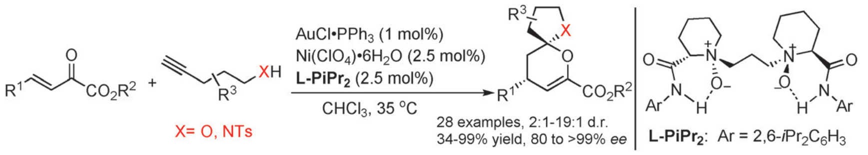
Labels of the reconstruction: The production of vinylated carboxylic compounds with a ^{13}C isotopic label in the C1 position enables the synthesis of vinyl acetate-1-^{13}C, a precursor for preparation of ^{13}C NMR hyperpolarized ethyl acetate-1-^{13}C. ^{13}C hyperpolarization of about 1.8 % is achieved using para-hydrogen-induced polarization side arm hydrogenation (PHIP-SAH) suggesting potential for medical imaging.

Isotopic Labeling

Relay Catalysis

J. Li, L. L. Lin, B. W. Hu, X. J. Lian, G. Wang, X. H. Liu,* X. M. Feng* ______ **6075 – 6078**

Bimetallic Gold(I)/Chiral *N*,*N*′-Dioxide Nickel(II) Asymmetric Relay Catalysis: Chemo- and Enantioselective Synthesis of Spiroketals and Spiroaminals

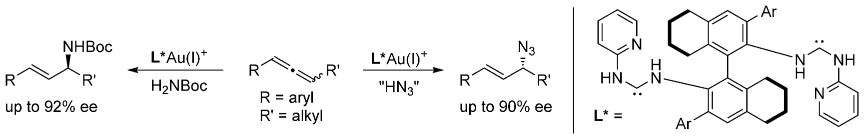


Running a relay: Highly efficient asymmetric cascade reactions of keto esters with alkynyl alcohols and amides were achieved using a gold(I)/chiral *N*,*N*′-dioxide nickel(II) complex as a bimetallic relay catalytic system. A variety of spiroketals and spiroaminals could be obtained using this method.

Gold Catalysis

D. A. Khrakovsky, C. Tao, M. W. Johnson, R. T. Thornbury, S. L. Shevick, F. D. Toste* ______ **6079 – 6083**

Enantioselective, Stereodivergent Hydroazidation and Hydroamination of Allenes Catalyzed by Acyclic Diaminocarbene (ADC) Gold(I) Complexes

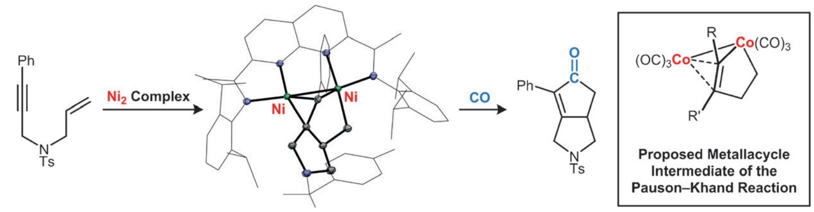


Chiral allylic azides and amines are obtained by enantioselective hydroazidation and hydroamination of allenes catalyzed by acyclic diaminocarbene gold(I) catalysts derived from BINAM. The sense of enantioinduction is reversed for the two different nucleophiles, allowing easy access to both enantiomers with a single catalyst enantiomer.

Pauson–Khand Reaction

D. R. Hartline, M. Zeller, C. Uyeda* ______ **6084 – 6087**

Well-Defined Models for the Elusive Dinuclear Intermediates of the Pauson–Khand Reaction

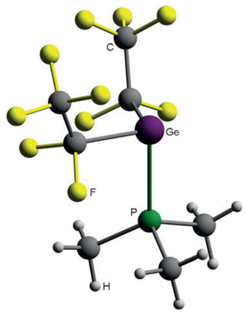


Key steps of the Pauson–Khand reaction are modelled using a supported Ni–Ni bond as a functional surrogate for the active site of $Co_2(CO)_8$. The direct characterization of a dinuclear alkene–alkyne oxidative coupling reaction is reported along with the solid-state structure of the resulting metallacycle complex.

Germylene Adducts

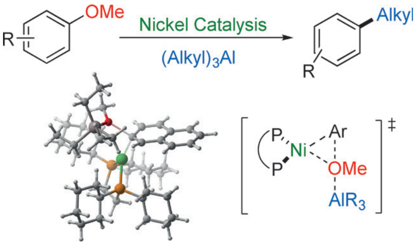
S. Pelzer, B. Neumann, H.-G. Stammler, N. Ignat′ev, B. Hoge* ______ **6088 – 6092**

The Bis(pentafluoroethyl)germylene Trimethylphosphane Adduct $(C_2F_5)_2Ge{\cdot}PMe_3$: Characterization, Ligand Properties, and Reactivity



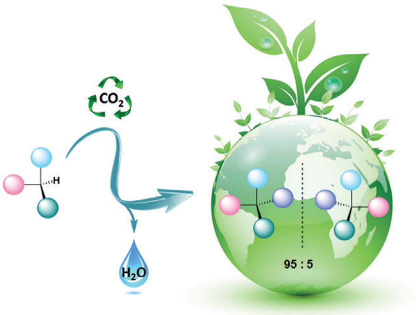
The germylene base adduct $(C_2F_5)_2Ge{\cdot}PMe_3$ was synthesized from $(C_2F_5)_3GeH$. Its structure was determined by X-ray diffraction and its ligand properties clarified through the use of Tolman's electronic parameter. Finally, its reactivity was also investigated.

The activation of the C—OMe bond in the title reaction is facilitated by Lewis acidic trialkylaluminum compounds, which enhance the oxidative-addition and transmetalation steps. A nickel catalyst with a bidentate P,P-ligand prevents the competing β-hydride elimination so that the alkyl-substituted products are obtained in high yields.



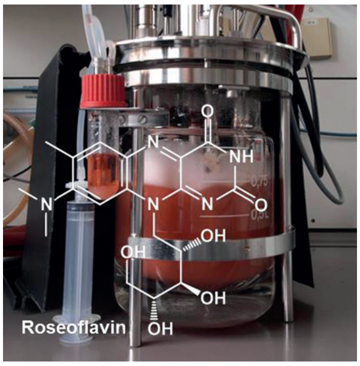
C(sp^2)–C(sp^3) Coupling

While indirect approaches are known, the direct catalytic asymmetric α-allylation of branched ketones has been elusive until today. By combining "enol catalysis" with the use of CO_2 as a formal catalyst, a solution to this problem was developed and a direct, highly enantioselective and highly atom-economic Tsuji–Trost allylation of branched ketones with simple allylic alcohol is reported.



Synthetic Methods

All by myself: Unexpectedly, a single enzyme (RosB) was found to catalyze several essential steps of the biosynthesis of the antibiotic roseoflavin from riboflavin (vitamin B2). RosB was identified in the bacterium *Streptomyces davawensis*, which was used to produce roseoflavin in a bioreactor containing a nutrient broth.



Enzymatic Synthesis

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

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

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