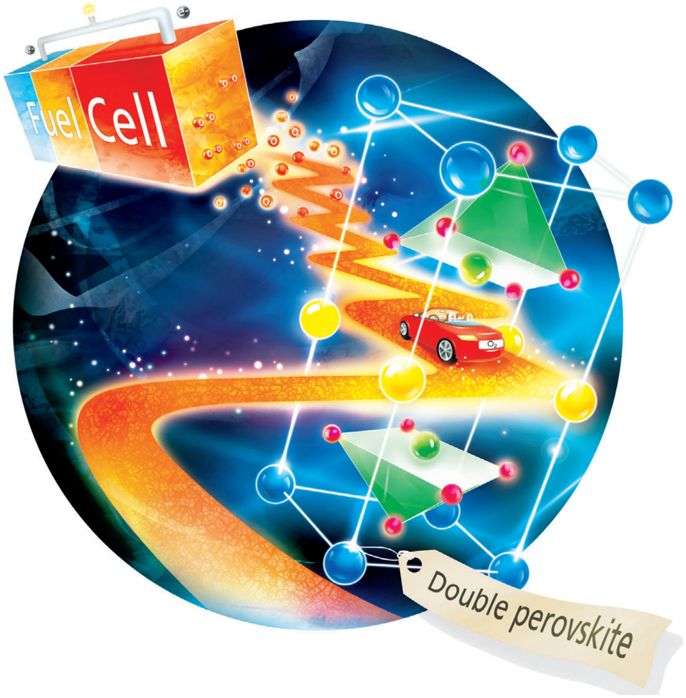
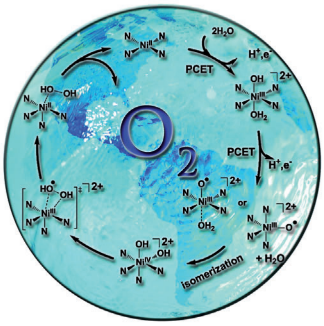
Double-perovskite compounds …

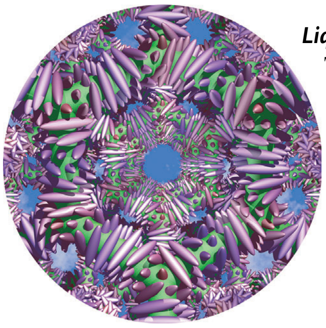


… are described by G. Kim and co-workers in their Communication on page 13064 ff. as a new class of cathode materials for solid oxide fuel cells. The enhanced stability of $NdBa_{0.75}Ca_{0.25}Co_2O_{5+\delta}$ can be ascribed to both the increased electron affinity of mobile oxygen species and the increased redox stability induced by Ca doping into the A site of $NdBaCo_2O_{5+\delta}$.

Water Oxidation

In their Communication on page 13042 ff., Z.-F. Ke, T.-B. Lu, and co-workers report a nickel-based homogeneous catalyst for water oxidation. This catalyst can efficiently electrocatalyze water oxidation at neutral pH in phosphate buffer.



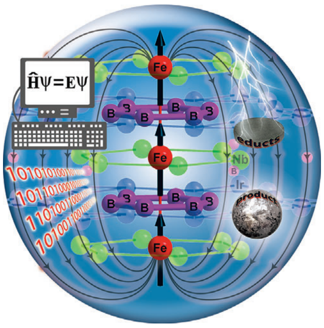


Liquid Crystals

Two types of liquid-crystalline phases consisting of two or three networks are presented by X. Zeng, G. Ungar, C. Tschierske et al. in their Communication on page 13115 ff. The three-network phase displays permanent chirality even though the constitutive molecules are achiral.

Boride Magnets

B. P. T. Fokwa et al. report in their Communication on page 13174 ff. a mutual dependency between ferromagnetic iron chains and stacked B_6 rings (see picture) found in the new ferromagnetic material, $Nb_6Fe_{1-x}Ir_{6+x}B_8$.



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Service

Author Profile

“My favorite molecule is C_{60}.
My favorite saying is ‘Results not published equals experiments not done’ …”
This and more about Lai-Sheng Wang can be found on page 12998.

News


F. Lloret


P. Samorì


C. Moberg

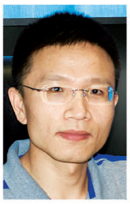

G. Férey


L. A. Oro


A. M. Bond


J. F. Rusling


M. Osawa


Y.-G. Guo


F. La Mantia


Y. Wang

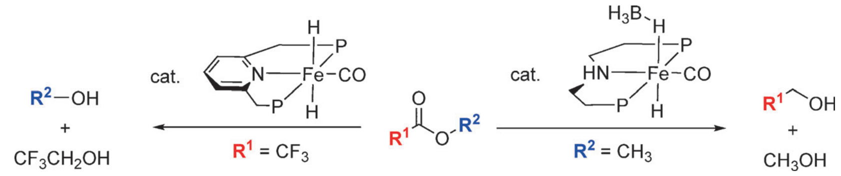
Books

Highlights

Homogeneous Catalysis

P. Dupau,* M.-L. Tran Do, S. Gaillard, J.-L. Renaud* ———— **13004 – 13006**

Iron-Catalyzed Hydrogenation of Esters to Alcohols

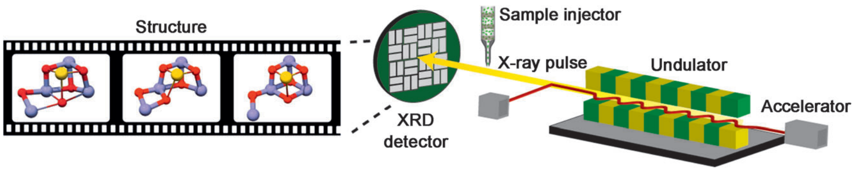


“Iron made it”: Recent breakthroughs in the hydrogenation of esters to alcohols by well-defined iron pincer complexes are highlighted. These complexes demonstrate promising efficiency and selectivities.

Enzyme Catalysis

H. Ogata, W. Lubitz* —— **13007 – 13008**

Protein Crystallography Using Free-Electron Lasers: Water Oxidation in Photosynthesis



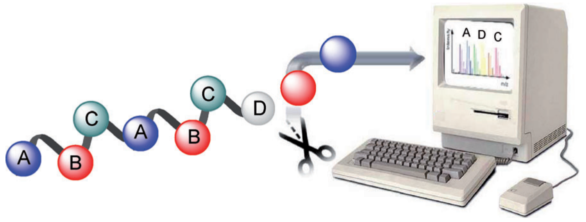
A new perspective on enzymes: Free-electron lasers are increasingly used to obtain crystal structures of interesting enzymes like photosystem II from nanocrystals at room temperature, to avoid radiation damage, and to detect structural differences between specific states in the catalytic cycle.

Minireviews

Polymer Sequencing

H. Mutlu, J.-F. Lutz* —— **13010 – 13019**

Reading Polymers: Sequencing of Natural and Synthetic Macromolecules



Read the small print: Sophisticated sequencing methods have been developed for deciphering the sequences of proteins and nucleic acids. Can these tools be transfered to the characterization of monomer sequences in synthetic polymers? The techniques employed in both fields are compared and critically analyzed.

For the USA and Canada:
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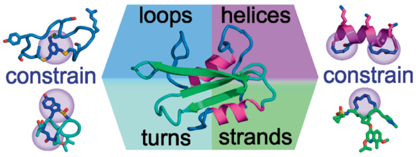
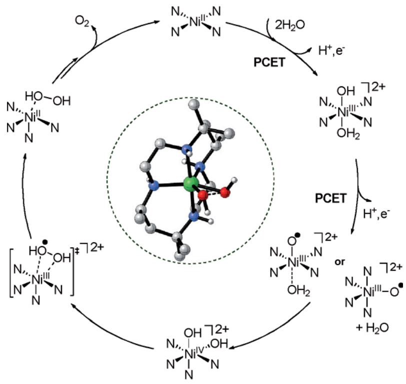
Reviews



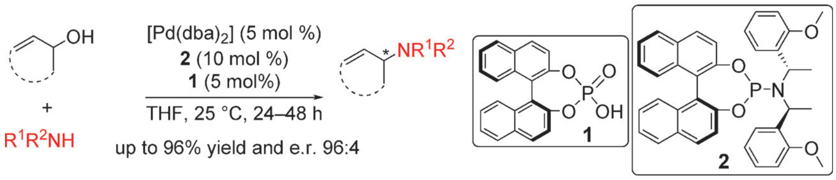
Short peptides can be constrained by cyclization to recreate key folded elements of protein structure, like β-strands and β-sheets, α-helices, and turn motifs. Coupled with internal molecular constraints, cyclization has led to many protease-resistant, potent and target-selective, biologically active compounds for use in biology and medicine.

Communications

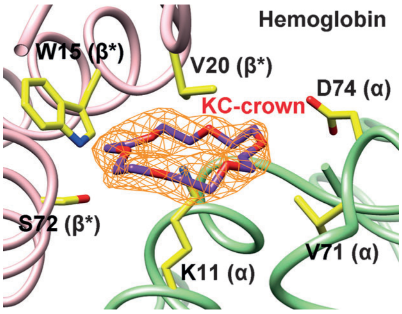
The first nickel-based homogeneous water oxidation catalyst has been reported, which can efficiently electrocatalyze water oxidation at neutral pH in phosphate buffer. The *cis* conformation of the catalyst is the key active intermediate (see scheme; PCET = proton-coupled electron transfer).



Frontispiece



Teamwork enantioselectivity: An asymmetric amination of racemic allylic alcohols with various functionalized amines proceeded with high regio- and enantioselectivity under cooperative catalysis by the chiral phosphoric acid **1** and a palladium complex with the phosphoramidite ligand **2** (see scheme; R^1 = aryl, R^2 = alkyl or H; dba = dibenzylideneacetone). The transformation was efficient even with less reactive alkyl allylic alcohols.



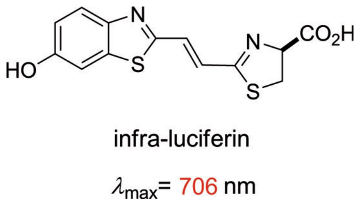
Crowning proteins: By a combination of structural and biophysical methods, it was observed that crown ethers modify protein surfaces dramatically, stabilizing molecular interactions. Hence, crown ethers could potentially be used to modulate a wide range of protein surface behaviors, such as oligomerization, domain–domain interactions, and crystallization.

Near-Infrared Bioluminescence

A. P. Jathoul, H. Grounds,
J. C. Anderson,*
M. A. Pule* __________ 13059 – 13063

A Dual-Color Far-Red to Near-Infrared Firefly Luciferin Analogue Designed for Multiparametric Bioluminescence Imaging

A stretched luciferin: Synthetic infra-luciferin is a dual-color, far-red to near-infrared (NIR) emitting analogue of beetle luciferin, which akin to native luciferin gives rise to different far-red to NIR emission maxima (up to $\lambda_{max} = 706$ nm) with different firefly luciferase mutants. This red-shifted bioluminescence is suitable for imaging in mammals with less attenuation than luciferin.

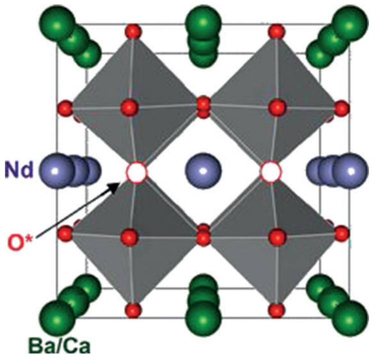


Perovskites

S. Yoo, A. Jun, Y.-W. Ju, D. Odkhuu,
J. Hyodo, H. Y. Jeong, N. Park, J. Shin,
T. Ishihara, G. Kim* _____ 13064 – 13067

Development of Double-Perovskite Compounds as Cathode Materials for Low-Temperature Solid Oxide Fuel Cells

Front Cover

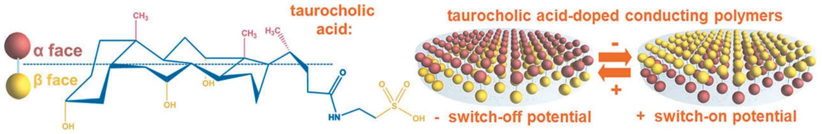


Ca doping into the A site of $NdBaCo_2O_{5+\delta}$ (NBCO) leads to $NdBa_{1-x}Ca_xCo_2O_{5+\delta}$ (NBCaCO), a new class of double-perovskite compounds that are highly stable both in air and in a CO_2-containing atmosphere. They display fast oxygen ion diffusion and high catalytic activity toward oxygen reduction while maintaining excellent compatibility with the electrolyte.

Protein Adsorption

J. Liao, Y. Zhu, Z. Zhou, J. Chen, G. Tan,*
C. Ning,* C. Mao* _____ 13068 – 13072

Reversibly Controlling Preferential Protein Adsorption on Bone Implants by Using an Applied Weak Potential as a Switch

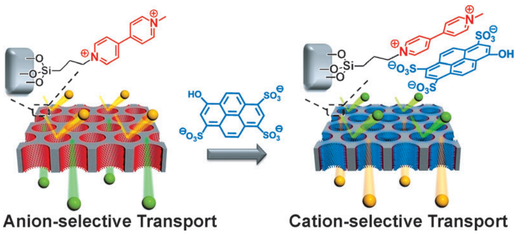


Face changer: Taurocholic acid (TCA), a biomolecule found in bile, is doped into 1D nanoarchitectured conducting polymers designed to aid cell growth on bone implants. The orientation of the hydrophobic α-face and hydrophilic β-face of TCA in the polymeric matrix can be changed by applying an electrical potential. This switching also causes a reversible change in wettability and protein adsorption as well as in adhesion and spreading of osteoblasts on the polymer surface.

Ion-Selective Channels

B. V. V. S. P. Kumar, K. V. Rao, S. Sampath,
S. J. George,*
M. Eswaramoorthy* _____ 13073 – 13077

Supramolecular Gating of Ion Transport in Nanochannels

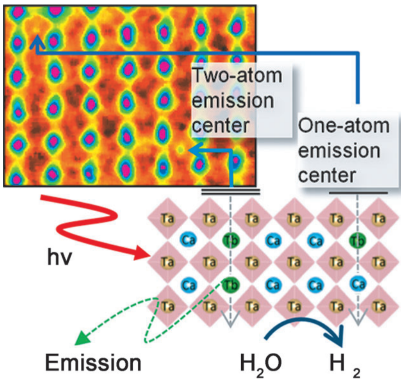


The charge-transfer interactions between dicationic viologen (acceptor) and trianionic pyranine (donor) were exploited to realize charge-reversal in nanochannels. Ion transport was switched from anion selective to ambipolar to cation selective by controlling the extent of viologen bound to the pyranine. Ion-transport regulation with respect to pH was achieved by selecting a donor with pH-responsive functional groups.

Photocatalysis

S. Ida,* S. Koga, T. Daio, H. Hagiwara,
T. Ishihara ———— 13078 – 13082

Direct Imaging of Light Emission Centers in Two-Dimensional Crystals and Their Luminescence and Photocatalytic Properties

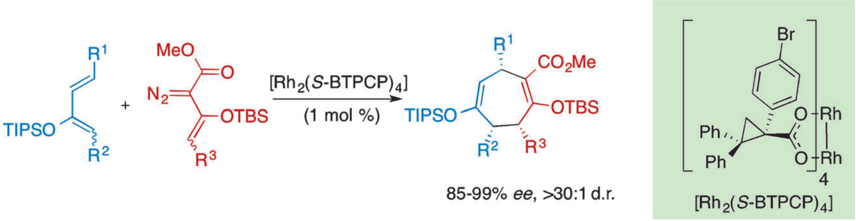


Luminescent materials: In a two-dimensional $Ca_{2-x}Tb_xTa_3O_{10}$ nanocrystal, the presence of one- and two-Tb-atom emission centers was confirmed. Although some Tb^{3+} emission centers existed in close proximity to each other, no concentration-based quenching was observed. The Tb^{3+}-doped nanosheets showed a higher photocatalytic activity relative to undoped nanosheets.

Carbenoids

P. E. Guzmán, Y. Lian,
H. M. L. Davies* ———— 13083 – 13087

Reversal of the Regiochemistry in the Rhodium-Catalyzed [4+3] Cycloaddition between Vinyldiazoacetates and Dienes

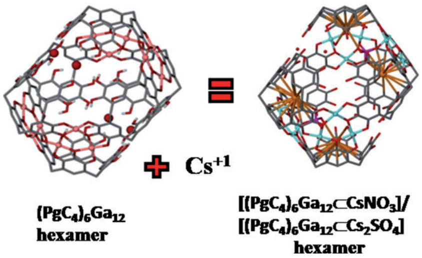


Put it in reverse: A regio-, diastereo-, and enantioselective [4+3] cycloaddition between vinylcarbenes and dienes was achieved using the dirhodium tetracarboxylate catalyst $[Rh_2(S\text{-BTPCP})_4]$. This method provides facile access to 1,4-cycloheptadienes which are regioisomers of those formed from the tandem cyclopropanation/Cope rearrangement reaction of vinylcarbenes with dienes. TBS = *tert*-butyldimethylsilyl, TIPS = triisopropylsilyl.

Calixarenes

H. Kumari, P. Jin, S. J. Teat, C. L. Barnes,
S. J. Dalgarno,
J. L. Atwood* ———— 13088 – 13092

Entrapment of Elusive Guests within Metal-Seamed Nanocapsules

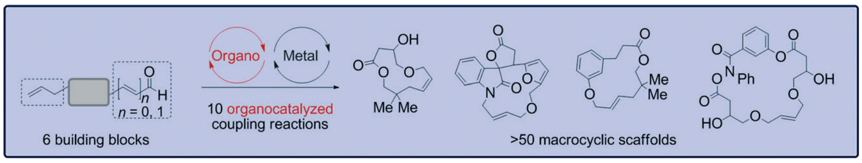


Anions play a crucial role in locking alkali metals on the interior of metal–organic capsules that contain structural water gates. This role is further evidenced when stitching-up the capsule seam, resulting in either expulsion or trapping of cesium ions depending on the anion employed.

Synthetic Methods

A. Grossmann, S. Bartlett, M. Janecek,
J. T. Hodgkinson,
D. R. Spring* ———— 13093 – 13097

Diversity-Oriented Synthesis of Drug-Like Macrocyclic Scaffolds Using an Orthogonal Organo- and Metal Catalysis Strategy



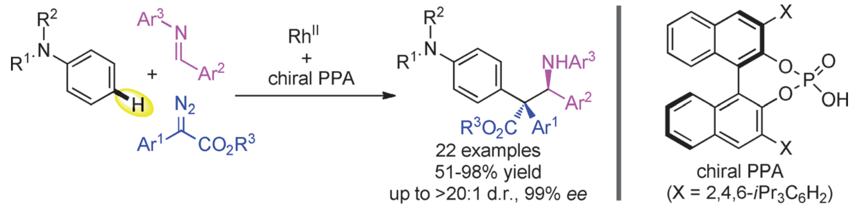
Hand in hand: The outlined diversity-oriented synthesis of a library of macrocycles is based on the orthogonal combination of multiple diversity-generating organocatalytic steps with alkene metathesis. In total, 51 macrocyclic structures bearing 48 unique scaffolds, drug-like chemophysical properties, and natural-product-like shape diversity were synthesized in only 2 to 4 steps without the need for protecting groups.

Asymmetric Catalysis

S. Jia, D. Xing,* D. Zhang,
W. Hu* ______________ 13098 – 13101

Catalytic Asymmetric Functionalization of Aromatic C–H Bonds by Electrophilic Trapping of Metal-Carbene-Induced Zwitterionic Intermediates

Inside Cover

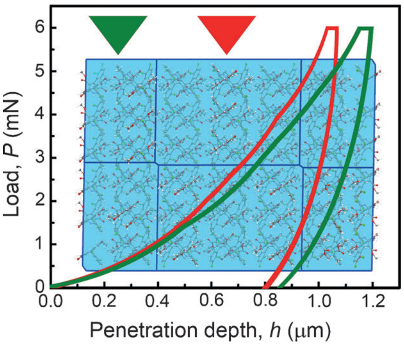


Caught in a trap: The title reaction of *N*,*N*-disubstituted anilines with diazo compounds and imines is reported for the efficient construction of α,α-diaryl benzylic quaternary stereocenters in good yields with high diastereoselectivities and excellent enantioselectivities. Efficient electrophilic trapping of the metal-carbene-induced zwitterionic intermediate is crucial for the enantiocontrol under Rh^{II}/chiral phosphoric acid (PPA) co-catalysis.

Polymorphism

M. K. Mishra, G. R. Desiraju,
U. Ramamurty,*
A. D. Bond* ____________ 13102 – 13105

Studying Microstructure in Molecular Crystals With Nanoindentation: Intergrowth Polymorphism in Felodipine

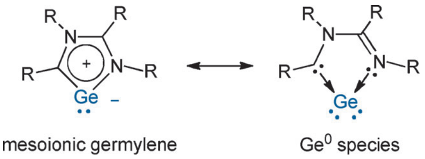


Two in one: Intergrowth polymorphism refers to the existence of distinct structural domains within a single crystal of a compound. For felodipine form II, the phenomenon is revealed by the nanoindentation technique which shows a bimodal response on specific single-crystal faces. The associated microstructure is a significant feature of the compound's structural identity, and has implications for structure–property correlations in molecular crystals.

Main-Group Elements

B. Su, R. Ganguly, Y. Li,
R. Kinjo* ______________ 13106 – 13109

Isolation of an Imino-N-heterocyclic Carbene/Germanium(0) Adduct: A Mesoionic Germylene Equivalent

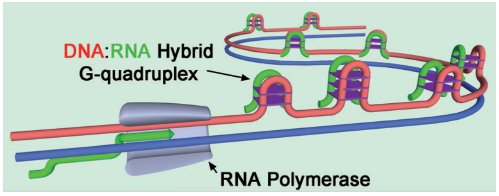


Germanium zero: Reduction of a chlorogermyliumylidene chelated by an imino-N-heterocyclic carbene ligand with potassium graphite produced a novel cyclic germenium species, which can be viewed as both a germanium(0) species and a mesoionic germylene. X-ray diffraction analysis and computational studies revealed one of the lone pairs on the Ge atom is involved in the π system on the GeC$_2$N$_2$ five-membered ring.

DNA Structures

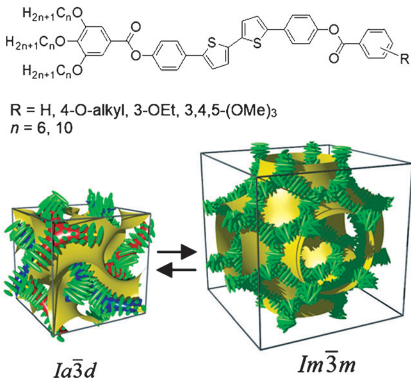
S. Xiao, J.-y. Zhang, J. Wu, R.-y. Wu, Y. Xia,
K.-w. Zheng, Y.-h. Hao, X. Zhou,
Z. Tan* ______________ 13110 – 13114

Formation of DNA:RNA Hybrid G-Quadruplexes of Two G-Quartet Layers in Transcription: Expansion of the Prevalence and Diversity of G-Quadruplexes in Genomes



Quartets unite to call the tune: The transcription of G-rich DNA produces G-rich RNA transcripts. G-tracts from DNA and RNA were found to form hybrid G-quadruplexes (HQs) of two or more G-quartets (see picture) with a possible role in transcription regulation. DNA:RNA HQs composed of two G-quartets were less stable and more flexible than HQs composed of three G-quartets, and their folding and unfolding were more responsive to transcription activity.

Cubics with a twist: Polycatenar 5,5′-diphenyl-2,2′-bithiophenes (see picture) form two types of bicontinuous cubic phases. Though the molecules are achiral the $Im\bar{3}m$ cubic phase is always chiral, while the $Ia\bar{3}d$ phase is achiral. The explanation is that in the $Ia\bar{3}d$ phase the opposing chiralities of the two enantiomorphic networks cancel, but not so in the three-network $Im\bar{3}m$ phase.



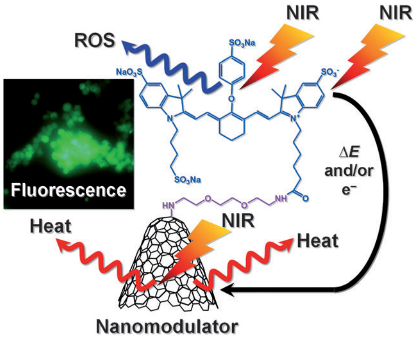
Chiral Induction

C. Dressel, F. Liu, M. Prehm, X. Zeng,* G. Ungar,* C. Tschierske* **13115 – 13120**

Dynamic Mirror-Symmetry Breaking in Bicontinuous Cubic Phases

Inside Back Cover

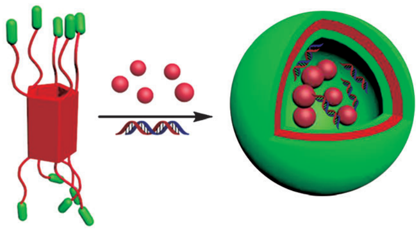
Carbon nanohorns were functionalized with a dye to develop a new type of light-driven nanomodulator. This system generates heat and reactive oxygen species (ROS) under biologically transparent near-infrared (NIR) laser irradiation. These properties can be applied for single-cell analyses and innovative cell therapies.



Nanotechnology

E. Miyako,* J. Russier, M. Mauro, C. Cebrian, H. Yawo, C. Ménard-Moyon, J. A. Hutchison, M. Yudasaka, S. Iijima, L. De Cola, A. Bianco* **13121 – 13125**

Photofunctional Nanomodulators for Bioexcitation



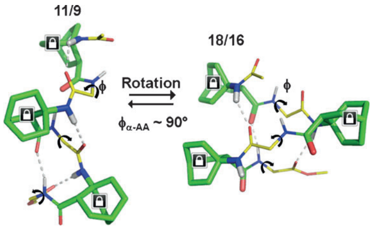
Simultaneous delivery of an anticancer drug and siRNA was achieved with cationic vesicles self-assembled from a novel ferrocenium-capped amphiphilic pillar[5]-arene. These systems exhibit low cytotoxicity to healthy cells and are redox-responsive in the presence of a reductant/oxidant.

Drug/siRNA Co-Delivery

Y. Chang, K. Yang, P. Wei, S. Huang, Y. Pei,* W. Zhao, Z. Pei* **13126 – 13130**

Cationic Vesicles Based on Amphiphilic Pillar[5]arene Capped with Ferrocenium: A Redox-Responsive System for Drug/siRNA Co-Delivery

The chain length of α,β-hybrid oligomers containing the highly constrained (*S*)-1-aminobicyclo[2.2.2]octane-2-carboxylic acid residue determines if either the 11/9 or the 18/16 helix is favored. The transition between these two helices involves a single ϕ angle rotation of the α residues.



Hybrid Peptides

B. Legrand, C. André, L. Moulat, E. Wenger, C. Didierjean, E. Aubert, M. C. Averlant-Petit, J. Martinez, M. Calmes,* M. Amblard* **13131 – 13135**

Unprecedented Chain-Length-Dependent Conformational Conversion Between 11/9 and 18/16 Helix in α/β-Hybrid Peptides

Multicomponent Reaction

X. Ma, J. Jiang, S. Lv, W. Yao, Y. Yang, S. Liu,* F. Xia, W. Hu* ___ **13136 – 13139**

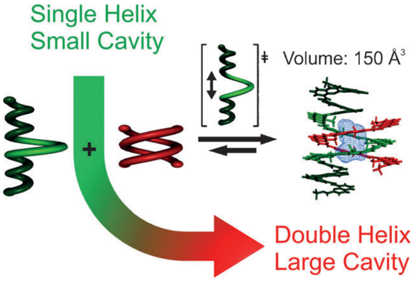
An Ylide Transformation of Rhodium(I) Carbene: Enantioselective Three-Component Reaction through Trapping of Rhodium(I)-Associated Ammonium Ylides by β-Nitroacrylates

Enantioselective trapping: The asymmetric three-component reaction of aryldiazoacetates, aromatic amines, and β-nitroacrylates affords γ-nitro-α-aminosuccinates in good yields and with high diastereo- and enantioselectivity. This reaction is proposed to proceed through the enantioselective trapping of Rh^I-associated ammonium ylides by nitroacrylates and represents the first example of Rh^I-carbene-induced ylide transformation.

Foldamer Heterodimerization

M. L. Singleton, G. Pirotte, B. Kauffmann, Y. Ferrand, I. Huc* ______ **13140 – 13144**

Increasing the Size of an Aromatic Helical Foldamer Cavity by Strand Intercalation

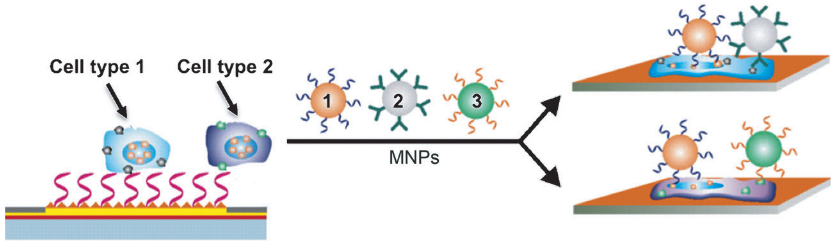


Making room for guests: By directing the heterodimerization of helically folded oligomers, the size of the foldamer cavity could be doubled on demand by the principle of maximal site occupancy. The postsynthetic modification in this way of capsules composed of helical aromatic oligoamide foldamers could potentially be used to control their receptor properties without altering the initial monomer sequences.

Electrochemical Biosensors

Y. Wan, Y.-G. Zhou, M. Poudineh, T. S. Safaei, R. M. Mohamadi, E. H. Sargent, S. O. Kelley* ___________ **13145 – 13149**

Highly Specific Electrochemical Analysis of Cancer Cells using Multi-Nanoparticle Labeling

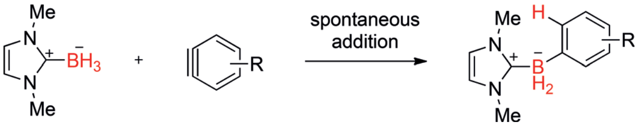


Needle in a haystack: A chip-based electrochemical assay using metal nanoparticles (MNPs, see picture) allows simultaneous detection of multiple different biomarkers on the surfaces of cancer cells, enabling discrimination between cancer cells and normal blood cells. As few as two cells captured per electrode can be detected.

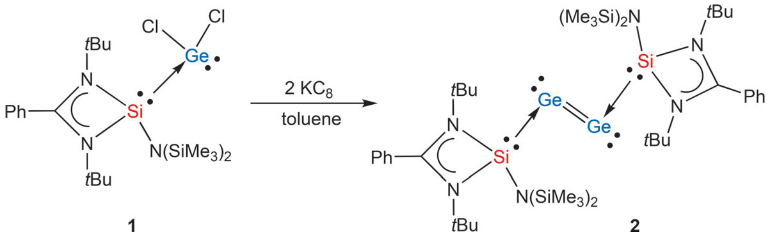
Hydroboration

T. Taniguchi,* D. P. Curran* ___________ **13150 – 13154**

Hydroboration of Arynes with N-Heterocyclic Carbene Boranes



A new partnership with a future: N-Heterocyclic carbene (NHC) boranes coupled with arynes in a hydroboration reaction to produce various B-aryl-substituted NHC-boranes (see scheme), which are stable and have many potential uses. The proposed hydride-transfer character of the mechanism was supported by the *ortho* regioselectivity observed for the hydroboration of arynes with an electron-withdrawing substituent.

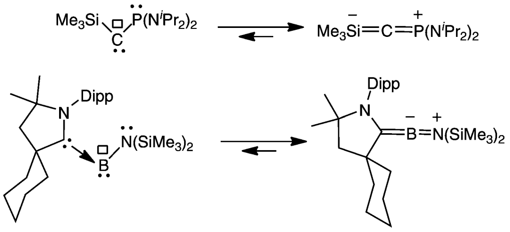


Silicon stabilizers: The reaction of the Si^{II}–Ge^{II} adduct **1** with KC_8 afforded the N-heterocyclic silylene-stabilized digermanium(0) complex **2**. X-ray crystallography and theoretical studies show conclusively that the N-heterocyclic silylene ligands stabilize the singlet digermanium(0) moiety by a weak synergic donor–acceptor interaction.

Group 14 Compounds

Y.-L. Shan, W.-L. Yim,*
C.-W. So* ______ 13155 – 13158

An N-Heterocyclic Silylene-Stabilized Digermanium(0) Complex



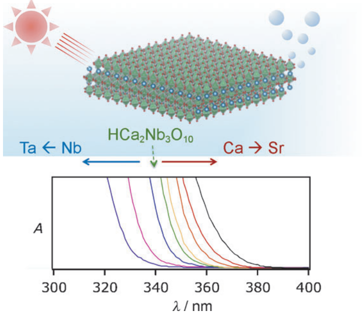
Boron can do it! The first carbene that was stable at room temperature had a pseudo allenic structure, but owing to its high flexibility, it featured classical carbene reactivity. Similarly, a stable boron compound, isoelectronic with singlet carbenes, has an allenic structure, and is able to activate CO and H_2.

Boron–Carbene Adducts

F. Dahcheh, D. Martin, D. W. Stephan,*
G. Bertrand* ______ 13159 – 13163

Synthesis and Reactivity of a CAAC–Aminoborylene Adduct: A Hetero-Allene or an Organoboron Isoelectronic with Singlet Carbenes

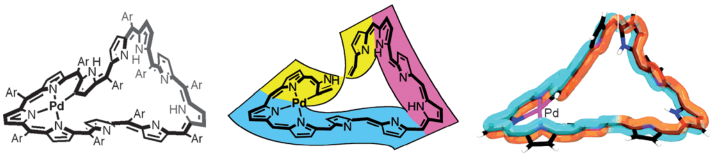
The sunny side of the sheet: Perovskite nanosheets of $HCa_{2-x}Sr_xNb_3O_{10}$ and $HCa_2Nb_{3-y}Ta_yO_{10}$ with tunable band-edge potentials were prepared. They worked as highly efficient heterogeneous photocatalysts for hydrogen evolution from water, with the maximum apparent quantum yield of approximately 80% at 300 nm, the highest value among nanosheet-based photocatalysts reported to date.



Water Splitting

K. Maeda,* M. Eguchi,
T. Oshima ______ 13164 – 13168

Perovskite Oxide Nanosheets with Tunable Band-Edge Potentials and High Photocatalytic Hydrogen-Evolution Activity



Decaphyrin Pd Complex

Pseudo-triangular 44π Möbius Aromatic Structure

A new twist: Reductive metalation of [44]decaphyrin with $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) provided a Hückel aromatic [46]decaphyrin Pd^{II} complex, which was quickly oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone to produce a Hückel antiaromatic [44]decaphyrin Pd^{II} complex. On standing in CH_2Cl_2 solution this complex slowly tautomerizes to a Möbius aromatic [44]decaphyrin Pd^{II} complex, giving an equilibrium mixture.

Expanded Porphyrins

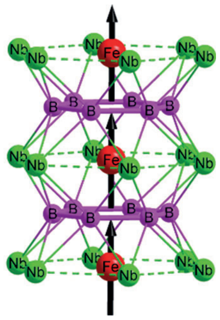
T. Yoneda, Y. M. Sung, J. M. Lim, D. Kim,*
A. Osuka* ______ 13169 – 13173

Pd^{II} Complexes of [44]- and [46]Decaphyrins: The Largest Hückel Aromatic and Antiaromatic, and Möbius Aromatic Macrocycles

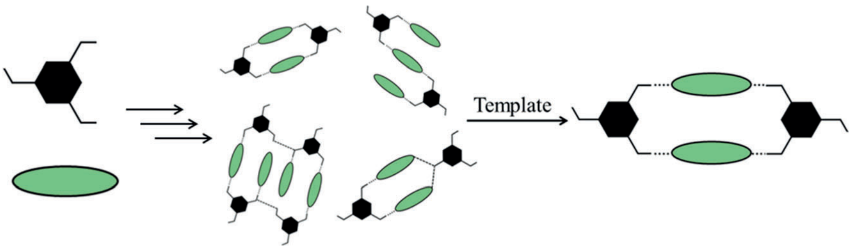
Boride Magnets

Back Cover

A mutual dependency between ferromagnetic iron chains and stacked B_6 rings (see picture) is found in the new ferromagnetic material, $Nb_6Fe_{1-x}Ir_{6+x}B_8$ ($T_C = 350$ K) by combining experiment and density functional theory (DFT). The strong magnetic Fe–Fe interactions found in the iron chains induce an unexpected strengthening of the B–B interactions in the B_6 rings.

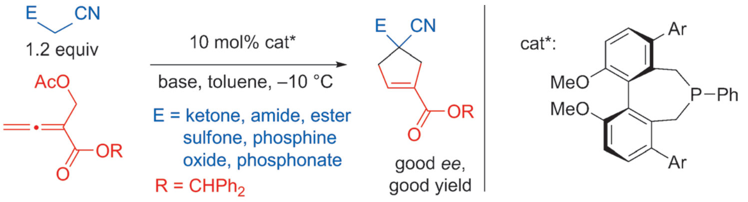


Polymorphism



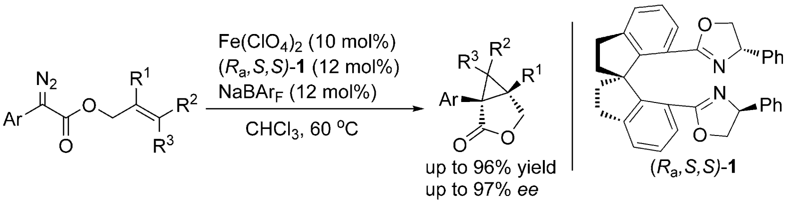
Crystal gazing: A study of the (pseudo)-polymorphs of cocrystals formed from binary and ternary phloroglucinol–dipyridylethylene and –phenazine systems has shown that polymorphism in multicomponent crystals is less likely than in single-component crystals. The generation of several crystal forms during the crystallization of a multicomponent system can be viewed as combinatorial crystal synthesis with synthon selection from a solution library.

Organocatalysis

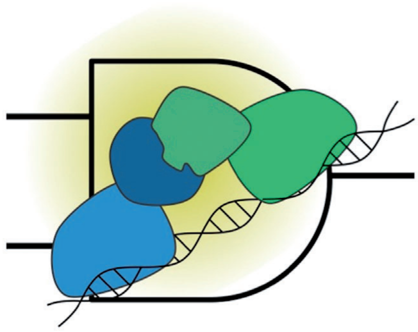


All in the family: A new family of chiral nucleophilic catalysts, biphenyl-derived phosphepines, and their use in the title reaction is reported. A range of one-carbon coupling partners can be employed to generate cyclopentenes bearing a fully substituted stereocenter. Initial mechanistic studies are described.

Asymmetric Catalysis



Ironed out: An iron-catalyzed asymmetric intramolecular cyclopropanation was realized in high yields and excellent enantioselectivity by using the iron complexes of chiral spiro-bisoxazoline ligands as catalysts. $NaBAr_F$ = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

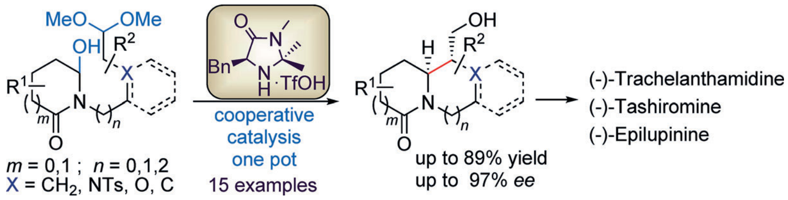


Gated Proteins: By using zinc-finger proteins, AND, OR, and NOR logic gates were created that respond to short oligonucleotide inputs by activating or deactivating a split-luciferase enzyme. The gate designs are simple and modular, thus enabling integration with larger multigate circuits and providing flexibility in the choice of protein outputs. Response to microRNA inputs was achieved through the use of translator circuits.

DNA Computation

A. Prokup, A. Deiters* —— **13192 – 13195**

Interfacing Synthetic DNA Logic Operations with Protein Outputs

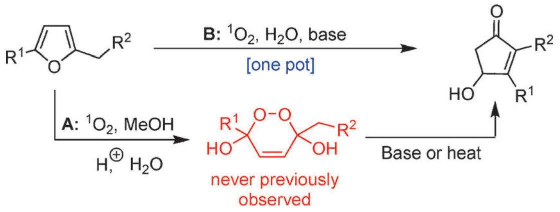


Double bonanza: The title reaction in the presence of an imidazolidinone-based catalyst furnished N-bridgehead bicyclic alkaloids bearing [3.3.0], [3.4.0], [4.4.0], and [4.5.0] skeletons. By using this protocol, the total syntheses of (−)-epilupinine, (−)-tashiromine, and (−)-trachelanthamidine were achieved.

Organocatalysis

D. Koley,* Y. Krishna, K. Srinivas,
A. A. Khan, R. Kant —— **13196 – 13200**

Organocatalytic Asymmetric Mannich Cyclization of Hydroxylactams with Acetals: Total Syntheses of (−)-Epilupinine, (−)-Tashiromine, and (−)-Trachelanthamidine

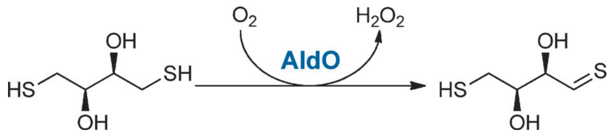


Green chemistry: A highly efficient one-pot transformation of readily accessible furans into 4-hydroxy-2-cyclopentenones in H_2O (see picture), using singlet oxygen as oxidant, has been developed.

Oxidation of Furans

D. Kalaitzakis, M. Triantafyllakis,
I. Alexopoulou, M. Sofiadis,
G. Vassilikogiannakis* —— **13201 – 13205**

One-Pot Transformation of Simple Furans into 4-Hydroxy-2-cyclopentenones in Water



An all-around player: Numerous classical flavin-dependent alcohol oxidases, such as alditol oxidase (AldO), which are well-known for their activity towards C—O and C—N bonds, can also catalyze the oxidation of thiols (see picture). This method provides a potential biocatalytic route to reactive thiocarbonyl compounds.

Biocatalysis

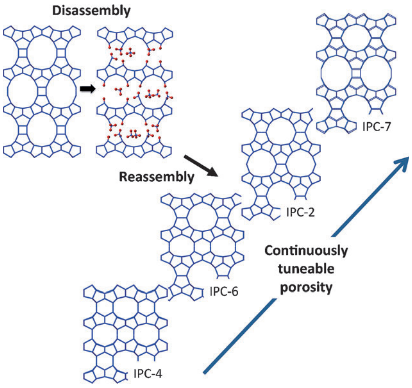
T. A. Ewing, W. P. Dijkman, J. M. Vervoort,
M. W. Fraaije,
W. J. H. van Berkel* —— **13206 – 13209**

The Oxidation of Thiols by Flavoprotein Oxidases: a Biocatalytic Route to Reactive Thiocarbonyls

Germanosilicates

P. S. Wheatley,* P. Chlubná-Eliášová, H. Greer, W. Zhou, V. R. Seymour, D. M. Dawson, S. E. Ashbrook, A. B. Pinar, L. B. McCusker, M. Opanasenko, J. Čejka, R. E. Morris* ———— **13210 – 13214**

Zeolites with Continuously Tuneable Porosity

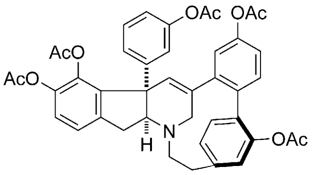


ADORable zeolites: A series of zeolites with continuously tuneable porosity was prepared using the assembly–disassembly–organization–reassembly (ADOR) method. The pores of the zeolites that are accessible with this method cover the whole range of useable sizes: from small to extra-large.

Natural Product Synthesis

Y. Momoi, K.-i. Okuyama, H. Toya, K. Sugimoto, K. Okano, H. Tokuyama* ———— **13215 – 13219**

Total Synthesis of (−)-Haouamine B Pentaacetate and Structural Revision of Haouamine B

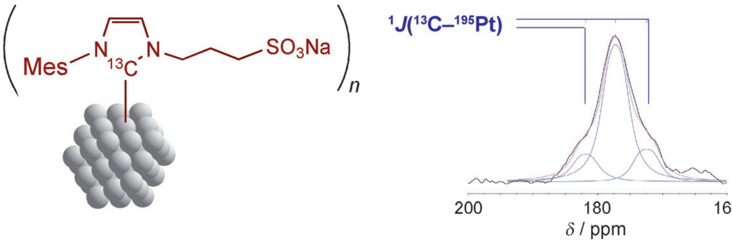


Revision: Key steps in the total synthesis of (−)-haouamine B pentaacetate (see structure) are the enantiocontrolled construction of indane-fused tetrahydropyridine based on Ellman's diastereoselective Mannich reaction and the newly developed mild Friedel–Crafts alkylation. The synthesis led to the revision of the structure, as proposed by Trauner and Zubía.

Water-Soluble Nanoparticles

E. A. Baquero, S. Tricard, J. C. Flores,* E. de Jesús,* B. Chaudret* ———— **13220 – 13224**

Highly Stable Water-Soluble Platinum Nanoparticles Stabilized by Hydrophilic N-Heterocyclic Carbenes

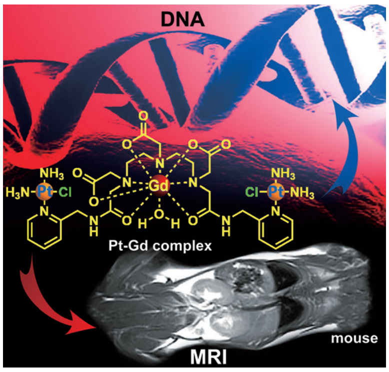


On the surface: The thermal decomposition of organometallic complexes with N-heterocyclic carbene ligands affords Pt nanoparticles that are soluble and stable in water for an indefinite period. The ^{13}C–^{195}Pt coupling observed by solid-state NMR spectroscopy confirms carbene coordination to the nanoparticle surface.

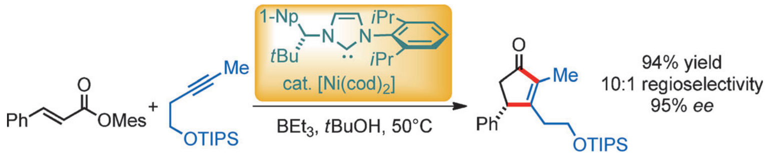
Antitumor Complexes

Z. Zhu, X. Wang,* T. Li, S. Aime, P. J. Sadler, Z. Guo* ———— **13225 – 13228**

Platinum(II)–Gadolinium(III) Complexes as Potential Single-Molecular Theranostic Agents for Cancer Treatment



Multitalented special agents: Cytotoxic *cis*-$[Pt(NH_3)_2(py)Cl]^+$ (py is a pyridyl ligand) was conjugated to the magnetic resonance imaging contrast agent Gd–DTPA (DTPA = diethylenetriaminepentaacetate) to form Gd–Pt complexes of the type shown in the picture. The conjugates satisfy the requirements for tumor therapy and imaging at the same dose and are thus promising theranostic agents for cancer treatment.

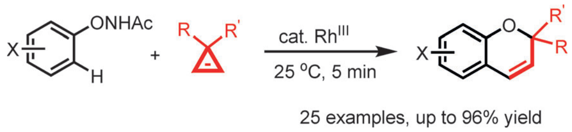


Asymmetric Catalysis

J. S. E. Ahlin, P. A. Donets, N. Cramer* ______ 13229 – 13233

Nickel(0)-Catalyzed Enantioselective Annulations of Alkynes and Arylenoates Enabled by a Chiral NHC Ligand: Efficient Access to Cyclopentenones

Cyclization: Nickel(0) catalysts with a chiral bulky C_1-symmetric N-heterocyclic carbene ligand enabled the efficient asymmetric reductive [3+2] cycloaddition of enoates and alkynes, providing substituted cyclopentenones under mild conditions. The system provided the products in very high enantioselectivity and led to a regioselective incorporation of unsymmetrically substituted alkynes.

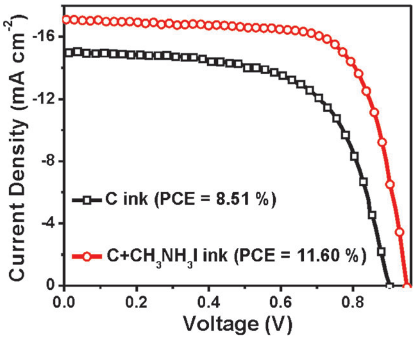


Carbenes

H. Zhang, K. Wang, B. Wang, H. Yi, F. Hu, C. Li, Y. Zhang, J. Wang* ______ 13234 – 13238

Rhodium(III)-Catalyzed Transannulation of Cyclopropenes with *N*-Phenoxyacetamides through C—H Activation

The three C's: An efficient rhodium(III)-catalyzed synthesis of 2*H*-chromenes from *N*-phenoxyacetamides and cyclopropenes has been developed. The reaction represents the first example of using cyclopropenes as a three-carbon unit in rhodium(III)-catalyzed C(sp^2)—H activations. Preliminary mechanistic investigations are discussed.

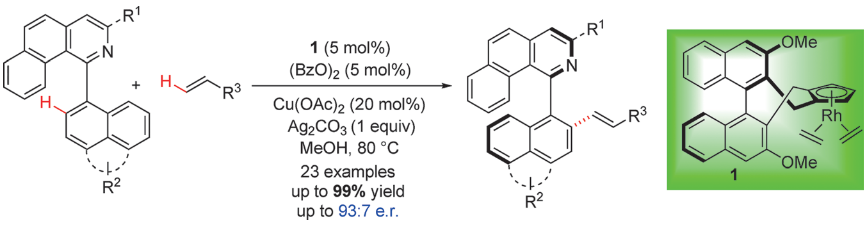


Nanotechnology

Z. Wei, H. Chen, K. Yan, S. Yang* ______ 13239 – 13243

Inkjet Printing and Instant Chemical Transformation of a $CH_3NH_3PbI_3$/Nanocarbon Electrode and Interface for Planar Perovskite Solar Cells

Inkjet-printing solar cells: By designing carbon plus CH_3NH_3I ink to transform PbI_2 in situ to $CH_3NH_3PbI_3$, an interpenetrating seamless interface between the $CH_3NH_3PbI_3$ active layer and the C hole-extraction electrode was instantly constructed, resulting in a 11.60% efficient, planar perovskite solar cell.



C—H Activation

J. Zheng, S.-L. You* ______ 13244 – 13247

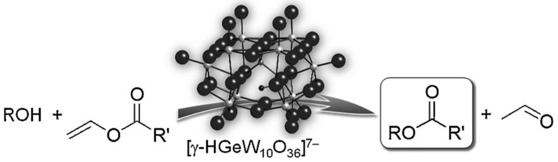
Construction of Axial Chirality by Rhodium-Catalyzed Asymmetric Dehydrogenative Heck Coupling of Biaryl Compounds with Alkenes

An axe to grind? Novel axially chiral biaryls were synthesized by the direct C—H bond olefination of biaryl compounds, using a chiral [Cp*Rh^{III}] catalyst (**1**), in good to excellent yields and enantioselectivities. The biaryls were found as suitable ligands for rhodium-catalyzed asymmetric conjugate addition reactions.

Polyoxometalates

K. Sugahara, N. Satake, K. Kamata,
T. Nakajima, N. Mizuno* **13248 – 13252**

A Basic Germanodecatungstate with a −7 Charge: Efficient Chemoselective Acylation of Primary Alcohols



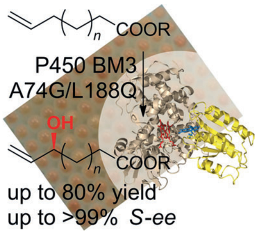
Charged up: The title germanodecatungstate $[\gamma\text{-HGeW}_{10}\text{O}_{36}]^{7-}$ was synthesized under non-aqueous conditions. The activities of germanodecatungstates for base-catalyzed reactions dramatically increased with an increase in the number of negative charges from −6 to −7. In the presence of $[\gamma\text{-HGeW}_{10}\text{O}_{36}]^{7-}$, various combinations of acylating agents and primary alcohols chemoselectively gave the desired acylated products in high yields.

C–H Oxidation

K. Neufeld, B. Henßen,
J. Pietruszka* ______ **13253 – 13257**

Enantioselective Allylic Hydroxylation of ω-Alkenoic Acids and Esters by P450 BM3 Monooxygenase

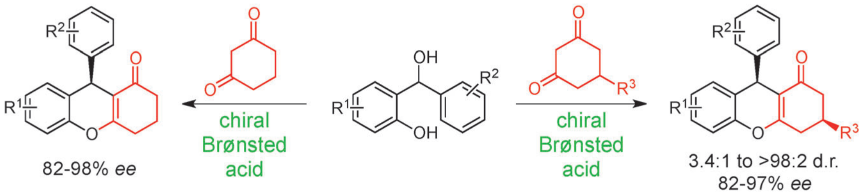
Modern biocatalysts on the rise: The P450 BM3 monooxygenase mutant A74G/L188Q catalyzes the enantioselective allylic hydroxylation of ω-alkenoic acids and esters under mild conditions using O_2 as an oxidant. This reaction offers access to important chiral building blocks for the synthesis of biologically active compounds and demonstrates the highest chemo- and enantioselectivity observed to date for the C–H oxidation of acyclic terminal olefins.



Organocatalysis

C.-C. Hsiao, H.-H. Liao,
M. Rueping* ______ **13258 – 13263**

Enantio- and Diastereoselective Access to Distant Stereocenters Embedded within Tetrahydroxanthenes: Utilizing *ortho*-Quinone Methides as Reactive Intermediates in Asymmetric Brønsted Acid Catalysis

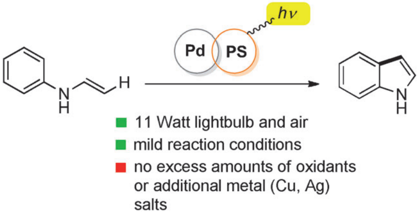


Procedures for the Brønsted acid catalyzed asymmetric synthesis of 9-substituted tetrahydroxanthenones and 3,9-disubstituted tetrahydroxanthenone derivatives have been developed. The procedures are based on the in situ generation of *ortho*-quinone methides and their subsequent reaction with 1,3-dicarbonyl compounds. The reaction provides products with a high level of asymmetric induction.

Combined Catalysis

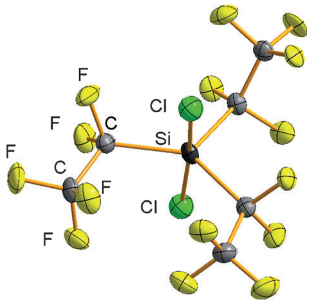
J. Zoller, D. C. Fabry, M. A. Ronge,
M. Rueping* ______ **13264 – 13268**

Synthesis of Indoles Using Visible Light: Photoredox Catalysis for Palladium-Catalyzed C–H Activation



Coupling without coinage metals: A combined palladium- and photoredox-catalyzed C–H olefination serves to synthesize indoles. Using visible light, direct C–H activation of aromatic enamines leads to a variety of indole derivatives in good yields under mild reaction conditions.

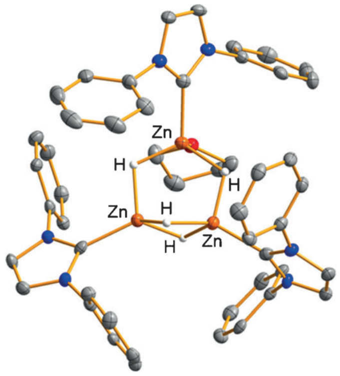
Pentacoordinate chlorosilicates are known to be reactive intermediates. They can be stabilized by the introduction of at least two electron-withdrawing C_2F_5 groups, which has allowed the characterization of a series of (pentafluoroethyl)-chlorosilicates (see example) in solution as well as in the solid state.



Stable Chlorosilicates

S. Steinhauer, T. Böttcher, N. Schwarze, B. Neumann, H.-G. Stammler, B. Hoge* ——— 13269 – 13272

Synthesis of Chlorosilicates



Competition for transition metals: A cationic trinuclear zinc hydride cluster with a Zn_3H_4 core efficiently catalyzes the hydrosilylation of aldehydes, ketones, and nitriles, and notably also carbon dioxide.

Zinc Catalysis

A. Rit, A. Zanardi, T. P. Spaniol, L. Maron,* J. Okuda* ——— 13273 – 13277

A Cationic Zinc Hydride Cluster Stabilized by an N-Heterocyclic Carbene: Synthesis, Reactivity, and Hydrosilylation Catalysis

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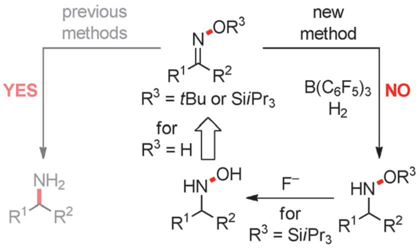

No NO cleavage: Transition-metal-free hydrogenation of oxime ethers with bulky groups at the oxygen atom (R^3 = tBu and $SiiPr_3$) can be achieved at mild temperatures by using the electron-deficient boron Lewis acid $B(C_6F_5)_3$ as a catalyst. The reduction is highly chemoselective, leaving the N–O bond intact. Subsequent fluoride-mediated cleavage of the Si–O bond (for $R^3 = SiiPr_3$) provides access to the free hydroxylamines (see scheme).

Hydrogenation

J. Mohr, M. Oestreich* ——— 13278 – 13281

$B(C_6F_5)_3$-Catalyzed Hydrogenation of Oxime Ethers without Cleavage of the N–O Bond

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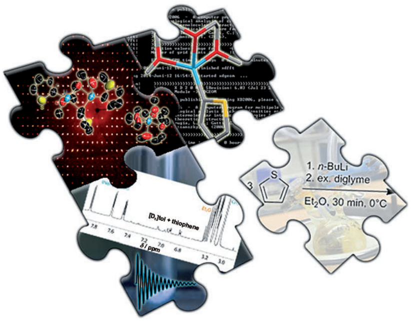


Aggregation is more than the sum of its parts! An unusual lithium lithiate, made up from three carbanions, two lithium cations, and a single donor base in the anion and a single lithium cation, and coordinated by two donor base molecules, was investigated in a combined study including X-ray diffraction, NMR spectroscopy, and computational approaches in solution and the solid state. Only the combination of this multitude of methods provides a firm picture of the whole.

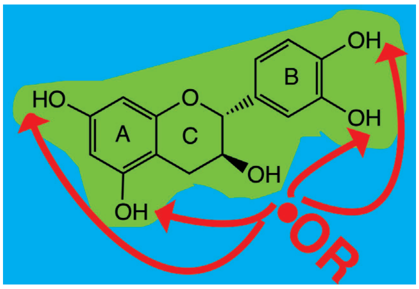
Lithium Lithiates

A.-C. Pöppler, M. Granitzka, R. Herbst-Irmer, Y.-S. Chen, B. B. Iversen, M. John, R. A. Mata, D. Stalke* ——— 13282 – 13287

Characterization of a Multicomponent Lithium Lithiate from a Combined X-Ray Diffraction, NMR Spectroscopy, and Computational Approach

Natural Antioxidants

How does tea fight dangerous radicals? Hydrogen abstraction from catechin and green-tea polyphenols by highly reactive O-centered H-abstracting species was studied at the molecular level and in real time by time-resolved EPR spectroscopy. Our results show that all phenolic OH groups display identical reactivity. Accordingly, statistical (entropic) factors essentially predominate in initial antioxidative events.



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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Angewandte Addendum

Anti-Electrostatic Hydrogen Bonds

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Following recent coverage in *Chemical & Engineering News* (September 22, **2014**, p. 10) the authors of this Communication were kindly informed by Prof. Ibon Alkorta (Madrid, Spain) and Prof. Steven R. Kass (Minneapolis) of earlier experimental[1,2] and theoretical[3,4] works pertaining to doubly-ionic H-bonded species in the gas phase that are peripherally related to this Communication. Their studies involve somewhat different species (such as large peptide clusters) and different theoretical focus than the central "What is H-bonding?" question of the present work, but should be recognized (along with crystallographic evidence on bicarbonate dimers[5] previously noted) as relevant to the attempted experimental and theoretical detection and characterization of paradoxical "anti-electrostatic" (or "electrostatics-defying"[3]) H-bond species that challenge current empirical modeling and pedagogy.

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