Service

Author Profile

"If I were not a scientist, I would be a painter. The most significant scientific advance of the last 100 years has been the Haber–Bosch process for ammonia synthesis …"
This and more about Atsuhiro Osuka can be found on page 9970.

News


D. Milstein


N. Martín

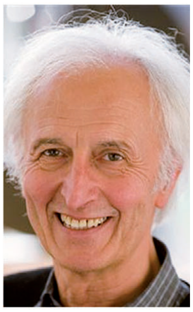

M. Taillefer


R. M. Waymouth


J. L. Hedrick


G. W. Coates

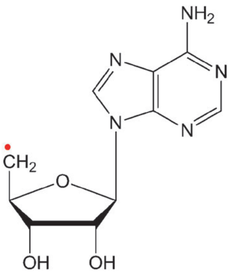

W. Thiel


H. Schwarz

Highlights

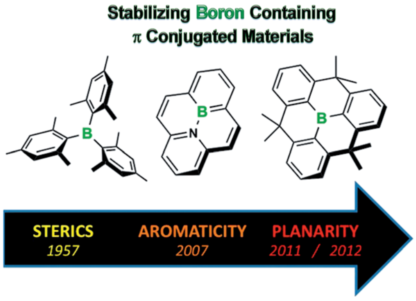
Radical Enzymes

Radical chaperone: Recent research reveals how the 5′-deoxyadenosyl radical (see structure) is generated by homolysis of the Co–C σ-bond of enzyme-bound coenzyme B_{12} and how it is guided to the substrate through pseudorotation of the ribose moiety and hydrogen-bonding interactions.



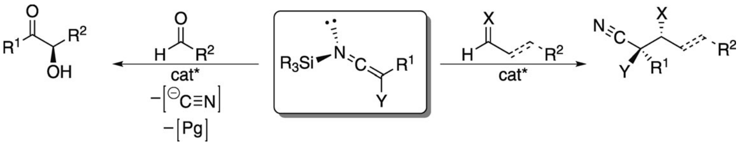
Boron Materials

Catching a plane: A new strategy for stabilizing the B–C bonds in boron-containing π-conjugated materials has been demonstrated. Encasing the boron in a rigid, planarized environment (see scheme) has been shown by Yamaguchi and co-workers to give air- and moisture-stable organoboranes that bring the boron's p orbital into full conjugation with the organic π framework.



Minireviews

Asymmetric Catalysis

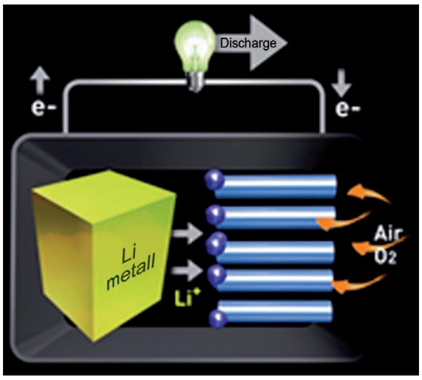


Teaching a middled-aged nucleophile new tricks: This Minireview provides an overview on the development of silyl ketene imines and their recent applications in catalytic, enantioselective reactions. The unique structure of ketene imines allow a diverse range of reactivity patterns and provide solutions to existing challenges in the enantioselective construction of quaternary stereogenic carbon centers and cross-benzoin adducts (see scheme; Pg = protecting group, Y = OPg).

Reviews

Batteries

TrueLi advanced: Modern energy storage technologies, such as lithium batteries and electrical double-layer capacitors are a central area of basic research. The aims being to develop new materials and electrochemical reactions for these energy storage units and to better understand the underlying processes. Latest developments include the Li–air (see picture) and the Li–S batteries



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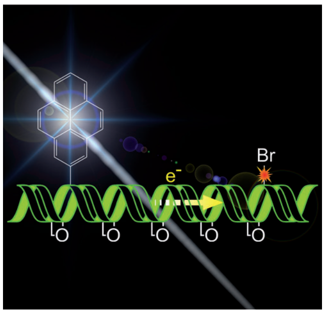
Communications

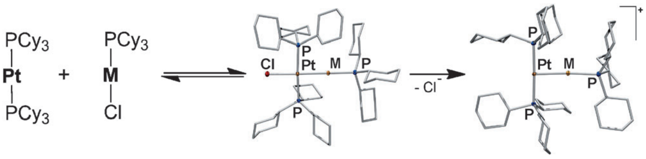
Electron Transfer

Frontispiece

Lock it, but not too much: LNA units (locked or bridging nucleic acids) in LNA:DNA hybrids lead to a negative effect on electron transfer (ET), but they also force the nucleic acid structure in the A-type double helix, which allows a better base stacking than the normal B-type and thus positively influences the ET. This result is significant for the design of nucleic acids of molecular electronics.



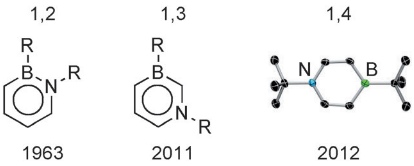
Heterobimetallic Complexes



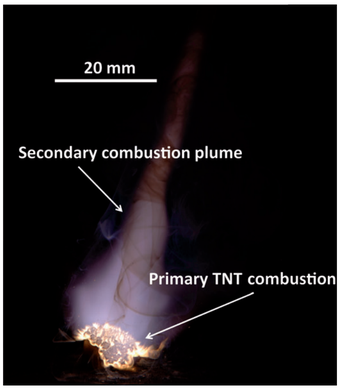
M&Ms: The reversible insertion of a platinum complex into coinage group metal–halogen bonds results in a series of unsupported metal-only Lewis pairs with a Lewis basic platinum(0) fragment and cationic copper, silver, and gold Lewis acids (see scheme; M = Cu, Ag, Au; Cy = cyclohexyl). This is a convenient route to mixed d^{10}–d^{10} complexes.

Boron Heterocycles

Completing the set: Although 1,2-azaborine is known, little is known about the 1,3- and 1,4-analogues. Now a simple, controlled synthesis of 1,2-di-*tert*-butyl-1,2-azaborine from acetylene and di-*tert*-butyliminoborane has been achieved by a metal-mediated formal [2+2+2] cycloaddition reaction. A 1,2-azaborete piano-stool complex was identified as an reaction intermediate.



Energetic Materials



Deceiving with TNT: Melt-cast pyrotechnic mixtures based on 2,4,6-trinitrotoluene (TNT)/$KClO_4$ (see picture for flame) spectrally matched infrared decoy flares and show superior performance and greatly reduced sensitivity in comparison to common pyrotechnic or double-base material currently in use for IR countermeasure flares.

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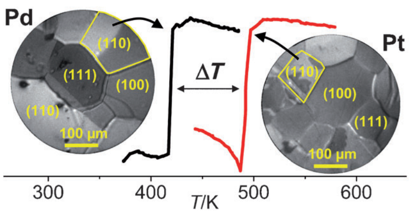
Heterogeneous Catalysis

D. Vogel, C. Spiel, Y. Suchorski, A. Trinchero, R. Schlögl, H. Grönbeck, G. Rupprechter* ______ **10041 – 10044**

Local Catalytic Ignition during CO Oxidation on Low-Index Pt and Pd Surfaces: A Combined PEEM, MS, and DFT Study

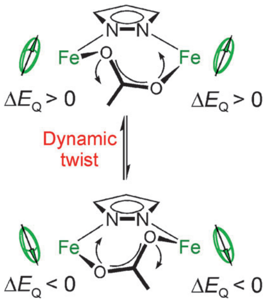


Shedding light on light-off: Photoemission electron microscopy, DFT, and microkinetic modeling were used to examine the local kinetics in the CO oxidation on individual grains of a polycrystalline sample. It is demonstrated that catalytic ignition ("light-off") occurs easier on Pd(*hkl*) domains than on corresponding Pt(*hkl*) domains. The isothermal determination of kinetic transitions, commonly used in surface science, is fully consistent with the isobaric reactivity monitoring applied in technical catalysis.

Molecular Nanoswitches

B. Burger, S. Demeshko, E. Bill, S. Dechert, F. Meyer* ___ **10045 – 10049**

The Carboxylate Twist: Hysteretic Bistability of a High-Spin Diiron(II) Complex Identified by Mössbauer Spectroscopy



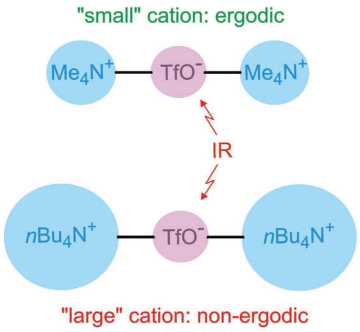
In a twist: The carboxylate ligand in the clamp of a highly preorganized diferrous site shows temperature-dependent dynamic behavior, coined the "carboxylate twist". It leads to a fluctuation of the electric field gradient and thus averaged Mössbauer resonances at higher temperatures, resulting in magnetic and spectroscopic hysteresis even without any spin-crossover or valence tautomerism.

Ion Pairs

C. J. Shaffer, Á. Révész, D. Schröder,* L. Severa, F. Teplý, E.-L. Zins, L. Jašíková, J. Roithová ______ **10050 – 10053**

Can Hindered Intramolecular Vibrational Energy Redistribution Lead to Non-Ergodic Behavior of Medium-Sized Ion Pairs?

Inside Back Cover

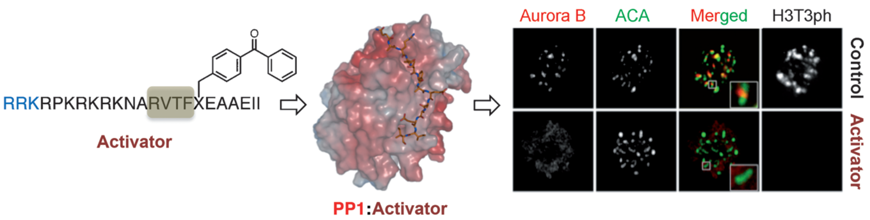


Communication breakdown: Ergodicity is the ability to predict the behavior of an ensemble from the behavior of its components. Infrared spectroscopy of mass-selected ion pairs in the gas phase suggests that intramolecular vibrational energy redistribution (IVR) is hindered in some of these noncovalently bound species, particularly when triflate anion is involved. The hindered IVR leads to a non-ergodic behavior on a timescale sufficient for the formation of new chemical bonds.

Drug Design

J. Chatterjee, M. Beullens, R. Sukackaite, J. Qian, B. Lesage, D. J. Hart, M. Bollen,* M. Köhn* ______ **10054 – 10059**

Development of a Peptide that Selectively Activates Protein Phosphatase-1 in Living Cells



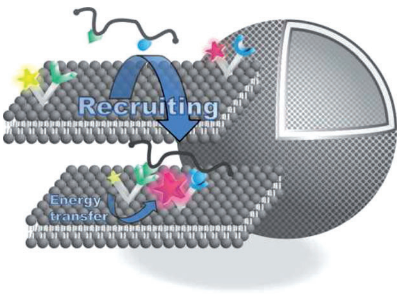
The first cell-penetrating peptide that activates protein phosphatase-1 (PP1) by disrupting a subset of PP1 complexes in living cells has been developed. Activated PP1 rapidly dephosphorylates its substrates, counteracting kinase activity inside cells. Activation of PP1 can thus be a novel approach to study PP1 function and to counteract Ser/Thr kinase activity under pathologically increased kinase signaling.

Artificial Membranes

B. Gruber, S. Balk, S. Stadlbauer, B. König* ______ **10060 – 10063**

Dynamic Interface Imprinting: High-Affinity Peptide Binding Sites Assembled by Analyte-Induced Recruiting of Membrane Receptors

Come together: Dynamic molecular recognition events at biological membrane receptors play a key role in cell signaling. Artificial membranes have been prepared with embedded synthetic receptors which dynamically arrange and selectively respond to external stimuli, such as, small peptide ligands.

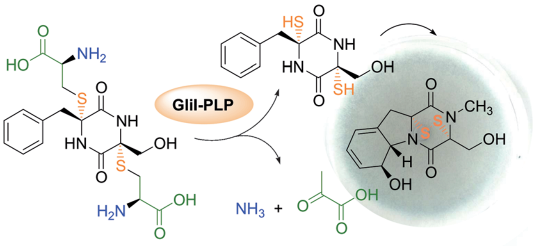


Natural Sulfur Compounds

D. H. Scharf, P. Chankhamjon, K. Scherlach, T. Heinekamp, M. Roth, A. A. Brakhage, C. Hertweck* ______ **10064 – 10068**

Epidithiol Formation by an Unprecedented Twin Carbon–Sulfur Lyase in the Gliotoxin Pathway

Front Cover

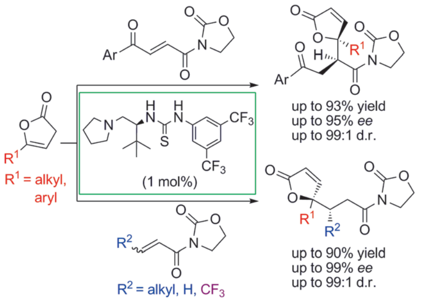


Two in one go: The elucidation of a key step in the biosynthesis of gliotoxin, the infamous virulence factor of the human pathogen *Aspergillus fumigatus*, provides insight into the formation of an epidithiol. Isolation of a bis(cysteine) S-conjugate from a Δ*gliI* mutant and in vitro studies show that GliI concomitantly cleaves two C–S bonds, along with the formation of ammonia and pyruvate (see scheme).

Asymmetric Synthesis

W. Zhang, D. Tan, R. Lee, G. Tong, W. Chen, B. Qi, K.-W. Huang,* C.-H. Tan,* Z. Jiang* ______ **10069 – 10073**

Highly Enantio- and Diastereoselective Reactions of γ-Substituted Butenolides Through Direct Vinylogous Conjugate Additions

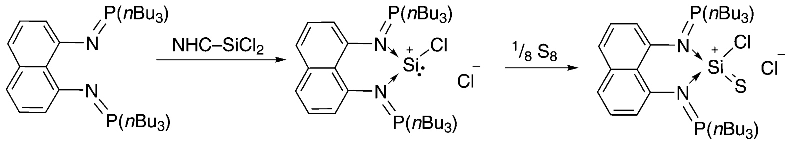


The strength of the weak: An L-*tert*-leucine-derived amine–thiourea catalyst (see scheme, green box) promotes the asymmetric vinylogous conjugate addition reaction between γ-aryl- and alkyl-substituted butenolides with the butenamides and enoates shown. Computational studies show the preference for the observed stereochemistry is a result of favourable weak non-bonding interactions, which stabilize the transition state.

Silicon Chemistry

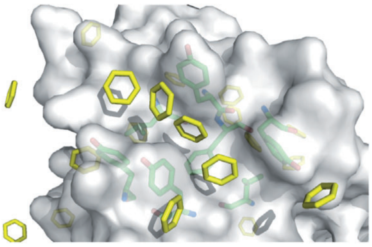
Y. Xiong, S. Yao, S. Inoue, E. Irran, M. Driess* ______ **10074 – 10077**

The Elusive Silyliumylidene [ClSi:]$^+$ and Silathionium [ClSi=S]$^+$ Cations Stabilized by Bis(Iminophosphorane) Chelate Ligand



1 2 3

Donor–acceptor trumps: The chlorosilyliumylidene salt **2** with a three-coordinate silicon(II) atom is accessible through ligand exchange between NHC–SiCl$_2$ and the electron-rich bis(ylide) ligand **1**. The cation in **2** represents a donor-stabilized form of the elusive [ClSi:] cation and could be fully characterized, including X-ray diffraction analysis. Oxidation of **2** with elemental sulfur furnished **3** as the sole product.



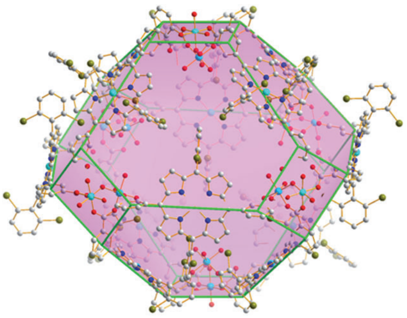
An explicit solvent ligand-mapping approach was used to reveal an otherwise hidden hydrophobic pocket in polo-like kinase 1 (Plk1). It predicted a novel ligand binding mode that was used for the design of a new ligand with high affinity for Plk1. X-ray crystallography confirmed that the binding was specific to the intended pocket.

Ligand Design

Y. S. Tan, P. Śledź, S. Lang, C. J. Stubbs, D. R. Spring, C. Abell,* R. B. Best* ——— **10078–10081**

Using Ligand-Mapping Simulations to Design a Ligand Selectively Targeting a Cryptic Surface Pocket of Polo-Like Kinase 1

A 12-connected fcu metal–organic framework (MOF), MMPF-3, has been prepared using a Co^{II} metalloporphyrin. MMPF-3 is comprised of the same polyhedral supermolecular building blocks as the prototypal **fcu**-MOF, **fcu**-MOF-1, and its nanoscale cavities feature 18 catalytically active cobalt centers. The high density (ca. 5 cobalt sites/nm^3) affords MMPF-3 superior performance in catalytic epoxidation of *trans*-stilbene compared to other MOFs.



Crystal Engineering

L. Meng, Q. Cheng, C. Kim, W.-Y. Gao, L. Wojtas, Y.-S. Chen, M. J. Zaworotko,* X. P. Zhang,* S. Ma* ——— **10082–10085**

Crystal Engineering of a Microporous, Catalytically Active **fcu** Topology MOF Using a Custom-Designed Metalloporphyrin Linker

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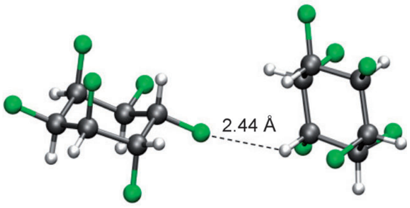
Six of the best: Benzene had been used by Faraday and Mitscherlich in their respective synthesis of hexachloro- and hexabromocyclohexane in the early 19th century. Also starting from benzene, η-1,2,3,4,5,6-hexafluorocyclohexane (benzene hexafluoride; see X-ray structure of a dimer) was now synthesized in five steps.



Benzene Hexafluoride

A. J. Durie, A. M. Z. Slawin, T. Lebl, D. O'Hagan* ——— **10086–10088**

The Synthesis of η-1,2,3,4,5,6-Hexafluorocyclohexane (Benzene Hexafluoride) from Benzene

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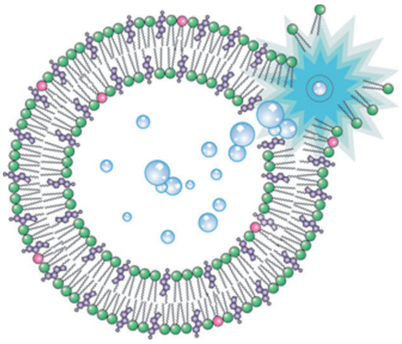


Bubbling over: After endocytosis and intracellular trafficking to lysosomes, liposomes containing ammonium bicarbonate can be thermally triggered to generate CO_2 bubbles (see scheme). These bubbles grow rapidly and collapse violently to induce transient cavitation, a process that can disrupt the lysosomal membrane and release lysosomal proteases, thus leading to cell necrosis.

Anticancer Agents

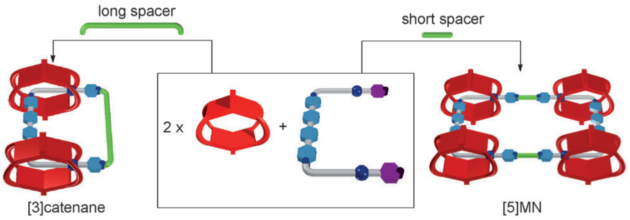
M. F. Chung, K. J. Chen, H. F. Liang, Z. X. Liao, W. T. Chia, Y. Xia,* H. W. Sung* ——— **10089–10093**

A Liposomal System Capable of Generating CO_2 Bubbles to Induce Transient Cavitation, Lysosomal Rupturing, and Cell Necrosis

Template Synthesis

C.-F. Chang, C.-J. Chuang, C.-C. Lai,
Y.-H. Liu, S.-M. Peng,
S.-H. Chiu* ______ **10094 – 10098**

Using Host–Guest Complexation to Fold a Flexible Linear Organic String: Kinetically Controlled Syntheses of [3]Catenanes and a Five-Membered Molecular Necklace

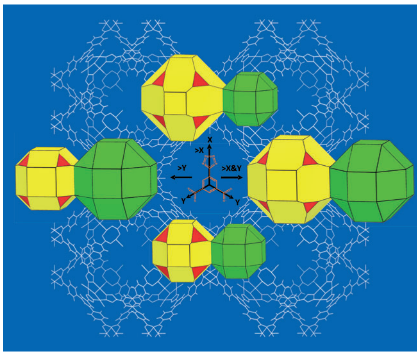


Rings and necklaces: Three [3]catenanes and a five-membered molecular necklace ([5]MN), with up to 60- and 92-membered rings as their centerpieces, respectively, have been synthesized. The synthesis started from the corresponding complexes in which the threaded flexible linear guests were bent at approximately right angles to facilitate kinetically controlled macrocyclizations.

Metal–Organic Frameworks

J. F. Eubank, F. Nouar, R. Luebke,
A. J. Cairns, L. Wojtas, M. Alkordi,
T. Bousquet, M. R. Hight, J. Eckert,
J. P. Embs, P. A. Georgiev,
M. Eddaoudi* ______ **10099 – 10103**

On Demand: The Singular **rht** Net, an Ideal Blueprint for the Construction of a Metal–Organic Framework (MOF) Platform

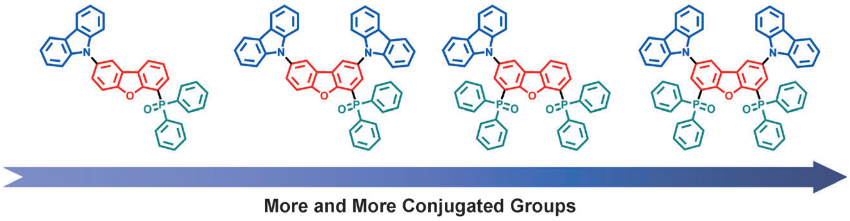


The exceptional nature of the **rht**-MOF platform, based on a singular edge-transitive net (the only net for the combination of 3- and 24-connected nodes), makes it an ideal target in crystal chemistry. The high level of control indicates an unparalleled blueprint for isoreticular functional materials (without concern for interpenetration) for targeted applications.

Excited-State Tuning

C. Han, Z. Zhang, H. Xu,* J. Li, G. Xie,
R. Chen, Y. Zhao,*
W. Huang ______ **10104 – 10108**

Controllably Tuning Excited-State Energy in Ternary Hosts for Ultralow-Voltage-Driven Blue Electrophosphorescence



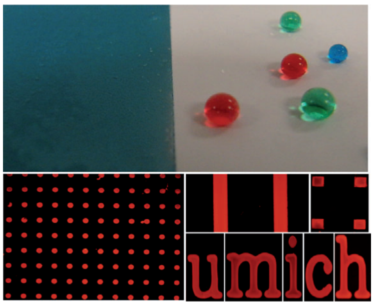
A series of dibenzofuran-based ternary hosts were designed and prepared. The singlet energy levels and carrier injecting/transporting abilities were adjusted on the basis of the mixed *meso* and short-axis linkages (see picture). By harmonizing the optical and electrical properties, the blue-emitting diodes realized highly efficient blue electrophosphorescence with ultralow driving voltages.

Smart Materials

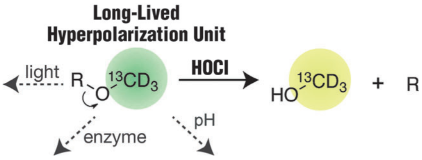
S. P. R. Kobaku, A. K. Kota, D. H. Lee,
J. M. Mabry, A. Tuteja* ___ **10109 – 10113**

Patterned Superomniphobic–Superomniphilic Surfaces: Templates for Site-Selective Self-Assembly

Patterned surfaces: The fabrication of patterned superomniphobic–superomniphilic surfaces is reported. Such patterned surfaces are expected to be useful in developing well-defined microreactors for liquid-phase reactions, significantly enhancing heat transfer during condensation and boiling of various low-surface-tension liquids, and in fabricating precisely tailored arrays of polymers and microparticles of different sizes and shapes.



How to live longer: A fully deuterated ^{13}C methoxy group ($^{13}CD_3O$) is presented as a new long-lived hyperpolarization unit for designing a sensitive ^{13}C magnetic resonance probe. By utilizing the unit, a hyperpolarized magnetic resonance probe for sensing hypochlorous acid was successfully designed.

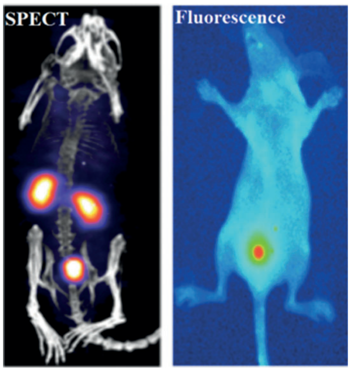


Magnetic Resonance Probes

T. Doura, R. Hata, H. Nonaka, K. Ichikawa,
S. Sando* ——— **10114 – 10117**

Design of a ^{13}C Magnetic Resonance Probe Using a Deuterated Methoxy Group as a Long-Lived Hyperpolarization Unit

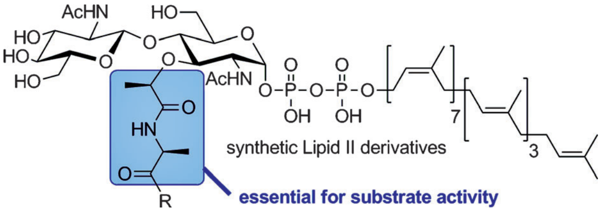
A molecular nanoprobe: Glutathione-coated near-infrared-emitting radioactive gold nanoparticles have been synthesized and behave like small-molecule contrast agents in pharmocokinetics. These nanoparticles show a rapid distribution half-life, a desirable elimination half-life, and hold promise for single-photon emission computed tomography (SPECT) and fluorescence imaging (see picture).



Imaging Agents

C. Zhou, G. Hao, P. Thomas, J. Liu, M. Yu,
S. Sun, O. K. Öz, X. Sun,*
J. Zheng* ——— **10118 – 10122**

Near-Infrared Emitting Radioactive Gold Nanoparticles with Molecular Pharmacokinetics

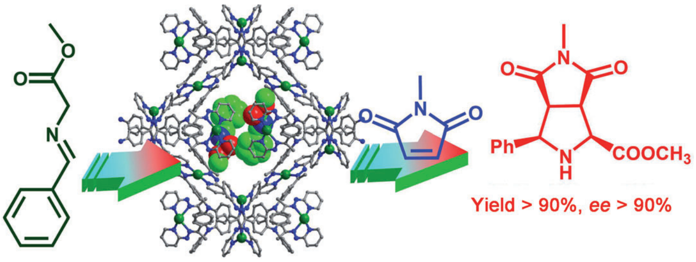


The writing's on the (cell) wall: A series of Lipid II analogues with modifications to the peptide moiety were evaluated as substrates of bacterial transglycosylase. The first two positions on the peptide, D-lactate and L-alanine (see scheme), especially their methyl groups, were found to be essential for substrate-binding activity, an important discovery for the design of antibiotics to inhibit cell-wall biosynthesis.

Structure-Activity Relationship

H.-W. Shih, Y.-F. Chang, W.-J. Li,
F.-C. Meng, C.-Y. Huang, C. Ma,
T.-J. R. Cheng, C.-H. Wong,*
W.-C. Cheng* ——— **10123 – 10126**

Effect of the Peptide Moiety of Lipid II on Bacterial Transglycosylase



Enantiomeric silver-based MOFs were obtained through a homochiral crystallization of cinchonine and cinchonidine enantiomers as chiral adducts with silver. These MOFs exhibited excellent catalytic activity for asymmetric [3+2] cycloaddition (see scheme), giving products with high enantioselectivity.

Asymmetric Catalysis

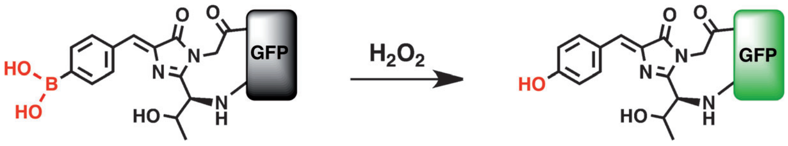
X. Jing, C. He, D. Dong, L. Yang,
C. Duan* ——— **10127 – 10131**

Homochiral Crystallization of Metal–Organic Silver Frameworks: Asymmetric [3+2] Cycloaddition of an Azomethine Ylide

Protein Engineering

F. Wang, W. Niu, J. Guo,*
P. G. Schultz* ________ 10132 – 10135

Unnatural Amino Acid Mutagenesis of Fluorescent Proteins

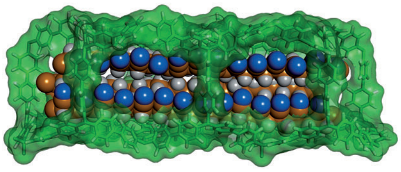


Tyrosine 66 of a green fluorescent protein (GFP) was substituted with unnatural amino acids carrying boronate, azido, nitro, and keto substituents. In general, the λ_{em}^{max} values of these GFP mutants is blue-shifted relative to that of GFP, and the fluorescence intensity of the boronate variant increases upon oxidation (see scheme). The X-ray crystal structures of the keto and boronate GFP mutants provide explanations of their altered fluorescence properties.

Polymerization in Frameworks

A. Comotti,* S. Bracco, M. Mauri,
S. Mottadelli, T. Ben, S. Qiu,
P. Sozzani ________ 10136 – 10140

Confined Polymerization in Porous Organic Frameworks with an Ultrahigh Surface Area

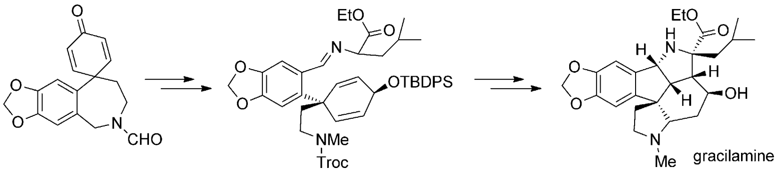


Polymers framed: Interpenetrated nanocomposites were formed by polymerization of acrylonitrile in a ultrahigh surface area (> 5000 $m^2 g^{-1}$) porous framework. The resulting material realizes a hyperextended interface with uniform interdigitation of the two structures at the size limit of the individual molecular moieties. The confined poly(acrylonitrile) chains could be transformed into light-absorbing polyconjugated ladder polymers.

Natural Products

S. Tian, W. Zi, D. Ma* ________ 10141 – 10144

Potentially Biomimetic Total Synthesis and Relative Stereochemical Assignment of (±)-Gracilamine



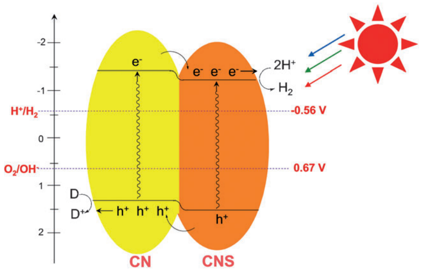
Gracil(e): The total synthesis of gracilamine features a potentially biomimetic intramolecular [3+2] cycloaddition to assemble its two fused five-membered rings and a debenzylation/ring-opening reaction to obtain the aldehyde intermediate (see scheme). The success of this synthesis provides a circumstantial evidence that supports the biosynthesis pathway of gracilamine proposed previously.

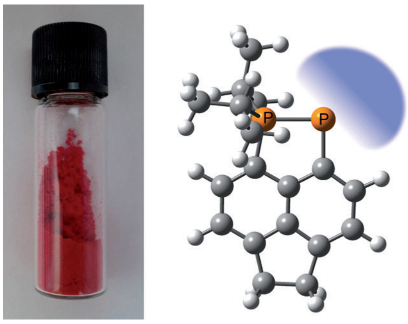
Polymeric Heterojunction

J. Zhang, M. Zhang, R. Sun,
X. Wang* ________ 10145 – 10149

A Facile Band Alignment of Polymeric Carbon Nitride Semiconductors to Construct Isotype Heterojunctions

Junction function: All-organic isotype heterojunctions are formed through the band alignment of polymeric carbon nitride semiconductors (CN and CNS, see scheme), improving the efficiency of charge separation and prolonging the lifetime of charge carriers. These polymeric heterostructures demonstrate an excellent performance for heterogeneous photocatalysis, as shown in a hydrogen-generation assay.

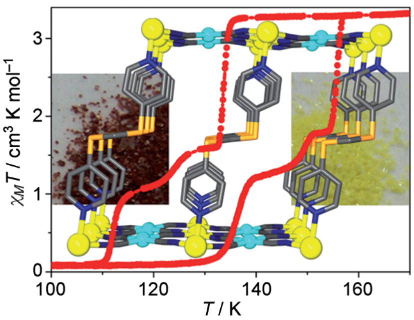




’P’ undressed: A stable phosphanylidene phosphorane with a sterically accessible (naked) two-coordinate P is reported (see structure). Coordination to Pd^0 reveals its phosphine donor/phosphinidene acceptor ($R_3P \rightarrow PR'$) nature by exposing its phosphinidene-like reactivity.

Donor-Acceptor Systems

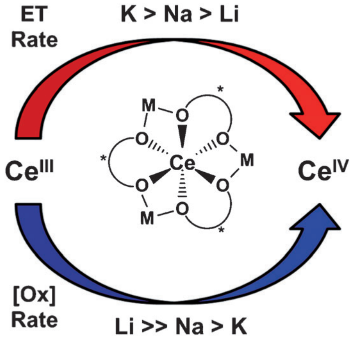
Multistability is exhibited by a metal–organic framework material that undergoes unique three-step spin crossover with 20 K thermal hysteresis (see picture). The stepwise transition is coupled to a three-step structural transformation that defines four distinct structural states. The material also exhibits reversible photo-induced spin crossover.



Multistable MOFs

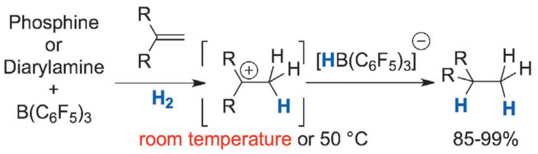
Inside Cover

Let’s get cerium: The role of ligand organization in the redox chemistry of Ce^{III} was investigated with a series of cerium(III)/alkali metal/1,1′-binolate (REMB) complexes. The electrochemical properties and chemical reactivity within the REMB framework are tunable through the choice of metal M, and the controlled redox behavior emphasizes the impact of ligand reorganization.



Rare Earths Redox Chemistry

Back Cover



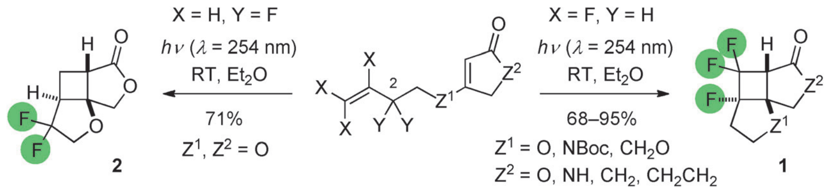
Weak nucleophiles for strong activation: The reversible activation of dihydrogen by an electron-deficient phosphine, $(C_6F_5)PPh_2$, in combination with the Lewis acid $B(C_6F_5)_3$ at −80 °C was accomplished. The catalytic hydrogenation of olefins proceeds through protonation and subsequent hydride attack. Electron-deficient phosphines and diarlyamines were demonstrated to be viable Lewis bases for the reaction, thus allowing catalyst loadings of 10 to 5 mol %.

Olefin Reduction

Photochemistry

D. A. Fort, T. J. Woltering, M. Nettekoven, H. Knust, T. Bach* ______ **10169 – 10172**

Synthesis of Fluorinated Tricyclic Scaffolds by Intramolecular [2+2] Photocycloaddition Reactions

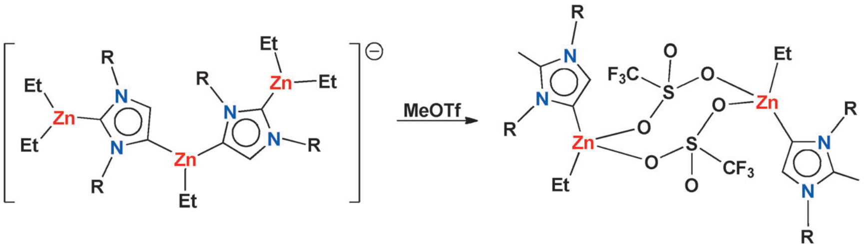


Fabulous Fluorine: The synthesis of fluorinated products **1** and **2** by [2+2] photocycloaddition was readily feasible after optimization of the irradiation conditions. The electron-deficient trifluoroolefin unit reacted intramolecularly to products **1** (nine examples, d.r. > 95:5). The reaction was also investigated after modification of position 2 of the side chain both with one or two fluoro substituents (e.g. to yield product **2**).

Group 12 Chemistry

Y. Wang, Y. Xie, M. Y. Abraham, R. J. Gilliard, Jr., P. Wei, C. F. Campana, H. F. Schaefer, III, P. von R. Schleyer, G. H. Robinson* ________ **10173 – 10176**

NHC-Stabilized Triorganozincates: Syntheses, Structures, and Transformation to Abnormal Carbene–Zinc Complexes

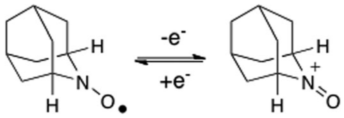


Anion is superior: NHC-based triorganozincates, from mononuclear to trinuclear, have been synthesized. The NHC-based triorganozincate chain (see scheme; left) was transformed into an abnormal carbene (*a*NHC)-complexed zinc ring (right) by reaction with MeOTf, closing the *a*NHC-Group 12 complexes gap.

Electrochemistry

F. Kato, A. Kikuchi, T. Okuyama, K. Oyaizu, H. Nishide* __ **10177 – 10180**

Nitroxide Radicals as Highly Reactive Redox Mediators in Dye-Sensitized Solar Cells

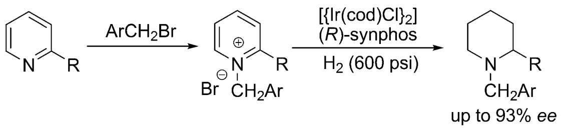


Exchanged: The organic radical 2-azaadamantan-*N*-oxyl (AZA; see picture) is found to be a stable and highly reactive redox mediator in dye-sensitized solar cell (DSSC) electrolytes. This radical has an appropriate redox potential and significantly high values for the diffusivity, heterogeneous electron-transfer rate, and electron self-exchange reaction rate. In a DSSC the AZA-based electrolyte achieves an excellent photovoltaic performance.

Asymmetric Hydrogenation

Z.-S. Ye, M.-W. Chen, Q.-A. Chen, L. Shi, Y. Duan, Y.-G. Zhou* ____ **10181 – 10184**

Iridium-Catalyzed Asymmetric Hydrogenation of Pyridinium Salts

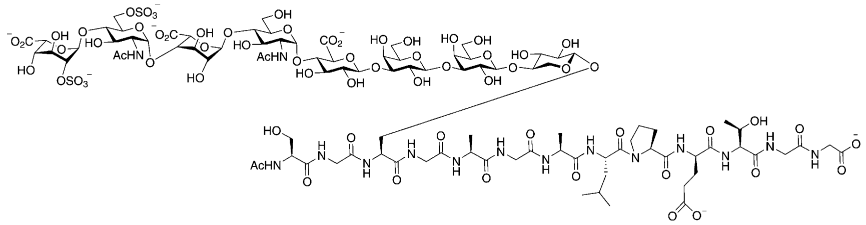


Highly efficient iridium-catalyzed asymmetric hydrogenations of simple 2-substituted pyridinium salts gives the chiral 2-substituted piperidines with up to 93 % *ee* (see picture; cod = 1,5-cyclooctadiene; synphos = (5,6),(5′,6′)-bis(ethylenedioxy)-2,2′-bis(diphenylphosphino)-1,1′-biphenyl). The key feature of this strategy is the activation of simple pyridines as the pyridinium salts, thus eliminating substrate inhibition and enhancing the reactivity.

Total Synthesis

B. Yang, K. Yoshida, Z. Yin, H. Dai,
H. Kavunja, M. H. El-Dakdouki,
S. Sungsuwan, S. B. Dulaney,
X. Huang* ______ **10185 – 10189**

Chemical Synthesis of a Heparan Sulfate Glycopeptide: Syndecan-1

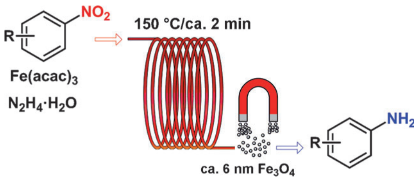


Finishing first: The highly complex structure of the title compound (see picture) was assembled. The protective groups utilized, as well as the sequences for formation of the glycosyl linkages and protecting group removal are critical to the success of the synthesis. This first preparation of a heparan sulfate glycopeptide lays the foundation for accessing other members of this class of molecules.

Iron Nanocatalysis

D. Cantillo, M. Baghbanzadeh,
C. O. Kappe* ______ **10190 – 10193**

In Situ Generated Iron Oxide Nanocrystals as Efficient and Selective Catalysts for the Reduction of Nitroarenes using a Continuous Flow Method



The best of both worlds: The benefits of homogeneous and heterogeneous nanocatalysis are combined, whereby highly reactive colloidal Fe_3O_4 nanocrystals are generated in situ that remain in solution long enough to allow the efficient and selective reduction of nitroarenes to anilines in continuous-flow mode (see scheme). After completion of the reaction, the nanoparticles aggregate and can be recovered by a magnet.

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 Corrigendum

Solid-State NMR Measurements of Asymmetric Dipolar Couplings Provide Insight into Protein Side-Chain Motion

P. Schanda, M. Huber, J. Boisbouvier,
B. H. Meier,* M. Ernst* _ **11005–11009**

Angew. Chem. Int. Ed. **2011**, *50*

DOI: 10.1002/anie.201103944

The authors of this communication wish to make an addition to their acknowledgement. The first sentence in this section must read as follows:

"This work was supported financially by the Swiss National Science Foundation, by ETH Zürich and the French Research Agency ANR (contract ANR-10-PDOC-011-01, ProtDynByNMR)".

In the main text, on page 11007, left column, second paragraph, the word "asymmetry" should be replaced by "anisotropy". The complete corrected sentence must read:

"This rotation leads to an averaged axially symmetric tensor with an aniosotropy $\delta_{\text{D,rigid axis}} = \delta_{\text{D,rigid}}/3 \approx 14.53$ kHz (based on the canonical tetrahedral angle $\theta_{\text{HCC}} = 109.47°$ and a C–H bond length of 1.115 Å)."

Furthermore, on page 8 of the Supporting Information, the equations for D_2 and D_3 should start with "1/4" instead of "−1/4". A corrected Supporting Information file is available with this corrigendum.

Angewandte Corrigendum

Enantioselective Synthesis of Tertiary α-Hydroxy Phosphonates Catalyzed by Carbohydrate/Cinchona Alkaloid Thiourea Organocatalysts

S. S. Kong, W. D. Fan, G. P. Wu,
Z. W. Miao* ______________ **8864–8867**

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

DOI: 10.1002/anie.201204287

The authors of this communication wish to insert additional citations as reference [14].

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[14] For selected examples of quinine **1** or cinchonine **2** organocatalyzed enantioselective reaction, see: a) Z. Y. Wang, X. Y. Sun, S. Q. Ye, W. Z. Wang, B. Wang, J. Wu, *Tetrahedron: Asymmetry* **2008**, *19*, 964 – 969; b) A. Russo, A. Perfetto, A. Lattanzi, *Adv. Synth. Catal.* **2009**, *351*, 3067 – 3071; for a review, see: c) M. D. Díaz de Villegas, J. A. Gálvez, P. Etayo, R. Badorrey, P. López-Ram-de-Viu, *Chem. Soc. Rev.* **2011**, *40*, 5564 – 5587. For catalysts **3a** and **3b**, see: d) K. Liu, H. F. Cui, J. Nie, K. Y. Dong, X. J. Li, J. A. Ma, *Org. Lett.* **2007**, *9*, 923 – 925. For Takemoto's thiourea **4**, see: e) T. Okino, Y. Hoashi, Y. Takemoto, *J. Am. Chem. Soc.* **2003**, *125*, 12672 – 12673. For thiourea catalysts of cinchona alkaloids **5a** and **5b**, selected examples: f) A. L. Tillman, J. Ye, D. J. Dixon, *Chem. Commun.* **2006**, 1191 – 1193; g) J. Ye, D. J. Dixon, P. S. Hynes, *Chem. Commun.* **2005**, 4481 – 4483; h) S. H. McCooey, S. J. Connon, *Angew. Chem.* **2005**, *117*, 6525 – 6528; *Angew. Chem. Int. Ed.* **2005**, *44*, 6367 – 6370; i) B. Vakulya, S. Varga, A. Csampai, T. Soos, *Org. Lett.* **2005**, *7*, 1967 – 1969; j) T. Marcelli, R. N. S. van der Haas, J. H. van Maarseveen, H. Hiemstra, *Angew. Chem.* **2006**, *118*, 943 – 945; *Angew. Chem. Int. Ed.* **2006**, *45*, 929 – 931; k) J. Song, Y. Wang, L. Deng, *J. Am. Chem. Soc.* **2006**, *128*, 6048 – 6049; l) S. J. Connon, *Chem. Commun.* **2008**, 2499 – 2510; m) M. Amere, M.-C. Lasne, J. Rouden, *Org. Lett.* **2007**, *9*, 2621 – 2624; n) T. Y. Liu, J. Long, B. J. Li, L. Jiang, R. Li, Y. Wu, L. S. Ding, Y. C. Chen, *Org. Biomol. Chem.* **2006**, *4*, 2097 – 2099.