The following Communications have been judged by at least two referees to be "very important papers" and will be published online at www.angewandte.org soon:

*V. Mazumder, M. Chi, K. L. More, S. Sun**
Synthesis and Characterization of Multimetallic Pd/Au and Pd/Au/FePt Core/Shell Nanoparticles

*S.-Y. Moon, J.-S. Bae, E. Jeon, J.-W. Park**
Organic Sol–Gel Synthesis: Solution-Processable Microporous Organic Networks

*D. V. Esposito, S. T. Hunt, A. L. Stottlemyer, K. D. Dobson, B. E. McCandless, R. W. Birkmire, J. G. Chen**
Low-Cost Hydrogen-Evolution Catalysts Based on Monolayer Platinum on Tungsten Monocarbide (WC) Substrates

R. Matsui, K. Seto, K. Fujita, T. Suzuki, A. Nakazaki, S. Kobayashi
Unusually *E*-Selective Ring-Closing Metathesis to Form Eight-Membered Rings

*T. J. Hebden, A. J. S. John, D. G. Gusev, W. Kaminsky, K. I. Goldberg, D. M. Heinekey**
Preparation of a Dihydrogen Complex of Cobalt

*S. Sun, G. Zhang, D. Geng, Y. Chen, R. Li, M. Cai, X. Sun**
A New Highly Durable Platinum Nanocatalyst for PEM Fuel Cells: Multiarmed Star-like Nanowire Single Crystals

*J. S. Chen, T. Zhu, C. M. Li, X. W. Lou**
Building Hematite Nanostructures Using Oriented Attachment

*Y. Zhang, G. M. Miyake, E. Y.-X. Chen**
Alane-Based Classical and Frustrated Lewis Pairs in Polymer Synthesis: Rapid Polymerization of Methyl Methacrylate and Naturally Renewable Methylene Butyrolactones to High-Molecular-Weight Polymers

*Y. Matsuki, M. T. Eddy, R. G. Griffin, J. Herzfeld**
Rapid 3D MAS NMR Spectroscopy at Critical Sensitivity

*S. Vellalath, I. Čorić, B. List**
***N*-Phosphinyl Phosphoramide: A Chiral Brønsted Acid Motif for the Direct Asymmetric *N,O*-Acetalization of Aldehydes**

K. Breuker, S. Brüschweiler, M. Tollinger*
Electrostatic Stabilization of Native Protein Structure in the Gas Phase

*J. Zeng, X. Xia, M. Rycenga, P. Henneghan, Q. Li, Y. Xia**
Successive Deposition of Silver on Silver Nanoplates: Lateral Versus Vertical Growth

News


M. Beller


S. V. Ley


J. Mulzer

Author Profile

*"My favorite subject at school was physics.
When I wake up I wish I could fall asleep again …"*
This and more about Xiaoming Feng can be found on page 8789.

Books

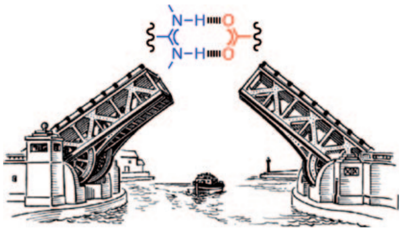
Contents

Highlights

Catenanes

I. M. Dixon, G. Rapenne* — **8792 – 8794**

Bridging the Gap: Making the Link in Mechanically Interlocked Chiral Molecules



Open the bridge: A [2]catenane has been synthesized around a salt-bridge template (see picture). Addition and sequestration of Zn^{2+} ions or variation of the pH value can reversibly trigger the formation and rupture of the salt bridge, thus inducing a major reorganization within the molecule. Suggestions as to the use of such systems as molecular logic gates or nanomechanical devices are made.

Genome Sequencing

U. Sundermann, S. Kushnir, F. Schulz* — **8795 – 8797**

The Development of DNA Sequencing: From the Genome of a Bacteriophage to That of a Neanderthal

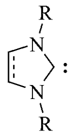
Them bones gonna rise again: Only a few weeks ago the Neandertal genome, deciphered from small amounts of ancient DNA, was published. This mileston was possible thanks to tremendous improvements in DNA-sequencing technologies. The picture shows a bone fragment from which genomic DNA was isolated for the sequencing experiment. (Picture copyright: Max-Planck-Institute of Evolutionary Anthropology).

Essays

N-Heterocyclic Carbenes

W. Kirmse* — **8798 – 8801**

The Beginnings of N-Heterocyclic Carbenes



A long time in the waiting: In 1960 Wanzlick brought N-heterocyclic carbenes to the point of take off. Experimental shortcomings, misunderstanding, and prejudgments, however, hindered their take off. Only 30 years later, with the isolation and structural elucidation of N-heterocyclic carbenes by Arduengo, did the flight begin.

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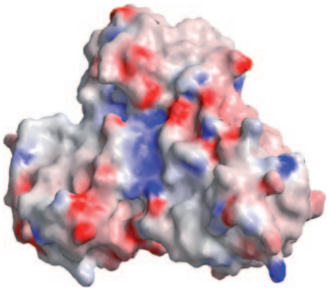
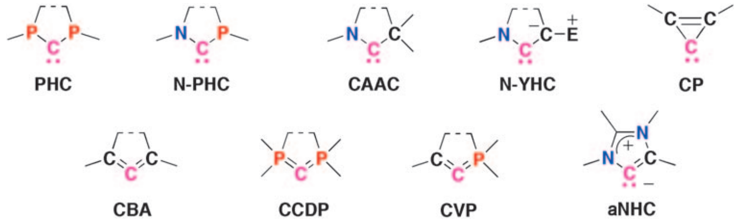
Minireviews

The way forward: In the last two decades a novel biosynthetic route to isopentenyl diphosphate and dimethylallyl diphosphate, the non-mevalonate or deoxyxylulose pathway, has been elucidated. The IspH protein (see space-filling model) catalyzes the terminal step of this biosynthetic pathway. The enzymes of this pathway are absent in mammals and are validated targets for new antibiotics.

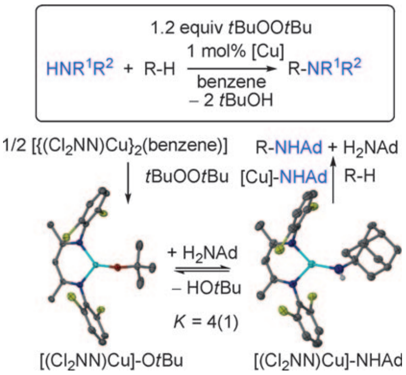


Reviews



A big family: Neutral carbon-based ligands are not restricted to classical cyclic diaminocarbenes (NHCs). Several other types of cyclic carbenes are stable and act as strong electron donors (see picture). Cyclic bent allenes (CBAs), carbodiphosphoranes (CCDPs), and vinylidenephosphorane (CVP) can even behave as four-electron donors. The gamut of electronic and steric properties available makes carbon ligands strong competitors to the phosphorus family.

Communications

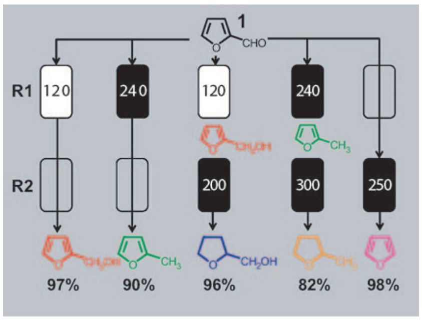


En route to catalysis: Two equivalents of the three-coordinate copper(II) amide [(Cl_2NN)Cu]-NHAd participate in stoichiometric C–H amination by a H-atom abstraction/radical capture sequence. This active species may be generated through a copper(II) *tert*-butoxide intermediate to allow for the unprecedented catalytic amination of sp^3-C–H bonds with unactivated alkylamines. This method greatly expands the range of amines for catalytic C–H amination since most protocols require N-based electron-withdrawing groups.

Continuous-Flow Reactors

J. G. Stevens, R. A. Bourne,* M. V. Twigg,
M. Poliakoff* ______________ **8856 – 8859**

Real-Time Product Switching Using a Twin Catalyst System for the Hydrogenation of Furfural in Supercritical CO$_2$

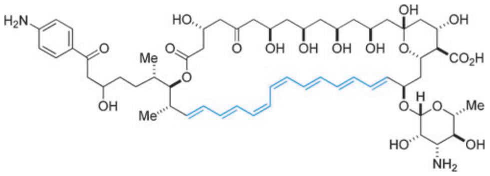


“Vending machine” chemistry: A tandem flow-reactor setup can be used to generate a choice of five products in high yield from a single biorenewable feedstock, furfural (**1**). “Real-time” switching to any of the products can be achieved rapidly by simply changing the reactor conditions.

Synthetic Methods

S. J. Lee, T. M. Anderson,
M. D. Burke* ______________ **8860 – 8863**

A Simple and General Platform for Generating Stereochemically Complex Polyene Frameworks by Iterative Cross-Coupling

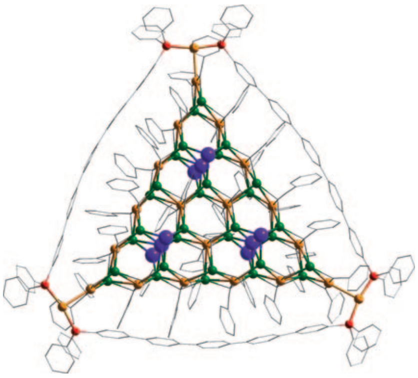


Not so complex: A novel iterative cross-coupling strategy provides access to useful building blocks that enable the simple preparation of complex polyene natural-product motifs in all possible stereoisomeric forms. The method was used to synthesize the polyene core of vacidin A (see structure).

Molecular Aggregates

I. O. Koshevoy,* A. J. Karttunen,
J. R. Shakirova, A. S. Melnikov,
M. Haukka, S. P. Tunik,*
T. A. Pakkanen* ______________ **8864 – 8866**

Halide-Directed Assembly of Multicomponent Systems: Highly Ordered Au^I–Ag^I Molecular Aggregates



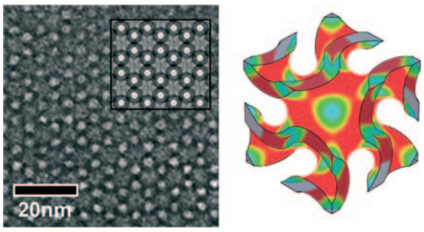
Triangular cationic belts [Au$_3${PPh$_2$-(C$_6$H$_4$)$_n$PPh$_2$}$_3$]$^{3+}$ enclose bimetallic clusters [Au$_w$Ag$_x$(C$_2$Ph)$_y$X$_z$] in molecular aggregates obtained by halide (X)-directed assembly of multicomponent systems. The largest aggregate consists of a central metal alkynyl halide cluster [Au$_{18}$Ag$_{30}$(C$_2$Ph)$_{36}$Cl$_9$]$^{3+}$ inside a [Au$_3$-{PPh$_2$(C$_6$H$_4$)$_5$PPh$_2$}$_3$]$^{3+}$ belt and comprises 51 metal atoms (see picture; Ag green, Au yellow, Cl violet, P red).

Mesoporous Crystals

K. Miyasaka,* O. Terasaki __ **8867 – 8871**

Self-Consistent Structural Solution of Mesoporous Crystals by Combined Electron Crystallography and Curvature Assessment

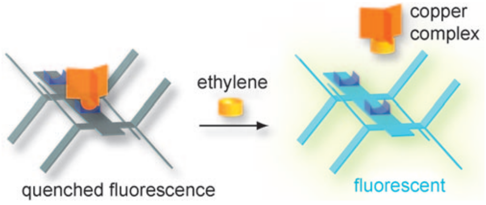
Pore and wall structures for ordered mesoporous crystalline materials can be obtained from electron crystallographic reconstruction based on transmission electron micrographs (see picture; left). Curvature and surface properties are then used to determine the mesostructures in a self-consistent manner within the data (right: color-coded distributions of Gaussian curvature on a surface viewed along [111]).



Sensors

B. Esser, T. M. Swager* ____ 8872 – 8875

Detection of Ethylene Gas by Fluorescence Turn-On of a Conjugated Polymer

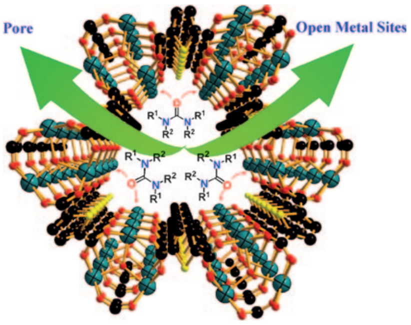


Ripe fruits: The fluorescence of a conjugated polymer is quenched by the presence of copper(I) moieties. Upon exposure to ethylene gas the copper complexes bind to ethylene and no longer quench the polymer fluorescence (see picture). This sensory concept can be used in solution and in thin films.

Metal–Organic Frameworks

J. Zhang, J. T. Bu, S. Chen, T. Wu, S. Zheng, Y. Chen, R. A. Nieto, P. Feng, X. Bu* ____ 8876 – 8879

Urothermal Synthesis of Crystalline Porous Materials

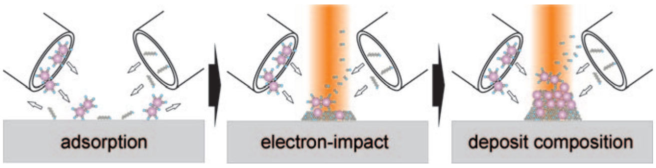


Pores from urea: Urea derivatives are shown to be a highly versatile solvent system for the synthesis of crystalline solids. In particular, reversible binding of urea derivatives to framework metal sites has been utilized to create a variety of materials that integrate both porosity and open metal sites (see picture).

Nanotechnology

L. Bernau, M. Gabureac, R. Erni, I. Utke* ____ 8880 – 8884

Tunable Nanosynthesis of Composite Materials by Electron-Impact Reaction

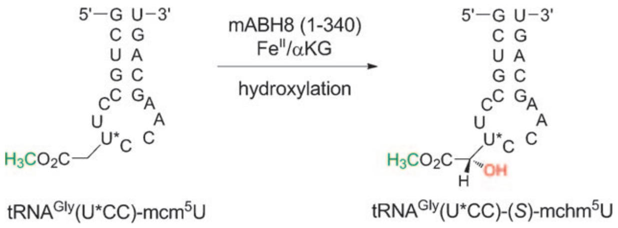


Impact factor: Electron-impact dissociation reactions in two-adsorbate systems were tuned by applying specific exposure conditions in electron microscopes. Pulsed electron-impact exposure could drive the dissociation reaction of one of the adsorbates into the molecule-limited regime while the reaction of the other adsorbate continued in the electron-limited regime. The pulse period gave control over the composition of the deposit (see scheme).

RNA Modification

Y. Fu, Q. Dai, W. Zhang, J. Ren, T. Pan,* C. He* ____ 8885 – 8888

The AlkB Domain of Mammalian ABH8 Catalyzes Hydroxylation of 5-Methoxycarbonylmethyluridine at the Wobble Position of tRNA



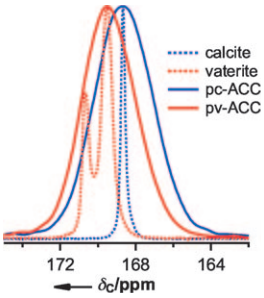
Family ties: The AlkB family of nonheme iron, α-ketoglutarate (αKG)-dependent dioxygenases is involved in biological processes such as DNA/RNA repair and obesity. The AlkB domain of ABH8 is shown to catalyze the hydroxylation of a modified uridine (mcm^{5}U) into (*S*)-mchm^{5}U at the wobble position of the anticodon stem–loop in tRNA (see scheme), thereby suggesting that this protein is a tRNA hypermodification enzyme.

Contents

Crystal Precursors

D. Gebauer,* P. N. Gunawidjaja,
J. Y. P. Ko, Z. Bacsik, B. Aziz, L. J. Liu,
Y. F. Hu, L. Bergström, C.-W. Tai,
T.-K. Sham, M. Edén,
N. Hedin* **8889 – 8891**

Proto-Calcite and Proto-Vaterite in Amorphous Calcium Carbonates



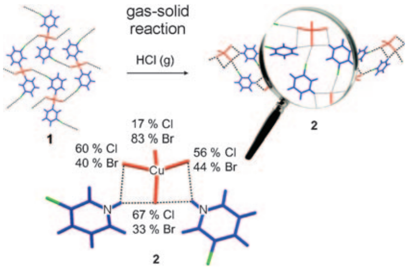
Amorphous order: Amorphous calcium carbonates (ACC) have an intrinsic structure relating to the crystalline polymorphs of calcite and vaterite. The proto-crystalline structures of calcite and vaterite (pc-ACC and pv-ACC) are analyzed by NMR (see picture), IR, and EXAFS spectroscopy, which shows that the structuring of ACC relates to the underlying pH-dependent equilibria.

Noncovalent Interactions

G. Mínguez Espallargas, J. van de Streek,
P. Fernandes, A. J. Florence, M. Brunelli,
K. Shankland, L. Brammer* **8892 – 8896**

Mechanistic Insights into a Gas–Solid Reaction in Molecular Crystals: The Role of Hydrogen Bonding

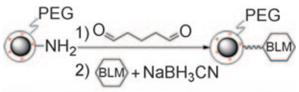
Hydrogen bonding leads the way: Reaction of nonporous crystalline coordination compound **1** with HCl gas results in conversion into the crystalline salt **2** (see picture) following chemisorption and insertion of HCl into Cu–N bonds. Powder diffraction studies show that $[CuBr_2Cl_2]^{2-}$ ions formed in **2** are reoriented to maximize the strength of hydrogen bonds and halogen bonds by preferentially involving Cl rather than Br ligands as acceptor sites.

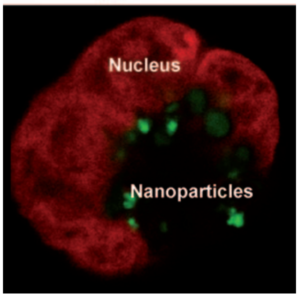


Drug Delivery

T. Georgelin, S. Bombard, J.-M. Siaugue,*
V. Cabuil **8897 – 8901**

Nanoparticle-Mediated Delivery of Bleomycin



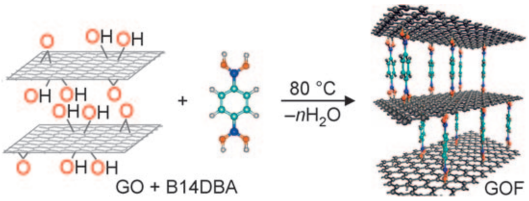


Direct delivery: Multifunctionalized magnetic nanoparticles, which are highly stable and positively charged, induce strong interactions with cells and nuclei, thus confining bleomycin (BLM) close to its DNA target (see picture; PEG = polyethylene glycol). Grafted BLM can induce significant damage in DNA and cancerous cells.

Graphene Oxide Frameworks

J. W. Burress, S. Gadipelli, J. Ford,
J. M. Simmons, W. Zhou,
T. Yildirim* **8902 – 8904**

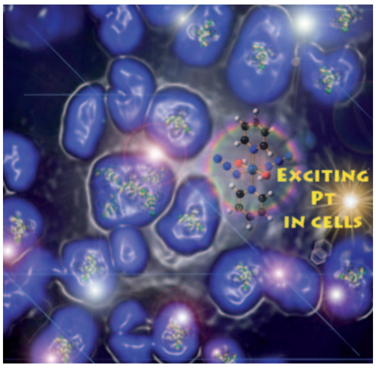
Graphene Oxide Framework Materials: Theoretical Predictions and Experimental Results



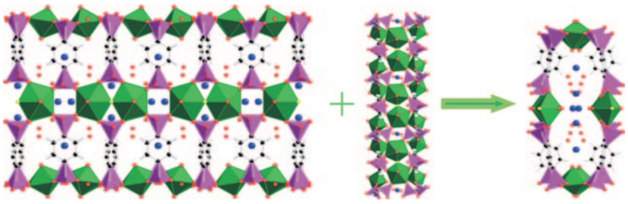
A promising storage medium for hydrogen and other gases is a graphene oxide framework (GOF) that consists of layers of GO connected by benzene-1,4-diboronic acid (B14DBA) pillars (see picture). Theoretical predictions and the initial experimental results are presented for this cheap and environmentally friendly building block for nanoporous materials with better gas adsorption properties.

Photoactivated Prodrugs

Activating platinum with light: An inert platinum(IV) diazido complex *trans*,*trans*-[Pt$(N_3)_2(OH)_2(py)_2$] becomes potently cytotoxic to cancer cells when activated by low doses of visible light.



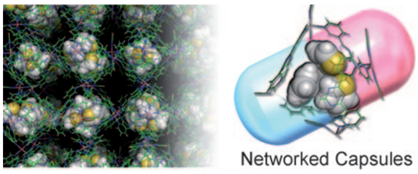
Elliptical Nanotubules



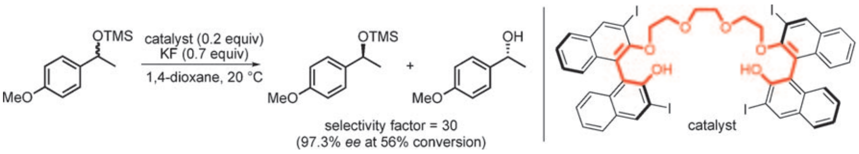
Nanotubular bells: A simple route to a uranyl diphosphonate with an elliptical nanotubular structure has been developed (see picture; C black, O red, Cs blue, F yellow, UO_7 green pentagonal bipyramids, phosphonate violet tetrahedra). The interior of the nanotubes provides a different chemical environment than the exterior with regards to the exchange of Cs^+ cations for Ag^+ cations, thus demonstrating that uranyl nanotubules are functional materials.

Molecular Capsules

The time capsule: A variety of guest molecules are stably trapped in networked coordination capsules up to 200 °C, which is above the boiling points of the guests. Networked capsules provide a distinctly different environment in the crystal form relative to that of pores, and are suitable for storing reactive molecules: Cyclopentadiene remains a monomer within the capsule even after heating, whereas dimerization through a Diels–Alder reaction takes place within the pore.



Chiral Anions

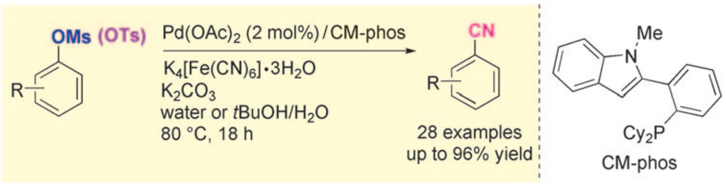


Getting the grips on fluoride: Chiral hydroxy-terminated polyethers bearing a 3,3′-halogen-substituted chiral 1,1′-bi-2-naphthol (BINOL) unit manifest a new structural motif for chiral-anion generators. Their unique properties are revealed through highly enantioselective desilylative kinetic resolution of a variety of silyl-protected racemic alcohols with KF (see scheme).

Cross-Coupling

P. Y. Yeung, C. M. So, C. P. Lau,
F. Y. Kwong* ______ **8918 – 8922**

A Mild and Efficient Palladium-Catalyzed Cyanation of Aryl Mesylates in Water or *t*BuOH/Water



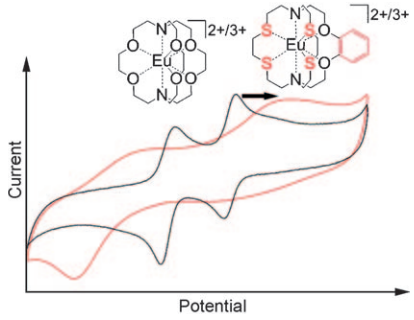
Cool and compatible: Aryl mesylates and tosylates underwent palladium-catalyzed cyanation under mild, aqueous conditions at 65–80 °C (see scheme). In many cases, water could be used as the reaction medium without a cosolvent, and a variety of substituents R, such as keto, aldehyde, ester, free amine, and nitrile groups, remained intact during the transformation. Cy = cyclohexyl, Ms = methanesulfonyl, Ts = *p*-toluenesulfonyl.

Cryptands

N.-D. H. Gamage, Y. Mei, J. Garcia,
M. J. Allen* ______ **8923 – 8925**

Oxidatively Stable, Aqueous Europium(II) Complexes through Steric and Electronic Manipulation of Cryptand Coordination Chemistry

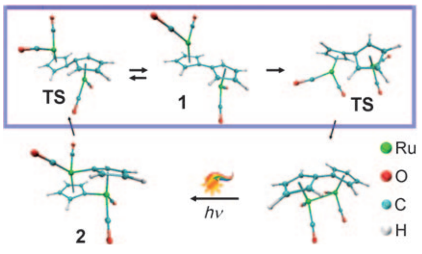
A series of cryptands has been prepared and they demonstrate the relationship between oxidative stability of aqueous Eu^{II} and ligand properties (see figure). One of these Eu^{II} complexes is more stable than Fe^{II} in hemoglobin and appears to be the most oxidatively-stable aqueous Eu^{II} species known. The high stability of Eu^{II} is expected to enable the use of the unique magnetic and optical properties of this ion in vivo.



Reaction Mechanisms

Y. Kanai,* V. Srinivasan, S. K. Meier,
K. P. C. Vollhardt,*
J. C. Grossman* ______ **8926 – 8929**

Mechanism of Thermal Reversal of the (Fulvalene)tetracarbonyldiruthenium Photoisomerization: Toward Molecular Solar–Thermal Energy Storage

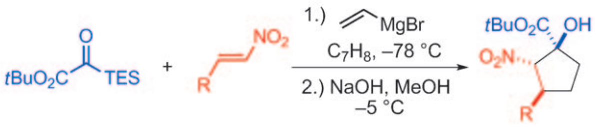


A closer look at the title reaction pinpoints a surprising mechanism—a relatively rapid preequilibrium between cyclopentadienyl complex **2** and fulvalene diradical complex **1** precedes the rate-determining *anti–syn* rotation and formation of the Ru–Ru bond. The computed energy values agree well with all experimental data, including saturation kinetics for the trapping of the intermediate by CCl_4. TS = transition state.

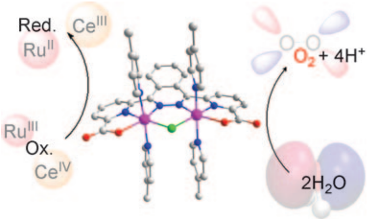
Multicomponent Reactions

G. R. Boyce, J. S. Johnson* _ **8930 – 8933**

Three-Component Coupling Reactions of Silyl Glyoxylates, Vinyl Grignard Reagent, and Nitroalkenes: An Efficient, Highly Diastereoselective Approach to Nitrocyclopentanols



Quick and easy: A regio- and stereoselective three-component coupling reaction generates functionalized (*Z*)-silyl enol ethers through a vinylation/[1,2]-Brook rearrangement/vinylogous Michael reaction cascade. These adducts can then undergo a diastereoselective deprotection/intramolecular Henry sequence to rapidly assemble densely functionalized nitrocyclopentanols with three contiguous stereocenters (see scheme; TES = triethylsilyl).

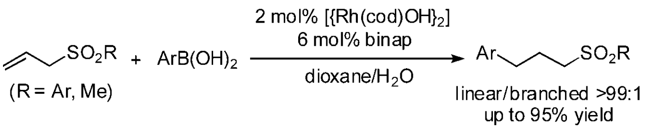


Here splits the sun: A dinuclear ruthenium complex has been synthesized and employed to catalyze the homogeneous water oxidation (see picture; purple Ru, green Cl, blue N, red O). An exceptionally high turnover number was observed both for chemical (Ce^{IV} as the oxidant) and light-driven ($[Ru(bpy)_3]^{2+}$-type photosensitizers) water splitting.

Water Oxidation

Y. Xu, A. Fischer, L. Duan, L. Tong, E. Gabrielsson, B. Åkermark, L. Sun* ———— **8934 – 8937**

Chemical and Light-Driven Oxidation of Water Catalyzed by an Efficient Dinuclear Ruthenium Complex



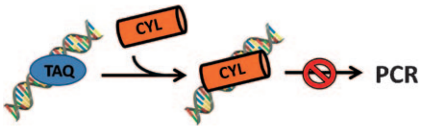
One step further: The rhodium(I)-catalyzed addition of readily available arylboronic acids to allyl sulfones affords the linear (formal) hydroarylated products in good yields and excellent regioselectivities. The reaction broadens the scope of unactivated alkenes that can participate in rhodium-catalyzed addition reactions.

Rhodium Catalysis

G. C. Tsui, M. Lautens* ———— **8938 – 8941**

Linear-Selective Rhodium(I)-Catalyzed Addition of Arylboronic Acids to Allyl Sulfones

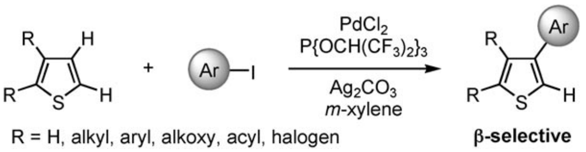
Supramolecular metal cylinders not only bind noncovalently to DNA inducing substantial coiling but are able to recognize specific DNA structures involved in biological processes as DNA replication. It is demonstrated that these molecules can inhibit the amplification of the DNA mediated by a Taq DNA polymerase and are even able to displace the enzyme from a double strand DNA (see scheme).



Supramolecular Metal Drug

C. Ducani, A. Leczkowska, N. J. Hodges,* M. J. Hannon* ———— **8942 – 8945**

Noncovalent DNA-Binding Metallo-Supramolecular Cylinders Prevent DNA Transactions in vitro



Open access: The normally less-reactive β position of thiophenes was previously inaccessible to direct functionalization. However, the β selectivity observed with the catalytic system $PdCl_2/P\{OCH(CF_3)_2\}_3/Ag_2CO_3$ in the arylation of thiophenes with iodoarenes (see scheme) is a remarkably general phenomenon applicable to unsubstituted, monosubstituted, and disubstituted thiophene derivatives, as well as thiophene-containing fused aromatic compounds.

C–H Functionalization

K. Ueda, S. Yanagisawa, J. Yamaguchi, K. Itami* ———— **8946 – 8949**

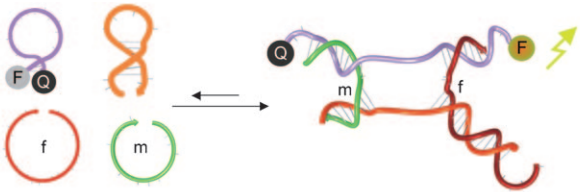
A General Catalyst for the β-Selective C–H Bond Arylation of Thiophenes with Iodoarenes

Contents

Single-Nucleotide Polymorphism

J. Grimes, Y. V. Gerasimova,
D. M. Kolpashchikov* ______ **8950 – 8953**

Real-Time SNP Analysis in Secondary-Structure-Folded Nucleic Acids

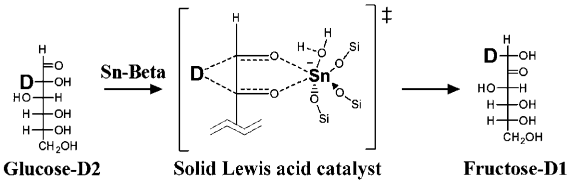


A tricomponent sensor was designed for genotyping stem-loop-structured DNA sequences. DNA adaptor strand f (see picture; red) hybridizes to the analyte (orange) with high affinity and unwinds its secondary structure; strand m (green) forms a stable complex only with the fully complementary analyte sequence. A fluorescing molecular beacon reports complex formation.

Biomass Conversion

Y. Román-Leshkov, M. Moliner,
J. A. Labinger, M. E. Davis* _ **8954 – 8957**

Mechanism of Glucose Isomerization Using a Solid Lewis Acid Catalyst in Water

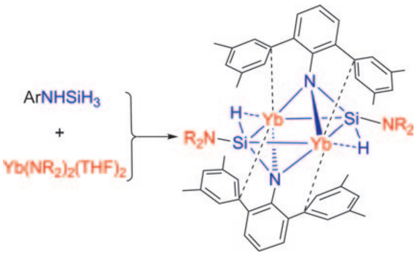


Other way round: ^{1}H and ^{13}C NMR spectroscopy on isotopically labeled glucose reveals that in the presence of tin-containing zeolite Sn-Beta, the isomerization reaction of glucose in water proceeds by way of an intramolecular hydride shift (see scheme) rather than proton transfer. This is the first mechanistic demonstration of Sn-Beta acting as a Lewis acid in a purely aqueous environment.

Lanthanide Silanimines

Y. Chen, H.-B. Song,
C.-M. Cui* ______________ **8958 – 8961**

Dehydrosilylation of $ArNHSiH_3$ with Ytterbium(II) Amide: Formation of a Dimeric Ytterbium(II) Silanimine Complex



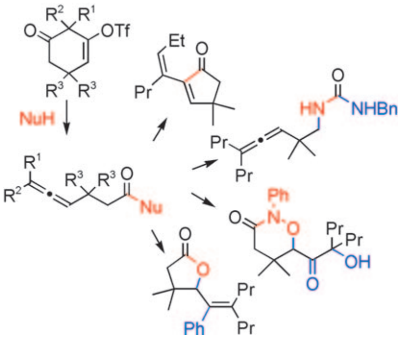
Agostic silanimine complexes: Reaction of $[Yb\{N(SiMe_3)_2\}_2(thf)_2]$ with $ArNHSiH_3$ resulted in the formation of the first lanthanide silanimine complex $[\{ArNSiH[N(SiMe_3)_2]\}_2Yb_2]$ (see picture), having a planar Yb_2Si_2 core with significant α-(SiH)···Yb interactions, as well as the monomeric homoleptic lanthanide(II) amide $[\{ArNSiH_2[N(SiMe_3)_2]\}_2Yb]$, showing β-agostic (SiH)···Yb interactions.

Domino Reactions

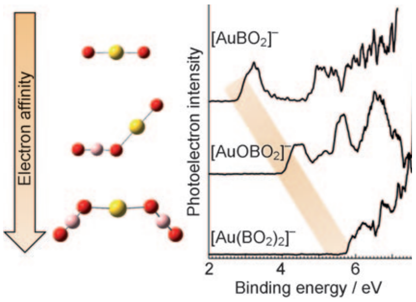
T. Saget, N. Cramer* ______ **8962 – 8965**

Heteroatom-Nucleophile-Induced C–C Fragmentations: Synthesis of Allenes and Entry to Domino Reactions

Blessed are the piece-makers: Heteroatom nucleophiles (NuH) induce Grob-type fragmentations of vinyl triflates under mild conditions and provide ω-allene-functionalized carboxylic acid derivatives. These products are a versatile starting point for domino and one-pot reactions accessing a range of structurally diverse scaffolds in good yields.



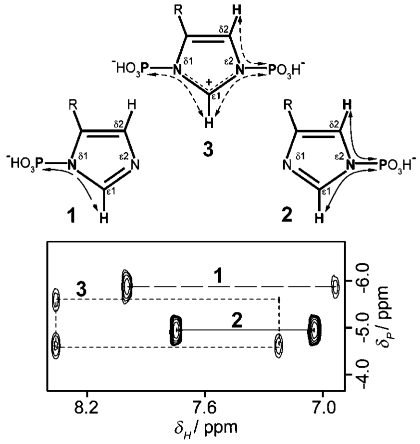
Hyperhalogens



Hyper trumps super: A central atom, typically a metal, surrounded by halogen or oxygen atoms is called a superhalogen. Theoretical calculations and experiments reveal that a new class of highly electronegative species can be created when the central metal atom is surrounded by superhalogen moieties. These hyperhalogens can have electron affinities even larger than those of their superhalogen building blocks.

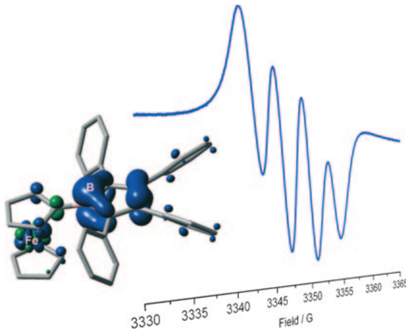
Histidine Phosphorylation

Three not of a kind: A NMR HNP experiment can distinguish between all three possible single- and double-phosphorylated histidines without requiring pK_a or chemical shift information (see picture). The method is tested on phosphorylated histidines and phosphocarrier protein HPr. It detects phosphorylation in phosphotransferase system regulation domain I (PRDI).

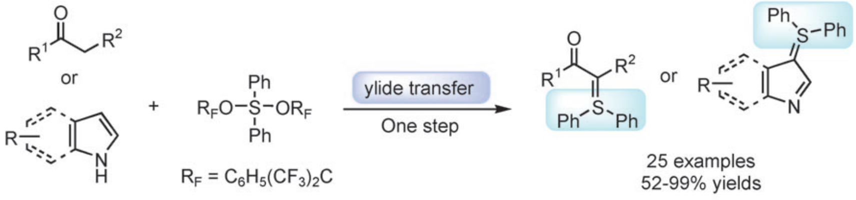


Boron-Centered Radicals

Time to B radical: One-electron reduction of 1-ferrocenyl-2,3,4,5-tetraphenylborole results in a radical anion with 5 π electrons in the borole ring. Both EPR spectroscopic investigations and spin density calculations confirm the formation of a borol radical (see picture). Further reduction stimulates an intramolecular $[(C_5H_5)Fe]$ migration from the cyclopentadienyl anion to the borole dianion.



Ylide Chemistry



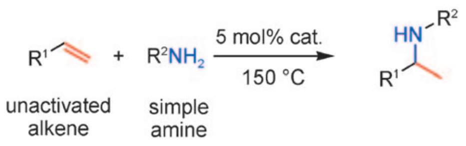
Power transfer: The title reaction proceeds under mild conditions (room temperature, short reaction times) and directly affords sulfonium ylides from active methylene compounds and heteroaromatics in a single step and in high yields. A detailed comparative structural analysis of a variety of ylides is presented and the implications of structure on the reactivity of these compounds are discussed.

Contents

Asymmetric Hydroamination

A. L. Reznichenko, H. N. Nguyen,
K. C. Hultzsch* ______ 8984 – 8987

Asymmetric Intermolecular Hydroamination of Unactivated Alkenes with Simple Amines

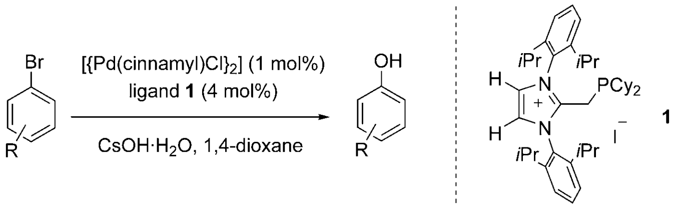


A hard nut to crack: The asymmetric intermolecular Markovnikov addition of simple amines to unactivated alkenes can be achieved utilizing binaphtholate rare-earth-metal catalysts with up to 61 % *ee* and 73 % *de* in the case where R^2 contains a stereogenic center.

Ligand Design

A. Dumrath, X.-F. Wu, H. Neumann,
A. Spannenberg, R. Jackstell,
M. Beller* ______ 8988 – 8992

Recyclable Catalysts for Palladium-Catalyzed C–O Coupling Reactions, Buchwald–Hartwig Aminations, and Sonogashira Reactions

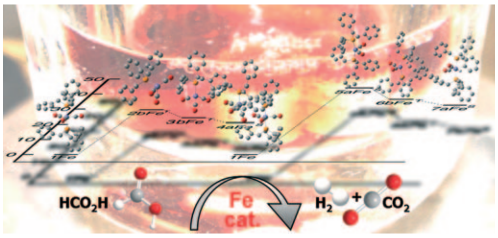


Simply reuse: Homogeneous palladium catalysts are effective and attractive tools for advanced organic synthesis (see example). Compound **1** belongs to a new class of ligands that enable recycling of the precious-metal catalyst directly from the reaction without any heterogenization.

Hydrogen Generation

A. Boddien, F. Gärtner, R. Jackstell,
H. Junge, A. Spannenberg, W. Baumann,
R. Ludwig,* M. Beller* ______ 8993 – 8996

ortho-Metalation of Iron(0) Tribenzylphosphine Complexes: Homogeneous Catalysts for the Generation of Hydrogen from Formic Acid

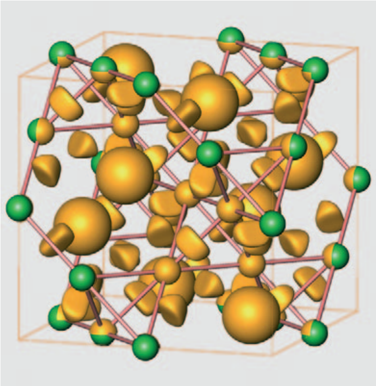


Without noble metals: A new catalyst derived from a non-noble metal has been developed for the selective generation of hydrogen from formic acid. DFT calculations and NMR spectroscopy support the formation of active *ortho*-metalated iron species as key intermediates during catalysis.

Laves Phases

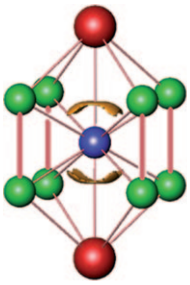
A. Ormeci, A. Simon,*
Yu. Grin* ______ 8997 – 9001

Structural Topology and Chemical Bonding in Laves Phases



A combined analysis of the electron localizability indicator (ELI; see isosurface ELI for $TiBe_2$) and electron density, the characteristic structural motif of the Laves phases MN_2 was shown to be mainly stabilized by charge transfer from *M* to *N*. In different groups of Laves phases, the bonding situation ranges from multicenter bonds between *M* and *N* atoms to the formation of $N^{\delta-}$ polyanions.

Eight-Connected Silicon



Under high-pressure high-temperature conditions, the title compounds with 4, 5, 6, or 8 Si–Si contacts are formed. The interatomic distances can be scaled to the number of homonuclear neighbors in the silicide framework. Analysis of the chemical bonding reveals multicenter bonds between metal and Si atoms (see figure for $CeSi_5$: Si blue and green, Ce red) and a contribution of semi-core states (the penultimate shell) of Ce to the chemical bonding.

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

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