Service

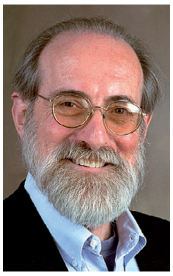
Author Profile

"What I look for first in a publication is a memorable discovery leading to a new idea.
The most important thing I learned from my parents is keep working for your goals and enjoy life (no matter what happens) …"
This and more about Kendall N. Houk can be found on page 9212.

News

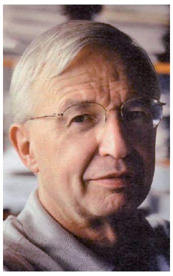

D. W. Stephan


D. S. Wright


J. L. Atwood


F. G. N. Cloke


S. C. E. Tsang


J.-M. Lehn


C. J. Moody


R. K. O'Reilly


R. J. K. Taylor


T. J. Colacot

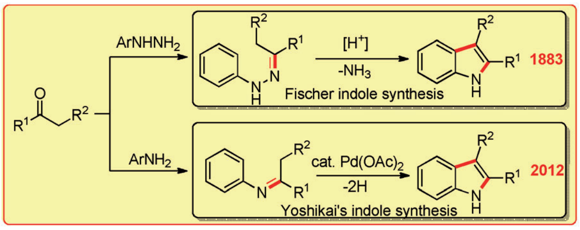
Obituaries

Rolf Appel, Emeritus Professor at University of Bonn, and pioneer of organophosphorus chemistry and discoverer of the Appel reaction for the transformation of alcohols into alkyl halides by means of PPh_3 and a tetrahalomethane, passed away on January 30, 2012.

Books

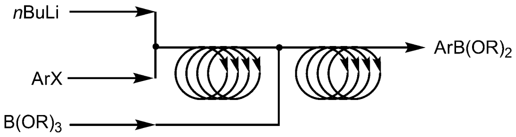
Highlights

Indole Synthesis



Complement for Fischer: An efficient palladium-catalyzed indole synthesis proceeds by the intramolecular cross-dehydrogenative coupling of *N*-aryl imines under mild conditions using molecular oxygen as the sole oxidant. This practical method relies on anilines and ketones as starting materials (and thus the same retrosynthetic disconnection as the Fischer indole synthesis) and will likely become a popular route.

Practical Lithiation Chemistry

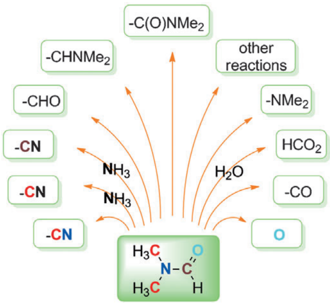


Quite a process: Recent pioneering reports establishing proof of concept for conducting lithiation chemistry to produce organoboron products in a continuous fashion are highlighted (see scheme).

Minireviews

Heterocycles

All-purpose reagent: In addition to being an effective polar solvent for chemical reactions, *N*,*N*-dimethylformamide (DMF) can serve as the source for a variety of units, such as CHO, $CHNMe_2$, $C(O)NMe_2$, NMe_2, and CN among others (see scheme). Recent developments in the employment of DMF as a reactant are reviewed.



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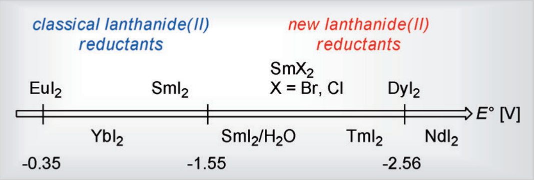
Reviews

Reductive Coupling

M. Szostak, D. J. Procter* ___ 9238 – 9256

Beyond Samarium Diiodide: Vistas in Reductive Chemistry Mediated by Lanthanides(II)



Electron dance: Lanthanide(II)-based electron-transfer reagents, beyond the classic reagent samarium(II) iodide (SmI$_2$, Kagan's reagent), are receiving increasing attention as new vehicles for the delivery of electrons and the orchestration of radical processes with power and precision (see scheme).

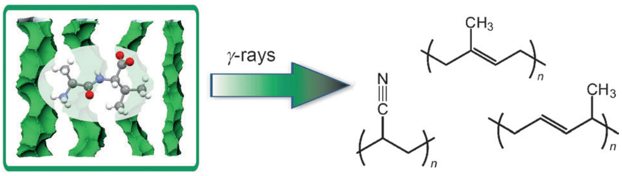
Communications

Polymerization in Biozeolites

G. Distefano, A. Comotti, S. Bracco, M. Beretta, P. Sozzani* ___ 9258 – 9262

Porous Dipeptide Crystals as Polymerization Nanoreactors

Frontispiece



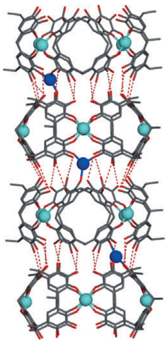
Channeling a good polymer: Dipeptide crystals have been used for solid-state polymerization reactions. The porosity of the crystals enables monomer absorption, followed by γ-irradiation to produce polymers with high molecular weights. The crystal channels induce stereoselective reactions to yield 1,4-*trans* polydienes and isotactic poly(acrylonitrile) with retention of fibrillar morphology (see scheme).

Tubular Assemblies

H. Kumari, S. R. Kline,* C. L. Dennis,* A. V. Mossine, R. L. Paul, C. A. Deakyne,* J. L. Atwood* ___ 9263 – 9266

Solution-Phase and Magnetic Approach towards Understanding Iron Gall Ink-like Nanoassemblies

Front Cover



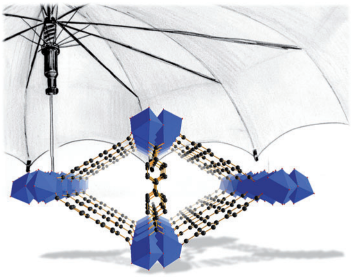
Metal-containing tubes: The structures of several iron-containing *C*-methylpyrogallol[4]arene (PgC$_1$) nanoassemblies were studied in both the solid and solution phases. The nanoassemblies have a tubular architecture with the iron as part of the framework (see picture; gray C, red O, turquoise/blue Fe), and magnetic analysis suggests a canted or spiral arrangement of the iron centers.

Metal–Organic Frameworks

V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross, C. Serre* ___ 9267 – 9271

A Series of Isoreticular, Highly Stable, Porous Zirconium Oxide Based Metal–Organic Frameworks

Inside Cover



Brolly good MOFs: A new series of hydrophobic isoreticular porous Zr oxide dicarboxylate MOFs have been prepared (see picture, Zr blue polyhedra, O red, C black). They have a one-dimensional pore system, a rare combination of Lewis acidity and hydrophobic character, and a higher hydrothermal and mechanical stability than their UiO MOF polymorph counterparts.

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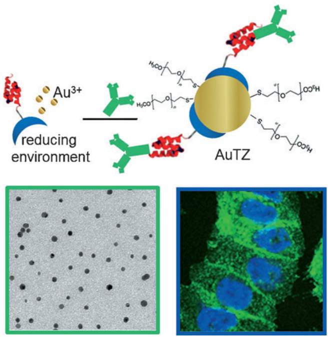
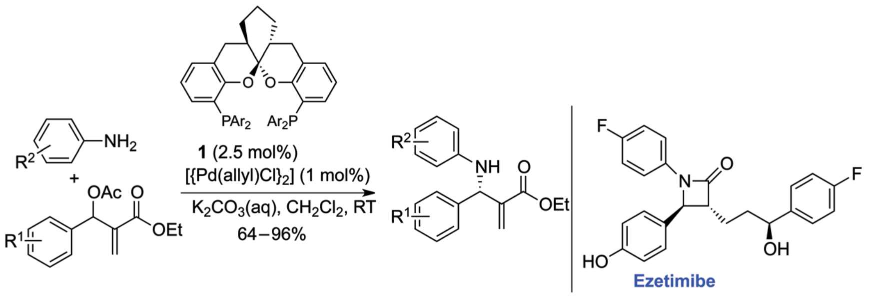
PSJ_12_42497_5_gu

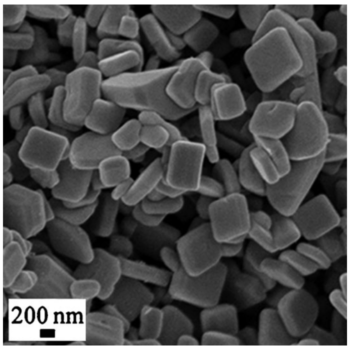
All bound up: A small variant of protein A (red; see picture) was used as a biotemplate for the synthesis and biofunctionalization of gold nanoparticles (AuNPs). These functionalized AuNPs were able to bind to antibodies (green blocks, trastuzumab; TZ) with a defined orientation, thus showing promise as bio-nanoparticle systems suitable for selective cell labeling by membrane-receptor-specific recognition.



Back Cover



Showing a backbone: The spiroketal backbone of the bis(phosphine) ligand **1** led to good regio- and enantioselectivity in the palladium-catalyzed asymmetric allylic amination of racemic Morita–Baylis–Hillman adducts with aromatic amines. The methodology provides a facile and efficient synthesis of precursors for optically active β-lactam derivatives, including the cholesterol drug Ezetimibe.

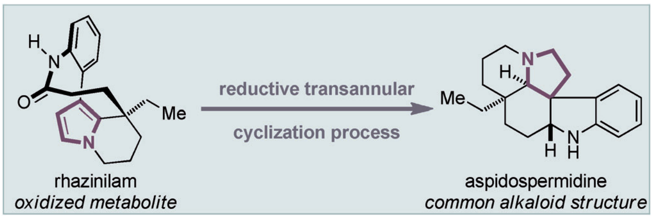


Free-standing single-crystal $PbTiO_3$ nanoplates (see picture) were synthesized by a facile hydrothermal method. A "self-templated" crystal growth is presumed to lead to the formation of the $PbTiO_3$ nanoplates, which have ferroelectric single-domain structures, whose polarization areas can be manipulated by writing and reading. The nanoplates are also effective catalysts for the oxidation of carbon monoxide.

Natural Product Synthesis

L. McMurray, E. M. Beck,
M. J. Gaunt* ______________ **9288 – 9291**

Chemical Synthesis of Aspidosperma Alkaloids Inspired by the Reverse of the Biosynthesis of the Rhazinilam Family of Natural Products

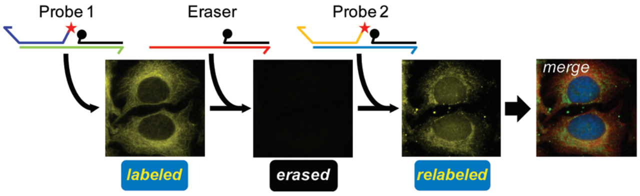


Pyrrole reduction: Iterative metal-catalyzed C–H functionalization reactions facilitated the preparation of a highly substituted pyrrole derivative. This derivative could be transformed into the pyrrole-containing secondary metabolite, rhazinilam, which could in turn be transformed through a reductive transannular cascade process into the structurally complex pyrrolidine-containing alkaloid natural product, aspidospermidine.

Fluorescence Imaging

R. M. Schweller, J. Zimak, D. Y. Duose,
A. A. Qutub, W. N. Hittelman,
M. R. Diehl* ______________ **9292 – 9296**

Multiplexed In Situ Immunofluorescence Using Dynamic DNA Complexes



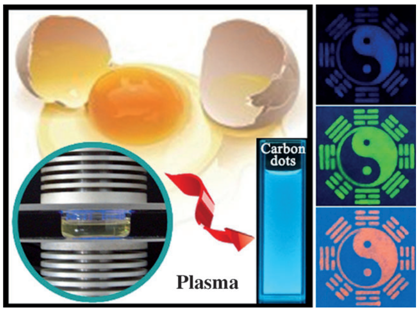
DNA-based erasers: The designed strand-displacement reactions between dynamic DNA probes (carrying fluorescent dyes (★) and quencher domains (●)) and DNA–antibody conjugates generate detachable immunofluoresence-reporting complexes that can be assembled (first image) and disassembled (second image) reversibly within fixed cells. With this system, different protein targets can be imaged sequentially within the same cells (third image).

Fluorescent Nanoparticles

J. Wang, C.-F. Wang,
S. Chen* ______________ **9297 – 9301**

Amphiphilic Egg-Derived Carbon Dots: Rapid Plasma Fabrication, Pyrolysis Process, and Multicolor Printing Patterns

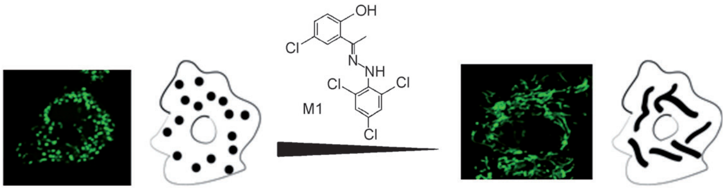
How do you like your eggs? Amphiphilic carbon dots (CDs) with intense blue fluorescence have been produced from chicken eggs by treatment with plasma. They are used as effective “fluorescent carbon inks” for multicolor luminescent inkjet and silk-screen printing (see image).



Drug Design

D. Wang, J. Wang, G. M. C. Bonamy,
S. Meeusen, R. G. Brusch, C. Turk,
P. Yang, P. G. Schultz* ______ **9302 – 9305**

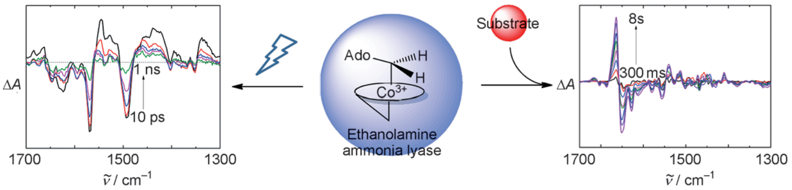
A Small Molecule Promotes Mitochondrial Fusion in Mammalian Cells



Fragmented mitochondria

Fused mitochondria

Mitochondrial dynamics: An image-based screen identified a small molecule, M1, that specifically promotes the fusion of fragmented mitochondria and protects cells from mitochondrial-fragmentation-associated cell death. Mechanistic studies revealed that M1 shifts the mitochondrial dynamic balance towards fusion (see picture).



The role of protein dynamics in promoting catalysis is hotly debated. Infrared data from both ultrafast flash photolysis and stopped-flow studies show that not only does there appear to be vibrational coupling between the cofactor and protein in B_{12}-dependent ethanolamine ammonia lyase, but also that there are significant protein motions coupled to the reaction that follows substrate binding (see picture).

Reaction Dynamics

H. J. Russell, A. R. Jones, S. Hay, G. M. Greetham, M. Towrie, N. S. Scrutton* ______ **9306 – 9310**

Protein Motions Are Coupled to the Reaction Chemistry in Coenzyme B_{12}-Dependent Ethanolamine Ammonia Lyase

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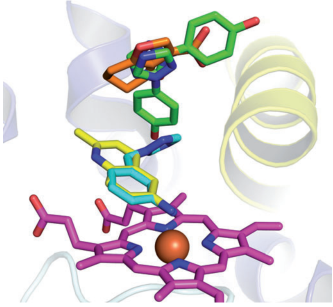


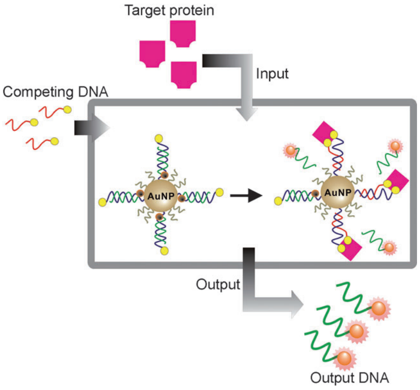
Pieces of the puzzle: The first fragment-based approach was used to target cytochrome P450 enzymes (CYPs) for drug development (see scheme). The experiments provide new insights into the binding site of the essential *Mycobacterium tuberculosis* CYP121 enzyme, and resulted in a promising novel lead compound based on fragment merging.

Drug Discovery

S. A. Hudson, K. J. McLean, S. Surade, Y.-Q. Yang, D. Leys, A. Ciulli, A. W. Munro, C. Abell* ______ **9311 – 9316**

Application of Fragment Screening and Merging to the Discovery of Inhibitors of the *Mycobacterium tuberculosis* Cytochrome P450 CYP121

Protein in, DNA out: A "binding-induced molecular translator" (see picture) is able to convert an input target protein into an output DNA that can be readily detected and potentially be used to assemble DNA nanodevices. Successful molecular translation is mediated by binding-induced DNA assembly on a gold nanoparticle (AuNP) scaffold, thereby achieving efficient target-dependent strand displacement.



DNA Structures

F. Li, H. Zhang, C. Lai, X.-F. Li, X. C. Le* ______ **9317 – 9320**

A Molecular Translator that Acts by Binding-Induced DNA Strand Displacement for a Homogeneous Protein Assay

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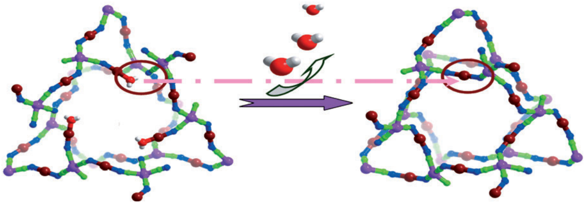


Two for one: Two unusual magnets based on the $[Mo(CN)_7]^{4-}$ building block with Mn^{II} linkers have been prepared with different topological 3D networks. Conversion of one into the other is triggered by dehydration during a single-crystal to single-crystal event (see picture; Mn: dark red, Mo: pink, C: green, N: blue, O: red).

Topological Magnetic Isomers

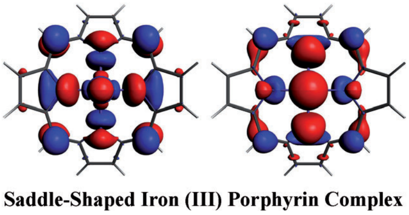
Q.-L. Wang, H. Southerland, J.-R. Li, A. V. Prosvirin, H. Zhao, K. R. Dunbar* ______ **9321 – 9324**

Crystal-to-Crystal Transformation of Magnets Based on Heptacyanomolybdate(III) Involving Dramatic Changes in Coordination Mode and Ordering Temperature

Coordination Chemistry

C.-C. Chen, P. P.-Y. Chen* ___ **9325 – 9329**

Paramagnetic NMR Shifts for Saddle-Shaped Five-Coordinate Iron(III) Porphyrin Complexes with Intermediate-Spin Structure

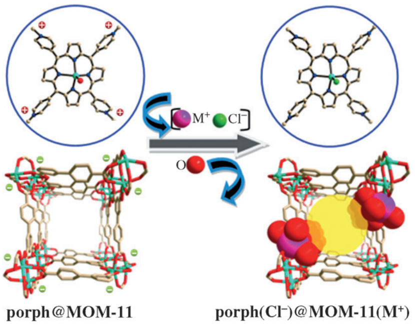


Calculable results: Complex density functional calculations and spin distribution analyses have been performed for planar and saddled iron(III) porphyrin complexes (see picture). The spin populations and the extent of the interactions between the metal and the porphyrin orbitals were determined, which can explain the large change of *meso*-carbon atom chemical shifts observed for different porphyrin ligands.

Metal–Organic Frameworks

Z. Zhang, W.-Y. Gao, L. Wojtas, S. Ma, M. Eddaoudi, M. J. Zaworotko* ___ **9330 – 9334**

Post-Synthetic Modification of Porphyrin-Encapsulating Metal–Organic Materials by Cooperative Addition of Inorganic Salts to Enhance CO_2/CH_4 Selectivity



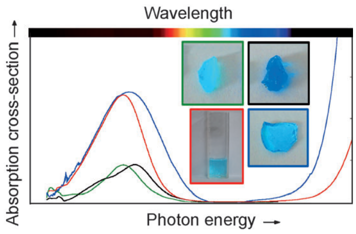
Keeping MOM: Reaction of biphenyl-3,4′,5-tricarboxylate and $Cd(NO_3)_2$ in the presence of *meso*-tetra(*N*-methyl-4-pyridyl)porphine tetratosylate afforded porph@MOM-11, a microporous metal–organic material (MOM) that encapsulates cationic porphyrins and solvent in alternating open channels. Porph@-MOM-11 has cation and anion binding sites that facilitate cooperative addition of inorganic salts (such as M^+Cl^-) in a stoichiometric fashion.

Coordination Chemistry

S. Gómez-Salces, F. Aguado,* R. Valiente, F. Rodríguez ___ **9335 – 9338**

Unraveling the Coordination Geometry of Copper(II) Ions in Aqueous Solution through Absorption Intensity

Strong colors: The solvation structure of copper(II) ions in water can be determined by optical absorption spectroscopy. Focus is placed on the absorption intensity (green: $Cs_2Cu(SO_4)_2{\cdot}6\,H_2O$, black: $CuSO_4{\cdot}5\,H_2O$, red: Cu^{2+} in aqueous solution, and blue: Cu^{2+} in glass). A dynamical model based on a Jahn–Teller-distorted complex describes the coordination of copper(II) ions in hydrate crystals and aqueous solution.

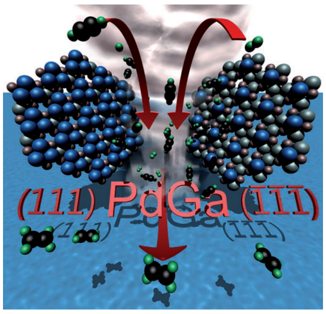


Intermetallic Compounds

J. Prinz, R. Gaspari, C. A. Pignedoli, J. Vogt, P. Gille, M. Armbrüster, H. Brune, O. Gröning, D. Passerone, R. Widmer* ___ **9339 – 9343**

Isolated Pd Sites on the Intermetallic PdGa(111) and PdGa($\bar{1}\bar{1}\bar{1}$) Model Catalyst Surfaces

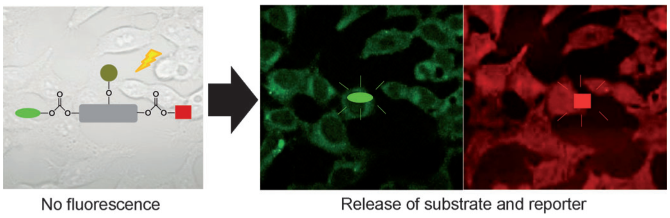
Scratching the surface: The high selectivity of PdGa catalysts towards the partial hydrogenation of acetylene was previously attributed to the separation of Pd atomic sites at the surfaces. The atomic structures of PdGa surfaces are determined by means of a combined experimental and computational approach, allowing investigation of the catalytic dissociation of hydrogen. The two opposite (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces show a very different arrangement of catalytic centers.



Chemical Biology

R. Labruère, A. Alouane, T. Le Saux,
I. Aujard, P. Pelupessy, A. Gautier,
S. Dubruille, F. Schmidt,*
L. Jullien* ——— 9344–9347

“Self-Immolative” Spacer for Uncaging with Fluorescence Reporting

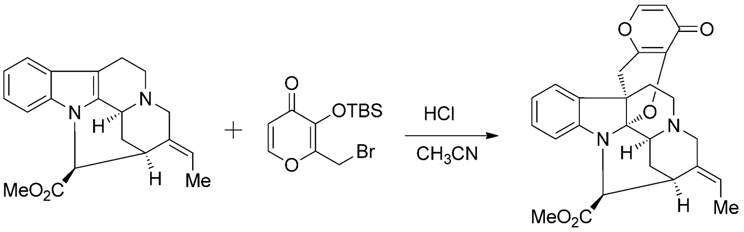


Dual photoliberation: A caged, branched, self-immolative spacer (see scheme, gray box) was designed to rapidly and simultaneously release a desired compound (green) and a fluorophore (red) upon photoactivation. Careful kinetic analysis of the disassembly of the spacer shows that it occurs on the shortest time scale reported to date.

Natural Product Synthesis

R. E. Ziegler, S.-J. Tan, T.-S. Kam,
J. A. Porco, Jr.* ——— 9348–9351

Development of an Alkaloid–Pyrone Annulation: Synthesis of Pleiomaltinine

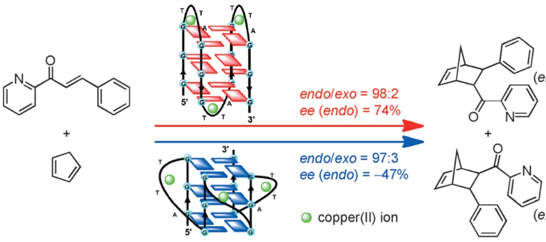


Odd Couple: A method for the synthesis of alkaloid-pyrones using a novel pyrone annulation of β-carbolines and indoles with 3-siloxy-4-pyrones is reported. The approach has enabled synthesis of the unusual alkaloid-pyrone pleiomaltinine from the plant-derived indole-alkaloid pleiocarpamine (see Scheme; TBS = *tert*-butyldimethylsilyl).

DNA-Based Catalysis

C. Wang, G. Jia, J. Zhou, Y. Li, Y. Liu, S. Lu,
C. Li* ——— 9352–9355

Enantioselective Diels–Alder Reactions with G-Quadruplex DNA-Based Catalysts

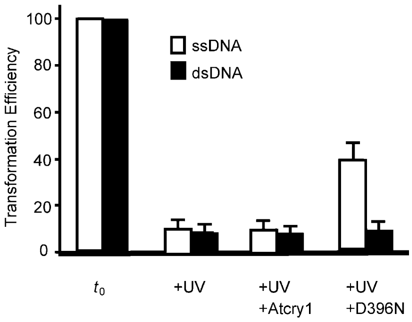


DNA in command: An enantioselective Diels–Alder reaction can be achieved using human telomeric G-quadruplex DNA-based catalysts. The absolute configuration of the product can be reversed when the conformation of G-quadruplex DNA is switched from antiparallel to parallel, and both the reaction rate and the enantioselectivity of the Diels–Alder reaction were found to be dependent on the DNA sequence.

Enzyme Mechanism

S. Burney, R. Wenzel, T. Kottke, T. Roussel,
N. Hoang, J.-P. Bouly, R. Bittl, J. Heberle,
M. Ahmad* ——— 9356–9360

Single Amino Acid Substitution Reveals Latent Photolyase Activity in *Arabidopsis* cry1



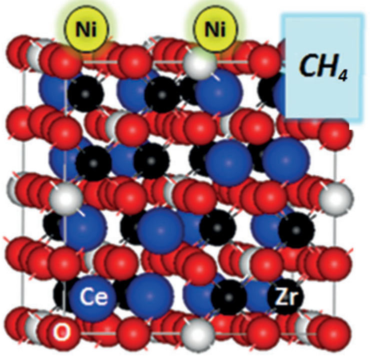
A quick switch: A single amino acid substitution at a conserved residue (D396N) of *Arabidopsis* cryptochrome-1 (Atcry1) confers single-stranded DNA repair activity in vitro, conferring photolyase activity onto the cryptochrome (see graph). The mutant protein undergoes photoreduction of flavin to the fully reduced anionic form, similar to photolyases and unlike wild-type cryptochromes.

Methane Reforming

M. Tada,* S. Zhang, S. Malwadkar,
N. Ishiguro, J. Soga, Y. Nagai, K. Tezuka,
H. Imoto, S. Otsuka-Yao-Matsuo,
S. Ohkoshi, Y. Iwasawa* ____ **9361–9365**

The Active Phase of Nickel/Ordered $Ce_2Zr_2O_x$ Catalysts with a Discontinuity ($x=7$–8) in Methane Steam Reforming

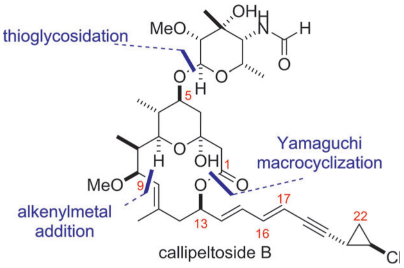
Breaking news: A unique discontinuous property and an active phase of Ni/ordered $Ce_2Zr_2O_x$ ($x=7$–8) solid-solution catalysts were observed during methane steam reforming. The catalytic performance of Ni/$Ce_2Zr_2O_x$ strongly depended on the phase and oxygen content of the $Ce_2Zr_2O_x$ support.



Natural Products

J. R. Frost, C. M. Pearson, T. N. Snaddon,
R. A. Booth, S. V. Ley* ______ **9366–9371**

Convergent Total Syntheses of Callipeltosides A, B, and C

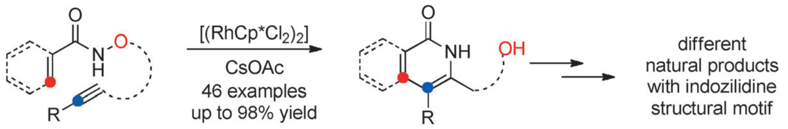


Going for the hat-trick: The synthesis of the entire callipeltoside family of natural products is described. Key to this synthesis was the coupling of the di-ene-yne and pyran fragments by a diastereoselective alkenylzinc addition allowing rapid access to the common aglycon. Attachment of each relevant L-configured sugar resulted in the first total synthesis of callipeltoside B (see scheme), and the syntheses of callipeltosides A and C.

C–H Activation

X. Xu, Y. Liu, C.-M. Park* ___ **9372–9376**

Rhodium(III)-Catalyzed Intramolecular Annulation through C–H Activation: Total Synthesis of (±)-Antofine, (±)-Septicine, (±)-Tylophorine, and Rosettacin

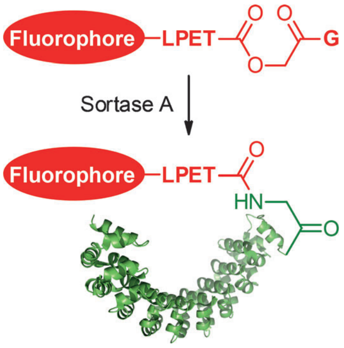


Annulation: The efficient synthesis of 3-hydroxyalkyl isoquinolones and 6-hydroxyalkyl 2-pyridones is enabled through the intramolecular annulation of alkyne-tethered hydroxamic esters (see scheme, Cp* = pentamethylcyclopentadienyl). The reaction features high regioselectivity, broad substrate scope, and excellent functional-group tolerance, proceeds under mild reaction conditions with low catalyst loading, and obviates the need for an external oxidant.

Protein Modification

D. J. Williamson, M. A. Fascione,
M. E. Webb,*
W. B. Turnbull* __________ **9377–9380**

Efficient N-Terminal Labeling of Proteins by Use of Sortase



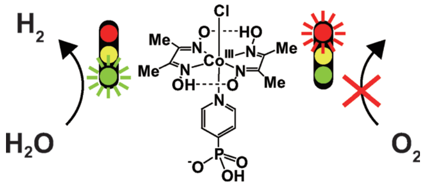
“Sorting out” N-terminal labeling: The reversibility of transpeptidase reactions makes protein N-terminal labeling challenging. Depsipeptide substrates for sortase A release alcohol by-products, which are poor nucleophiles for the reverse reaction, during ligation. Proteins with an unhindered N-terminal glycine residue can be labeled efficiently with only a minimal excess of the labeling reagent (see scheme).

Water Splitting

F. Lakadamyali, M. Kato, N. M. Muresan, E. Reisner* ——— 9381 – 9384

Selective Reduction of Aqueous Protons to Hydrogen with a Synthetic Cobaloxime Catalyst in the Presence of Atmospheric Oxygen

Inside Back Cover



Protons preferred: A cobalt catalyst is reported that evolves H_2 electro- and photocatalytically at room temperature, in pH-neutral water, and in the presence of atmospheric O_2 (see scheme). The catalyst shows respectable Faradaic efficiencies under N_2 and 21% O_2 in N_2, and can be used under both homogeneous and heterogeneous conditions.

Synthetic Methods

VIP

A. J. J. Lennox, G. C. Lloyd-Jones* ——— 9385 – 9388

Preparation of Organotrifluoroborate Salts: Precipitation-Driven Equilibrium under Non-Etching Conditions

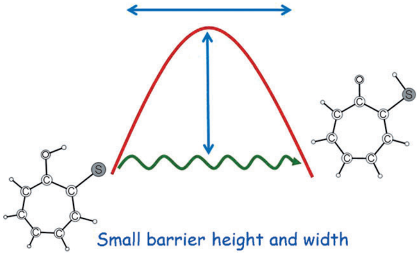
Simple, rapid, and scaleable: In contrast to current procedures using corrosive HF/MF or MHF_2 reagents (M = e.g. K), a wide range of trifluoroborates can be rapidly, simply, and safely prepared from MF (M = K, Cs), RCO_2H, and a boronic acid/ester in regular glassware (see figure; left versus right). The use of L-(+)-tartaric acid as an alkali-metal sponge is key and allows isolation of RBF_3M by a simple stir/filter/evaporate sequence.

Quantum Mechanics

D. Jose, A. Datta* ——— 9389 – 9392

Tunneling Governs Intramolecular Proton Transfer in Thiotropolone at Room Temperature

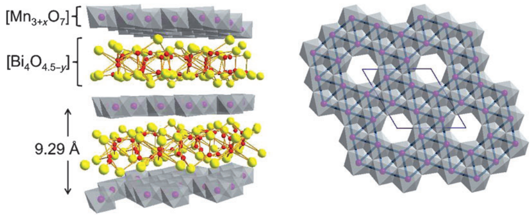
Successfully tunneled: The rapid and temperature-independent intramolecular proton transfer in thiotropolone occurs entirely through quantum mechanical tunneling (see picture). For tropolone, tunneling across a smaller yet broader barrier leads to a slower rate of proton transfer for temperatures smaller than 240 K.



Solid-State Structures

A. Aliev, M. Huvé, S. Colis, M. Colmont, A. Dinia, O. Mentré* ——— 9393 – 9397

Two-Dimensional Antiferromagnetism in the $[Mn_{3+x}O_7][Bi_4O_{4.5-y}]$ Compound with a Maple-Leaf Lattice



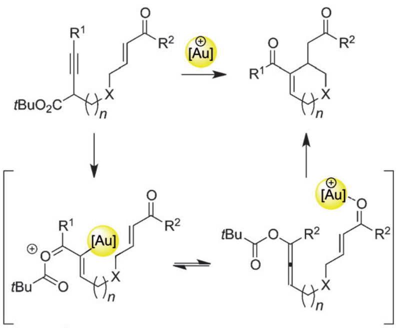
The modular compound $[Mn_{3+x}O_7][Bi_4O_{4.5-y}]$ contains a rare example of true 2D maple-leaf lattice of edge-sharing $Mn^{3+/4+}$ (see picture). This compound displays a magnetic transition at 210 K without evidence for a Néel ordering, which indicates in-plane 2D antiferromagnetism.

Synthetic Methods

J. W. Cran,* M. E. Krafft ____ **9398 – 9402**

Regioselective Cyclizations Utilizing a Gold-Catalyzed [3,3] Propargyl Ester Rearrangement

Switch-Au-roo: A new strategy for the regioselective synthesis of unsaturated carbocycles by chemoselective activation of a Rauhut–Currier zwitterion surrogate, formed from the Au-catalyzed [3,3] sigmatropic rearrangement of propargylic esters, has been achieved. By reversing the regiochemistry of the propargyl ester the synthesis of either the endo- or exocyclic enones is feasible.

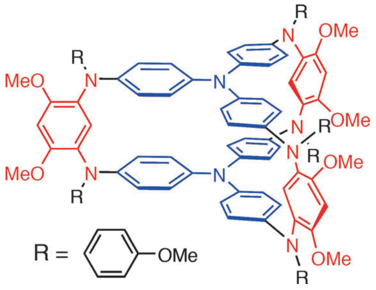


R^1 can be more electrophilic, less electrophilic, or equal in electrophilicity to R^2

Radical Ions

Y. Yokoyama, D. Sakamaki, A. Ito,* K. Tanaka, M. Shiro ________ **9403 – 9406**

A Triphenylamine Double-Decker: From a Delocalized Radical Cation to a Diradical Dication with an Excited Triplet State

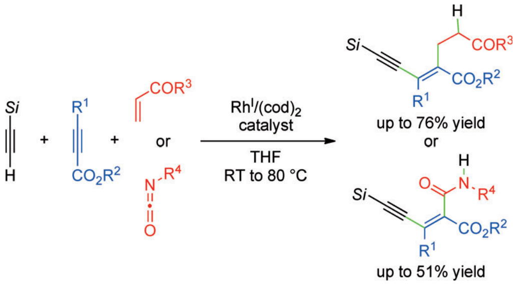


The redox properties and electronic structures of polycationic species were examined using a triphenylamine double-decker species. The double-decker has a strong electron-donating ability, and the spin in the radical cation is delocalized over the whole caged skeleton, despite no direct transannular π–π interaction between two TPA decks. Moreover, the diradical dication has spin-singlet character, despite the *meta*-phenylene linkage.

Multicomponent Reactions

Y. Hoshino, Y. Shibata, K. Tanaka* ________________ **9407 – 9411**

Rhodium-Catalyzed Three-Component Cross-Addition of Silylacetylenes, Alkynyl Esters, and Electron-Deficient Alkenes or Isocyanates

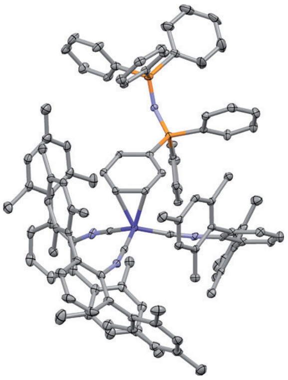


'Rh'oad crossing: A cationic Rh^{I}/(cod)$_2$ complex catalyzes the chemo-, regio-, and stereoselective title reaction with electron-deficient alkenes leading to substituted 1,3-dienes. The analogous three-component cross-addition involving isocyanates instead of alkenes has also been developed.

Metallates

A. E. Carpenter, G. W. Margulieux, M. D. Millard, C. E. Moore, N. Weidemann, A. L. Rheingold, J. S. Figueroa* ____________ **9412 – 9416**

Zwitterionic Stabilization of a Reactive Cobalt Tris-Isocyanide Monoanion by Cation Coordination

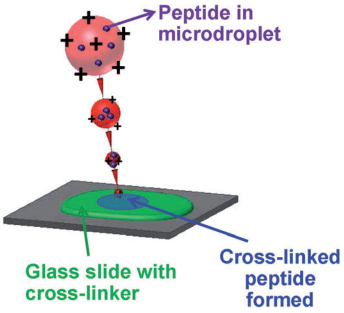


A break with tradition: The cation, [Ph$_3$P=N=PPh$_3$]$^+$ ([PPN]$^+$), was found to provide a stabilizing η^2-arene interaction to the coordinatively unsaturated, tris-isocyanide monoanion, [Co(CNAr^{Mes2})$_3$]$^-$ (Ar^{Mes2}=2,6-(2,4,6-Me$_3$C$_6$H$_2$)C$_6$H$_3$); Co = purple, N = light purple, and P = orange). The resulting zwitterion is a source of [Co(CNAr^{Mes2})$_3$]$^-$ anions, performing nucleophilic additions, carbon–element bond activations, and multistep decarbonylations.

Ambient Ion–Surface Reactions

A. K. Badu-Tawiah, A. Li, F. P. M. Jjunju, R. G. Cooks* 9417–9421

Peptide Cross-Linking at Ambient Surfaces by Reactions of Nanosprayed Molecular Cations

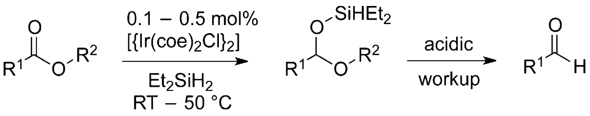


Chemical synthesis with ambient ions: Peptide cross-linking is achieved nearly instantaneously and quantitatively by delivering solvated peptide cations in microdroplets to a cross-linker present on a glass surface (see picture) or vice versa. The reaction can be carried out in an open laboratory environment.

Homogeneous Catalysis

C. Cheng, M. Brookhart* 9422–9424

Efficient Reduction of Esters to Aldehydes through Iridium-Catalyzed Hydrosilylation

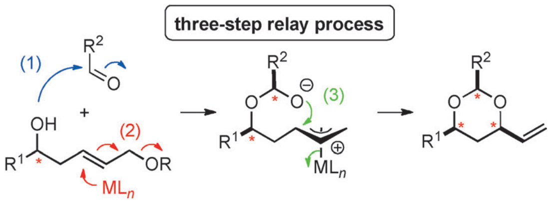


Trumping DIBALH: A new method for reduction of esters to aldehydes through silyl acetal intermediates involves a single-step hydrosilylation catalyzed by a readily available iridium complex, $[\{Ir(coe)_2Cl\}_2]$ (see scheme; coe = cyclooctene). The low catalyst loading, mild reaction conditions, high conversions, and broad substrate scope make this method a superior alternative to ester reduction using DIBALH.

Domino Reactions

L. Wang, D. Menche* 9425–9427

Concise Synthesis of Acetal-Protected *syn* 1,3-Diols by a Tandem Hemiacetal Formation/Tsuji–Trost Reaction

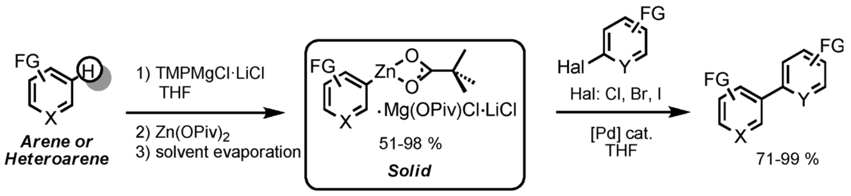


Designed, developed, and applied: A novel domino sequence was used for the rapid assembly of acetal-protected *syn* 1,3-diols. The convergent synthesis of a polyol fragment of the macrolide antibiotic RK-397 demonstrates that this method is suitable for the rapid and stereoselective preparation of polyketide-type diol motifs.

Organozinc Reagents

C. I. Stathakis, S. Bernhardt, V. Quint, P. Knochel* 9428–9432

Improved Air-Stable Solid Aromatic and Heterocyclic Zinc Reagents by Highly Selective Metalations for Negishi Cross-Couplings

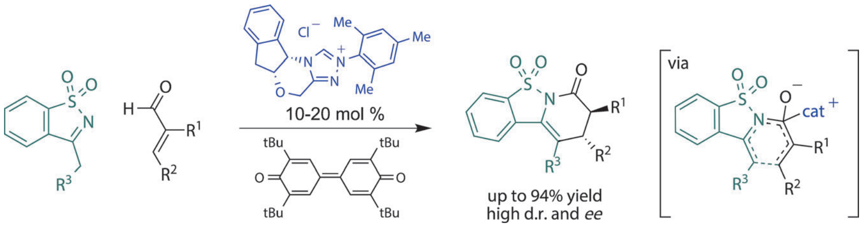


Directed metalation using TMPMgCl·LiCl (TMP = 2,2,6,6-tetramethylpiperidide) and subsequent transmetalation with $Zn(OPiv)_2$ leads to aryl and heteroaryl zinc pivalates. After solvent evaporation, easy-to-handle fine powders are obtained that retain most of their activity (> 85 %) when exposed to air for 4 h. They smoothly undergo Negishi cross-couplings, and technical-grade solvents can be used without significant loss of yield.

NHC Catalysis

A. G. Kravina, J. Mahatthananchai, J. W. Bode* ______ **9433 – 9436**

Enantioselective, NHC-Catalyzed Annulations of Trisubstituted Enals and Cyclic *N*-Sulfonylimines via α,β-Unsaturated Acyl Azoliums

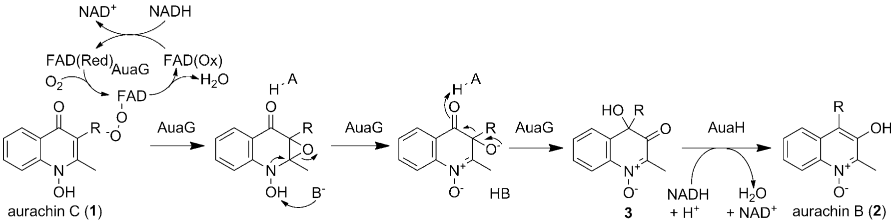


All aboard please! A new reaction of enals and cyclic sulfonylimines, as the nucleophiles(!), is the first highly enantioselective NHC-catalyzed annulation of trisubstituted enals. The catalytically generated α,β-unsaturated acyl azolium undergoes a reaction with the enamine tautomer of the imine via an aza-Claisen rearrangement as the key C–C bond-forming step. High yields and enantioselectivities were achieved using β-, α,β-, and β,β′-substituted enals.

Biosynthesis

Y. Katsuyama, K. Harmrolfs, D. Pistorius, Y. Li, R. Müller* ______ **9437 – 9440**

A Semipinacol Rearrangement Directed by an Enzymatic System Featuring Dual-Function FAD-Dependent Monooxygenase



The biosynthesis of aurachins includes the intriguing migration of the prenyl group by a pinacol-type rearrangement. In vitro analysis of AuaGH revealed that these enzymes catalyze epoxidation coupled with semipinacol rearrangement (see scheme) and ketoreduction. Thus, the AuaGH system was revealed to be a novel enzymatic system for establishing semipinacol rearrangements.

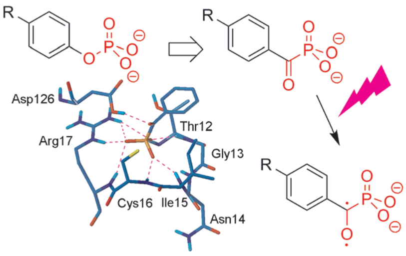
VIP

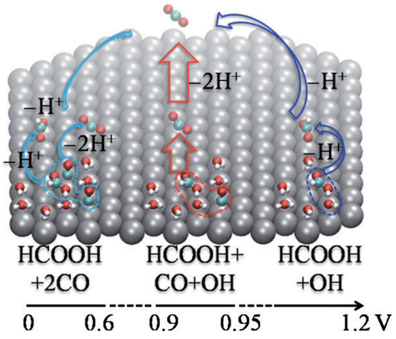
Photoactive Bioisosters

A. Horatscheck, S. Wagner, J. Ortwein, B. G. Kim, M. Lisurek, S. Beligny, A. Schütz, J. Rademann* ___ **9441 – 9447**

Benzoylphosphonate-Based Photoactive Phosphopeptide Mimetics for Modulation of Protein Tyrosine Phosphatases and Highly Specific Labeling of SH2 Domains

A light switch for phosphotyrosine-recognizing proteins: Irradiation of the bioisosteric benzoylphosphonate suffices to "turn off" the activity of target proteins and to label them covalently (see scheme). Photoactive bioisosters may find applications in functional cell biology, bioanalytics, and proteome research.





Synergy with potential: Analysis of relevant mechanistic pathways by density functional theory, reveals the synergistic role of co-adsorbed CO and OH in promoting HCOOH electrooxidation on Pt(111). Kinetic models derived from these studies show the atomistic surface phenomena underlying the experimental CV observation in the potential range between 0.0 and 1.2 V (see picture).

Electrocatalysis

W. Gao, J. E. Mueller, Q. Jiang, T. Jacob* **9448 – 9452**

The Role of Co-Adsorbed CO and OH in the Electrooxidation of Formic Acid on Pt(111)

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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