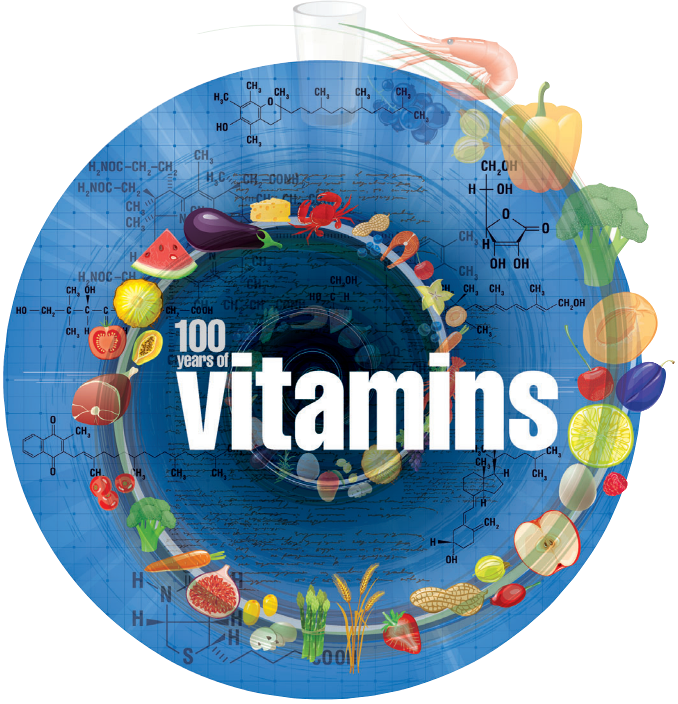
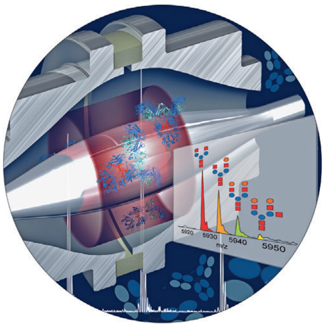
In 1912, the name vitamins ...

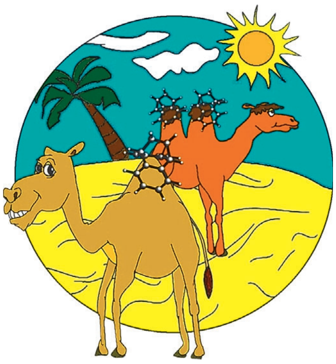


... was coined by Casimir Funk to describe essential bioactive substances contained in food. The use of vitamins has since resulted in an enormous improvement in human health. Their structures provided challenging synthetic problems for chemists in academia and industry. In the Review on page 12960 ff., W. Bonrath et al. present 100 years of achievement in vitamin preparation, from the first synthesis to manufacture on an industrial scale.



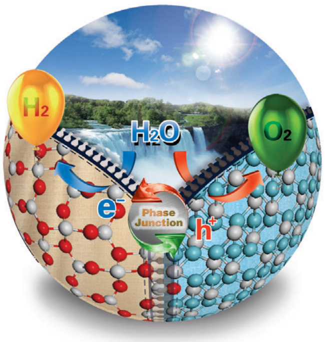
Protein Mass Spectrometry

In their Communication on page 12992 ff., A. J. R. Heck and co-workers use orbitrap mass spectrometry to analyze intact native antibodies. This approach enables the direct characterization of the glycan profile of antibodies.



Zimmerman Di-π-Methane Rearrangement

The di-π-methane rearrangement of dibenzobarrelene to dibenzosemibullvalene by density functional calculation is studied by R. A. Matute and K. N. Houk in their Communication on page 13097 ff.



Photocatalysis

In their Communication on page 13089 ff., C. Li et al. show that the phase junction formed between two phases of Ga_2O_3 can facilitate charge separation, resulting in high photocatalytic activity for overall water splitting.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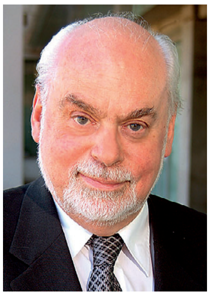
Editorial



"... The time has come for us to embrace complexity—despite the fact that everyone has their own definition of it—and put much more of our effort into studying complex mixtures of interacting molecules ...".
Read more in the Editorial by Fraser Stoddart.

Service

Author Profile

"My favorite place on earth is Yosemite National Park. The most significant scientific advance of the last 100 years has been the identification of the Higgs Boson ..."
This and more about Jonathan R. Nitschke can be found on page 12928.

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News


S. E. Reisman


C. R. J. Stephenson


G. Gauglitz


R. Eisenberg

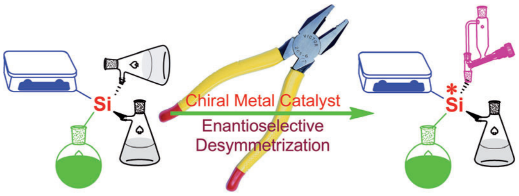

D. W. C. Macmillan


T. Ritter

Books

Highlights

Asymmetric Catalysis



Prochiral silanes: Recent work has demonstrated the powerful potential of enantioselective desymmetrization catalyzed by transition-metal complexes in the stereoselective formation of silicon-stereogenic silanes. These methods offer new possibilities for asymmetric synthesis of any functionalized chiral silanes that possess tetraorganosilicon stereocenters.

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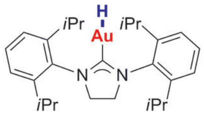
Gold Hydrides

Good as gold: Gold hydrides were long considered unstable. In the past few years reports have appeared on not only the stable NHC gold(I) monohydride complex **1** (see structure; NHC = N-heterocyclic carbene) but also a dinuclear gold(I) hydride and most recently the gold(III) monohydride complex **2** with a C-N-C pincer ligand. One can expect new and important impulses for inorganic and organometallic chemistry and homogeneous gold catalysis.



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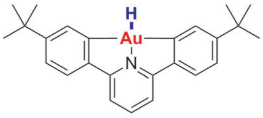

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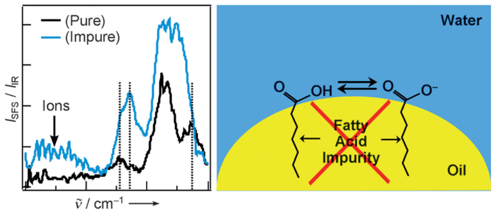
Correspondence

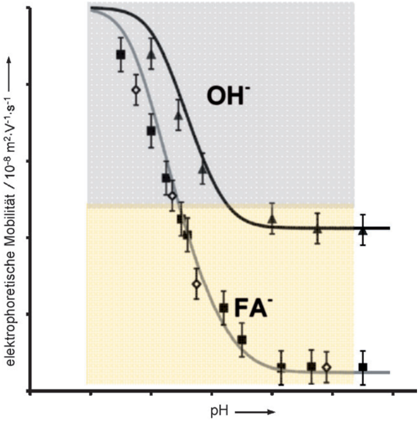
Oil/Water Interface (1)



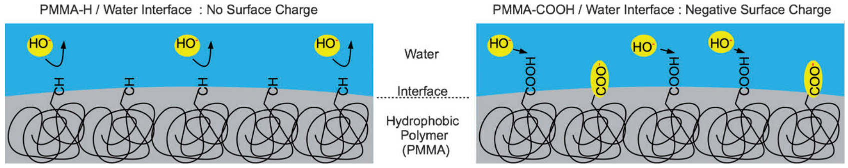
The origin of the charge on oil/water interfaces that can be found from electrokinetic mobility measurements is a long-standing issue that has invoked different explanations. Sum frequency scattering (SFS) shows that impurities are likely not a general cause for the charge (see picture).

Oil/Water Interface (2)

The effect of fatty acid impurities on the electrophoretic mobility of hexadecane in water emulsions is reinterpreted, occasioned by an error in the surface charge attributed to the fatty acids. The results are consistent with a surface charge contributed by both hydroxide ions and deprotonated fatty acids (see picture).



Oil/Water Interface (3)



Pure is uncharged: Uncontaminated hydrophobic interfaces, such as PMMA-H/water interfaces, are uncharged. If the macromolecules have instead ionizable carboxylic acid endgroups, such as PMMA-COOH, a surface charge similar to the contaminated oil/water interface is obtained.

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Essays

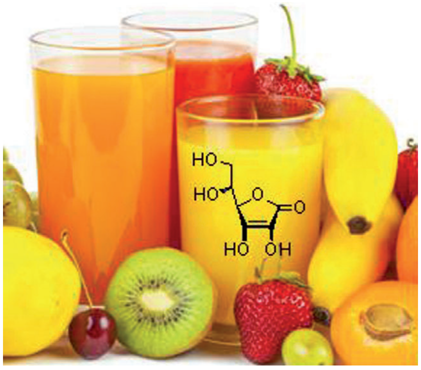
William Lawrence Bragg

A new age dawned when 22-year-old William Lawrence Bragg (see picture) realized that the observations of X-ray diffraction by a crystal can be interpreted very simply as arising from the reflection of the X-rays by planes of atoms in the crystal. In the 100 years since this insight X-ray diffraction has transformed chemistry, mineralogy, metallurgy, and most recently, biology.

Reviews

Vitamins

Front Cover



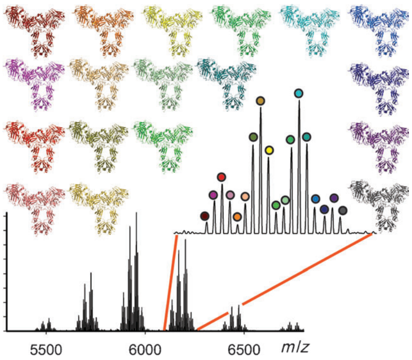
Essential: The discovery of vitamins was a scientific breakthrough that changed the world! The synthesis of vitamins on a commercial scale and their application in diets had a dramatically positive impact on human and animal health as well as economic development. The key achievements in research of vitamins are highlighted in this Review, starting from the first industrial synthesis of L-ascorbic acid up to modern catalytic methods.

Communications

Protein Mass Spectrometry

Frontispiece

Antibody profiling: Native mass spectrometry analysis of intact antibodies can be achieved with improved speed, sensitivity, and mass resolution by using a modified orbitrap instrument. Complex mixtures of monoclonal antibodies can be resolved and their glycan "fingerprints" can be profiled (see picture). Noncovalent interactions are maintained, thus allowing antibody–antigen binding to be measured.



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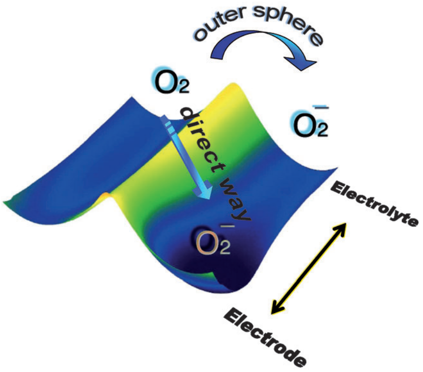
Reduction of Oxygen

P. Quaino, N. B. Luque, R. Nazmutdinov,
E. Santos,
W. Schmickler* ________ **12997 – 13000**

Why is Gold such a Good Catalyst for Oxygen Reduction in Alkaline Media?

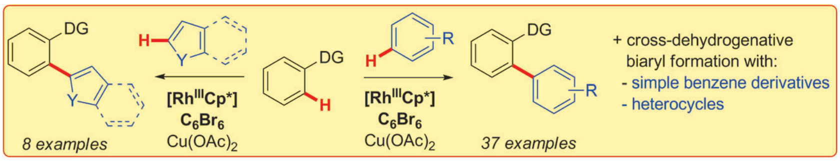


The two faces of gold: The reduction of oxygen on gold electrodes in alkaline solutions has been investigated theoretically. The most favorable reaction leads directly to adsorbed O_2^-, but the activation energy for a two-step pathway, in which the first step is an outer-sphere electron transfer to give solvated O_2^-, is only slightly higher. d-band catalysis, which dominates oxygen reduction in acid media, plays no role. The reason why the reaction is slow in acid media is also explained.

Double C–H Activation

J. Wencel-Delord, C. Nimphius, H. Wang,
F. Glorius* ____________ **13001 – 13005**

Rhodium(III) and Hexabromobenzene—A Catalyst System for the Cross-Dehydrogenative Coupling of Simple Arenes and Heterocycles with Arenes Bearing Directing Groups



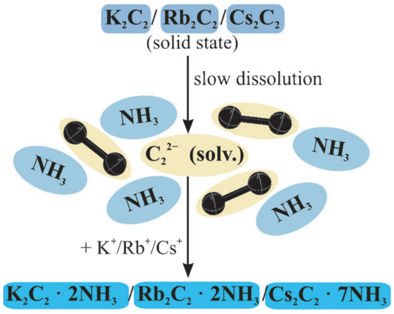
C_6Br_{six} & drugs! C_6Br_6 can be used as the cooxidant/catalyst modifier for the [Rh^{III}Cp*]-catalyzed (Cp* = C_5Me_5) dehydrogenative cross-coupling of benzamides with simple benzene derivatives (see scheme, DG = directing group). Similarly, heterocycles can be coupled and druglike structures formed. Mechanistic studies suggest a unique and multiple role of the $Cu(OAc)_2/C_6Br_6$ system and a nonchelate-assisted C–H activation as the rate-determing step.

Acetylide Chemistry

M. Hamberger, S. Liebig, U. Friedrich,
N. Korber,*
U. Ruschewitz* ________ **13006 – 13010**

Evidence of Solubility of the Acetylide Ion C_2^{2-}: Syntheses and Crystal Structures of $K_2C_2{\cdot}2\,NH_3$, $Rb_2C_2{\cdot}2\,NH_3$, and $Cs_2C_2{\cdot}7\,NH_3$

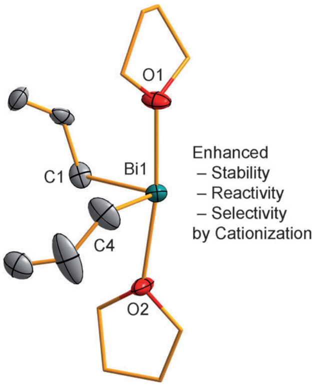
Carbon anions in solution: C_2^{2-} dumbbells are well-known in solid-state compounds. The crystallization of the title compounds now shows that acetylide ions are existent in solution and therefore chemistry with small dissolved carbon anions may be within reach.



Organobismuth Chemistry

C. Lichtenberg, F. Pan, T. P. Spaniol,
U. Englert, J. Okuda* ____ **13011 – 13015**

The Bis(allyl)bismuth Cation: A Reagent for Direct Allyl Transfer by Lewis Acid Activation and Controlled Radical Polymerization



A positive effect: The bis(allyl)bismuth cation (see picture) in $[Bi(C_3H_5)_2(thf)_2][B(C_6H_3Cl_2)_4]$ is superior to neutral tris(allyl)bismuth in the additive-free allylation of unsaturated C-heteroatom functionalities and the controlled living radical polymerization of activated olefins.

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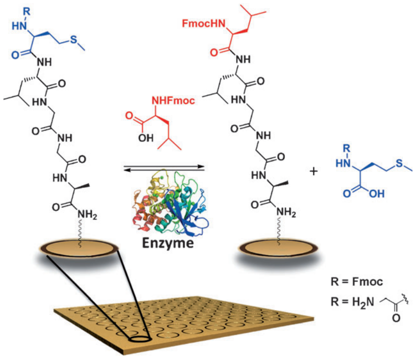
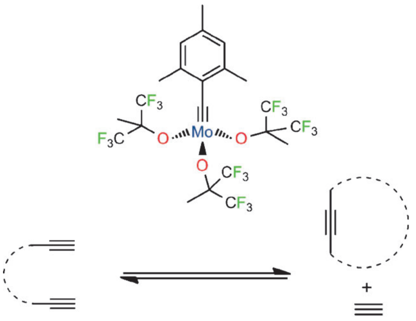


Reversible as well as stereo- and chemoselective: Various proteases such as thermolysin and chymotrypsin catalyze amine acyl exchange in peptides. This acyl exchange can be used to modify amino-functionalized surfaces under physiological reaction conditions and provides an alternative mechanism for posttranslational transpeptidation reactions such as peptide-splicing reactions in the proteasome.

Enzyme Catalysis

R. Castangia, M. Austeri,
S. L. Flitsch* ———— **13016 – 13018**

Enzymatic Amine Acyl Exchange in Peptides on Gold Surfaces



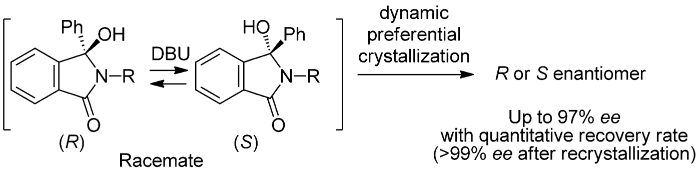
Now even terminal: The 2,4,6-trimethylbenzylidyne complexes $[\mathrm{MesC{\equiv}M\{OC(CF_3)_2Me\}_3}]$ (M = Mo, W) were synthesized from $[\mathrm{Mo(CO)_6}]$ and $[\mathrm{W(CO)_6}]$, respectively. The molybdenum complex is an efficient catalyst for the metathesis of internal and terminal alkynes and also for the ring-closing metathesis of internal and terminal α,ω-diynes at room temperature and low catalyst concentrations.

Alkyne Metathesis

B. Haberlag, M. Freytag, C. G. Daniliuc,
P. G. Jones, M. Tamm* — **13019 – 13022**

Efficient Metathesis of Terminal Alkynes

Inside Cover

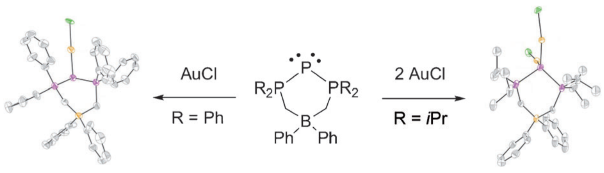


Separated: 3-Hydroxy-3-phenylisoindolin-1-ones have been resolved by dynamic preferential crystallization. The compounds were effectively racemized through ring-opening and ring-closing reactions via achiral intermediates under basic conditions. Crystallization from a toluene solution containing 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with stirring and evaporation of the solvent gave optically active crystals quantitatively with high *ee* values.

Chiral Resolution

F. Yagishita, H. Ishikawa, T. Onuki,
S. Hachiya, T. Mino,
M. Sakamoto* ———— **13023 – 13025**

Total Spontaneous Resolution by Deracemization of Isoindolinones



Go for the gold! Incorporating a borate anion into the backbone of a triphosphenium cation produces a unique zwitterionic phosphanide that can coordinate to one or two {AuCl} fragments depending on the steric bulk of the ligand (see picture; Au yellow, P purple, Cl green). Computational investigations show that in this μ-type ligand, the phosphorus atom behaves only as a σ,π donor.

Phosphanide Ligands

J. W. Dube, C. L. B. Macdonald,
P. J. Ragogna* ———— **13026 – 13030**

Accessing the Coordination Chemistry of Phosphorus(I) Zwitterions

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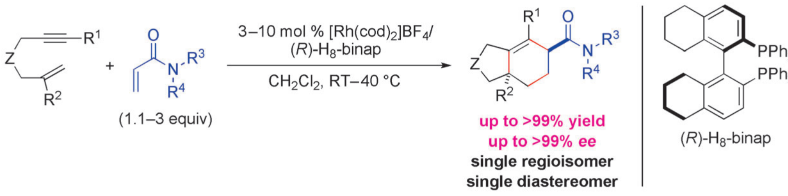
Asymmetric Catalysis

K. Masutomi, N. Sakiyama, K. Noguchi, K. Tanaka* ———— 13031 – 13035

Rhodium-Catalyzed Regio-, Diastereo-, and Enantioselective [2+2+2] Cycloaddition of 1,6-Enynes with Acrylamides

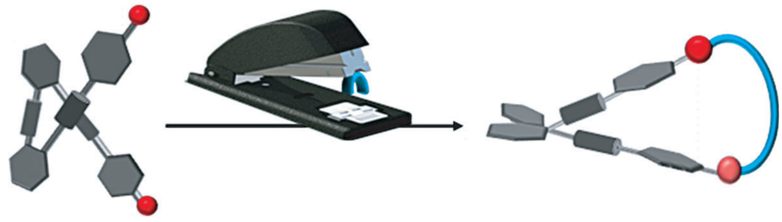


Ring ring: Annulated cyclohexenes were synthesized by using the title reaction with the cationic rhodium(I)/(*R*)-H$_8$-binap complex as a catalyst. In this catalysis, regioselective insertion of the acrylamide into a rhodacyclopentene intermediate and the coordination of the carbonyl group of the acrylamide to the cationic rhodium center suppress the undesired β-hydride elimination.

Structure Elucidation

N. Fuentes, A. Martin-Lasanta, L. Alvarez de Cienfuegos, R. Robles, D. Choquesillo-Lazarte, J. M. García-Ruiz, L. Martínez-Fernández, I. Corral, M. Ribagorda, A. J. Mota, D. J. Cárdenas, M. C. Carreño, J. M. Cuerva* ———— 13036 – 13040

Versatile Bottom-up Approach to Stapled π-Conjugated Helical Scaffolds: Synthesis and Chiroptical Properties of Cyclic *o*-Phenylene Ethynylene Oligomers

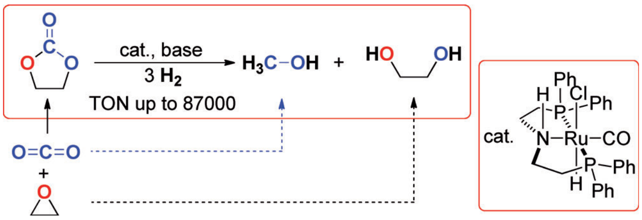


Spring loaded: The smallest members of a family of carbon nanocoils (CNCs), adopting a fixed helical structure, have been synthesized by introduction of one or two staples in *o*-phenylene ethynylene oligomers. The chiroptical responses of the systems having enantiopure L-tartrate-derived staples confirmed the induced helicity. Theoretical studies suggest that these CNCs are pseudoelastic.

Homogeneous Catalysis

Z. B. Han, L. C. Rong, J. Wu, L. Zhang, Z. Wang, K. Ding* ———— 13041 – 13045

Catalytic Hydrogenation of Cyclic Carbonates: A Practical Approach from CO$_2$ and Epoxides to Methanol and Diols



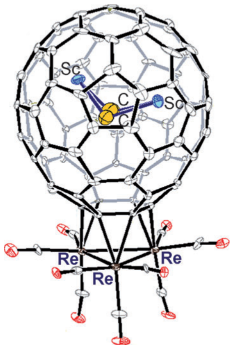
Two birds with one stone: The simultaneous production of two important bulk chemicals, methanol and ethylene glycol, from CO$_2$ and ethylene oxide has been achieved under mild conditions by the highly efficient homogeneous catalytic hydrogenation of ethylene carbonate in the presence of a (PNP)Ru^{II} catalyst (see scheme).

Fullerene Complexes

C.-H. Chen, W.-Y. Yeh,* Y.-H. Liu, G.-H. Lee ———— 13046 – 13049

[$(\mu\text{-H})_3Re_3(CO)_9(\eta^2,\eta^2,\eta^2\text{-}Sc_2C_2@C_{3v}(8)\text{-}C_{82})$]: Face-Capping Cluster Complex of an Endohedral Fullerene

Like a miniature trophy, the complex pictured was obtained as the sole product from the reaction of $Sc_2C_2@C_{3v}(8)\text{-}C_{82}$ and [$(\mu\text{-H})_3Re_3(CO)_{11}(NCMe)$] and characterized by IR, visible/near-infrared, and NMR spectroscopy, mass spectrometry, and X-ray diffraction. Coordination of the Re$_3$ cluster to the unique hexagon oriented perpendicular to the C_3 axis of the fullerene core altered the geometry and electronic properties of $Sc_2C_2@C_{3v}(8)\text{-}C_{82}$.



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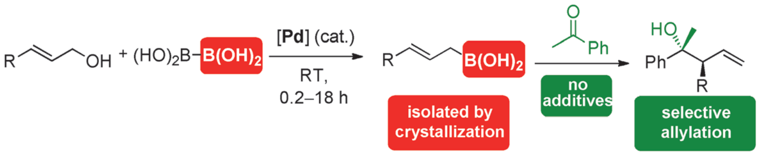

Textbook revision: Allylboronic acids, which are easily prepared from allylic alcohols, react readily and selectively with ketones without Lewis acid catalysts.

Allylboration

M. Raducan, R. Alam,
K. J. Szabó* ———— **13050 – 13053**

Palladium-Catalyzed Synthesis and Isolation of Functionalized Allylboronic Acids: Selective, Direct Allylboration of Ketones

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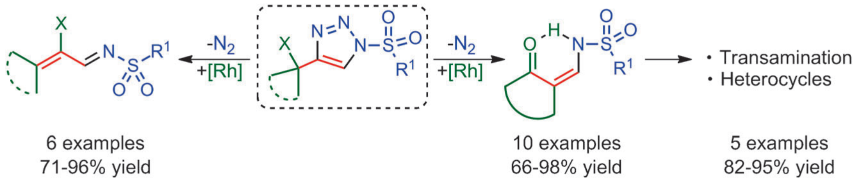

Room for expansion: An efficient, regioselective, and convergent method for the ring expansion and rearrangement of 1-sulfonyl-1,2,3-triazoles under rhodium(II)-catalyzed conditions is described. These denitrogenative reactions form substituted enaminone and olefin-based products (see scheme). The enaminone products can be further functionalized to give various heterocycles and ketone derivatives, thus rendering the sulfonyl triazole traceless.

Rhodium(II) Catalysis

N. Selander, B. T. Worrell,
V. V. Fokin* ———— **13054 – 13057**

Ring Expansion and Rearrangements of Rhodium(II) Azavinyl Carbenes

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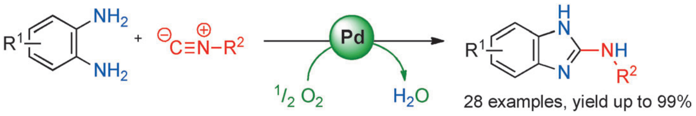


O_2 in, H_2O out: Various diamines and related bisnucleophiles readily undergo oxidative isocyanide insertion with Pd(OAc)$_2$ (1 mol%) as the catalyst and O_2 as the terminal oxidant to give a diverse array of medicinally relevant N heterocycles. The utility of this highly sustainable method is demonstrated by a formal synthesis of the antihistamines astemizole and norastemizole.

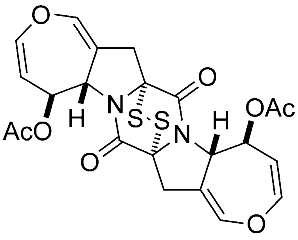
Homogeneous Catalysis

T. Vlaar, R. C. Cioc, P. Mampuys,
B. U. W. Maes,* R. V. A. Orru,*
E. Ruijter* ———— **13058 – 13061**

Sustainable Synthesis of Diverse Privileged Heterocycles by Palladium-Catalyzed Aerobic Oxidative Isocyanide Insertion

---

The key step in this total synthesis of (−)-acetylaranotin is the efficient formation of the characteristic dihydrooxepine ring from cyclohexenone through an unusual vinylogous Rubottom oxidation and a regioselective Baeyer–Villiger oxidation. (−)-Acetylaranotin is obtained in 22 steps from commercially available L-Cbz-tyrosine (Cbz = benzyloxycarbonyl).



(−)-Acetylaranotin

Natural Product Synthesis

H. Fujiwara, T. Kurogi, S. Okaya, K. Okano,
H. Tokuyama* ———— **13062 – 13065**

Total Synthesis of (−)-Acetylaranotin

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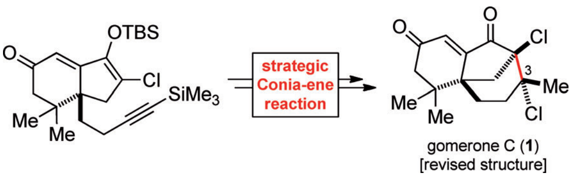
Natural Product Synthesis

N. Huwyler,
E. M. Carreira* ________ **13066 – 13069**

Total Synthesis and Stereochemical Revision of the Chlorinated Sesquiterpene (±)-Gomerone C

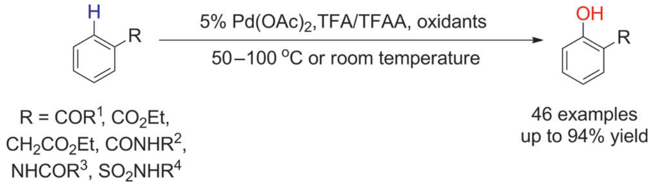


Revised: The total synthesis of gomerone C results in revision of the stereochemical assignment at C3 (see scheme). The synthetic strategy relies on a late-stage Conia-ene reaction, which efficiently forms the bicyclo[3.2.1]octane containing the bridgehead chloride and generates an exocyclic olefin, which can be used as a flexible handle for further elaboration. The two contiguous quaternary centers are installed by means of a Diels–Alder reaction.

Catalytic Hydroxylation

G. Shan, X. Yang, L. Ma,
Y. Rao* ________ **13070 – 13074**

Pd-Catalyzed C–H Oxygenation with TFA/TFAA: Expedient Access to Oxygen-Containing Heterocycles and Late-Stage Drug Modification

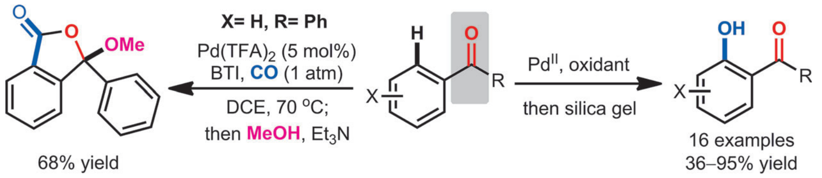


Acid brings the oxygen: A general method for palladium-catalyzed C–H oxygenation has been developed for the facile synthesis of a wide range of functionalized phenols with readily available aryl ketones, benzoates, benzamides, acetanilides, and sulfonamides. A trifluoroacetic acid/trifluoroacetic acid anhydride solvent system serves as the oxygen source and is the critical factor for C–H activation.

C–H Activation

F. Mo, L. J. Trzepkowski,
G. Dong* ________ **13075 – 13079**

Synthesis of *ortho*-Acylphenols through the Palladium-Catalyzed Ketone-Directed Hydroxylation of Arenes

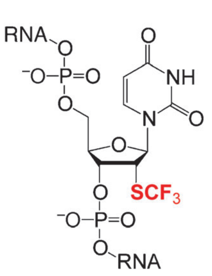


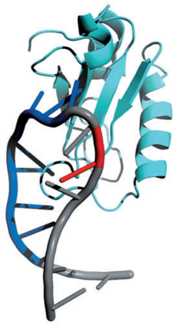
Ketone in charge: A formal ketone-directed palladium-catalyzed *ortho*-hydroxylation of arenes has been developed as an effective approach to access *o*-acylphenols from simple arylketones. A Pd-catalyzed oxidative *ortho*-carbonylation reaction using ketone directing groups to access a ketal–lactone motif is also demonstrated. The ubiquity and versatile nature of ketones make these methods attractive. BTI = PhI(TFA)$_2$; DCE = 1,2-dichloroethane.

RNA Labeling

K. Fauster, C. Kreutz,
R. Micura* ________ **13080 – 13084**

2′-SCF$_3$ Uridine—A Powerful Label for Probing Structure and Function of RNA by ^{19}F NMR Spectroscopy





Fluorishing: The Togni reagent allows efficient synthetic access to fluorine-labeled RNA molecules (see picture). These are in turn highly useful for NMR spectroscopic analyses of secondary and tertiary structures, RNA–protein interactions, and functionality of riboswitch modules.

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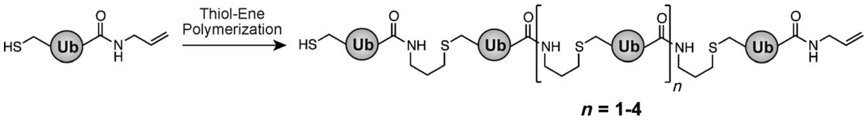
Thiol-Ene Polymerization

V. H. Trang, E. M. Valkevich, S. Minami,
Y. Chen, Y. Ge,
E. R. Strieter* ——— 13085 – 13088

Nonenzymatic Polymerization of Ubiquitin: Single-Step Synthesis and Isolation of Discrete Ubiquitin Oligomers



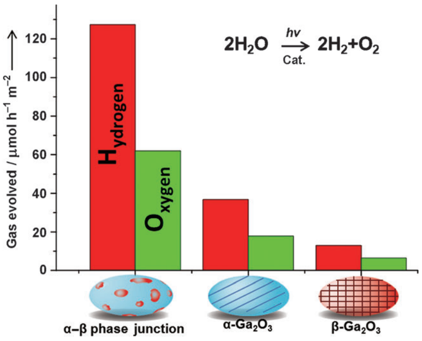
Linked: A method based on thiol-ene chemistry enables the synthesis and purification of ubiquitin oligomers with ≥ 4 units. This approach, which employs free-radical polymerization, can be applied towards the synthesis of homogeneous Lys6-linked ubiquitin oligomers currently inaccessible by enzymatic methods. By using these chains, one can study their roles in the ubiquitin proteasome system and the DNA damage response pathway.

Photocatalysis

X. Wang, Q. Xu, M. Li, S. Shen, X. Wang,
Y. Wang, Z. Feng, J. Shi, H. Han,
C. Li* ——— 13089 – 13092

Photocatalytic Overall Water Splitting Promoted by an α–β phase Junction on Ga_2O_3

Back Cover

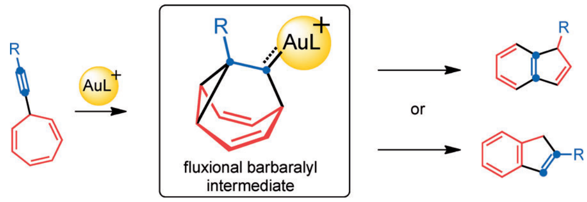


When Alpha met Beta: A tuneable α—β surface phase junction on Ga_2O_3 can significantly improve photocatalytic overall water splitting into H_2 and O_2 over individual α-Ga_2O_3 or β-Ga_2O_3 surface phases. This enhanced photocatalytic performance is mainly attributed to the efficient charge separation and transfer across the α–β phase junction.

Fluxional Intermediates

P. R. McGonigal, C. de León, Y. Wang,
A. Homs, C. R. Solorio-Alvarado,
A. M. Echavarren* ——— 13093 – 13096

Gold for the Generation and Control of Fluxional Barbaralyl Cations



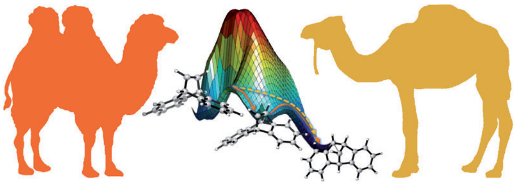
The frog prince with his two identities pales in comparison with the shape-shifting barbaralyl cation, which exists as a mixture of 181 400 degenerate forms. Gold-catalyzed cycloisomerizations of 7-alkynyl cyclohepta-1,3,5-trienes were found to proceed via fluxional barbaralyl intermediates (see scheme). The evolution of the intermediates into 1- or 2-substituted indenes could be controlled by the choice of gold complex.

Photorearrangements

R. A. Matute,
K. N. Houk* ——— 13097 – 13100

The Triplet Surface of the Zimmerman Di-π-Methane Rearrangement of Dibenzobarrelene

Inside Back Cover



High-level calculations: The Zimmerman di-π-methane rearrangement of dibenzobarrelene occurs via a triplet state to form dibenzosemibullvalene, overcoming two barriers connecting two biradicals. The shape of the triplet potential-energy surface shows that the rearrangement involves two transition states. The first triplet diradical intermediate may bypass in the passive of the alkene triplet to the final intermediate (see picture).

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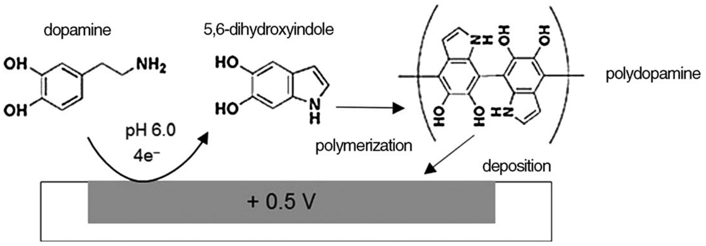
Polydopamine

K. Kang, S. Lee, R. Kim, I. S. Choi,*
Y. Nam* ———— 13101 – 13104

Electrochemically Driven, Electrode-Addressable Formation of Functionalized Polydopamine Films for Neural Interfaces

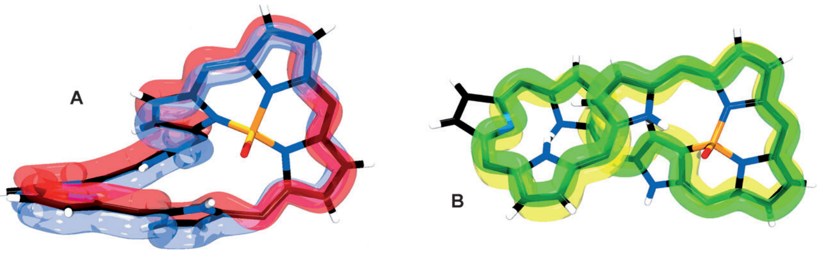


The electrode-specific formation of polydopamine films is achieved by applying positive voltage to the target electrodes at pH 6.0. The functionalization of the films is simultaneously carried out by co-depositing dopamine with molecules of interest onto the electrode.

Antiaromaticity

T. Higashino, B. S. Lee, J. M. Lim, D. Kim,*
A. Osuka* ———— 13105 – 13108

A Möbius Antiaromatic Complex as a Kinetically Controlled Product in Phosphorus Insertion to a [32]Heptaphyrin

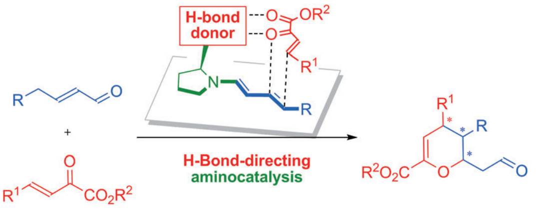


Singly twisted Möbius antiaromatic [34]heptaphyrin **A** and doubly twisted Hückel aromatic [34]heptaphyrin **B** were formed by a phosphorus insertion reaction. **A** rearranges thermally to give the more stable **B** with P=O migration from NNN to NNC, and thus **A** is a rare case of a kinetically controlled Möbius antiaromatic molecule.

Asymmetric Catalysis

Ł. Albrecht, G. Dickmeiss, C. F. Weise,
C. Rodríguez-Escrich,
K. A. Jørgensen* ———— 13109 – 13113

Dienamine-Mediated Inverse-Electron-Demand Hetero-Diels–Alder Reaction by Using an Enantioselective H-Bond-Directing Strategy

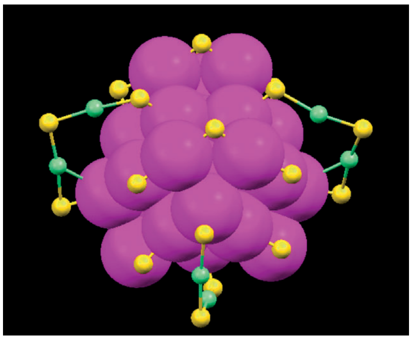


Giving directions: Optically active dihydropyrans bearing three contiguous stereogenic centers can be efficiently prepared by the title reaction. High stereo- and regiocontrol can be achieved by employing a bifunctional H-bond-directing aminocatalyst.

Nanocluster Structure

C. Zeng, H. Qian, T. Li, G. Li, N. L. Rosi,
B. Yoon, R. N. Barnett, R. L. Whetten,
U. Landman, R. Jin* ———— 13114 – 13118

Total Structure and Electronic Properties of the Gold Nanocrystal $Au_{36}(SR)_{24}$



A golden opportunity: The total structure of a $Au_{36}(SR)_{24}$ nanocluster (see figure) reveals an unexpected face-centered-cubic tetrahedral Au_{28} kernel (magenta). The protecting layer exhibits an intriguing combination of binding modes, consisting of four regular arch-like staples and the unprecedented appearance of twelve bridging thiolates (yellow). This unique protecting network and superatom electronic shell structure confer extreme stability and robustness.

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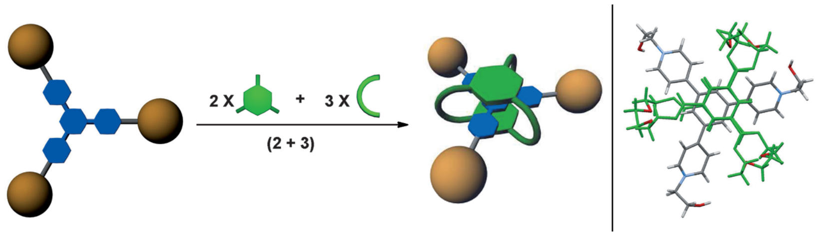

Encaged! Three-terminal interlocked molecular species were obtained by dynamic (2+3) assembly of a cagelike macro-bicycle around a trifurcated tris-pyridinium π guest. The complex is stabilized by π–π interactions and multiple [C–H···O] and [C–H···N] interactions. Uncomplexed guest molecules cocrystallize alongside the threaded complexes in the solid state, thus giving extended π-stacked columns.

Self-Assembly

A. Pun, D. A. Hanifi, G. Kiel, E. O'Brien,
Y. Liu* **13119–13122**

Facile Route to an All-Organic, Triply Threaded, Interlocked Structure by Templated Dynamic Clipping

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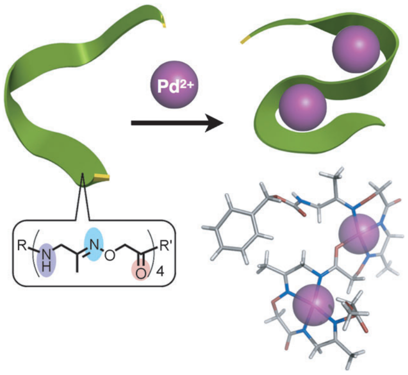


Metal-mediated secondary structures of peptide-based foldamers were constructed using artificial backbone-coordinative oxime peptides. Complexation of the peptides with Pd^{II} afforded several mononuclear and dinuclear secondary structures such as helices and hairpins as confirmed by single-crystal XRD and NMR analyses (see picture).

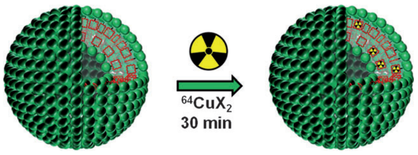
Metallo-Foldamers

S. Tashiro, K. Matsuoka, A. Minoda,
M. Shionoya* **13123–13127**

Metallo-Foldamers with Backbone-Coordinative Oxime Peptides: Control of Secondary Structures

---

PET friendly: Labels for PET imaging are incorporated into completely organic porphysomes by using a fast (30 min), one-pot, high-yielding (>95%) procedure to produce highly stable (>48 h) radiolabeled nanoparticles that show the highest specific activity ever reported for a ^{64}Cu-labeled nanoparticle. These ^{64}Cu-porphysomes can be accurately and noninvasively tracked in vivo.



Imaging Agents

VIP

T. W. Liu, T. D. MacDonald, J. Shi,
B. C. Wilson, G. Zheng* **13128–13131**

Intrinsically Copper-64-Labeled Organic Nanoparticles as Radiotracers

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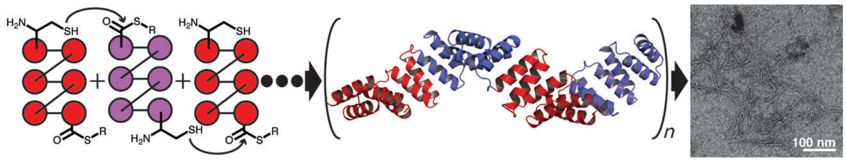

Single-protein-chain superhelical filaments are obtained from monomeric repeat proteins by controlling the chemistry and solvent exposure at their terminal interfaces. The assembly was achieved in aqueous solution, at neutral pH value, and at room temperature. The building block was a recombinantly engineered designed tetratricopeptide repeat protein. Directed head-to-tail self-assembly was driven by genetically encoded orthogonal native chemical ligation.

Biomaterials

J. J. Phillips, C. Millership,
E. R. G. Main* **13132–13135**

Fibrous Nanostructures from the Self-Assembly of Designed Repeat Protein Modules

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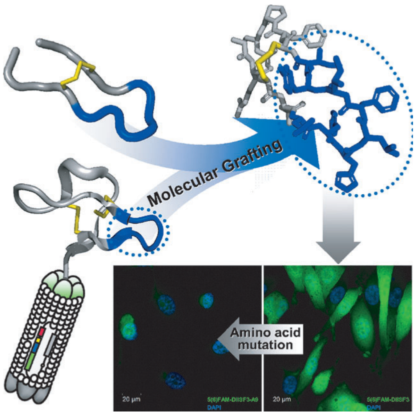
Peptide Design

F. Zoller, A. Markert, P. Barthe, W. Zhao, W. Weichert, V. Askoxylakis, A. Altmann, W. Mier, U. Haberkorn* ___ **13136–13139**

Combination of Phage Display and Molecular Grafting Generates Highly Specific Tumor-Targeting Miniproteins

Frankenstein's peptide: The grafting of the binding domain from miniprotein Min-23 into the sunflower trypsin inhibitor (SFTI-I) peptide scaffold (see scheme) preserved its in vitro and in vivo binding specificity and proteolytic stability. The combination of these peptides was shown to be tumor-specific with a good binding affinity for delta-like ligand 4 (Dll4) protein. The use of SFTI-I as a peptide scaffold is ideal for hit-to-lead development.

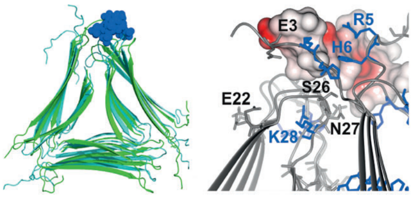


Amyloid β-Peptides

J. Madine, M. J. Pandya, M. R. Hicks, A. Rodger, E. A. Yates, S. E. Radford, D. A. Middleton* ___ **13140–13143**

Site-Specific Identification of an Aβ Fibril–Heparin Interaction Site by Using Solid-State NMR Spectroscopy

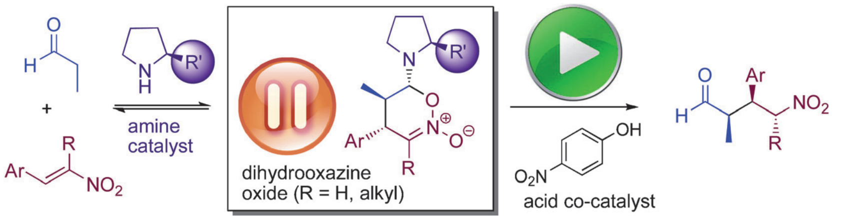
At the surface of $A\beta_{1-40}$ amyloid fibrils that have a threefold molecular symmetry (green in the left picture) a site of interaction of the glycosaminoglycan analogue heparin (blue) was identified. The binding site consists of residues at the N terminus and the turn regions defining the apices of the triangular geometry. Heparin has a lower affinity for $A\beta_{1-40}$ fibrils having twofold molecular symmetry, thus revealing a remarkable morphological selectivity.



Reaction Mechanisms

G. Sahoo, H. Rahaman, Á. Madarász, I. Pápai,* M. Melarto, A. Valkonen, P. M. Pihko* ___ **13144–13148**

Dihydrooxazine Oxides as Key Intermediates in Organocatalytic Michael Additions of Aldehydes to Nitroalkenes



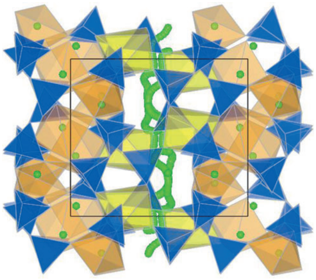
Pause and play: Dihydrooxazine oxides are stable intermediates that are protonated directly, without the intermediacy of the zwitterions, in organocatalytic Michael additions of aldehydes and nitroalkenes (see scheme, R = alkyl). Protonation of these species explains both the role of the acid co-catalyst in these reactions, and the observed stereochemistry when the reaction is conducted with α-alkylnitroalkenes.

Lithium Batteries

J. M. Clark, S. Nishimura, A. Yamada, M. S. Islam* ___ **13149–13153**

High-Voltage Pyrophosphate Cathode: Insights into Local Structure and Lithium-Diffusion Pathways

Ion-transport paths: Combined modeling and neutron diffraction studies provide atomic-scale insights into $Li_2FeP_2O_7$, a material proposed for a new lithium-battery cathode with reversible electrode operation at the highest voltage of all known Fe-based phosphates. The results indicate that Li^+ ions are transported rapidly through a 2D network along the paths shown in green in the picture.



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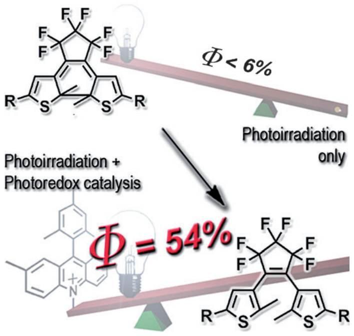
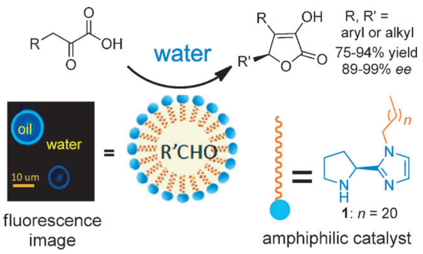


An open and shut case: Photoirradiation of the 9-mesityl-10-methylacridinium ion, which acts as a photoredox catalyst, evoked catalytic cycloreversion of the photochromic 1,2-dithienylethene (DTE) compounds with one order of magnitude enhancement in quantum yields. Mechanistic studies revealed that the back electron transfer and electron transfer from the neutral closed form of DTE compounds to the open-form radical cation are key steps.

Photochromism

S. Lee, Y. You,* K. Ohkubo, S. Fukuzumi,* W. Nam* ________ 13154 – 13158

Photoelectrocatalysis to Improve Cycloreversion Quantum Yields of Photochromic Dithienylethene Compounds



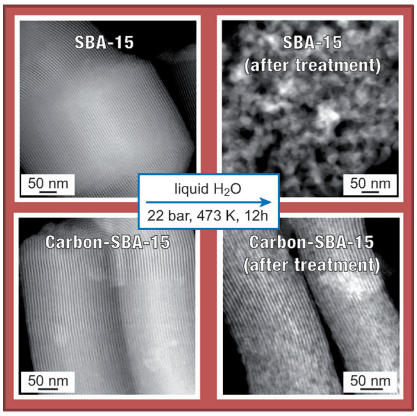
Drop it! A highly enantioselective catalytic cascade reaction of α-ketoacids and aldehydes is achieved using the title catalyst and water as the solvent. Fluorescence imaging shows that the catalyst is mainly distributed on the surface of emulsion droplets. Optically active isotetronic acids can be obtained with this method and the emulsion droplets are responsible for the high reactivity and enantioselectivity.

Asymmetric Catalysis

B. Zhang, Z. Jiang, X. Zhou, S. Lu, J. Li, Y. Liu,* C. Li* ________ 13159 – 13162

The Synthesis of Chiral Isotetronic Acids with Amphiphilic Imidazole/Pyrrolidine Catalysts Assembled in Oil-in-Water Emulsion Droplets

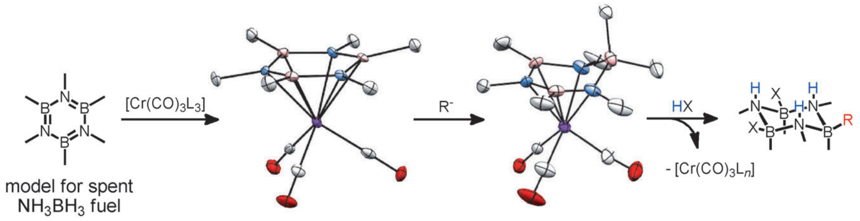
A simple and inexpensive approach is used to coat metal oxide surfaces (SBA-15) with thin films of carbon. These carbon films provide improved hydrothermal stability to oxides, such as silica and alumina, which are not otherwise stable at elevated temperatures in the presence of liquid water (see picture). Furthermore, the carbon film changes the surface chemistry of the support.



Surface Chemistry

H. N. Pham, A. E. Anderson, R. L. Johnson, K. Schmidt-Rohr, A. K. Datye* ________ 13163 – 13167

Improved Hydrothermal Stability of Mesoporous Oxides for Reactions in the Aqueous Phase



Recharging spent BN fuel: {Cr(CO)$_3$} mediates the reduction of borazines by hydride and methyl nucleophiles to generate anionic complexes of dearomatized hexamethylborazine. Subsequent quenching leads to the release of a substituted cyclotriborazane, successfully demonstrating the stepwise reduction of a B=N bond.

Chemical Hydrogen Storage

T. J. Carter, J. W. Kampf, N. K. Szymczak* ________ 13168 – 13172

Reduction of Borazines Mediated by Low-Valent Chromium Species

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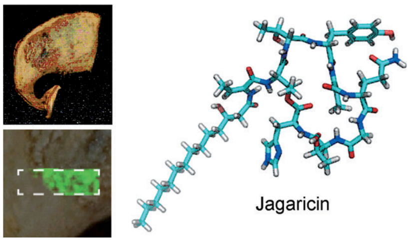
Natural Products

K. Graupner, K. Scherlach,
T. Bretschneider, G. Lackner, M. Roth,
H. Gross, C. Hertweck* __ **13173 – 13177**

Imaging Mass Spectrometry and Genome Mining Reveal Highly Antifungal Virulence Factor of Mushroom Soft Rot Pathogen



Caught in the act: Imaging mass spectrometry of a button mushroom (see picture) infected with the soft rot pathogen *Janthinobacterium agaricidamnosum* in conjunction with genome mining revealed jagaricin as a highly antifungal virulence factor that is not produced under standard cultivation conditions. The structure of jagaricin was rigorously elucidated by a combination of physicochemical analyses, chemical derivatization, and bioinformatics.

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

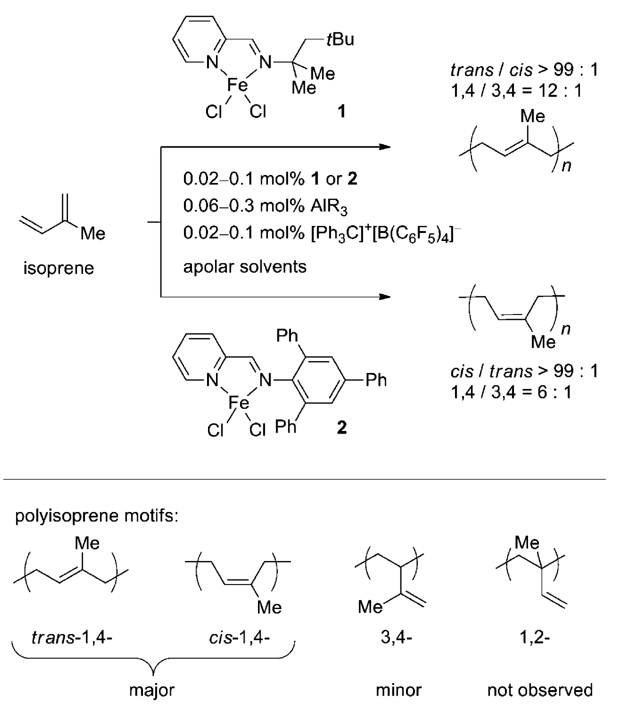
Iron-Catalyzed Polymerization of Isoprene and Other 1,3-Dienes

J. Raynaud, J. Y. Wu,
T. Ritter* ______________ **11805–11808**

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

DOI: 10.1002/anie.201205152

In Scheme 1 of this communication an error was introduced in the course of the editorial typesetting process. Polymerization of isoprene in the presence of catalyst **2** yields 1,4-polyisoprene not with a *trans*/*cis* ratio of > 99:1 but with a *cis*/*trans* ratio of > 99:1, as is shown in the corrected version of Scheme 1 below.



Scheme 1. Polymerization of isoprene using precatalysts **1** and **2**. Complex **1** affords *trans*-1,4-polyisoprene preferentially, whereas complex **2** affords *cis*-1,4-polyisoprene preferentially. The 3,4-insertion motif is a minor component in both polymers (7–8% content for 1, and 15% content for 2). R = *i*Bu for **1** and Et for **2**.

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