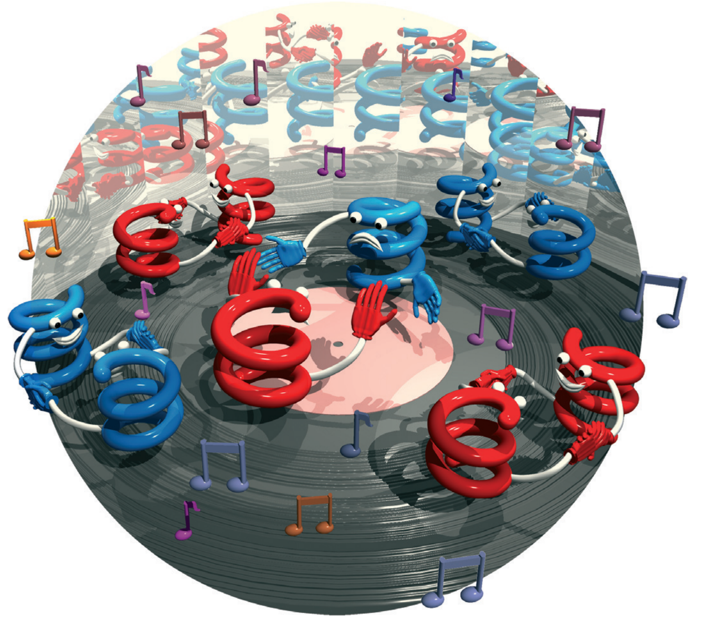
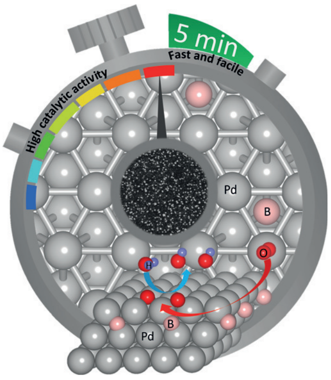
To form couples to get into the dance, …

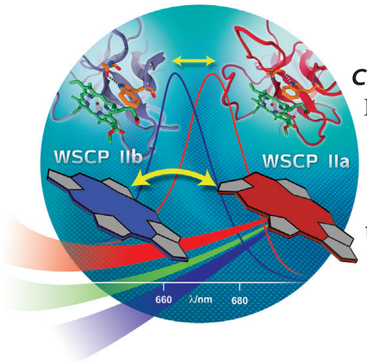


… helices have to have the same handedness. In their Communication on page 6848 ff., I. Huc and co-workers show that at the molecular scale, right-handed foldamer helices with two right hands (in blue) and left-handed helices with two left hands (in red) cannot join hands to form dimeric macrocycles. The outcome is a remote communication of handedness between helices bound in the same macrocycle. Graphic credit: Dr. V. Maurizot.

Oxygen Reduction

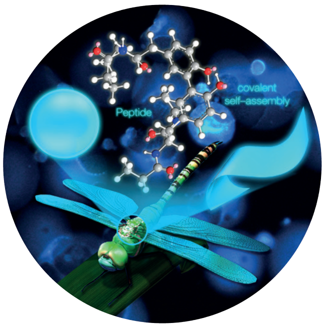
H. Su, H. Sato, and co-workers show in their Communication on page 6842 ff. that B doping of Pd nanoparticles lowers the barrier to O_2 dissociation for the oxygen reduction reaction (ORR).





Chlorophyll

In their Communication on page 6901 ff., D. Noy and co-workers provide the first direct demonstration that aromatic ring deformation of the chlorophyll macrocycle causes significant absorption red shifts.



Nanostructures

The direct synthesis of fluorescent peptide hollow nanocages and free-standing thin films by installation of a biomimetic dityrosine bond in short peptide assemblies is reported by D.-P. Kim and co-workers in their Communication on page 6925 ff.

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Editorial

“… Just over 50 years ago, Robert S. Cahn, Sir Christopher Ingold, and Vladimir Prelog published the Review ‘Specification of Molecular Chirality’ in Angewandte Chemie. The article would change the everyday language of the chemist by bringing the term chirality to their attention. Today, the CIP system is the specification tool in organic chemistry …”
Read more in the Editorial by Günter Helmchen.

Service

Author Profile

“If I were not a scientist, I would be bored. My motto is ‘Keep it short!’ …”
This and more about Jeroen S. Dickschat can be found on page 6818.

News


D. Bourissou


C. Picart


E. Métay


G. Nocton


V. Fourmond


H. F. Sleiman


I. Aprahamian

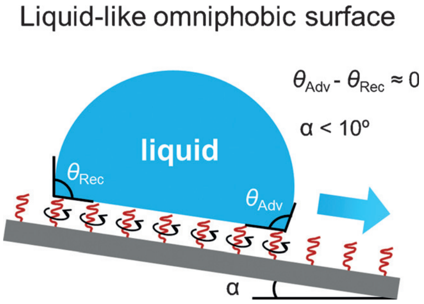
Highlights

Omniphobic Surfaces

S. Wooh, D. Vollmer* ____ **6822 – 6824**

Silicone Brushes: Omniphobic Surfaces with Low Sliding Angles

Losing contact: Omniphobic surfaces can be readily produced by acid-catalyzed graft polycondensation of dimethyldimethoxysilane (PDMS). Droplets show a very small contact angle hysteresis as well as a low sliding angle of only a few degrees. The nm-thick PDMS layer is neither easily washed away nor depleted. This method offers a novel approach towards the preparation of super-liquid-repelling surfaces.



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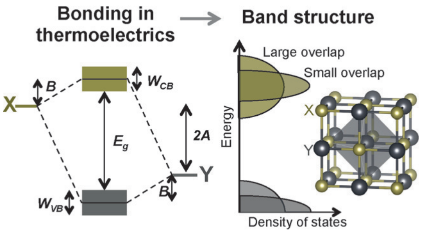
Reviews

Solid-State Chemistry

W. G. Zeier, A. Zevalkink, Z. M. Gibbs, G. Hautier, M. G. Kanatzidis,* G. J. Snyder* ______ 6826 – 6841

Thinking Like a Chemist: Intuition in Thermoelectric Materials



Bonding interactions in thermoelectrics: Chemical bonding concepts and molecular orbital theory are used to understand electronic structures and the electronic and thermal transport in semiconductors. Emphasis is placed on the influence of local bonding interactions, such as bond length and orbital overlap, coordination environment, and the expression of lone-pairs.

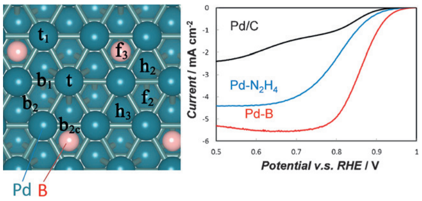
Communications

Oxygen Reduction Reaction

T. T. Vo Doan, J. Wang, K. C. Poon, D. C. L. Tan, B. Khezri, R. D. Webster, H. Su,* H. Sato* ______ 6842 – 6847

Theoretical Modelling and Facile Synthesis of a Highly Active Boron-Doped Palladium Catalyst for the Oxygen Reduction Reaction

Frontispiece



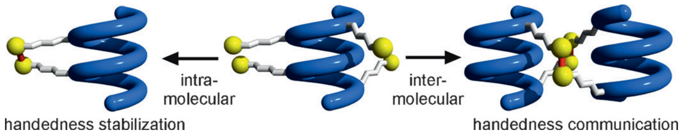
Better with a B in its bonnet: Theoretical modelling shows that B doping negatively shifts the surface core level of Pd and lowers the barrier to O_2 dissociation for the oxygen reduction reaction (ORR). A B-doped Pd nanoparticle catalyst was then rationally designed, synthesized in a facile manner by electroless deposition, and shown to be a highly active ORR catalyst compared to commercial Pd and Pt catalysts.

Chirality

C. Tsiamantas, X. de Hatten, C. Douat, B. Kauffmann, V. Maurizot, H. Ihara, M. Takafuji, N. Metzler-Nolte, I. Huc* ______ 6848 – 6852

Selective Dynamic Assembly of Disulfide Macrocyclic Helical Foldamers with Remote Communication of Handedness

Front Cover



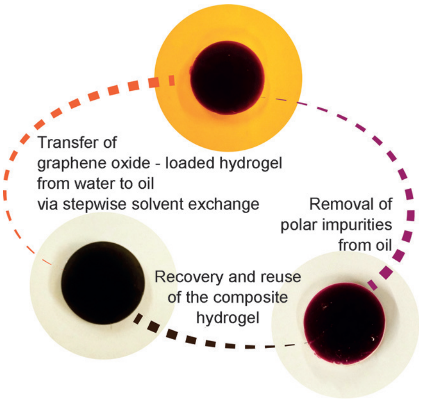
Hand signals: Remote chiral communication of handedness is conveyed between aromatic helical foldamers through disulfide-bridged side chains without any direct contact between helices.

Oil Decontamination

C. Cheng, D. Wang* ______ **6853 – 6857**

Hydrogel-Assisted Transfer of Graphene Oxides into Nonpolar Organic Media for Oil Decontamination

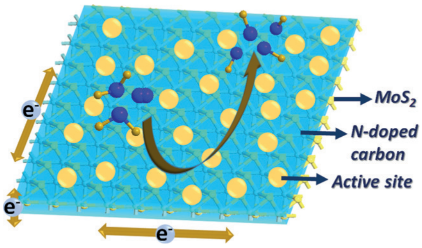
New adsorption strategy: Graphene oxide (GO) loaded agarose hydrogels are readily transferred from water to oil by stepwise solvent exchange, which enables the GOs, loaded in the agarose network, to effectively adsorb polar impurities in oil.



Noble-Metal-Free Electrocatalysts

K. Yuan, X. Zhuang, H. Fu, G. Brunklaus, M. Forster, Y. Chen, X. Feng,* U. Scherf* ______ **6858 – 6863**

Two-Dimensional Core-Shelled Porous Hybrids as Highly Efficient Catalysts for the Oxygen Reduction Reaction

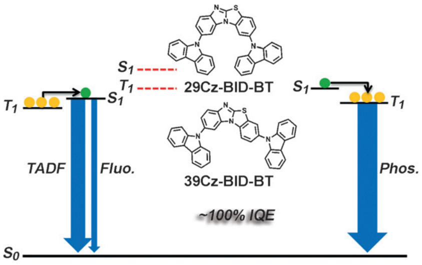


Hierarchically porous MoS_2/N-doped carbon hybrids were fabricated by pyrolysis of MoS_2-templated microporous polymer sandwiches. The hybrids are characterized by high specific surface areas and aspect ratios and show promising oxygen reduction reaction and supercapacitor performances.

Light-Emitting Diodes

L.-S. Cui, J. U. Kim, H. Nomura, H. Nakanotani, C. Adachi* **6864 – 6868**

Benzimidazobenzothiazole-Based Bipolar Hosts to Harvest Nearly All of the Excitons from Blue Delayed Fluorescence and Phosphorescent Organic Light-Emitting Diodes

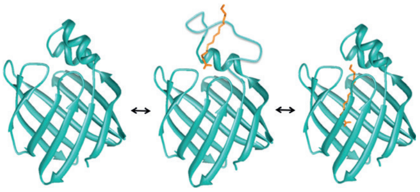


Gotta catch them all: Over 20% external quantum efficiencies were achieved in both blue thermally activated delayed fluorescence (TADF) and phosphorescent organic light-emitting diodes (OLEDs) using benzimidazobenzothiazole bipolar host materials.

Fatty Acid Binding Proteins

T. Xiao, J. Fan, H. Zhou, Q. Lin, D. Yang* ______ **6869 – 6872**

Local Unfolding of Fatty Acid Binding Protein to Allow Ligand Entry for Binding

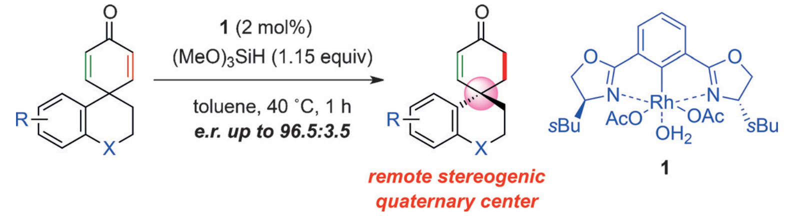


Open and shut case: Fatty acid binding proteins exist mainly in a closed conformation that is in equilibrium with two minor states: one native-like and one locally unfolded. Local unfolding of the second helix generates an opening to allow ligands to enter or leave the protein cavity and controls ligand association and dissociation rates.

Desymmetrization

Y. Naganawa,* M. Kawagishi, J.-i. Ito, H. Nishiyama* ———— 6873 – 6876

Asymmetric Induction at Remote Quaternary Centers of Cyclohexadienones by Rhodium-Catalyzed Conjugate Hydrosilylation



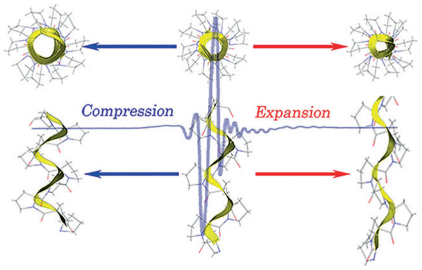
Remote control: The catalytic asymmetric construction of a quaternary stereocenter—one of the most challenging issues in synthetic organic chemistry—was possible by the desymmetrizing conjugate hydrosilylation of prochiral differently γ,γ-disubstituted cyclohexadienones in the presence of a chiral rhodium complex (see scheme). The cyclohexenone products with a remote stereogenic quaternary center were formed with high stereoselectivity.

Biopolymers

M. T. Ruggiero, J. Sibik, R. Orlando, J. A. Zeitler, T. M. Korter* ———— 6877 – 6881

Measuring the Elasticity of Poly-L-Proline Helices with Terahertz Spectroscopy

Inside Cover

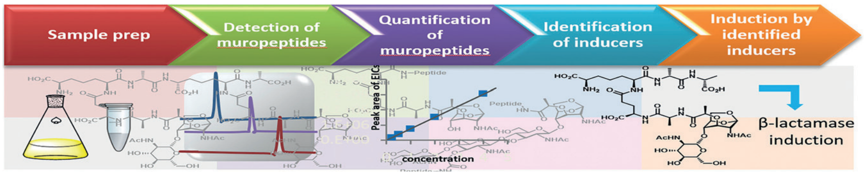


Spring fever: The experimental Young's moduli of two known poly-L-proline helical forms were determined in the crystalline state by using an approach that combines terahertz time-domain spectroscopy, X-ray diffraction, and solid-state density functional theory. Contrary to expectations, the helices were found to be considerably less rigid than many other natural and synthetic polymers, as well as differing greatly from each other.

Peptidoglycan

M. Lee, S. Dhar, S. De Benedetti, D. Hesek, B. Boggess, B. Blázquez, K. Mathee,* S. Mobashery* ———— 6882 – 6886

Muropeptides in *Pseudomonas aeruginosa* and their Role as Elicitors of β-Lactam-Antibiotic Resistance

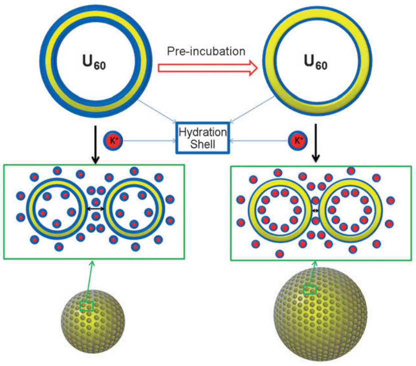


Muropeptides: A total of 20 muropeptides, which are breakdown products of peptidoglycan, were isolated from *Pseudomonas aeruginosa* and their structures were elucidated. The least abundant of these metabolites is present at 100 and the most abundant at 55 000 molecules per bacterium. Two of these compounds were shown to be involved in the induction of β-lactamase expression. This effect is the basis for resistance to β-lactam antibiotics in *P. aeruginosa*.

Ion Channel Mimics

Y. Gao, J. E. S. Szymanowski, X. Sun, P. C. Burns,* T. Liu* ———— 6887 – 6891

Thermal Responsive Ion Selectivity of Uranyl Peroxide Nanocages: An Inorganic Mimic of K^+ Ion Channels

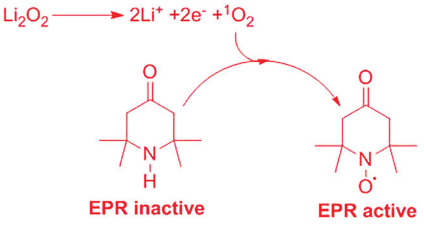


U_{60} clusters demonstrate tunable ion selectivity at different temperatures that can mimic the function of protein ion channels. Adjustable permeability toward different alkali ions is mainly attributed to the thermal responsiveness of the U_{60} cluster's hydration shell thickness.

Lithium–Air Batteries

J. Wandt,* P. Jakes,* J. Granwehr,
H. A. Gasteiger, R.-A. Eichel **6892 – 6895**

Singlet Oxygen Formation during the Charging Process of an Aprotic Lithium–Oxygen Battery

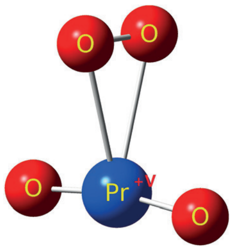


The missing link: Evidence found for the evolution of substantial amounts of highly reactive singlet oxygen at potentials above 3.5 V during the charging of Li–O_2 cells (see scheme) might complete our understanding of electrolyte degradation and carbon corrosion reactions hampering the development of reversible lithium–air batteries. Measures to eliminate ${}^1O_2$-induced side reactions could thus improve the cycle life of such batteries.

Lanthanides

Q. Zhang, S.-X. Hu, H. Qu, J. Su, G. Wang,
J.-B. Lu, M. Chen, M. Zhou,*
J. Li* **6896 – 6900**

Pentavalent Lanthanide Compounds: Formation and Characterization of Praseodymium(V) Oxides



Very im-Pr-essive: Infrared spectroscopic studies and quantum chemical calculations show that PrO_4 and PrO_2^+ oxide species involve the unprecedented Pr^V oxidation state. In the gas phase, species such as $[(PrO)^+(O_2)_n]$ and $[(PrO_2)^+(O_2)_n]$ ($n = 1$–7), which contain the linear PrO_2^+ ion, are formed. These studies demonstrate that the pentavalent state is viable for lanthanide elements in a suitable coordination environment.

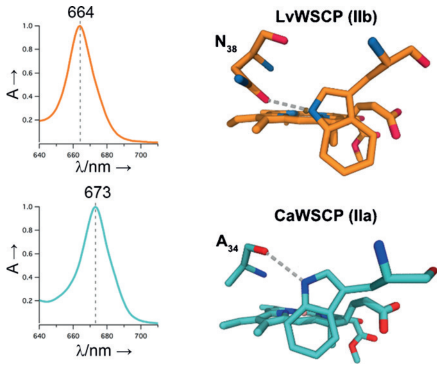
Chlorophyll

D. Bednarczyk, O. Dym, V. Prabahar,
Y. Peleg, D. H. Pike, D. Noy* **6901 – 6905**

Fine Tuning of Chlorophyll Spectra by Protein-Induced Ring Deformation

Inside Back Cover

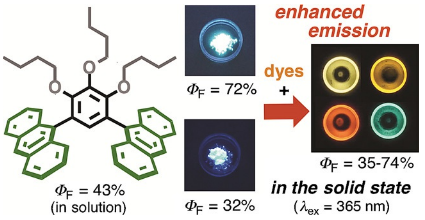
A change for the redder: A new crystal structure of type IIa water-soluble chlorophyll binding protein (WSCP) from cauliflower is compared to the type IIb WSCP structure. It reveals how ring deformation is exploited for red shifting the red-most chlorophyll absorption peak. A single mutation of asparagine to alanine changes the hydrogen-bonding pattern of a tryptophan residue repositioning it to perturb the planarity of the chlorophyll macrocycle.



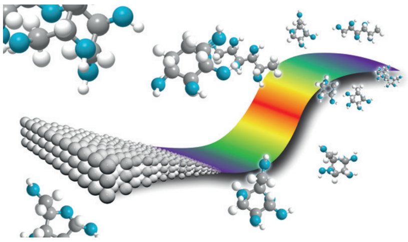
Solid-State Fluorescence

S. Sekiguchi, K. Kondo, Y. Sei, M. Akita,
M. Yoshizawa* **6906 – 6910**

Engineering Stacks of V-Shaped Polyaromatic Compounds with Alkyl Chains for Enhanced Emission in the Solid State



Stacking up: Two types of fluorescent solids were generated from a V-shaped bisanthracene derivative with three butyl groups. The highly emissive solid ($\Phi_F > 70\%$) adopts a head-to-head arrangement with discrete stacks of the anthracene moieties. Furthermore, large enhancements of dye emissions (up to 45-fold) were achieved in the solid state by adding various fluorescent dyes to the V-shaped compound.



Color vision: A photonic crystal that recognizes saccharides specifically allows abundant optical information to be obtained in the form of structural color. The use of a multiangle analysis method enables fluorescence signals in various spectral regions to be differentially enhanced. This approach enabled 12 saccharides with similar structures, as well as saccharides at different concentrations and in mixtures, to be successfully discriminated.

Analytical Methods

M. Qin, Y. Huang, Y. Li, M. Su, B. Chen,
H. Sun, P. Yong, C. Ye, F. Li,*
Y. Song* ________ **6911 – 6914**

A Rainbow Structural-Color Chip for Multisaccharide Recognition

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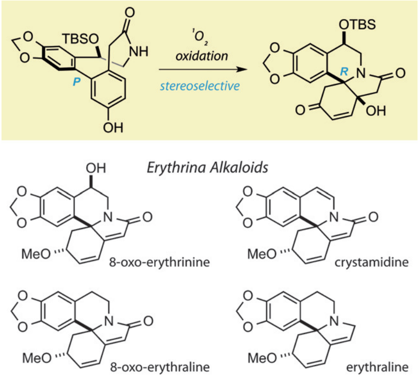

Then there were four: The fixed atropisomeric stereochemistry of a medium-sized biaryl intermediate was fully transferred to the central point chirality of a helical intermediate as a result of singlet oxygen oxidation and transannulation. This finding enabled the asymmetric synthesis of a common intermediate, which is amenable to a variety of oxidation-reduction transformations, thus giving rise to the first asymmetric syntheses of four erythrina alkaloids.

Total Synthesis

H. Umihara, T. Yoshino, J. Shimokawa,
M. Kitamura,*
T. Fukuyama* ________ **6915 – 6918**

Development of a Divergent Synthetic Route to the Erythrina Alkaloids: Asymmetric Syntheses of 8-Oxo-erythrinine, Crystamidine, 8-Oxo-erythraline, and Erythraline

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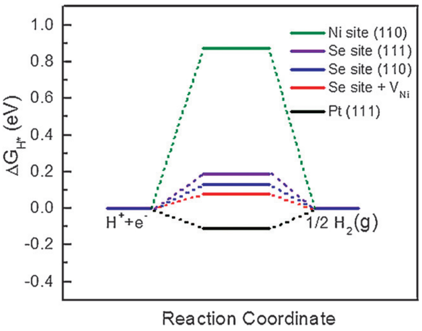


Excess selenium: Although the under-coordinated surface metal centers of pyrite-type transition-metal dichalcogenides have been suggested to be the main active sites for H_2 production, the ligand composition also plays a decisive role. The Se sites and excessive Se atoms on the surface of pyrite-type $NiSe_2$ are now corroborated to be the active sites for electrochemical H_2 evolution.

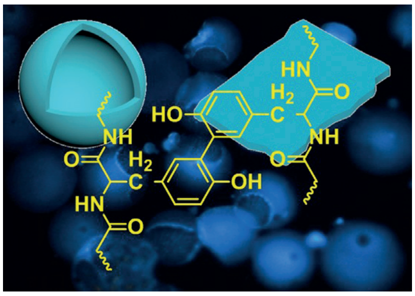
Electrocatalysis

F. M. Wang, Y. Li, T. A. Shifa, K. Liu,
F. Wang, Z. Wang, P. Xu, Q. Wang,
J. He* ________ **6919 – 6924**

Selenium-Enriched Nickel Selenide Nanosheets as a Robust Electrocatalyst for Hydrogen Generation

---

Covalent self-assembly of peptides: Direct synthesis of fluorescent peptide nanocapsules and free-standing thin films by bioinspired one-step photopolymerization of peptides is reported. The crosslinked peptides showed superior mechanical strength compared to non-covalent peptides, and were used to design robust peptidosomes.



Nanocapsules

K.-I. Min, G. Yun, Y. Jang, K.-R. Kim,
Y. H. Ko, H.-S. Jang, Y.-S. Lee, K. Kim,
D.-P. Kim* ________ **6925 – 6928**

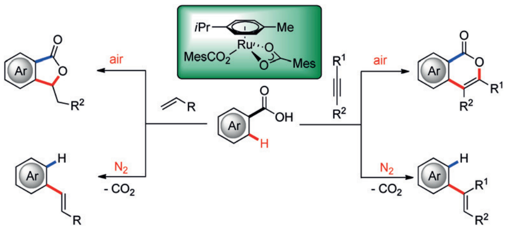
Covalent Self-Assembly and One-Step Photocrosslinking of Tyrosine-Rich Oligopeptides to Form Diverse Nanostructures

Back Cover

C–H Activation

N. Y. P. Kumar, A. Bechtoldt,
K. Raghuvanshi,
L. Ackermann* ________ **6929 – 6932**

Ruthenium(II)-Catalyzed Decarboxylative C–H Activation: Versatile Routes to *meta*-Alkenylated Arenes

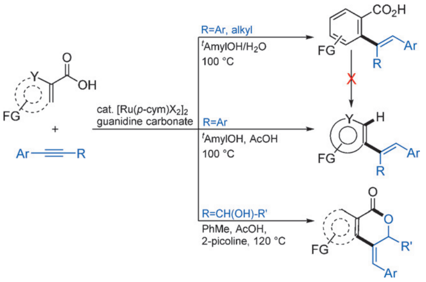


Two birds with one Ru: Ruthenium(II) catalysis enabled decarboxylative C–H olefinations by carboxylate assistance at low temperature. It is applicable to both alkenes for oxidative olefinations, as well as alkynes for redox-neutral hydroarylations. Neither silver nor copper salts are required and *meta*-substituted products can be accessed with this method.

C–H Activation

L. Huang, A. Biafora, G. Zhang,
V. Bragoni, L. J. Gooßen* ___ **6933 – 6937**

Regioselective C–H Hydroarylation of Internal Alkynes with Arenecarboxylates: Carboxylates as Deciduous Directing Groups

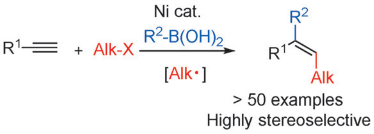


Make the switch: A simple ruthenium(II) complex catalyzes the regioselective hydroarylation of internal alkynes with benzoic acids. The conditions can be tuned to switch from a non-decarboxylative to a decarboxylative pathway. Aryl(alkyl)acetylenes react regioselectively with formation of the alkyl-branched 2-vinylbenzoic acids, and propargylic alcohols cyclize to γ-alkylidene-δ-lactones.

Alkynes

Z. Li, A. García-Domínguez,
C. Nevado* ____________ **6938 – 6941**

Nickel-Catalyzed Stereoselective Dicarbofunctionalization of Alkynes

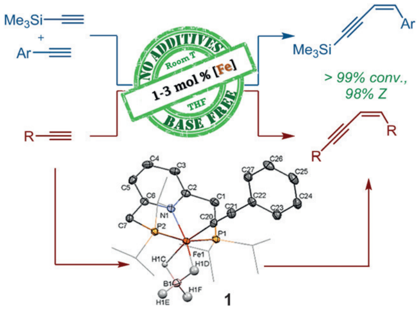


Triple whammy: A nickel-catalyzed three-component reaction involving terminal alkynes, boronic acids, and alkyl halides produces trisubstituted alkenes in a highly regio- and stereocontrolled fashion. The reaction, devoid of air- and moisture-sensitive organometallic reagents and catalysts, is operationally simple and offers a broad scope and functional-group tolerance.

C–C coupling

O. Rivada-Wheelaghan, S. Chakraborty,
L. J. W. Shimon, Y. Ben-David,
D. Milstein* ____________ **6942 – 6945**

Z-Selective (Cross-)Dimerization of Terminal Alkynes Catalyzed by an Iron Complex

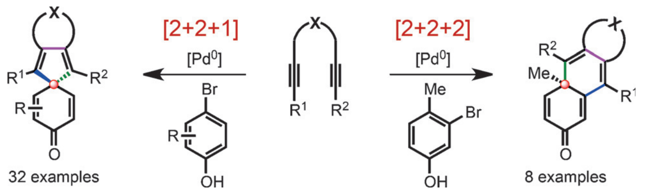


Ironing out the kinks: Iron-catalyzed homocoupling of terminal alkynes and cross-dimerization of aryl acetylenes with a silylacetylene avoided problems of precious metal catalysis, usage of additives, and selectivity issues encountered with other catalysts in the past. The complex [Fe(H)(BH$_4$)(*i*Pr-PNP)] (**1**) operated efficiently at room temperature without a base or other additives to give the corresponding products with *Z* selectivity in 79–99 % yield (see scheme).

Cyclizations

L. Bai, Y. Yuan, J. Liu, J. Wu, L. Han, H. Wang, Y. Wang, X. Luan* **6946 – 6950**

Palladium(0)-Catalyzed Intermolecular Carbocyclization of (1,*n*)-Diynes and Bromophenols: An Efficient Route to Tricyclic Scaffolds

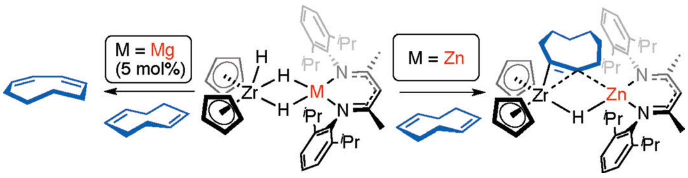


Tricycles: A novel palladium(0)-catalyzed dearomative cyclization reaction of bromophenols with (1,*n*)-diynes ($n = 6$–9) has been developed for building two new types of tricyclic architectures containing a quaternary carbon center. This method employs inexpensive bromophenols and easily accessible diynes and tolerates various functional groups. Preliminary results with commercially available chiral ligands indicate that enantioselective variants are feasible.

Zirconocenes

M. J. Butler, A. J. P. White, M. R. Crimmin* **6951 – 6953**

Isomerization of Cyclooctadiene to Cyclooctyne with a Zinc/Zirconium Heterobimetallic Complex

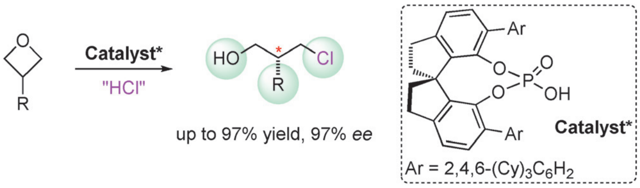


Zn/Zr shows its mettle: Reaction of a Zn/Zr heterobimetallic complex with 1,5-cyclooctadiene (1,5-COD) results in slow isomerization to 1,3-cyclooctadiene (1,3-COD), along with the formation of a new complex that includes a cyclooctyne ligand bridging two metal centers. While analogous Mg/Zr and Al/Zr heterobimetallic complexes are competent for the catalytic isomerization of 1,5-COD to 1,3-COD, only the zinc species gives the cyclooctyne adduct.

Organocatalysis

W. Yang, Z. Wang, J. Sun* **6954 – 6958**

Enantioselective Oxetane Ring Opening with Chloride: Unusual Use of Wet Molecular Sieves for the Controlled Release of HCl

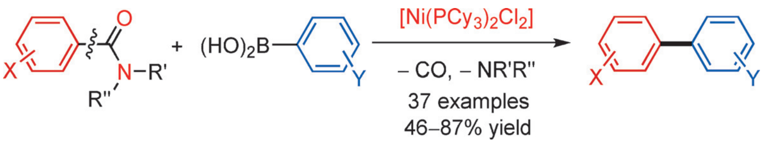


The enantioselective ring opening of oxetanes with chloride provides access to a range of highly functionalized three-carbon building blocks. The use of a new catalyst in combination with wet molecular sieves for the controlled release of HCl leads to high enantioselectivities.

Suzuki–Miyaura Coupling

S. Shi, G. Meng, M. Szostak* **6959 – 6963**

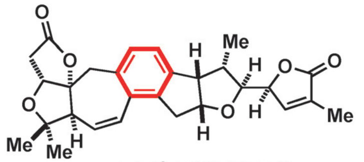
Synthesis of Biaryls through Nickel-Catalyzed Suzuki–Miyaura Coupling of Amides by Carbon–Nitrogen Bond Cleavage



Breaking and making: The first nickel-catalyzed Suzuki–Miyaura coupling of amides for the synthesis of biaryl compounds through N–C amide bond cleavage is reported. The reaction tolerates a wide range of sensitive and electronically diverse substituents on both coupling partners.

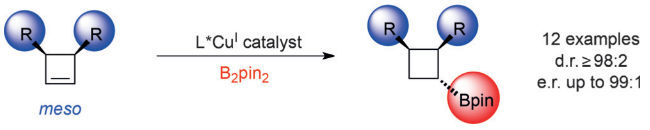
Natural Product Synthesis

Going round in circles: The first total synthesis of rubriflordilactone B, a heptacyclic *Schisandraceae* bisnortriterpenoid with a tetrasubstituted arene moiety, was accomplished in a highly convergent fashion. A 6π electrocyclization/aromatization process was exploited as a key step.



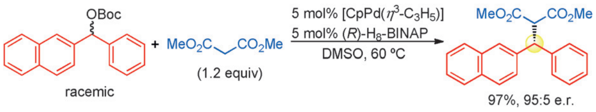
rubriflordilactone B

Asymmetric Catalysis



Squared away: The first catalytic enantioselective synthesis of cyclobutylboronates was achieved by using a chiral copper(I) complex. A broad variety of cyclobutanes are prepared with high levels of diastereo- and enantiocontrol. Moreover, this is the first method for the enantioselective desymmetrization of *meso*-cyclobutenes to prepare chiral cyclobutanes.

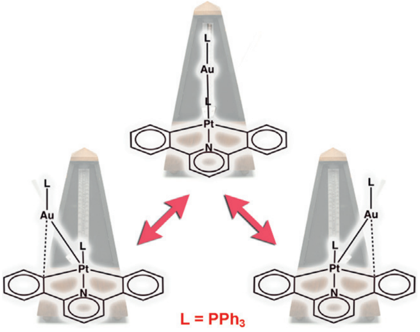
Asymmetric Catalysis



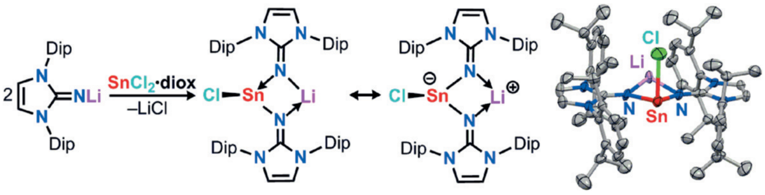
New dynamics: A Pd/(*R*)-H$_8$-BINAP-catalyzed asymmetric benzylic alkylation of active methylene compounds has been developed. The reaction proceeds without the use of an external base, and the starting racemic diarylmethyl carbonates are converted into optically active coupling products, containing a benzylic chiral stereocenter, by a dynamic kinetic asymmetric transformation.

Heterobimetallic Complexes

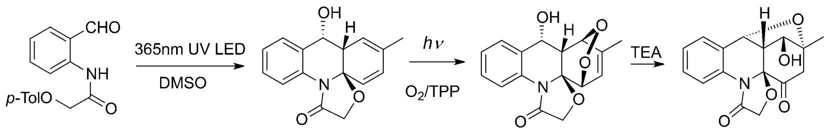
The swing of a rare metronome: A bimetallic Pt–Au complex was synthesized and its electronic structure studied by DFT methods. In solution, it showed unusual fluxional behavior involving the formation and cleavage of Au–C bonds (see picture). The complex can be viewed as a model for an intermediate in a transmetalation process promoted by cooperative metal catalysts, whereby the Pt–Au bond anchors the two metallic fragments.



Tin Compounds



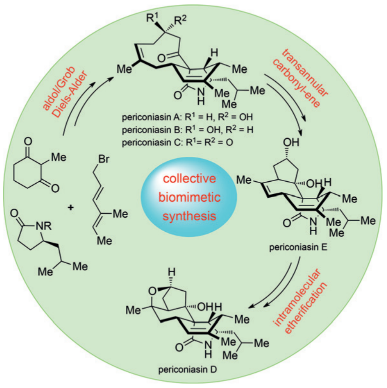
Ambiphilic tin(II): An elusive bis(imino)stannylenoid, a tin carbenoid analogue, was synthesized by using the highly basic imidazolin-2-imino group. Through investigations into the reactivity of the system and computational studies, the ambiphilic character of the stannylenoid was demonstrated.



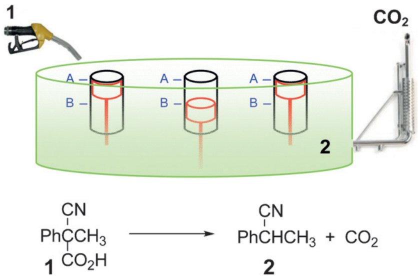
I'm so excited: Photoinduced dearomatization of arenes was achieved through intramolecular cycloaddition with aza-*o*-xylylenes generated by excited-state intramolecular proton transfer in the readily available photoprecursors. The [2+4] topology of this cycloaddition is unprecedented for photo-dearomatizations of benzenoid aromatic carbocycles and produces the novel heterocycles cyclohexadieno-oxazolidino-quinolinols.

Photochemistry

Family members: The collective total syntheses of periconiasins A–E, a group of newly identified cytochalasans, are presented. An array of rationally designed or bioinspired transformations, including a tandem aldol condensation/Grob fragmentation, a Diels–Alder, and a transannular carbonyl–ene reaction allows rapid access to the targets from readily accessible building blocks.



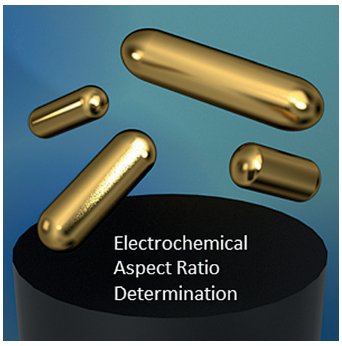
Natural Products



Poetry in motion: Carboxylic acid **1** was found to be a convenient fuel for the operation of a molecular switch that moves under the influence of protonation–deprotonation steps. The cyclic motions of the catenane switch were induced solely by the chemical energy supplied by the decarboxylation of **1**, without recourse to additional stimuli.

Molecular Switches

Shaping up: The electrochemical determination of the aspect ratio of gold nanorods on an individual basis through nano-impact experiments is demonstrated. The measured dimensions are in excellent agreement with electron microscopy results, establishing the use of nanoparticle impact electrochemistry for the characterization of anisotropic nanomaterials.



Gold Nanorod Analysis

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

Enzyme- and Ruthenium-Catalyzed Enantioselective Transformation of α-Allenic Alcohols into 2,3-Dihydrofurans

B. Yang, C. Zhu, Y. Qiu, J.-E. Bäckvall* **5568–5572**

Angew. Chem. Int. Ed. **2016**, *55*

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Reference [14] of this Communication has to be corrected as shown below: In part a), "(where the allene is the medium group)" was added for clarification, and additional studies are cited in part b).

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[14] a) After the completion of this study, a KR of allenic alcohols (where the allene is the medium group) was reported that gave good enantioselectivity in 1–5 days: W. Li, Z. Lin, L. Chen, X. Tian, Y. Wang, S.-H. Huang, R. Hong, *Tetrahedron Lett.* **2016**, *57*, 603. b) For efficient enzymatic kinetic resolution of α-allenic alcohols, where the allene is the large group, see: D. Xu, Z. Li, S. Ma, *Chem. Eur. J.* **2002**, *8*, 5012; D. Xu, Z. Li, S. Ma, *Tetrahedron: Asymmetry* **2003**, *14*, 3657.