Service

Author Profile

"My not-so-secret passion is electronic gadgets. The greatest scientific advance in the next decade will be catalytic C–O activation. …"
This and more about Oliver Reiser can be found on page 11416.

News

T. Nozoe

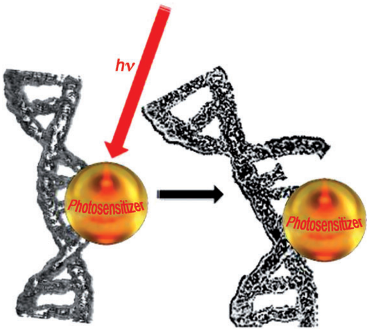
A. B. Holmes

Books

Highlights

Cancer Therapy

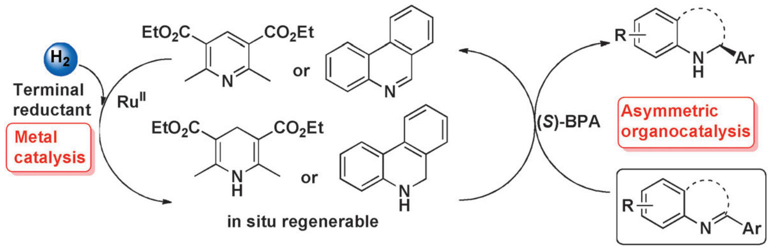
Cell death by visible light: Photodynamic therapy (PDT) is a relatively underemployed method for treatment of diseases including cancer. Recent improvements in synthetic and analysis methods of metal complexes provide for red-light-activated drugs with potential application in PDT (see picture).



Relay Catalysis

F. Shi, L.-Z. Gong* ________ **11423 – 11425**

Relay Catalysis Enables Hydrogen Gas to Participate in Asymmetric Organocatalytic Hydrogenation



Teamwork: Through relay catalysis by a Ru^{II} complex and a chiral phosphoric acid ((*S*)-BPA in the scheme) recently developed by Zhou's group, hydrogen gas can act as the terminal reductant in the catalytic asymmetric hydrogenation of heterocycles. This is a completely new concept in the area of asymmetric hydrogenation.

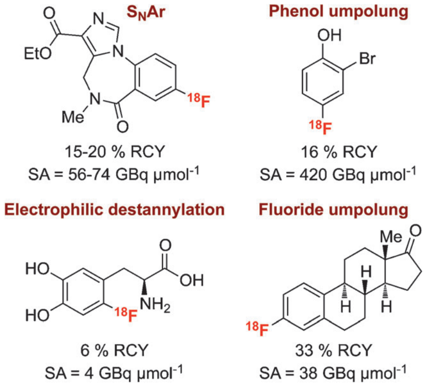
Minireviews

^{18}F Radiochemistry

M. Tredwell,*
V. Gouverneur* ________ **11426 – 11437**

^{18}F Labeling of Arenes

On the radio: The ^{18}F labeling of arenes is formally carried out by nucleophilic fluorination with [^{18}F]fluoride (S_NAr) and electrophilic fluorination with [^{18}F]F_2, [^{18}F]OF, or [^{18}F]NF reagents. Imposing a reactivity switch (umpolung) on either the ^{18}F source or the arene substrate allows for the long-awaited labeling of electron-neutral and electron-rich arenes with [^{18}F]fluorides (see examples; RCY = radiochemical yield, SA = specific activity).

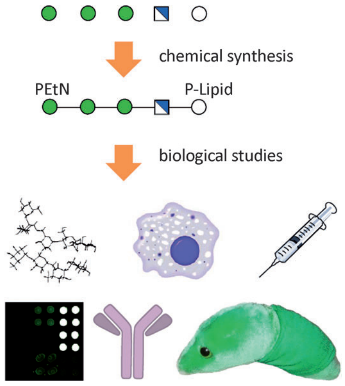


Reviews

Posttranslational Modifications

Y.-H. Tsai, X. Liu,
P. H. Seeberger* ________ **11438 – 11456**

Chemical Biology of Glycosylphosphatidylinositol Anchors



Protein anchors: Glycosylphosphatidylinositol (GPI) glycolipids anchor proteins on the extracellular membrane. This mode of protein posttranslational modification is common and important in eukaryotes. Insight into the structure and function of GPIs is discussed, with an emphasis on the recent progress in using structurally defined synthetic GPIs as tools to dissect their biological functions.

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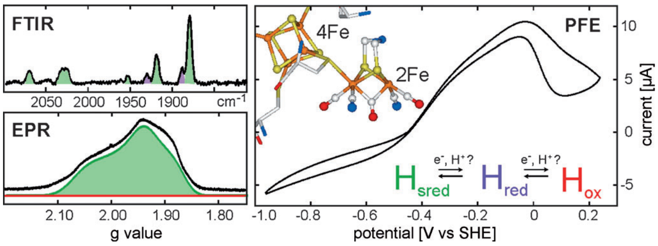
[FeFe] Hydrogenase Mechanism

A. Adamska, A. Silakov,* C. Lambertz, O. Rüdiger, T. Happe, E. Reijerse,* W. Lubitz* ——— 11458 – 11462

Identification and Characterization of the "Super-Reduced" State of the H-Cluster in [FeFe] Hydrogenase: A New Building Block for the Catalytic Cycle?



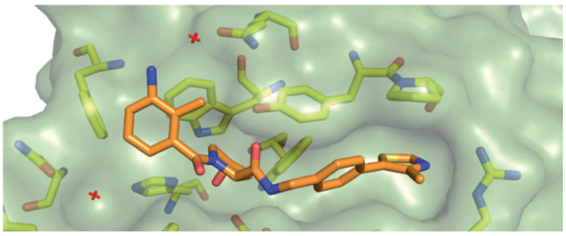
Super-reduced and super-active: A new redox state in the active site of algal [FeFe] hydrogenases has been identified and characterized by EPR and FTIR spectroscopy. Electrochemical and in vitro essays show that this species is highly active in hydrogen production and suggest that it is a key intermediate in the catalytic cycle of all [FeFe] hydrogenases.

Frontispiece

Drug Design

D. L. Buckley, J. L. Gustafson, I. Van Molle, A. G. Roth, H. S. Tae, P. C. Gareiss, W. L. Jorgensen, A. Ciulli, C. M. Crews* ——— 11463 – 11467

Small-Molecule Inhibitors of the Interaction between the E3 Ligase VHL and HIF1α

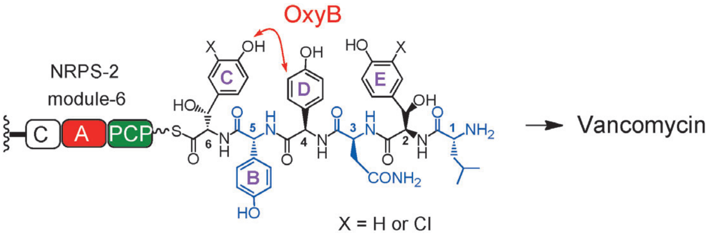


By design: Novel small-molecule inhibitors of the interaction between the von Hippel–Lindau ligase (VHL) and its molecular target HIF1α, a transcription factor involved in oxygen sensing, have been developed and studied. The most potent inhibitor binds with an IC_{50} value of 0.9 µM and is thus the first sub-micromolar inhibitor of the VHL–HIF1α interaction.

Vancomycin Biosynthesis

P. C. Schmartz, K. Wölfel, K. Zerbe, E. Gad, E. S. El Tamany, H. K. Ibrahim, K. Abou-Hadeed, J. A. Robinson* ——— 11468 – 11472

Substituent Effects on the Phenol Coupling Reaction Catalyzed by the Vancomycin Biosynthetic P450 Enzyme OxyB



Oxidative phenol coupling reactions are required to establish the cross-linked heptapeptide backbone of vancomycin. The first cross-linking reaction, catalyzed by the P450 enzyme OxyB, is dramatically slower when a chlorine substituent is present in the hexapeptide-*S*-PCP substrate and is abolished when chlorine is introduced into a potential heptapeptide-*S*-PCP substrate.

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Roald Hoffmann (Nobel Prize 1981)

Susumu Kitagawa

Jean-Marie Lehn (Nobel Prize 1987)

E.W. “Bert” Meijer

Frank Schirrmacher (Publisher, *FAZ*)

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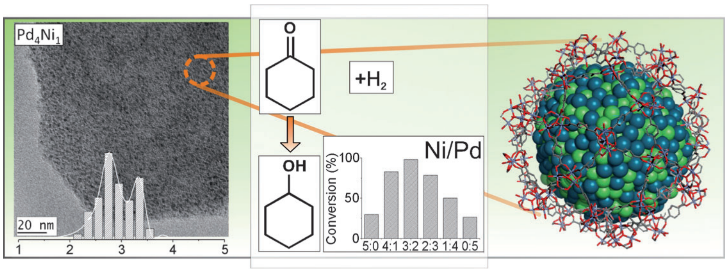
Bimetallic Catalysis

J. Hermannsdörfer, M. Friedrich,
N. Miyajima, R. Q. Albuquerque,
S. Kümmel, R. Kempe* ___ **11473 – 11477**

Ni/Pd@MIL-101: Synergistic Catalysis with Cavity-Conform Ni/Pd Nanoparticles

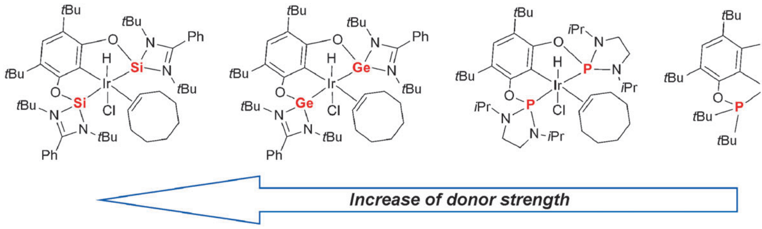


A perfect fit: Cavity-conform bimetallic Ni/Pd nanoparticles of different composition were generated in the metal–organic framework MIL-101. Experimental evidence and molecular dynamic simulations indicate the existence of mixed bimetallic particles. Pronounced synergistic effects have been observed in liquid-phase catalysis.

Pincer Ligands

A. Brück, D. Gallego, W. Wang, E. Irran,
M. Driess,*
J. F. Hartwig* ___ **11478 – 11482**

Pushing the σ-Donor Strength in Iridium Pincer Complexes: Bis(silylene) and Bis(germylene) Ligands Are Stronger Donors than Bis(phosphorus(III)) Ligands

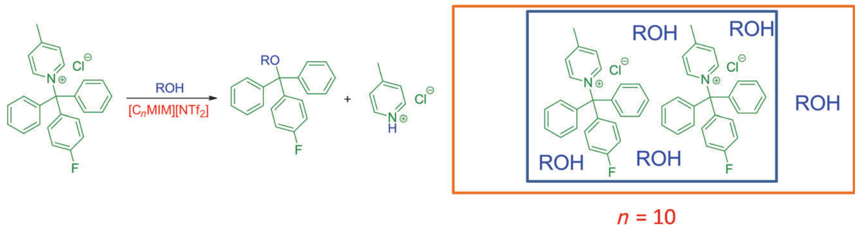


Breaking the donor limits: The remarkable coordination chemistry of ECHE (E = Si, Ge) ligands with Group 9 metals (Ir, Rh) and their application in catalytic C–H borylation of arenes was investigated. The spectroscopic and structural features of the first [ECE] iridium complexes show the stronger σ-donating properties of the divalent Si and Ge pincer ligands compared to analogous P^{III}-based ligands.

Ionic Liquids

C. C. Weber, A. F. Masters,
T. Maschmeyer* ___ **11483 – 11486**

Pseudo-Encapsulation—Nanodomains for Enhanced Reactivity in Ionic Liquids

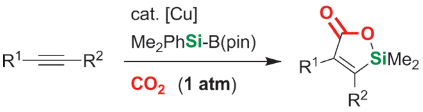


Domain constrained: Polar and nonpolar domains within 1-alkyl-3-methylimidazolium ionic liquids can affect reaction outcomes by pseudo-encapsulation of reactants and this has been explored for a nucleophilic substitution reaction using a cationic substrate and a range of nucleophiles. The significant rate enhancements observed correlate with the concentration of the polar reactants within the ionic liquid's polar domain. ([C$_n$MIM] = 1-alkyl-3-methylimidazolium).

Homogeneous Catalysis

T. Fujihara, Y. Tani, K. Semba, J. Terao,
Y. Tsuji* ___ **11487 – 11490**

Copper-Catalyzed Silacarboxylation of Internal Alkynes by Employing Carbon Dioxide and Silylboranes

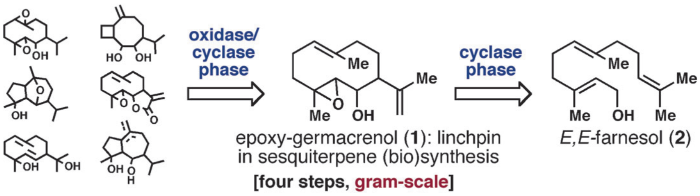


Silalactones: The copper-catalyzed reaction of internal alkynes with (dimethylphenylsilyl)pinacolborane (Me$_2$PhSi-B(pin)) as the silicon source and CO$_2$ at atmospheric pressure afforded silalactones selectively in good to high yields. The silalactones can be used as substrates for the Hiyama cross-coupling reaction as demonstrated for one substrate.

Sesquiterpenes

K. Foo, I. Usui, D. C. G. Götz,
E. W. Werner, D. Holte,
P. S. Baran* ____________ **11491 – 11495**

Scalable, Enantioselective Synthesis of Germacrenes and Related Sesquiterpenes Inspired by Terpene Cyclase Phase Logic



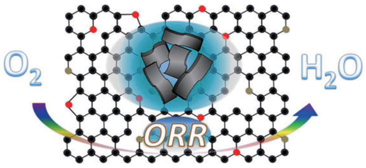
Terpene cyclase phase: Inspired by this logic, a scalable and enantioselective divergent synthesis of germacrane-type sesquiterpenes is developed. Salient features of this work include: 1) the direct ring closure of a farnesol derivative to the 10-membered carbocycle **1**, and 2) subsequent synthetic operations on **1** to gain access to different bicyclic frameworks such as guaianes, cadinanes, selinanes, and elemenes.

Heterogeneous Catalysis

J. Liang, Y. Jiao, M. Jaroniec,
S. Z. Qiao* ____________ **11496 – 11500**

Sulfur and Nitrogen Dual-Doped Mesoporous Graphene Electrocatalyst for Oxygen Reduction with Synergistically Enhanced Performance

Back Cover



Doping duo: Mesoporous graphene doped with both N and S atoms (N-S-G) was prepared in one step and studied as an electrochemical catalyst for the oxygen reduction reaction (ORR). The catalyst shows excellent ORR performance comparable to that of commercial Pt/C. The outstanding activity of N-S-G results from both the large number and the synergistic effect of the dopant heteroatoms.

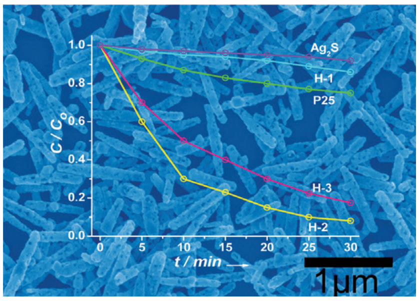
Nanotubes

W. L. Yang, L. Zhang, Y. Hu,* Y. J. Zhong,
H. B. Wu, X. W. Lou* ____ **11501 – 11504**

Microwave-Assisted Synthesis of Porous Ag_2S–Ag Hybrid Nanotubes with High Visible-Light Photocatalytic Activity

Inside Back Cover

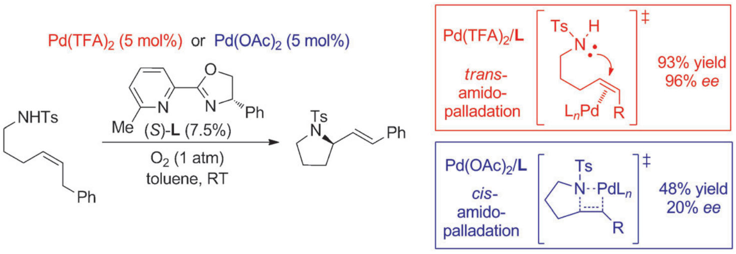
Brought to light: Ag_2S–Ag hybrid nanotubes were synthesized by rapid microwave-assisted sulfidation of Ag_2CO_3 nanorods. The relative amounts of Ag_2S and Ag in the hybrid structure can be controlled easily by varying the concentration of the sulfur precursor. The optimized Ag_2S–Ag hybrid structure has superior photocatalytic activity (yellow) for both degradation of methyl orange (see graph) and reduction of aqueous Cr^{VI} under visible-light irradiation.



Asymmetric Catalysis

A. B. Weinstein,
S. S. Stahl* ____________ **11505 – 11509**

Reconciling the Stereochemical Course of Nucleopalladation with the Development of Enantioselective Wacker-Type Cyclizations

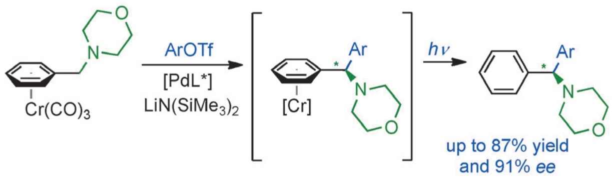


A stereochemical substrate probe was used to assess the factors that affect the stereochemical course of nucleopalladation in the context of an enantioselective Wacker-type reaction. The enantioselectivity correlates directly with the nucleopalladation pathway, and both the neutral-donor and anionic ligands on palladium are capable of controlling selectivity for *cis*- or *trans*-nucleopalladation (see scheme; TFA = trifluoroacetate).

Synthetic Methods

G. I. McGrew, C. Stanciu, J. Zhang,
P. J. Carroll, S. D. Dreher,*
P. J. Walsh* ______ 11510–11513

Asymmetric Cross-Coupling of Aryl Triflates to the Benzylic Position of Benzylamines

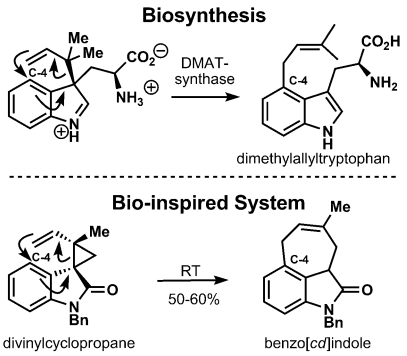


Ligand in a haystack: The first catalytic asymmetric cross-coupling of benzyllithiums α to tertiary amines using [Cr(CO)$_3$] activation of benzylic C$_{sp^3}$–H bonds is described. The stabilized organolithium undergoes Pd-catalyzed coupling with aryl triflates (ArOTf) by a novel dynamic kinetic resolution to yield enantioenriched diarylmethylamines. The chiral ligand for this reaction was identified using high-throughput experimentation with 192 ligands.

Biosynthetic Mechanism

D. D. Schwarzer, P. J. Gritsch,
T. Gaich* ______ 11514–11516

Mimicking Dimethylallyltryptophan Synthase: Experimental Evidence for a Biosynthetic Cope Rearrangement Process

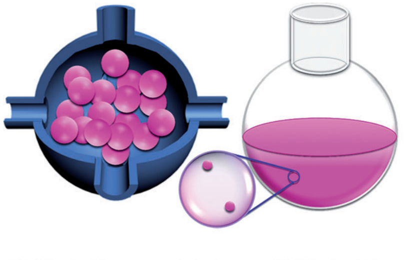


Easy to cope with: Experimental evidence was found to support an enzymatic [3,3]-sigmatropic rearrangement catalyzed by dimethylallyltryptophan (DMAT) synthase (see scheme). A bio-inspired system showed the feasibility of Cope rearrangement to the C-4 position of the indole nucleus. The tricyclic benzo[*cd*]indole core of welwitindolinones and dragmacidin E was synthesized using this transformation.

Heterogeneous Catalysis

B. Li, S. Bai, X. Wang, M. Zhong, Q. Yang,*
C. Li* ______ 11517–11521

Hydration of Epoxides on [Co^{III}(salen)] Encapsulated in Silica-Based Nanoreactors

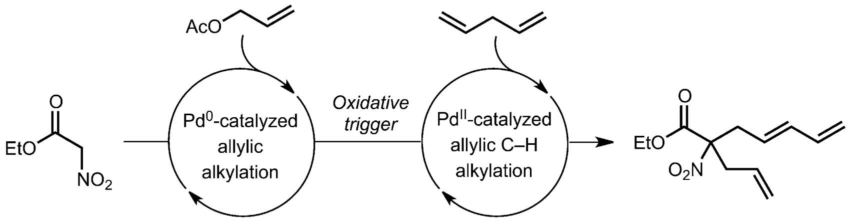


A confined workspace has its benefits in the case of a non-acid solid catalyst prepared by encapsulating [Co^{III}(salen)] in the nanocages of mesoporous silica. The catalytic activity and selectivity of [Co^{III}(salen)] were increased significantly owing to the enhanced cooperative activation effect in the nanoreactors. Thus, ethylene oxide (EO) underwent hydration at a low 2:1 H$_2$O/EO molar ratio to give ethylene glycol in up to 96% yield.

Assisted Tandem Catalysis

B. M. Trost,* D. A. Thaisrivongs,
M. M. Hansmann ______ 11522–11526

Tandem Palladium(0) and Palladium(II)-Catalyzed Allylic Alkylation Through Complementary Redox Cycles

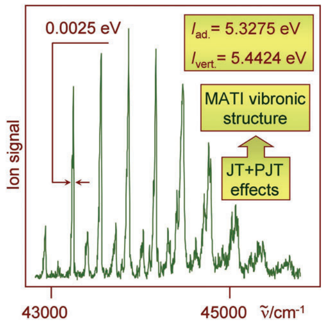


Here it goes again: A tandem catalytic process effects sequential Pd^0-catalyzed allylic alkylations through leaving group ionization and Pd^{II}-catalyzed allylic alkylations by C–H activation. By employing an oxidative trigger to convert the catalytic species from Pd^0 into Pd^{II}, both transformations can be conducted in a single reaction vessel using the same precatalyst. This allows for the selective introduction of otherwise indistinguishable allyl groups.

Sandwich Complexes

S. Y. Ketkov,* H. L. Selzle **11527 – 11530**

Threshold Ionization of Cobaltocene: The Metallocene Molecule Revealing Zero Kinetic Energy States

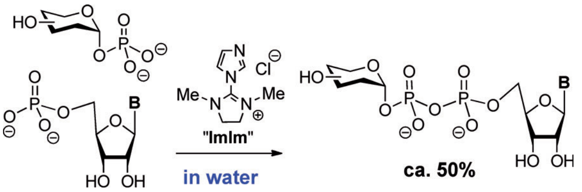


Playing it cool: The mass-analyzed threshold ionization (MATI) spectrum of jet-cooled cobaltocene shows a surprisingly rich vibronic structure which provides high-resolution adiabatic ($I_{ad.}$) and vertical ($I_{vert.}$) ionization energies of the neutral molecule, as well as vibrational frequencies of the gas-phase cation. The spectrum is indicative of both Jahn–Teller (JT) and pseudo-Jahn–Teller (PJT) activity in the 19-electron [Cp_2Co] sandwich complex.

Synthetic Methods

H. Tanaka, Y. Yoshimura, M. R. Jørgensen, J. A. Cuesta-Seijo, O. Hindsgaul* ________ **11531 – 11534**

A Simple Synthesis of Sugar Nucleoside Diphosphates by Chemical Coupling in Water



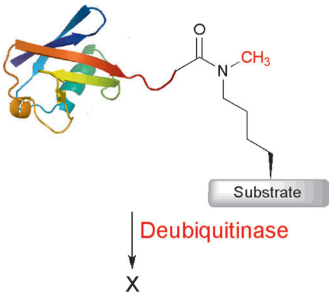
Sugar nucleotides made easy: The new reagent “ImIm”, which is formed in situ in water, is shown to activate nucleoside 5′-phosphates to their imidazolides, these can subsequently couple with sugar-1-phosphates; the whole procedure takes place in water. This truly simple method yields a crude product mixture that can be used directly as a source of donors for glycosyltransferase-mediated oligsaccharide synthesis. In the scheme, **B** stands for the nucleobases U, A, or G.

Stable Isopeptide Bond

M. Haj-Yahya, N. Eltarteer, S. Ohayon, E. Shema, E. Kotler, M. Oren, A. Brik* ________ **11535 – 11539**

N-Methylation of Isopeptide Bond as a Strategy to Resist Deubiquitinases

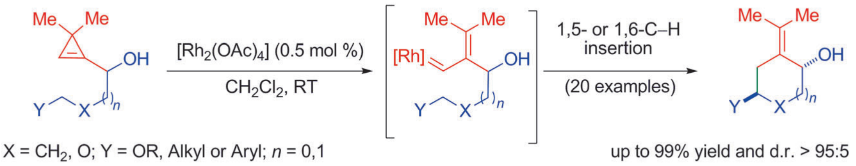
Stable like a rock: An efficient method to generate N-methylated isopeptide bonds has been developed. The strategy was used to generate highly stable ubiquitinated peptides and proteins that are resistant to deubiquitinases (DUBs; see scheme). Thus, the behavior of several stable ubiquitin conjugates with different DUBs was studied in vitro and within a cellular environment.



Homogeneous Catalysis

A. Archambeau, F. Miege, C. Meyer,* J. Cossy* ________ **11540 – 11544**

Highly Efficient Stereoselective Catalytic $C(sp^3)$–H Insertions with Donor Rhodium Carbenoids Generated from Cyclopropenes

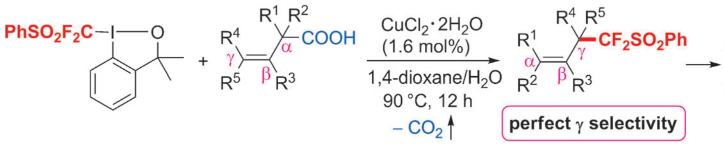


Rings of five and six: Donor alkenyl rhodium carbenoids generated from 3,3-dimethylcyclopropenylcarbinols exhibit high reactivity in intramolecular C–H insertions. The reactions proceed under remarkably mild conditions, tolerate the presence of the free hydroxy group, and afford an efficient and stereoselective access to a variety of functionalized carbocycles and oxygen heterocycles.

Synthetic Methods

Z. He, M. Hu, T. Luo, L. Li,
J. Hu* ―――――― **11545 – 11547**

Copper-Catalyzed Difluoromethylation of β,γ-Unsaturated Carboxylic Acids: An Efficient Allylic Difluoromethylation

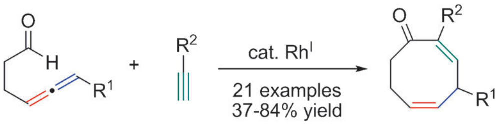


Not one but two! A new strategy for the regiospecific construction of compounds with allylic CF_2H groups has been developed. The decarboxylative (phenylsulfonyl)difluoromethylation of β,γ-unsaturated carboxylic acids is catalyzed by a Lewis acid ($CuCl_2 \cdot 2H_2O$), and the resulting product easily undergoes desulfonylation.

Cycloaddition

Y. Oonishi,* A. Hosotani,
Y. Sato* ―――――― **11548 – 11551**

Construction of Monocyclic Eight-Membered Rings: Intermolecular Rhodium(I)-Catalyzed [6+2] Cycloaddition of 4-Allenals with Alkynes

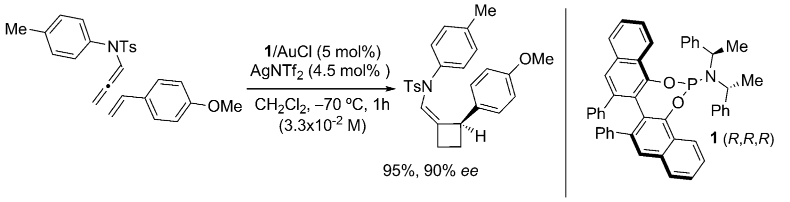


Rounding up: A Rh^I-catalyzed intermolecular cycloaddition of 4-allenals with alkynes has been developed that provides various monocyclic eight-membered rings in good to high yields in a stereoselective manner (see scheme). In addition, the chirality of the starting allene is transferred in this reaction, thereby giving optically active monocyclic eight-membered ring compounds.

Asymmetric Catalysis

S. Suárez-Pantiga, C. Hernández-Díaz,
E. Rubio, J. M. González* **11552 – 11555**

Intermolecular [2+2] Reaction of *N*-Allenylsulfonamides with Vinylarenes: Enantioselective Gold(I)-Catalyzed Synthesis of Cyclobutane Derivatives

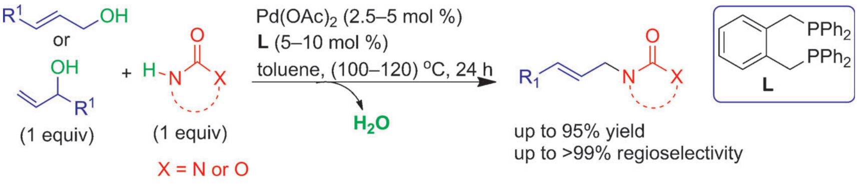


Golden touch: *N*-allenylsulfonamides react with styrene derivatives to furnish chiral cyclobutanes in both high yield and enantioselectivity at −70 °C. Phosphoramidite ligands such as **1**, facilitate this asymmetric gold(I)-catalyzed [2+2] cycloaddition. Tf = trifluoromethanesulfonyl.

Homogeneous Catalysis

D. Banerjee, R. V. Jagadeesh, K. Junge,
H. Junge, M. Beller* ―― **11556 – 11560**

Efficient and Convenient Palladium-Catalyzed Amination of Allylic Alcohols with N-Heterocycles

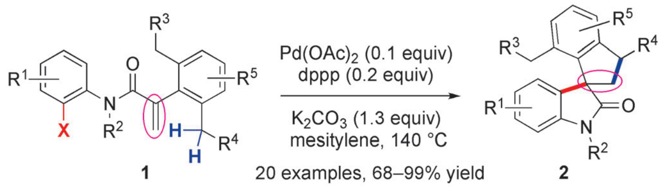


Atom economic: A commercially available palladium catalyst system is applied for an environmentally benign allylation of electron-deficient N-heterocycles using allylic alcohols (see scheme). The system is also applied for the N-allylation of biologically important uridine and thymidine derivatives.

Synthetic Methods

T. Piou, L. Neuville,*
J. Zhu* ______________ **11561 – 11565**

Activation of a C(sp^3)–H Bond by a Transient σ-Alkylpalladium(II) Complex: Synthesis of Spirooxindoles Through a Palladium-Catalyzed Domino Carbopalladation/C(sp^3)–C(sp^3) Bond-Forming Process

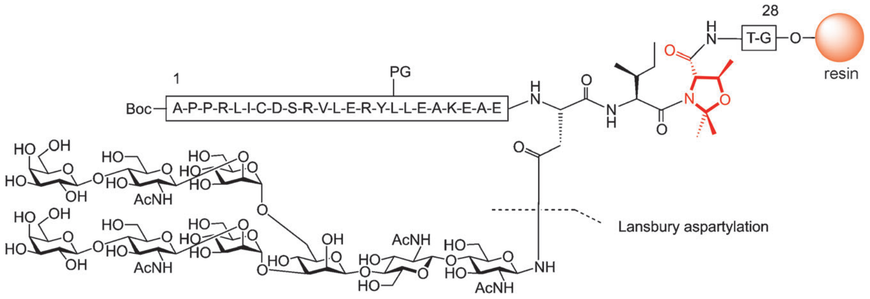


Heck shortens the distance: A method for the palladium-catalyzed activation of a C(sp^3)–H bond by a σ-alkyl Pd^{II} complex generated in situ from a remote arylhalide function has been developed. This approach allows a novel domino carbopalladation/C(sp^3)–C(sp^3) bond-forming process to provide rapid access to biologically relevant spirooxindoles.

Peptide Synthesis

V. Ullmann, M. Rädisch, I. Boos, J. Freund,
C. Pöhner, S. Schwarzinger,
C. Unverzagt* __________ **11566 – 11570**

Convergent Solid-Phase Synthesis of N-Glycopeptides Facilitated by Pseudoprolines at Consensus-Sequence Ser/Thr Residues

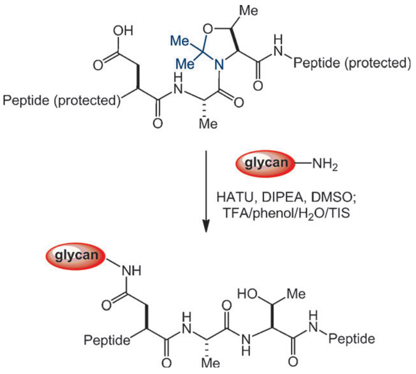


Remote control: The formation of aspartimides is greatly decreased during peptide elongation and during convergent sugar couplings of Asp-X-Ser/Thr peptides that contain a pseudoproline (red; see scheme). The robust approach efficiently joins complex peptides and N-glycans on the solid phase thus facilitating the availability of glycopeptides and glycoproteins.

Glycoprotein Synthesis

P. Wang, B. Aussedat, Y. Vohra,
S. J. Danishefsky* _______ **11571 – 11575**

An Advance in the Chemical Synthesis of Homogeneous N-Linked Glycopolypeptides by Convergent Aspartylation

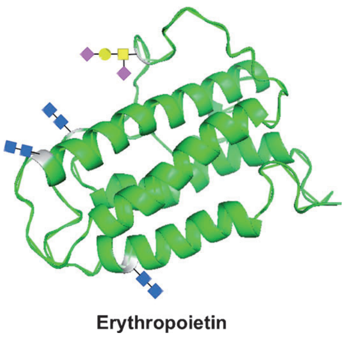


Like a Pro: A one-flask aspartylation/deprotection method, wherein long peptide fragments, bearing proximal pseudoproline functionality, are merged with complex glycan domains has been developed. Following aspartylation, acid-mediated global deprotection reveals the elaborated glycopeptide. The temporary pseudoproline functionality serves to suppress formation of aspartimide side products during solid-phase peptide synthesis and aspartylation.

Total Synthesis

P. Wang, S. Dong, J. A. Brailsford, K. Iyer, S. D. Townsend, Q. Zhang, R. C. Hendrickson, J. Shieh, M. A. S. Moore, S. J. Danishefsky* ______ **11576–11584**

At Last: Erythropoietin as a Single Glycoform



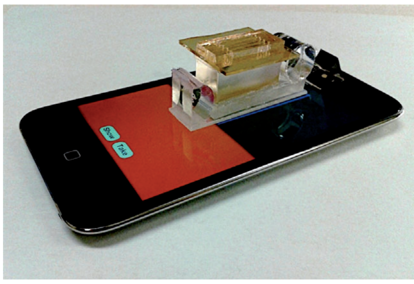
Wild thing: The first total synthesis of wild-type erythropoietin glycoprotein (see picture) has been accomplished. The erythropoietic activity of the synthetic folded protein has been demonstrated.

Front Cover

Sensors

P. Preechaburana,* M. C. Gonzalez, A. Suska, D. Filippini* ______ **11585–11588**

Surface Plasmon Resonance Chemical Sensing on Cell Phones

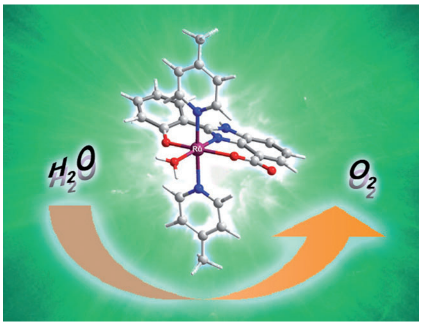


Chemosensing based on angle-resolved surface plasmon resonance is demonstrated on intact cell phones using a disposable optical coupler and software to configure illumination and acquisition. This coupler operates on different cell phones and is applied for classical affinity assays with commercial chips and custom-made tests with embedded calibration. Measured performance (2.14x10^{-6} refractive index units) is comparable with compact SPR systems.

Catalytic Oxidation

M. D. Kärkäs, T. Åkermark, E. V. Johnston, S. R. Karim, T. M. Laine, B.-L. Lee, T. Åkermark, T. Privalov, B. Åkermark* ______ **11589–11593**

Water Oxidation by Single-Site Ruthenium Complexes: Using Ligands as Redox and Proton Transfer Mediators

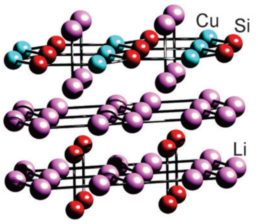


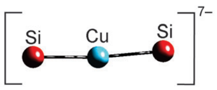
Light me up: Through the use of an imidazole motif it is possible to introduce a combined redox and proton-transfer mediator into single-site ruthenium water-oxidation catalysts. With the complex (see picture), high turnover numbers and high initial turnover frequencies were attained with the mild oxidant $[\mathrm{Ru(bpy)_3}]^{3+}$ (bpy = 2,2′-bipyridine).

Lithium-Rich Compounds

A. Slabon, S. Budnyk, E. Cuervo-Reyes, M. Wörle, C. Mensing, R. Nesper* ______ **11594–11596**

Copper Silicides with the Highest Lithium Content: $\mathrm{Li_7CuSi_2}$ Containing the 16-Electron Group $[\mathrm{CuSi_2}]^{7-}$ and $\mathrm{Li_{7.3}CuSi_3}$ with Heterographene Nets ${}^{2}_{\infty}[\mathrm{CuSi}]^{3.3-}$



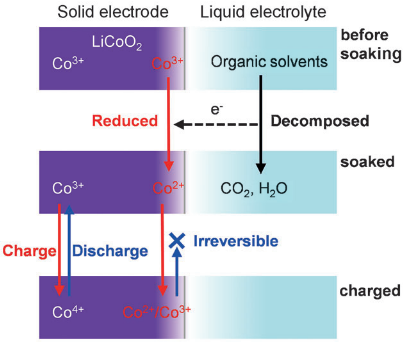


Incredibly rich in lithium: The ternary silicides $\mathrm{Li_7CuSi_2}$ with the linear $[\mathrm{Si\text{-}Cu\text{-}Si}]^{7-}$ Zintl anion (see picture) and $\mathrm{Li_{7.3}CuSi_3}$ are compounds with the highest lithium content in the ternary system. The crystal and electronic structures of both compounds are discussed.

Solid–Liquid Interface

D. Takamatsu,* Y. Koyama, Y. Orikasa,
S. Mori, T. Nakatsutsumi, T. Hirano,
H. Tanida, H. Arai, Y. Uchimoto,
Z. Ogumi ________ **11597 – 11601**

First In Situ Observation of the $LiCoO_2$ Electrode/Electrolyte Interface by Total-Reflection X-ray Absorption Spectroscopy



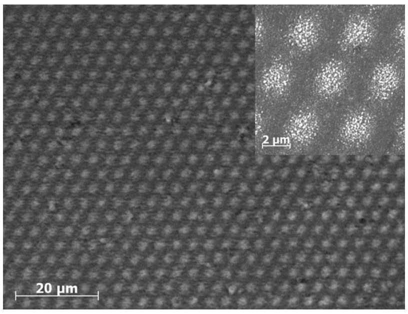
Surface analysis: In situ total-reflection fluorescence X-ray absorption spectroscopy showed that reduction of cobalt at the surface of a $LiCoO_2$ electrode occurs by contact with a liquid electrolyte. An irreversible behavior was observed at the surface of $LiCoO_2$ during a first charge/discharge process whereas the bulk material showed a reversible behavior. This Co reduction is an initial electrode deterioration.

Electrochemical Lithography

A. A. Eliseev,* N. A. Sapoletova,
I. Snigireva, A. Snigirev,
K. S. Napolskii ________ **11602 – 11605**

Electrochemical X-ray Photolithography

Best of both worlds: Electrochemical X-ray photolithography combines the advantages of X-ray photolithography with the versatility of electrochemical processing. A proof-of-concept was carried out by electrochemical deposition of nickel under coherent X-ray illumination guided through a lithographic mask with a 4 micrometer pitch, resulting in formation of a nickel grating (see picture).



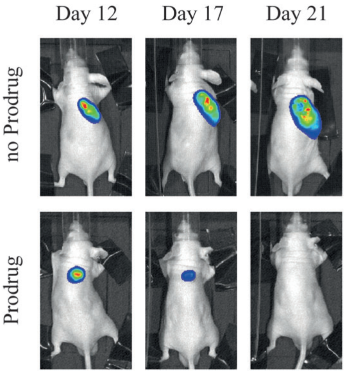
Tumor Targeting

T. Legigan, J. Clarhaut, I. Tranoy-Opalinski,
A. Monvoisin, B. Renoux, M. Thomas,
A. Le Pape, S. Lerondel,
S. Papot* ________ **11606 – 11610**

The First Generation of β-Galactosidase-Responsive Prodrugs Designed for the Selective Treatment of Solid Tumors in Prodrug Monotherapy

Inside Cover

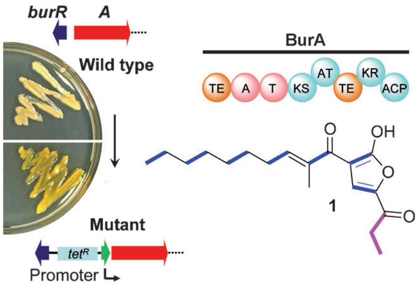
Massive attack: Galactoside prodrugs have been designed that can be selectively activated by lysosomal β-galactosidase located inside cancer cells expressing a specific tumor-associated receptor. This efficient enzymatic process triggers a potent cytotoxic effect, releasing the potent antimitotic agent MMAE and allowing the destruction of both receptor-positive and surrounding receptor-negative tumor cells.



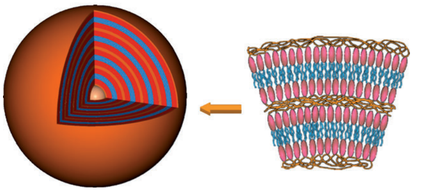
Natural Products

J. Franke, K. Ishida,
C. Hertweck* ________ **11611 – 11615**

Genomics-Driven Discovery of Burkholderic Acid, a Noncanonical, Cryptic Polyketide from Human Pathogenic *Burkholderia* Species



Biosynthetic secrets unveiled: Targeted promoter exchange in a cryptic biosynthesis gene cluster conserved among certain pathogenic *Burkholderia* species yielded a highly unstable, structurally unprecedented polyketide, burkholderic acid (**1**). Labeling experiments, gene knock-outs, and bioinformatics analyses grant first insights into a fascinating polyketide pathway. BurA is an unusual nonribosomal peptide synthetase/polyketide synthase featuring internal thioesterase domains.



Polymeric onions: A concept of vesicle fabrication based on nonstoichiometric complexation of a polybase with an amphiphilic ligand bearing a sulfonic acid group is developed (see picture). In contrast to conventional polymersomes, the polymer backbones are oriented mainly parallel to the vesicle walls. The vesicles can collapse under UV irradiation because of a UV-triggered *trans–cis* isomerization of the azo-group-containing ligand.

Polymersomes

L. Li, M. Rosenthal, H. Zhang, J. J. Hernandez, M. Drechsler, H. Phan, S. Rütten, X. Zhu,* D. A. Ivanov,* M. Möller ———— **11616 – 11619**

Light-Switchable Vesicles from Liquid-Crystalline Homopolymer–Surfactant Complexes

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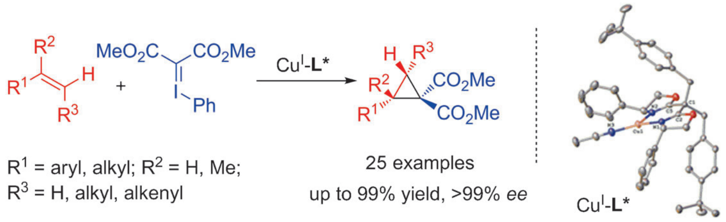

Triangulation method: The catalytic enantioselective cyclopropanation of multisubstituted olefins with phenyliodonium ylide malonate has been achieved in the presence of a chiral bisoxazoline copper(I) complex (see scheme). A wide range of substrates undergo the reaction to provide optically active 1,1-cyclopropane diesters in high yield with up to $>99\,\%$ *ee*. A rationale for the enantioselective induction has been proposed.

Asymmetric Catalysis

C. Deng, L.-J. Wang, J. Zhu, Y. Tang* ———— **11620 – 11623**

A Chiral Cagelike Copper(I) Catalyst for the Highly Enantioselective Synthesis of 1,1-Cyclopropane Diesters

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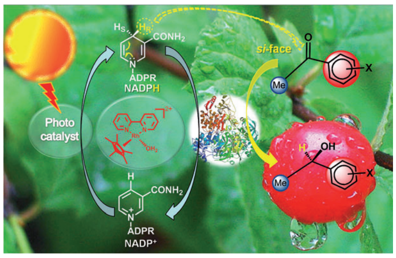
Artificial Photosynthesis System: A novel photocatalyst/enzyme-coupled artificial photosynthesis system harvests solar energy as seen in green plants through the combination of photocatalysis and biocatalysis and induces asymmetry in an achiral substrate (see picture; ADPR = adenosine diphosphate ribose, NADP = nicotinamide adenine dinucleotide phosphate).



Synthetic Methods

S. Choudhury, J.-O. Baeg,* N.-J. Park, R. K. Yadav ———— **11624 – 11628**

A Photocatalyst/Enzyme Couple That Uses Solar Energy in the Asymmetric Reduction of Acetophenones

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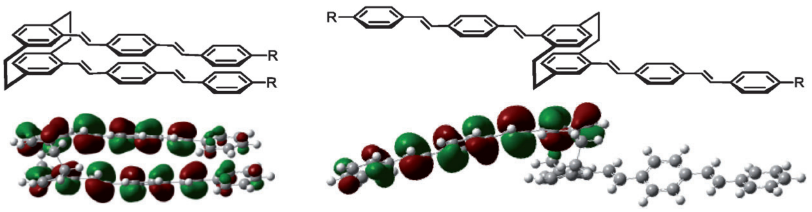


A clever combination: A series of phenylene vinylene oligomers, in which the conjugated segments are held in a well-defined stacked arrangement along their entire length, was studied experimentally and theoretically (see picture). The impact of the extended interchain interactions on the photophysics of the π-stacked systems is reported.

Electronic Structure

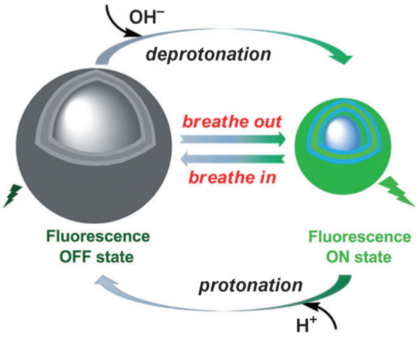
S. Mukhopadhyay, S. P. Jagtap, V. Coropceanu, J.-L. Brédas, D. M. Collard* ———— **11629 – 11632**

π-Stacked Oligo(phenylene vinylene)s Based on Pseudo-Geminal Substituted [2.2]Paracyclophanes: Impact of Interchain Geometry and Interactions on the Electronic Properties

Vesicles

R. Dong, B. Zhu, Y. Zhou,* D. Yan,
X. Zhu* ______________ **11633 – 11637**

"Breathing" Vesicles with Jellyfish-like On–Off Switchable Fluorescence Behavior



Controlled, deep breathing: Polymeric vesicles that exhibit reversible pH-induced "breathing" behavior accompanied by switchable fluorescence (see picture) were prepared through the aqueous self-assembly of an amphiphilic block copolymer. Mechanistic studies showed that this jellyfish-like breathing and light-emitting behavior originates from protonation- or deprotonation-induced changes in the conformation of the azobenzene chromophores.

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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